9th International Symposium on Polymer Electrolytes

CSP-03-5043
DTIC Copy
Distribution A:
Approved for public release;
distribution is unlimited

August 22–27, 2004
Mrągowo–Poland

E X T E N D E D A B S T R A C T S

Organized by:

Polymer Ionics Research Group

PIRG

at

Chemical Faculty

Warsaw University of Technology

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE *(DD-MM-YYYY)*
20-01-2005

2. REPORT TYPE
Conference Proceedings

3. DATES COVERED *(From – To)*
22 August 2004 - 27 August 2004

4. TITLE AND SUBTITLE
9th Symposium on Polymer Electrolytes (ISPE 9)

5a. CONTRACT NUMBER
FA8655-03-1-5043

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Program Committee:
Zbigniew Florjanczyk
Franciszek Krok
Janusz Plocharski

5d. PROJECT NUMBER

5d. TASK NUMBER

5e. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Warsaw University of Technology
Noakowskiego 3
Warszawa 00-664
Poland

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
EOARD
PSC 802 BOX 14
FPO 09499-0014

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
CSP 03-5043

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The Final Proceedings for 9th Symposium on Polymer Electrolytes (ISPE 9), 22 August 2004 - 27 August 2004

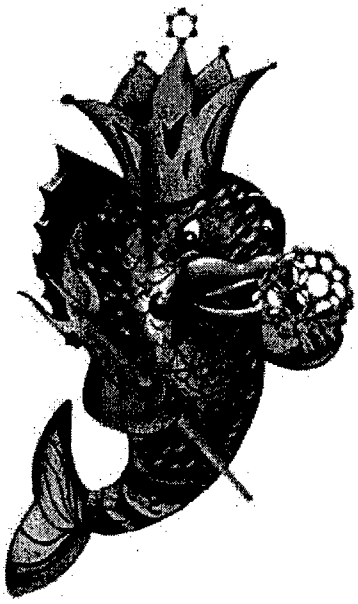
This is an interdisciplinary conference. Topics include 1) basic theory including modeling and simulation techniques; 2) physical and electrochemical methods of characterization; 3) structural studies; 4) investigations of ion transport mechanisms; 5) new polymer electrolytes; 6) existing and expected engineering applications in electrochemical energy storage systems, fuel cells, display systems, multipurpose sensors, electrochemical devices of potential importance for medicine biology.

15. SUBJECT TERMS
EOARD, Polymer Chemistry, Electrochemistry, Batteries

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			WILLIAM B. McCLURE, Col, USAF
UNCLAS	UNCLAS	UNCLAS	UL	232	19b. TELEPHONE NUMBER *(Include area code)* +44 (0)20 7514 4376

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39-18

9th International Symposium on Polymer Electrolytes



August 22–27, 2004
Mrągowo–Poland

E X T E N D E D A B S T R A C T S

Organised by:
Polymer Ionics Research Group
PIRG
at
Chemical Faculty
Warsaw University of Technology

20050217 032

AQ F05-05-0757

International Advisory Committee

Michel Armand	University of Montreal, Montreal, Canada
Peter Bruce	University of St. Andrews, United Kingdom
Maria Forsyth	Monash University, Australia
Diana Golodnitsky	Tel Aviv University, Tel Aviv, Israel
Steve Greenbaum	CUNY, New York, USA
Per Jacobsson	Chalmers University, Goeteborg, Sweden
Hiroyuki Ohno	Tokyo University of Agriculture & Technology, Japan
Lawrance Scanlon	US Air Force Lab, Dayton, USA
Bruno Scrosati	University of Rome, Rome, Italy
Jean M. Tarascon	CNRS, Amiens, France
Josh Thomas	Uppsala University, Uppsala, Sweden
Masayoshi Watanabe	Yokohama National University, Yokohama, Japan
Peter Wright	University of Sheffield, Sheffield, United Kingdom

Programme Committee

Prof. Władysław Wieczorek	*Chairperson of the Programme Committee*
Prof. Zbigniew Florjańczyk	Co-chairperson of the Programme Committee
Prof. Franciszek Krok	Co-chairperson of the Programme Committee
Prof. Janusz Płocharski	Conference Secretary

Organising Committee

Dr Maciej Siekierski	*Chairperson of the Organising Committee*
M.Sc. Marcin Ciosek	Technical advisory and consulting
Dr Marek Marcinek	Public relations and contact with sponsors

We wish to thank the following for their contribution to the success of this conference:

FACULTY OF CHEMISTRY
Warsaw University of Technology
Noakowskiego 3, 00-664 Warsaw, Poland • tel. +48 22 6607372, 6607507 • fax. +48 22 6282741

kbn
STATE COMMITTEE FOR SCIENTIFIC RESEARCH

PLASTICS REVIEW
MIESIĘCZNIK MENEDŻERÓW POLSKIEGO PRZEMYSŁU TWORZYW SZTUCZNYCH I KAUCZUKÓW

ZOBACZ ŚWIAT W NOWYM ŚWIETLE OSRAM

Book DTP : Marcin Ciosek (admin@soliton.ch.pw.edu.pl)

Conference programme

Monday, August 23	
8:45 – 9:00	Opening and Introductory remarks by P. V. Wright
ORDERED STRUCTURES	chairperson: **P. V. Wright**
9:00 – 9:45	Conductivity and Structure of Crystalline Polymer Electrolytes *P. G. Bruce, Y. Andreev*
9:45 – 10:30	Lithium Ion Conducting Channel as Solid-State Electrolytes *L. G. Scanlon, L. R. Lucente, W. A. Feld, G. Sandi, P. Balbuena, A. Turner*
10:30 – 10:50	Study of Ion Conduction Mechanism in Ordered Poly(Ethylene Oxide) Based Polymer Electrolytes *E. Livshits, R. Kovarsky, D. Golodnitsky, E. Peled*
10:50 – 11:10	Polymer Electrolyte Single-Ion Conductors with Decoupled Li^+ Motion *A. M. Mayes, S.W. Ryu, S. Kumar, Y. Shao-Horn*
11:10 – 11:30	**Coffee**
MODELLING	chairperson: **A. M. Mayes**
11:30 – 12:15	MD Simulation of the Crystalline Short- and Long- Chain Systems $(LiPF_6)_{1-X}\bullet(Li_2SiF_6)_X\bullet PEO_6$ *D. Brandell, I. Thomas, H. Kasemägi, A. Liivat, A. Aabloo*
12:15 – 12:45	Molecular Modelling Studies of Polymer Electrolytes for Power Sources *P. B. Balbuena, E. J. Lamas, Y. Wang*
12:45 – 13:15	Ab initio Studies on Complexation of Anions to Neutral Species *P. Johansson, P. Jacobsson*
13:15 – 13:35	Modelling Defect-Assisted Conductivity in Organic Ionic Plastic Crystals *A. J. Hill, S. J. Pas, M. Forsyth, D. R. MacFarlane*
13:45 – 14:45	**Lunch**
NEW POLYMER ARCHITECTURE	chairperson: **J. Thomas**
16:30 – 17:15	Improved Lithium Ion Transport in Polyelectrolytes *M. Forsyth, N. Byrne, C. Tiyapiboonchaiya, P. Howlett, D. R.MacFarlane*
17:15 – 17:35	Synthesis, Molecular Structure, Microphase Stability And Conduction Mechanism in Solvent-Free Low-Dimensional Copolymer - Li Salt Systems with High Ambient Conductivity *J. Liu, Y Zheng, Y-P. Liao, G. Ungar, P. V. Wright*
17:35 – 17:55	Polymer-in-Salt Electrolytes Based on Acrylonitrile and Butyl Acrylate Copolymers *E. Zygadlo-Monikowska, Z. Florjanczyk, W. Wieczorek, N. Langwald, A. Tomaszewska*
17:55 – 18:10	**Coffee**
NEW POLYMER ARCHITECTURE *continued*	chairperson: **L. G. Scanlon**
18:10 – 18:40	New Insights into Structural and Electrochemical Properties of Anisotropic Polymer Electrolytes *D. Golodnitsky, E. Livshits, R. Kovarsky, E. Peled, S. H. Chung, S. Suarez, S. Greenbaum*
18:40 – 19:00	Polymer Electrolytes Based on Poly(N-Ethylethylenimine) and Poly(N-Methylethylenimine) *R. Frech, G. A. Giffin, R. Sanders, J. Eisenblätter, D. T. Glatzhofer*
19:00 – 19:20	Lithium Migration Property of Phase-separated Polymer Gel Electrolyte *Y. Saito, K. Hirai, T. Sakai, S. Murata, K. Kii*
19:45	**Dinner (BBQ)**

Tuesday, August 24	
IONIC LIQUIDS	chairperson: **M. Forsyth**
9:00 – 9:45	Ionic Liquids as New Salts for Polymer Electrolytes; the Scope and Prospects *M. Watanabe*
9:45 – 10:15	Ionic Solids - a New Class of Fast Ion Conductors *I. Adebahr, D. R. MacFarlane, M. Forsyth*
10:15 – 10:35	Development of Polymeric Gel Electrolytes Containing Magnesium Salt and Ionic Liquid *N. Yoshimoto, T. Shirai, M. Morita*
10:35 – 10:55	Ion Transport Properties of Lithium Ionic Liquids and Ion Gels *H. Shobukawa, H. Tokuda, M. Watanabe*
10:55 – 11:15	NMR Studies on Diffusion of Individual Ions of Lithium-salt doped Room Temperature Ionic Liquids correlating with the Ionic Conductivity *K. Hayamizu, H. Nakagawa*
11:15 – 11:35	**Coffee**
OPTICAL PROPERTIES	chairperson: **D. Golodnitsky**
11:35 – 12:05	Bringing Light to Polymer Electrolytes: the Light-Emitting Electrochemical Cell *L. Edman*
12:05 – 12:35	Electrochromism in Visors and Goggles, Electrolytes for Electrochromic Applications *I. Stevens*
12:35 – 12:55	Polymer Electrolyte with Large Temperature-Dependent Conductivity for Novel Electrochromic Imaging *N. Kobayashi, M. Nishimura, H. Ohtomo*
13:15– 14:15	Lunch
NEW POLYMER ARCHITECTURE *continued*	chairperson: **A. Reiche**
16:00 – 16:20	Polyacrylonitrile-Molybdenum Disulfide Polymer Electrolyte Nanocomposites *G. González, E. Benavente, M. A. Santa Ana*
16:20 – 16:40	Influence of the Plasticizer Contents on the Properties of HEC Based Solid Polymeric Electrolytes *G.O. Machado, H.C.A. Ferreira, A. Pawlicka*
16:40 – 17:00	Solid Polymer Electrolytes Prepared From a Hyper-Branched Graft Polymer Using Atom Transfer Radical *M. Higa, Y. Fujino, T. Koumoto, R. Kitani, S. Egashira*
17:00 – 19:15	**POSTER SESSION**
19:45	**Dinner (BBQ)**

Wednesday, August 25	
COMPOSITES	chairperson: **M. Watanabe**
9:00 – 9:30	Synthesis and Electrochemical Characterization of Novel Nanocomposite Polymeric Membranes *G. Sandi, R. Kizilel, K. A. Carrado, N. Castagnola*
9:30 – 10:00	Modelling of Conductivity in Composites with Random Resistor Networks *M. Siekierski, K. Nadara*
10:00 – 10:20	Nanocomposite Polymer Electrolytes Based on Poly(oxyethylene) and Cellulose Nanocrystals *E. Alloin, M. A. S. Azizi Samir, W. Gorecki, A. Dufresne, J.-Y. Sanchez*
10:20 – 10:40	Effect of High Pressure CO_2 on the Structural and Electrical Properties of ORMOCERS-APE Systems Based on Zr and Al. *V. Di Noto, K. Vezzù, M. Vittadello, S. Lavina, A. Bertucco*
10:40 – 11:00	**Coffee**
COMPOSITES *continued*	chairperson: **R. Frech**
11:00 – 11:20	Increasing lithium ion in electrolyte materials through the use of additives *N. Byrne, J.M. Pringle, C. Tiyapiboonchaiya, D. R. MacFarlane, M. Forsyth*
11:20 – 11:40	Determination of the lithium transference number in PEO-DME-$LiClO_4$ modified with alumina powder of different surface acidity. *M. Ciosek, M. Siekierski*
11:40 – 12:00	Properties of Highly Pigmented Electrolytes with Large Porosity for Rechargeable Li-Polymer Batteries *J. Schulz, M. Popall, B. Olsowski, C. Cronauer*
12:00 – 12:20	Facile Preparation of Organoboron-based Ion Conductive Polymers *T. Mizumo, K. Sakamoto, N. Matsumi, H. Ohno*
12:20 – 12:40	Model Composite Polymer Electrolytes Containing Triphenylborane *M. Marcinek, G. Z. Żukowska, W. Wieczorek*
13:00	**Lunch and EXCURSION**
20:00	**Dinner**

Thursday, August 26	
METHODS	chairperson: S.H.Chung
9:00 – 9:45	NMR Studies of Mass Transport in Polymer Electrolytes for Batteries and Fuel Cells *S. G. Greenbaum*
9:45 – 10:05	Quantitative Infrared Studies of PEO Based Electrolytes *I. E. Furneaux, A. M. McCoy, V. Seneviratne, R. Frech*
10:05 – 10:25	Radiotracer Diffusion and Ionic Conduction in the Polymer Electrolyte $PEO_{30}NaI$ *S. Obeidi, B. Zazoum, N.A. Stolwijk*
10:25 – 10:45	Relaxation of Ions and Dipoles in LiTFSI Salt-in-Polymer and Polymer-in-Salt Electrolytes *J. R. Dygas, M. Marzantowicz, F. Krok, A. Lasinska, Z. Florjanczyk, A. Affek, E. Zygadlo-Monikowska*
10:45 – 11:05	Free Volume and Conductivity in Polymer Electrolytes: A Temperature and Pressure Dependent Study *S. J. Pas, M. D. Ingram, K. Funke, A. J. Hill*
11:05 – 11:25	**Coffee**
PROTON CONDUCTORS & FUEL CELLS	chairperson: S. G. Greenbaum
11:25 – 12:10	Overcoming performance limitations of membrane-electrode assemblies for direct methanol fuel cells *P. Zelenay*
12:10 – 12:30	NMR Studies of Mass Transport in High Acid Content Fuel Cell Membranes Based on PBI/Phosphoric Acid *S.H. Chung, L. Durantino, J.R.P. Jayakody, H. Zhang, L. Xiao, B. Benicewicz, S.G. Greenbaum*
12:30 – 12:50	Proton Conductors for Low Humidity Conditions *T. Rager, M. Schuster, A. Noda, K.-D. Kreuer, J. Maier*
12:50 – 13:10	Brønsted Acid-Base Ionic Liquids and Ion Gels as Proton Conducting Nonaqueous Electrolytes *Md. A. B. H. Susan, A. Noda, M. Watanabe*
13:10 – 14:00	**Lunch**
PROTON CONDUCTORS & FUEL CELLS *continued*	chairperson: V. Di Noto
16:30 – 17:00	Inorganic-Organic Hybrid Protonic Polymeric Materials for Fuel Cells Based on Polycondensed and Organically Cross-Linked Sulfonyl- and Styrene Functionalized Alkoxysilanes *S. Jacob, C. Poinsignon, M. Popall*
17:00 – 17:20	Prediction of Methanol and Water Fluxes Through a Direct Methanol Fuel Cell Polymer Electrolyte Membrane *S.S. Sandhu, R.O. Crowther, J.P. Fellner*
17:20 – 17:40	A Spectroscopic Study of Proton Conducting Polymer Membranes Based on PVDF/PAN Blends. *A. Martinelli, A. Matic, P. Jacobsson, L. Börjesson, M. A. Navarra, S. Panero, B. Scrosati*
17:40 – 18:00	**Coffee**
PROTON CONDUCTORS & FUEL CELLS *continued*	chairperson: M. Popall
18:00 – 18:20	Stability Study of PEMFC Ionomers through Model Molecules Mimicking Polymer Repeat Units *M. Maréchal, J. Guindet, J.-Y. Sanchez*
18:20 – 18:40	Synthesis and Structural Characterization of Two New Siloxanic Proton Conducting Membranes *V. Di Noto, M. Vittadello, S. Lavina*
18:40 – 19:00	The Influence of The Solvent Composition on the Viscosity, Glass Temperature and Vibrational Spectra in PC-H_3PO_4 Anhydrous Electrolytes *G. Z. Żukowska, K. Nadara, K. R. Jeffrey, J. R. Stevens*
20:00	**Conference banquet**

Friday, August 27	
APPLICATIONS	chairperson: **Z. Florjańczyk**
9:00 – 9:45	From Plastic Li-Ion to Plastic Li Metal Cells Operating at Room Temperature *L. Sannier, R. Bouchet, M. Chami, S. Grugeon, J-M. Tarascon*
9:45 – 10:05	Proposal of a New Actuator Using Ion Gel Driven at Low Voltage under Atmospheric Condition *S. Nanjo, M. Watanabe*
10:05 – 10:35	Recent Development of ENEA Lithium Metal Battery Project *W. H. Henderson, J.H. Shin, G. B. Appetecchi, F. Alessandrini, S. Passerini*
10:35 – 10:55	Research and Development of All-Solid-State Lithium Polymer Batteries - Degradation Analysis and Fabrication of High-voltage, High-capacity batteries *S. Seki, Y. Kobayashi, H. Miyashiro, A. Yamanaka, Y. Mita, T. Iwahori*
10:55 – 11:15	**Coffee**
APPLICATIONS *continued*	chairperson: **F. Krok**
11:15 – 11:45	Dip-coating of battery materials by deposition of nanoparticles on polymer-conditioned surfaces *I. Besenhard, A. Basch, B. Gollas, J.-H. Han, K. Leitner, K.-C. Möller, M. Winter*
11:45 – 12:05	Cellulose Derivatives as Lithium Ion Conductor *M. Chelmecki, W. H. Meyer, G. Wegner*
12:05 – 12:35	Electroanalytical Characterisation of Nonaqueous Proton Conducting Gel Containing Dodecatungstophosphoric Redox Centres for Applications in Supercapacitors *P. J. Kulesza, A. Lewera, G. Z. Zukowska, W. Wieczorek, M. Chojak, K. Miecznikowski*
12:35 – 12:45	**CLOSING**
13:00 – 13:45	**Lunch**

CONTENTS

LECTURES

1. A Spectroscopic Study of Proton Conducting Polymer Membranes Based on PVdF/PAN Blends.
   A. Martinelli, A. Matic, P. Jacobsson, L. Börjesson, M. A. Navarra, S. Panero, B. Scrosati 105
2. Ab initio Studies on Complexation of Anions to Neutral Species
   P. Johansson, P. Jacobsson 27
3. Bringing Light to Polymer Electrolytes: the Light-Emitting Electrochemical Cell
   L. Edman 53
4. Brønsted Acid-Base Ionic Liquids and Ion Gels as Proton Conducting Nonaqueous Electrolytes
   Md. A. B. H. Susan, A. Noda, M. Watanabe 99
5. Cellulose Derivatives as Lithium Ion Conductor
   M. Chelmecki, W. H. Meyer, G. Wegner 123
6. Conductivity and Structure of Crystalline Polymer Electrolytes
   P. G. Bruce, Y. Andreev 15
7. Determination of the lithium transference number in PEO-DME-$LiClO_4$ modified with alumina powder of different surface acidity.
   M. Ciosek, M. Siekierski 75
8. Development of Polymeric Gel Electrolytes Containing Magnesium Salt and Ionic Liquid
   N. Yoshimoto, T. Shirai, M. Morita 47
9. Dip-coating of battery materials by deposition of nanoparticles on polymer-conditioned surfaces
   J.O. Besenhard, A. Basch, B. Gollas, J.-H. Han, K. Leitner, K.-C. Möller, M. Winter 121
10. Effect of High Pressure CO_2 on the Structural and Electrical Properties of ORMOCERS-APE Systems Based on Zr and Al.
    V. Di Noto, K. Vezzù, M. Vittadello, S. Lavina, A. Bertucco 71
11. Electroanalytical Characterisation of Nonaqueous Proton Conducting Gel Containing Dodecatungstophosphoric Redox Centres for Applications in Supercapacitors
    P. J. Kulesza, A. Lewera, G. Z. Zukowska, W. Wieczorek, M. Chojak, K. Miecznikowski 125
12. Electrochromism in Visors and Goggles, Electrolytes for Electrochromic Applications
    J. Stevens 55
13. Facile Preparation of Organoboron-based Ion Conductive Polymers
    T. Mizumo, K. Sakamoto, N. Matsumi, H. Ohno 79
14. Free Volume and Conductivity in Polymer Electrolytes: A Temperature and Pressure Dependent Study
    S. J. Pas, M. D. Ingram, K. Funke, A. J. Hill 91
15. From Plastic Li-Ion to Plastic Li Metal Cells Operating at Room Temperature
    L. Sannier, R. Bouchet, M. Chami, S. Grugeon, J-M. Tarascon 113
16. Improved Lithium Ion Transport in Polyelectrolytes
    M. Forsyth, N. Byrne, C. Tiyapiboonchaiya, P. Howlett, D. R.MacFarlane 31
17. Increasing lithium ion in electrolyte materials through the use of additives
    N. Byrne, J.M. Pringle, C. Tiyapiboonchaiya, D. R. MacFarlane, M. Forsyth 73
18. Influence of the Plasticizer Contents on the Properties of HEC Based Solid Polymeric Electrolytes
    G.O. Machado, H.C.A. Ferreira, A. Pawlicka 61
19. Inorganic-Organic Hybrid Protonic Polymeric Materials for Fuel Cells Based on Polycondensed and Organically Cross-Linked Sulfonyl- and Styrene Functionalized Alkoxysilanes
    S. Jacob, C. Poinsignon, M. Popall 101
20. Ion Transport Properties of Lithium Ionic Liquids and Ion Gels
    H. Shobukawa, H. Tokuda, M. Watanabe 49
21. Ionic Liquids as New Salts for Polymer Electrolytes; the Scope and Prospects
    M. Watanabe 43
22. Ionic Solids - a New Class of Fast Ion Conductors
    I. Adebahr, D. R. MacFarlane, M. Forsyth 45
23. Lithium Ion Conducting Channel as Solid-State Electrolytes
    L. G. Scanlon, L. R. Lucente, W. A. Feld, G. Sandi, P. Balbuena, A. Turner 17
24. Lithium Migration Property of Phase-separated Polymer Gel Electrolyte
    Y. Saito, K. Hirai, T. Sakai, S. Murata, K. Kii 41
25. MD Simulation of the Crystalline Short- and Long- Chain Systems $(LiPF_6)_{1-X}\cdot(Li_2SiF_6)_X\cdot PEO_6$
    D. Brandell, I. Thomas, H. Kasemägi, A. Liivat, A. Aabloo 23

26. Model Composite Polymer Electrolytes Containing Triphenylborane
M. Marcinek, G. Z. Żukowska, W. Wieczorek 81
27. Modelling Defect-Assisted Conductivity in Organic Ionic Plastic Crystals
A. J. Hill, S. J. Pas, M. Forsyth, D. R. MacFarlane 29
28. Modelling of Conductivity in Composites with Random Resistor Networks
M. Siekierski, K. Nadara 67
29. Molecular Modelling Studies of Polymer Electrolytes for Power Sources
P. B. Balbuena, E. J. Lamas, Y. Wang 25
30. Nanocomposite Polymer Electrolytes Based on Poly(oxyethylene) and Cellulose Nanocrystals
F. Alloin, M. A. S. Azizi Samir, W. Gorecki, A. Dufresne, J.-Y. Sanchez 69
31. New Insights into Structural and Electrochemical Properties of Anisotropic Polymer Electrolytes
D. Golodnitsky, E. Livshits, R. Kovarsky, E. Peled, S. H. Chung, S. Suarez, S. Greenbaum 37
32. NMR Studies of Mass Transport in High Acid Content Fuel Cell Membranes Based on PBI/Phosphoric Acid
S. H. Chung, L. Durantino, J.R. P. Jayakody, H. Zhang, L. Xiao, B. Benicewicz, S.G. Greenbaum 95
33. NMR Studies of Mass Transport in Polymer Electrolytes for Batteries and Fuel Cells
S. G. Greenbaum 83
34. NMR Studies on Diffusion of Individual Ions of Lithium-salt doped Room Temperature Ionic Liquids correlating with the Ionic Conductivity
K. Hayamizu, H. Nakagawa 51
35. Overcoming performance limitations of membrane-electrode assemblies for direct methanol fuel cells
P. Zelenay 93
36. Polyacrylonitrile-Molybdenum Disulfide Polymer Electrolyte Nanocomposites
G. González, E. Benavente, M. A. Santa Ana 59
37. Polymer Electrolyte Single-Ion Conductors with Decoupled Li^+ Motion
A. M. Mayes, S.W. Ryu, S. Kumar, Y. Shao-Horn 21
38. Polymer Electrolyte with Large Temperature-Dependent Conductivity for Novel Electrochromic Imaging
N. Kobayashi, M. Nishimura, H. Ohtomo 57
39. Polymer Electrolytes Based on Poly(N-Ethylethylenimine) and Poly(N-Methylethylenimine)
R. Frech, G. A. Giffin, R. Sanders, J. Eisenblätter, D. T. Glatzhofer 39
40. Polymer-in-Salt Electrolytes Based on Acrylonitrile and Butyl Acrylate Copolymers
E. Zygadlo-Monikowska, Z. Florjanczyk, W. Wieczorek, N. Langwald, A. Tomaszewska 35
41. Prediction of Methanol and Water Fluxes Through a Direct Methanol Fuel Cell Polymer Electrolyte Membrane
S.S. Sandhu, R.O. Crowther, J.P. Fellner 103
42. Properties of Highly Pigmented Electrolytes with Large Porosity for Rechargeable Li-Polymer Batteries
J. Schulz, M. Popall, B. Olsowski, C. Cronauer 77
43. Proposal of a New Actuator Using Ion Gel Driven at Low Voltage under Atmospheric Condition
S. Nanjo, M. Watanabe 115
44. Proton Conductors for Low Humidity Conditions
T. Rager, M. Schuster, A. Noda, K.-D. Kreuer, J. Maier 97
45. Quantitative Infrared Studies of PEO Based Electrolytes
J. E. Furneaux, A. M. McCoy, V. Seneviratne, R. Frech 85
46. Radiotracer Diffusion and Ionic Conduction in the Polymer Electrolyte $PEO_{30}NaI$
S. Obeidi, B. Zazoum, N.A. Stolwijk 87
47. Recent Development of ENEA Lithium Metal Battery Project
W. H. Henderson, J.H. Shin, G. B. Appetecchi, F. Alessandrini, S. Passerini 117
48. Relaxation of Ions and Dipoles in LiTFSI Salt-in-Polymer and Polymer-in-Salt Electrolytes
J. R. Dygas, M. Marzantowicz, F. Krok, A. Lasinska, Z. Florjanczyk, A. Affek, E. Zygadlo-Monikowska 89
49. Research and Development of All-Solid-State Lithium Polymer Batteries - Degradation Analysis and Fabrication of High-voltage, High-capacity batteries
S. Seki, Y. Kobayashi, H. Miyashiro, A. Yamanaka, Y. Mita, T. Iwahori 119
50. Solid Polymer Electrolytes Prepared From a Hyper-Branched Graft Polymer Using Atom Transfer Radical
M. Higa, Y. Fujino, T. Koumoto, R. Kitani, S. Egashira 63
51. Stability Study of PEMFC Ionomers through Model Molecules Mimicking Polymer Repeat Units
M. Maréchal, J. Guindet, J.-Y. Sanchez 107
52. Study of Ion Conduction Mechanism in Ordered Poly(Ethylene Oxide) Based Polymer Electrolytes
E. Livshits, R. Kovarsky, D. Golodnitsky, E. Peled 19
53. Synthesis and Electrochemical Characterization of Novel Nanocomposite Polymeric Membranes
G. Sandí, R. Kizilel, K. A. Carrado, N. Castagnola 65
54. Synthesis and Structural Characterization of Two New Siloxanic Proton Conducting Membranes
V. Di Noto, M. Vittadello, S. Lavina 109

55. Synthesis, Molecular Structure, Microphase Stability And Conduction Mechanism in Solvent-Free Low-Dimensional Copolymer - Li Salt Systems with High Ambient Conductivity
J. Liu, Y Zheng, Y-P. Liao, G. Ungar, P. V. Wright 33
56. The Influence of The Solvent Composition on the Viscosity, Glass Temperature and Vibrational Spectra in PC-H_3PO_4 Anhydrous Electrolytes
G. Z. Żukowska, K. Nadara, K. R. Jeffrey, J. R. Stevens 111

POSTERS

1. A Fully Polymeric Proton Conductor Based on Benzimidazole-Functionalized Polysiloxanes
C. Persson, P. Jannasch 129
2. A Spectroscopic, Thermal, and Conductivity Study of Branched Poly(ethylenimine) – Sodium Triflate complexes.
N. M. Rocher, R. Frech 131
3. Activating effect of boron trifluoride on the ionic conductivity of lithium carboxylates
A. Affek, A. Tomaszewska, E. Zygadło-Monikowska, Z. Florjańczyk 133
4. Brønsted Acid-Base and -Polybase Complexes as Electrolytes for Fuel Cells
H. Matsuoka, H. Nakamoto, M. Watanabe 135
5. Characterisation of new ormolytes for zinc Batteries
S. C. Nunes, V. de Zea Bermudez, M. M. Silva, S. C. Barros, M. J. Smith, R. A. Sá Ferreira, L. D. Carlos J. Rocha 137
6. Characterisation of sulfonated bisphenol-a-polysulfone
P. Genova-Dimitrova, C. Iojoiu, M. Maréchal, C. Poinsignon, J.-Y. Sanchez 139
7. Comparison between ab Initio results and crystallographic data in Ionomers.
C. Chauvin, I. Gautier-Luneau, C. Perez del Valle, F. Alloin, C.Iojoiu, J.Y. Sanchez 141
8. Conductivity studies on PMMA based proton conducting gel electrolytes
S.L. Agrawal, S. Pandey 143
9. Dependence of the proton conductivity and methanol permeability of a PVA based cation-exchange membrane on its water content
M. Higa, S. Egashira, K. Hatemura, N. Endo, K. Matsusaki 145
10. Design of Ion Conductive Ionic Liquid Domain using Phosphate Groups on DNA Strand
N. Nishimura, Y. Nomura, H. Ohno 147
11. Dielectric Study on the system PEG(400):LiTf and PEG(400):$MgTf_2$
M. Fredriksson, J. Carlsson, M. Furlani, I. Albinsson, B.-E. Mellander 149
12. Effect of lewis acids on the conductivity of polymer-in-salt type electrolytes
A. Tomaszewska, A. Affek, E. Zygadło-Monikowska, Z. Florjańczyk 151
13. Effects of minimal water content in lithium and potassium triflate-PEG400 systems
N. Saei, P. Siewert, S. Thernström, M. Furlani, I. Albinson, B.-E. Mellander 153
14. Electrochemical synthesis of polypyrrole in ionic liquids
J. M. Pringle, D. R. MacFarlane, G. G. Wallace, M. Forsyth 155
15. Electrolytes Based on PEO-Boronate Ester Polymers for Application in Electrochromic Windows
P.-Y. Pennarun, P. Jannasch, S. Papaefthimiou, P. Yianoulis 157
16. Electrorheological fluids based on polymer electrolytes
A. Krztoń-Maziopa, J. Płocharski 159
17. Electrorheological studies of polymer electrolytes in liquid crystalline matrix
M. Ciszewska, J. Płocharski 161
18. Free Volume Studies of Polymer–Ionic Liquid Mixtures
A. J. Hill, S. J Pas, S. Seki, M. Watanabe 163
19. High Frequency Dielectric Study on PEG400, PPG400 and the Statistical Copolymer P(EP)G 600
C. Stappen, M. Furlani, G. Niklasson 165
20. Improved conductivity measurements of fuel cell polymer electrolytes
M. Maréchal, J. Guindet, J.-P. Diard, J.-Y. Sanchez 167
21. In-situ impedance and optical study of crystallization and melting of PEO:LiTFSI polymer electrolytes
M. Marzantowicz, J.R. Dygas, F. Krok, A. Łasińska, Z. Florjańczyk, A. Affek 169
22. Intercalation of Polyacrylonitrile into Bentonite
E. Benavente, M. A. Santa Ana, G. González 171
23. Investigations on the ion transport mechanism in PVOH-based polymer gels
R. A. Vargas, I. Palacios, V. H. Zapata 173
24. Ion-conductive Properties of Mesoporous Silica-filled Composite Polymer Electrolytes
S. Igawa, Y. Tominaga, S. Asai, M. Sumita 175
25. Ion-Gels Prepared by Incorporation of Protic Ionic Liquids in Polymer Networks as Anhydrous Proton Conducting Non-aqueous Electrolytes
N. Ishibashi, Md. A. B. H. Susan, H. Nakamoto, M. Watanabe 177

26. Ion Transport Properties of Lithium Ionic Liquids and Ion Gels
H. Shobukawa, H. Tokuda, M. Watanabe 49
27. Ionic Conduction of Polyether-Based Electrolytes Under High-Pressure CO_2
Y. Tominaga, S. Hirahara, S. Asai, M. Sumita 179
28. Ionic Conductivity in the Crystalline Polymer Electrolytes PEO_6:$LiXF_6$, X=P, As, Sb
E. Staunton, A.M. Christie, Y. G. Andreev, P. G. Bruce 181
29. Li^+ transport in amphiphilic copolymer mixtures - the influence of copolymer sequencing.
Y-P. Liao, Y. Zheng, J. Liu, G. Ungar, P.V. Wright 183
30. Molecular dynamics simulation of the layered vanadium pentoxide/PEO/lithium-salt system
H. Kasemägi, A. Aabloo, B. Dunn, J. Thomas 185
31. New proton conducting composite membranes for polymer fuel cells
A. Magistris, A. Carollo, S. Grandi, C. Tomasi, P. Mustarelli, E. Quartarone 187
32. New salts based on lithium oligoether sulfate ester.
C. Chauvin, X. Ollivrin, F. Alloin, J-F.Le Nest, J.Y. Sanchez 188
33. Novel composite polymer-in-salt electrolytes based on PVdF matrix obtained with a solvent free technique.
M. Malinowska, J. Piekarska, M. Siekierski, G. Z. Żukowska 191
34. Novel "polymer in salt" electrolytes based on acrylonitrile – butyl acrylate copolymers and LiTFSI
A. Łasińska, A. Affek, J.R. Dygas, Z. Florjańczyk, F. Krok, M. Marzantowicz, A. Tomaszewska, E. Zygadło-Monikowska 193
35. Novel Composite Proton-Exchange Membranes (C-PEM) for Fuel-Cell Applications
E. Peled, T. Duvdevani, M. Philosoph, M. Rakhman, T. Feiglin 195
36. Nuclear Magnetic Resonance study of plasticized HEC/Lithium salt polymer electrolytes
L.V.S. Lopes, G.O. Machado, A. Pawlicka, J.P. Donoso 197
37. PEO based nano-composite solid polymer electrolytes containing copper salts
M.A.K.L. Dissanayake, P.A.R.D. Jayathilaka, B.-E. Mellander, I. Albinson 199
38. Performance of ionic liquids and ion gels as electrolytes in dye-sensitized solar cells
C. Matsuyama, R. Kawano, A. Sato, M. Watanabe 201
39. Physicochemical Properties and Structures of Room Temperature Ionic Liquids
H. Tokuda, K. Hayamizu, Md. A. B. H. Susan, M. Watanabe 203
40. Proposal of a New Actuator Using Ion Gel Driven at Low Voltage under Atmospheric Condition
S. Nanjo, M. Watanabe 115
41. Protic ion gels as proton conducting electrolyte under anhydrous condition
H. Nakamoto, M. Watanabe 205
42. Proton-conducting ionomers by chemical grafting reactions on arylene main chain polymers
B. Lafitte, L. E. Karlsson, M. Puchner, P. Jannasch 207
43. Protonic Conductors on the basis of polybenzimidazole (PBI) - H_3PO_4, Crosslinked membranes
R.Kalim, U.Maehr, A.Reiche 209
44. Protonic Conductors on the basis of polybenzimidazole (PBI) - H_3PO_4 membranes - Solid State NMR and Conductivity Study
C.Hughes, R.Kalim, S.Haufe, U.Maehr, B.Angerstein, M.Baldus, A.Reiche 211
45. Solid polymer electrolytes based on blends of poly(trimethylene carbonate) and poly(ethylene oxide)
M. M. Silva, S. C. Barros, D. N. Januário, A. Evans, M. J. Smith, J. R. MacCallum 213
46. Specific Charge Transport of an I^- / I_3^- Redox Couple in an Ionic Liquid and Ion gels
R. Kawano, M. Watanabe 215
47. Study on acidity and conductivities of systems consisting of [bmim][Cl] and an alcohol
E. Bogel-Łukasik, R. Bogel-Łukasik, U. Domańska-Żelazna 217
48. Supramolecular additives as a method to improve ionic transport properties in composite electrolytes based on lithium salts and PEO matrix.
M. Ciosek, M. Kalita, M. Bukat, M. Siekierski, A. Plewa, G. Rokicki, W. Wieczorek 219
49. Synthesis of novel lithium salt monomers based on sulfonamide and single-ion conductivity of their polymer electrolytes
S.I. Hwang, Md. K. Rahman, S. Tabata, M. Watanabe 221
50. The Synthesis of a New Family of Aluminum-Based Anion Receptors and the Study of Their Effects on Ion Conductivity in Liquid Electrolytes
Y. M. Lee, J.-E. Seo, N.-S. Choi, W.-H. Seol, J. A. Lee, J.-K. Park 223
51. Transparent Chitosan Based Polymer Electrolites
S. Fuentes, J. Retuert, G. González 225
52. Zwitterion effect in polyelectrolyte gels based on lithium methacrylate-N,N-dimethyl acrylamide copolymer
J. Sun, D.R. MacFarlane, M. Forsyth 227

9th International Symposium on Polymer Electrolytes

Lecture Abstracts

Conductivity and Structure of Crystalline Polymer Electrolytes

Peter G. Bruce and **Yuri Andreev**
School of Chemistry, University of St. Andrews, KY16 9ST Scotland, UK
e-mail: **p.g.bruce@st-and.ac.uk**, tel (+) 44 1334 463825, fax (+) 44 1334 463808

A number of structures of crystalline polymer electrolytes have been solved with the help of the simulated annealing method for *ab initio* structure determination from powder diffraction data [1]. Establishing the structures of poly(ethylene oxide)$_6$:$LiXF_6$, X=P, As, Sb [2-3] led to the recent discovery that ionic conduction can occur in the crystalline phase of these materials [4-5]. This challenged the established view that conduction occurred exclusively in amorphous materials above their glass transition temperature and that crystalline complexes were insulators. The 6:1 crystalline complexes mentioned above not only conduct but do so better than the analogous amorphous phases [4] (Fig.1).

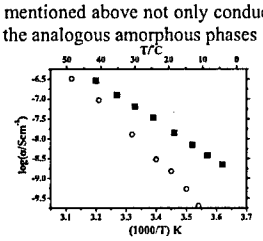


Fig. 1 Ionic conductivity of crystalline (squares) and fully amorphous (circles) phases of P(EO)$_6$:$LiSbF_6$

The conduction mechanism in amorphous polymer electrolytes relies on relatively slow local solvent reorganization (segmental motion) which limits the level of conductivity that can be achieved. Indeed, despite strenuous efforts, the maximum conductivity (10^{-4} Scm^{-1} at 25°C) in such amorphous polymer electrolytes has remained too low for many applications. In contrast relatively higher conductivities may be possible for crystalline systems.

Further investigation of the crystalline materials has shown an increase in ionic conductivity with reduction of molecular weight of the crystalline polymer electrolyte.

Although the pure 6:1 crystalline complexes are interesting because they support ionic conductivity, the level of conductivity is not high! However, we have found that it is possible to raise the conductivity to a significant degree by modifying the 6:1 complexes. Various strategies will be discussed. For example replacing a proportion of the $LiXF_6$ salt with a different Li salt leads to conductivity 2 orders of magnitude higher, Fig.2. By modifying the system still further, yet higher conductivities may be achieved.

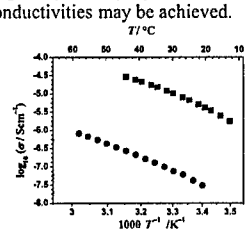


Fig. 2 Ionic conductivity of pure (circles) and doped (squares) P(EO)$_6$:$LiAsF_6$.

References

[1] Y.G. Andreev, P. Lightfoot, P.G. Bruce Chem Commun (1996), p. 148.

[2] G.S. MacGlashan, Y.G. Andreev, P.G. Bruce Nature **398** (1999), p. 792.

[3] Z. Gadjourova, D. Martin y Marero, K.H. Andersen, P.G. Bruce Chem. Mater. **13** (2001), p. 1282.

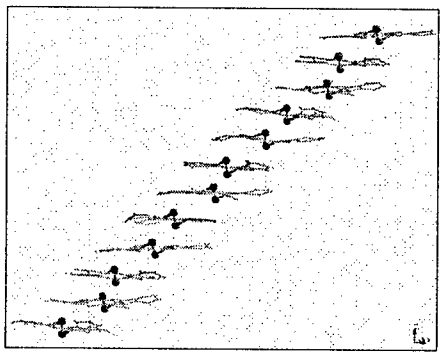
[4] Z. Gadjourova, Y.G. Andreev, D.P. Tunstall, P.G. Bruce Nature **412** (2001), p. 520.

[5] Z. Stoeva, I. Martin-Litas, E. Staunton, Y.G. Andreev, P.G. Bruce J. Am. Chem. Soc. **125** (2003), p. 4619.

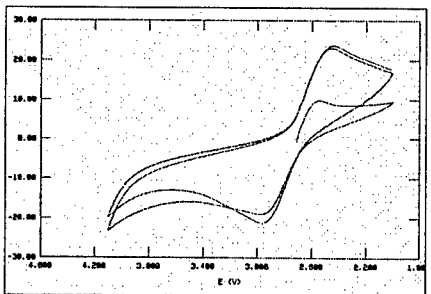
Lithium Ion Conducting Channel as Solid-State Electrolyte for Rechargeable Lithium Batteries

L. G. Scanlon, L. R. Lucente, W. A. Feld, G. Sandí, P. Balbuena, and A. Turner
[a]Air Force Research Laboratory, Energy Storage & Thermal Sciences Branch, Wright-Patterson Air Force Base, OH 45433; [b]University of Dayton Research Institute, 300 College Park, Dayton, OH 45469; [c]Department of Chemistry, Wright State University, Dayton, OH 45435; [d]Chemistry Divison, Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 40439; [e]Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208
e-mail: **lawrence.scanlon@wpafb.af.mil**, tel 937-255-2832, fax 937-656-7529

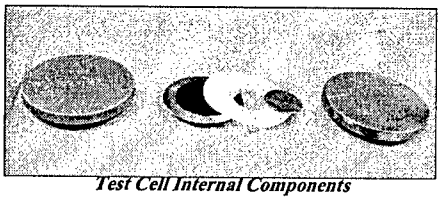
Theoretical calculations have been used in the development of a lithium ion conducting channel as a solid-state electrolyte for rechargeable lithium batteries. Results of ab initio and molecular dynamics calculations illustrate the importance of molecular self-assembly in channel formation based on a large array of molecules of dilithium phthalocyanine (Li_2Pc). Four calculated crystalline structures, as possible candidates for the ionically conducting channels, are compared to experimental X-Ray spectra of Li_2Pc. These same structures are to be considered for explaining the irreversible structural change of Li_2Pc at 200°C as demonstrated through small angle X-ray scattering. In addition, the importance of an asymmetric structure will be discussed in terms of facilitating ionic connectivity between Li_2Pc and a solid-state MnO_2 cathode. Experimental cyclic voltammograms will be shown which demonstrates that Li_2Pc functions as a solid-state lithium ion conducting channel.



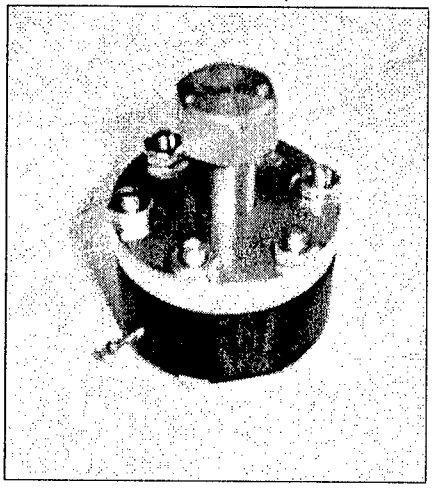
Molecular Dynamics Calculations
Lithium chain along the [5,5,7] direction
Li – Li: 5.84 – 6.88 A



Cyclic voltammogram of $Li/Li_2Pc/MnO_2$ cell at 75°C, scan rate 280 μV/s



Test Cell Internal Components



Monday, August 23
10:30 - 10:50

Study of ion conduction mechanism in ordered poly(ethylene oxide) based polymer electrolytes.

E. Livshits[1], R. Kovarsky[1], D. Golodnitsky[1,2], E. Peled[1]
[1]*School of Chemistry, Tel Aviv University,*
[2]*Wolfson Applied Materials Research Center, Tel Aviv 69978, Israel*

Introduction

The possibility of using polymer electrolytes (PE), as the basis of high energy-density batteries was first recognized by Armand about two decades ago and is a driving force behind the research performed on these materials. Most of the research on new polymer electrolytes has been guided by the principle that ion transport is strongly dependent on local motion of the polymer in the vicinity of the ion. In contrast to this, it has been recently shown by us that ionic conductivity in the static, ordered environment of the crystalline phase can be greater than that in the equivalent amorphous material above the glass transition point. In this work we present the effect of salt anion on the mechanism of ion transport in semicrystalline and amorphous PEs.

Experimental

The electrolytes were prepared from poly(ethylene oxide) (P(EO)) with incorporation of different lithium salts by casting from acetonitrile solution on teflon tray. All handling of PEs took place under an argon atmosphere in a VAC glove box with water content < 10 ppm. A high precision compact-load Motorized Horizontal Test Stand MH-100BA tester for tensile strength measurements was used for stretching the polymer electrolyte films.

Results and discussion

In all the electrolytes studied, including semicrystalline complexes of poly(ethylene oxide) (PEO) with different salts, such as, lithium iodide, lithium trifluoromethanesulfonate (LiTF) and lithium trifluoromethanesulfonimide (LiTFSI), stretching induced longitudinal DC conductivity enhancement was observed, in spite of the formation of more ordered polymer electrolyte (PE) structure. It was found that the more amorphous the PE, the less its lengthwise conductivity is influenced by stretching. The results of our investigation suggest that ionic transport occurs preferentially along the PEO helical axis, at least in the crystalline phase, and the rate-determining step of the lithium ion conduction in LiI:$P(EO)_{20}$, LiTF:$P(EO)_{20}$ and LiTFSI:$P(EO)_{16}$ polymer electrolytes below T_m is "interchain" hopping. As it was expected there is an influence of stretching rate on conductivity enhancement: the higher the stretching rate of PE the lower the conductivity enhancement.

Polymer Electrolyte Single-Ion Conductors with Decoupled Li^+ Motion

Anne M. Mayes*[1], Sang-Woog Ryu[1], Sundeep Kumar[2] and Yang Shao-Horn[2]
Department of Materials Science and Engineering[1] and Department of Mechanical Engineering[2]
Massachusetts Institute of Technology, Cambridge, MA 02139
*e-mail: **amayes@mit.edu**, tel (+) 1-617-253-3318, fax (+) 1-617-452-3432

Introduction

At high discharge rates, lithium batteries fitted with "dry" polymer electrolytes suffer from reduced capacities arising from gradients in salt concentration that form in the electrolyte, causing mass transfer overpotential. One strategy to address this problem is to employ a single-ion conductor as the electrolyte. By tethering the counterion to the polymer backbone, salt concentration gradients can be eliminated, and the full current carried by mobile lithium cations. This gain in Li transference number is typically accompanied by a drop in the A.C. conductivity, however, due to strong ion pairing interactions.

Improving the performance of single-ion polymer electrolytes requires a means to promote charge dissociation, thereby enhancing Li^+ mobility. One approach is to employ bulky, low charge density counterions. For example, Florjanczyk et al. reported significant enhancements in the conductivity of single-ion gel polymer electrolytes by incorporating BF_3, which complexed with the carboxylate anions of the polymer network [1]. Recently, we demonstrated that equivalent charge separation could be achieved by spatially isolating the carboxylate counter ion in a secondary polymer domain adjacent to the ion-conducting (PEO-based) domain, using self-assembling block copolymer electrolytes of tailored molecular architecture [2]. Still, room temperature conductivities for these materials remain in the range of 10^{-6} S/cm.

It appears that further enhancement in conductivity for "dry" macromolecular Li^+ conductors may require structures that encourage both ion dissociation and lithium ion motion that is decoupled from the local segmental motions of the PEO chains. In a series of recent papers [3], Wright and coworkers reported room temperature conductivities up to 10^{-3} S/cm for electrolytes incorporating an amphiphilic, PEO-based copolymer component doped with $LiClO_4$ or $LiBF_4$. Alkyl side chains of these copolymers induce self-assembly, thereby generating fast conduction pathways for Li^+. Interestingly, the high reported conductivities are obtained only after thermal cycling.

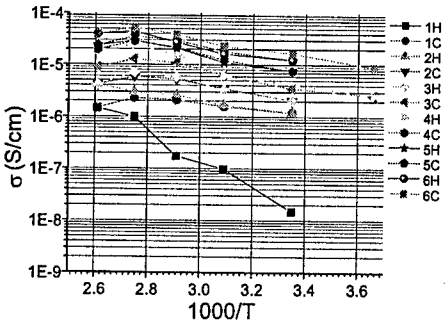
Inspired by the work of Wright, we have undertaken the development of a self-assembling amphiphilic copolymer electrolyte that exhibits single-ion conduction and Li^+ motion decoupled from the PEO segmental dynamics. This paper will report our initial results of this effort.

Experimental

An amphiphilic, self-assembling single-ion polymer electrolyte was made by free radical copolymerization of methacrylic acid and a methacrylate macromonomer of oligo(ethylene oxide) end-capped with octadecane, followed by lithiation. Some systems were complexed with BF_3 to enhance ion dissociation. Conductivities were measured by impedance spectroscopy as a function of temperature. Wide-angle and small-angle x-ray scattering (WAXS and SAXS) and differential scanning calorimetry (DSC) were employed to characterize morphology.

Results and discussion

Conductivity data for a single-ion conductor complexed with BF_3 and having a Li:EO ratio of 1:17 are shown in the figure below, for 6 heating-cooling cycles. While initial conductivity is quite low at room temperature (~10^{-8} S/cm) and strongly temperature dependent, upon cooling, a hysteresis in the conductivity is seen, with little temperature dependence, similar to the findings by Wright [3]. A steady increase in conductivity is found with further thermal cycling, achieving a value of $>10^{-5}$ S/cm at room temperature after 6 cycles.



Conclusions

The amphiphilic single-ion conductors show substantial promise as new electrolyte materials for battery applications involving high-current densities. Ongoing work aims to uncover the origin of the conductivity hysteresis. This work was supported by ONR grant no. N00014-02-1-0343.

References

[1] Z. Florjanczyk et al., Electrochim. Acta **45** (2000), p. 3563
[2] S.-W. Ryu et al., J. Electrochem. Soc., submitted.
[3] F. Chia et al., Electrochim. Acta **48** (2003), p. 1939 and references therein.

Monday, August 23
11:30 - 12:15

MD simulation of the crystalline short- and long-chain systems $(LiPF_6)_{1-x}\bullet(Li_2SiF_6)_x\bullet PEO_6$

Daniel Brandell, **Josh Thomas**
Department of Materials Chemistry, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden.
Heiki Kasemägi, Anti Liivat and Alvo Aabloo
Institute of Physics, Tartu University, Tähe 4, 51010 Tartu, Estonia.
e-mail: **josh.thomas@mkem.uu.se** tel: (+46) 18 471 3763 fax: (+46) 18 513548

Introduction

It has been found that significantly increased Li-ion conductivities are obtained in the crystalline systems $LiXF_6{\cdot}PEO_6$ for X = P, As and Sb if the monovalent anions are partially substituted by some divalent anion; typically, SiF_6^{2-}, *e.g.*, [1]. Moreover, crystal structures have been published for the unsubstituted systems, showing them to involve cylindrical channels, each comprising pairs of hemi-helical PEO chains [2-3]. These channels are found to host the Li ions, while the XF_6^- ions occupy the interchain space. These various structure determinations and conductivity measurements used a range of different PEO chain-lengths in the MW-range 500-100.000. On the basis of these experiments, we have embarked upon a series of MD simulations to explain this enhancement of ionic conductivity in the SiF_6^{2-}-doped system, and to shed some light on the effect of methyl chain-termination in these materials.

The calculations

Molecular dynamics (MD) simulations have been made of the systems $LiPF_6.PEO_6$, both for infinite PEO chains and for methyl-terminated polymer chains of MW *ca.* 1100 (~22 EO units). Simulations have also been made for the corresponding SiF_6^{2-}-doped system, charge-compensated by the insertion of extra Li^+ ions. Simulations have also been made under imposed electric field to reproduce the situation experienced by the electrolyte in a battery application. These simulations have used periodic boundary conditions and an Ewald summation to treat long-range electrostatic forces. Each simulation has involved an equilibration period of 200ps at constant volume (NVT thermostat), followed by an NpT simulation for a sampling period of 1ns.

All simulations have been made on our local PC-Wulfkit cluster comprising 4 Pentium III's and 4 Athlon MP 2000+ double-processor nodes, using the software package DL_POLY.

Results and discussion

Our simulations have revealed the same modes of Li-ion hopping along the hemi-helical channels in $LiPF_6.PEO_6$ as were seen in earlier simulations [4], and supported by Stoeva *et al.* [5]. The lithium ions move through four-fold coordination sites in the double hemi-helix. It is shown that the dynamics of the PEO chain is intimately coupled to lithium-ion motion. Chain-ends are also seen to influence ion mobility in the undoped compound.

The ionic conductivity in the system is also greatly influenced by doping with a divalent anion; the interstitial Li ions giving rise to enhanced ion mobility. The effect of the methyl end-groups in the low MW PEO system is also analyzed. They are shown to play a decisive role in controlling Li-ion hopping between different chains.

Surprisingly, we have been unsuccessful in accurately reproduce the detail of the published crystal structures [3]. Generally, our simulations exhibit a higher lithium-oxygen coordination number, which would suggest a polymer backbone configuration somewhat diffrent from that determined by diffraction. This can be related to the fact that the derived experimental models neglect chain-end effects, and/or that our MD potentials are inadequate in describing the rather unusual polymer conformation found at some points along the PEO chains in this system.

Conclusions

Although clear discrepancies are found between the results of the earlier diffraction study of the $LiPF_6{\cdot}PEO_6$ structure and our MD simulation, these differences can be rationalised in terms of neglect of the effect of chain-ends and the use of inadequate polymer potentials. The enhancement effect of divalent-anion doping on the Li^+ transport mechanism has also been demonstrated.

References

[1] P.G. Bruce, *Private communication.*
[2] G.S. MacGlashan, Y. Andreev & P.G. Bruce, *Nature,* **398** (1999) 792.
[3] Z. Gadjourova, D.M. y. Marero, K.H. Andersen, Y. Andreev & P.G. Bruce, *Chem. Materials,* **13** (2001) 1282.
[4] ISPE-8 Proceedings, Santa Fe, USA, 2002.
[5] Z. Stoeva, I. Martin-Litas, E. Staunton, Y. Andreev & P.G. Bruce, *JACS,* **125** (2003) 4619.

Monday, August 23
12:15 - 12:45

Molecular modeling studies of polymer electrolytes for power sources

Perla B. Balbuena, E. J. Lamas, and Y. Wang
Department of Chemical Engineering, Texas A&M University, College Station, TX, 78743
e-mail: **balbuena@tamu.edu**, tel (+) 979-845-3361, fax (+) 979-845-6446

Introduction

Understanding the mechanisms of ionic and molecular transport in polymer electrolyte phases is crucial for the development of improved power sources. Here we consider two systems of current interest: transport of oxygen and protons through hydrated nafion in the vicinity of a catalyst phase, and ionic transport in a polyphosphazene membrane that should be a good ionic carrier but a bad water carrier.

Theoretical methods such as density functional theory and molecular dynamics simulations permit us to elucidate details of ionic and molecular transport which can be used for the design of alternative membranes and/or devices.

Theoretical

We use density functional theory calculations on representative models of the systems to determine the force field parameters (bond lengths, charges, force constants) for classical molecular dynamics (MD) simulations. The MD simulations provide information about structural and dynamical properties of systems involving thousands of atoms.

Results and discussion

The conformation of the nafion membrane over Pt nanoparticles deposited on a carbon substrate is examined under various degrees of hydration. Similarly, the water structure in this restricted environment is closely analyzed and its diffusivity is calculated and compared with those of bulk water and water diffusing in a polymer medium. In addition, we calculate the diffusion of O_2 through the hydrated nafion medium, and especially the possible mechanisms of transport in the cathode side of low-temperature fuel cells.

In a second study, we investigate the transport of lithium ions through polyphosphazene membranes. We are mainly interested in determining the competition of adsorption of lithium ions on membrane sites with lithium hydration. The possible existence of contact ion pairs, solvent-separated and solvent-shared ion pairs, is thoroughly investigated.

Conclusions

It is found that Nafion interacts strongly with the catalytic metal nanoparticles directing the side chain towards the catalyst surface. The flow of oxygen is observed to take place through the hydrophobic sites of the membrane. Water adopts a well-ordered structure on the exposed graphite surface and solvates the hydrophilic sites of the membrane.

In the polyphosphazene membranes, ether-oxygen and nitrogen atoms of the membrane compete with water oxygen atoms for binding to the lithium ions. At conditions of slat concentration and humidity expected for lithium-water batteries, it is found that the nitrogen atoms are the strongest adsorption points to bind lithium ions.

Monday, August 23
12:45 – 13:15

Ab initio studies on complexation of anions to neutral species

Patrik Johansson and **Per Jacobsson**
Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, SWEDEN
E-mail: **patrikj@fy.chalmers.se**, Tel (+46) 31 772 3178, Fax (+46) 31 772 2090

Introduction

Various ways to enhance the ion conductivity of non-aqueous electrolytes and especially solid polymer electrolytes have been explored. Special focus should be put on increasing the low cation transference numbers, which are major obstacles for real battery applications. The origin of the low cation conductivity is to be found in the way the salt is solvated – by the cation coordinating strongly to the functional groups of the polymers (*e.g.* the ether oxygens of PEO). As a new concept aiming at increased ion conductivity as well as increased cation transference numbers we tentatively suggested anion encapsulation [1]. This uses the host-guest scheme to create supermolecules, traditionally used for cation guests (*e.g.* crown ethers), but here with anion guest species and neutral hosts based on oriented dipoles. Here we present a more thorough study of differently sized neutral host molecules with and without anion guests. In order to accomplish this we use neutral cryptand molecules *e.g.* the $(H_3BN)_4[(CH_2)_n]_6$, (n=3-6) [2] to enclose simple anions (F^-, Cl^-, BF_4^-, and ClO_4^-). As general sub-tasks crucial for obtaining a correct picture of anion enclosure and the resulting properties we have identified: i) conformer generation, ii) geometry optimization and energy minima verification, iii) evaluation and decomposition of formation energies, and iiii) internal dynamics of the resulting complexes. In addition we have computed the lithium ion affinities of the resulting supramolecular anions.

Computational

The first task has been completed by exploring the conformational space of all the hosts using molecular mechanics calculations prior to any quantum mechanical (QM) calculations. A systematic study of the conformational space rapidly becomes insurmountable even for medium sized molecular systems. We therefore applied a Monte-Carlo based conformation search using the MMFF force field. To address the second stage the resulting structures were geometry re-optimized using MMFF. Subsequently, unique structures from each sub-study were transferred to full QM optimisations using HF methods employing the standard 6-31G* basis set (HF/6-31G*). The computational task of ~100 atoms is easily handled with the resources at hand. However, as all the structures are very flexible and have flat potential energy landscapes the geometry optimisations are very time-consuming due to the large number of iterations needed; a typical case demanded ~80 cycles. Only for the most stable structures for each sub-study analytical second derivatives with respect to nuclear displacements were evaluated to validate the energy minima. To address the third task single-point (SP) energy calculations using larger basis sets (6-311+G*) and electron correlation (B3LYP hybrid functional) were performed for the most stable host-guest combinations. The formation energies were obtained at each QM computational level as the differences in total electronic energies (ΔE_{el}) between the supermolecules formed and the separate components, all in their minimum energy geometries. In order to in more depth analyse interactions Morokuma-Kitaura decompositions of the supermolecules were performed as implemented in GAMESS [3]. The interaction energies are this way interpretable in physically relevant terms: Pauli repulsion, Coulombic attraction, polarisation, and charge-transfer. The dynamics of the host-guest complexes as revealed by SP or MD calculations provide data on the escape possibilities and associated barriers for the anion guests.

Results

We show the formation of supramolecular anions to be possible using a wide range of host-guest combinations. The relative energy contributions from the decomposition analysis are also presented. Overall the most stable complexes are obtained using the F^- anion and some complexes have remarkable lithium ion affinities – as low as ~58% of that computed for the PF_6^- anion is obtained. For the larger hosts the smaller anions become less shielded towards the lithium cation and the escape barrier becomes crucial.

Conclusions

The use of neutral encapsulating agents can provide stable anionic supramolecular complexes with very low lithium ion affinities. The chloride anion, together with an appropriate host, may be a practical choice for better lithium ion conducting electrolytes – especially as LiCl is both inexpensive and obtainable as a highly pure salt.

References

[1] P. Johansson Electrochimica Acta **48** (2003).
[2] K. Worm, F. P. Schmidtchen, A. Schier, A. Schäfer and M. Hesse Angew. Chem. Int. Ed. Engl. **33** (1994).
[3] M. W. Schmidt *et al.* J. Comp. Chem. **14** (1993).

Modeling Defect-Assisted Conductivity in Organic Ionic Plastic Crystals

Anita J. Hill,[1,2] Steven J. Pas,[3] Maria Forsyth,[4] Douglas R. MacFarlane[2]
[1] CSIRO Manufacturing and Infrastructure Technology, Private Bag 33, South Clayton MDC, Victoria 3169, Australia
[2] Monash University, School of Chemistry, Wellington Rd, Clayton, Victoria 3800, Australia
[3]University of Münster, Institute of Physical Chemistry, Corrensstrasse 30, 48149 Münster, Germany
[4]Monash University, School of Physics and Materials Engineering, Wellington Rd, Clayton, Victoria 3800, Australia

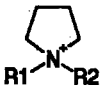
e-mail: anita.hill@csiro.au, tel (+61) 3 9545-2777, fax (+61) 3 9544-1128
e-mail: stpas@uni-muenster.de, tel (+49) 251 83 23433 fax (+49) 251 83 29138
e-mail: maria.forsyth@spme.monash.edu.au, tel (+61) 3 9905-4939, fax (+61) 3 9905-4940
e-mail: douglas.macfarlane@sci.monash.edu.au, tel (+61) 3 9905-4540, fax (+61) 3 9905-4597

Introduction

Ion conductive organic plastic crystals have generated much interest due to the observation of significant conductivities in their plastic crystal phases [1-3]. Their combined mechanical and transport properties make them suitable for use in lithium batteries and other electrochemical devices.

Quaternary ammonium based salts coupled with symmetric anions have been investigated by Ikeda *et al.* [2] and many of these exhibit plastic crystal phases as determined by thermal analysis and nuclear magnetic resonance (NMR) measurements. Some of these compounds have also shown substantial ionic conductivity in their high temperature plastic phases (*e.g.* Et_2NH_2Br has $\sigma = 2.5 \times 10^{-7}$ S cm^{-1} at 127°C). Conductivity has been attributed to a vacancy migration model, although no direct evidence for this has been presented.

Organic ionic plastic crystal (OIPC) electrolytes based on pyrrolidinium ring cations:



where R groups are R_1 = methyl or ethyl, and R_2 = methyl, ethyl, propyl *etc.*, and anions including bis(trifluoromethanesulfonyl) amide (TFSA), hexafluorophosphate (PF_6) and tetrafluoroborate (BF_4), have displayed conductivities as high as 10^{-3} S cm^{-1} at 20°C [3,4]. These materials have interesting phase behaviour with several solid-solid phase transitions often being observed which are, at least partially, attributed to the onset of increasing degrees of rotational disorder and finally complete isotropic rotation of the ions *on their lattice sites*. The latter leads to high diffusivities in many cases and thereby also to high ionic conductivities and plastic mechanical behaviour.

Recently we have investigated a simple tetramethyl ammonium dicyanamide compound (Me_4NDCA) as an archetypal plastic crystal electrolyte for which the crystal structure could be readily determined. This, together with an NMR second moment analysis, was used to understand the nature of the rotational and translational motions which lead to high plasticity and conductivity [5]. Conductivity appears to be dominated by the Me_4N cation diffusion and this is correlated to the number of vacancies as determined from the relative fraction of mobile cation species observed in the NMR linewidth measurement.

Scanning electron microscopy (SEM) of pyrrolidinium BF_4 and TFSA compounds has suggested that different degrees of plasticity occur in these materials and that this is manifested in the SEM by the observation of dislocations and parallel slip planes [6]. In cases where plastic behaviour is not expected (eg. N-methyl N-butyl pyrrolidinium BF_4) the SEM indicates a more well defined crystalline material with slip planes noticeably absent. Most recently, rotator motions (rotational disorder) and defects (point and extended lattice defects), as directly probed using orthoPositronium, have been shown to aid ionic conduction in plastic crystal phases of N,N dimethyl, pyrrolidinium TFSA and N,N methyl, ethyl pyrrolidinium TFSA [7].

The semi-stable orthoPositronium (oPs) atom was first shown to be sensitive to solid-solid phase transitions in molecular crystals by Cooper *et al.* [8]. Subsequent work in molecular plastic crystals attributed this to oPs trapped in defects, and depending on the system, and its phase behaviour, these defects could be vacancies, divacancies or dislocations [9]. From this work, it was established that a relationship existed between the oPs lifetime (τ_{oPs}) and defect size [9]. The statistical weight of the oPs component (I_{oPs}) reflects the formation probability and trapping rate, the latter of which is proportional to the defect concentration. A range of organic plastic crystals have been studied by positron annihilation lifetime spectrscopy (PALS). The PALS data as a function of temperature through the solid-solid phase transformations has been used to derive vacancy formation energies for these systems [10].

Defect assisted conductivity has been discussed for organic ionic plastic crystal (OIPC) systems [2,3,11] and has been supported by electron microscopy [6], (NMR) [5] and (PALS) [7]; however, a model relating chemistry (ion size, symmetry, interionic interaction) to defect structure and conductivity has not been proposed. Such a model would facilitate design of optimum OIPC systems.

Experimental

N-methyl N-ethyl pyrrolidinium TFSA was synthesized as described in reference [3]. The compounds were prepared by a metathesis reaction from the corresponding iodide salt. PALS measurements were performed using an automated EG&G Ortec fast-fast coincidence system. Two identical samples were placed on either side of a ^{22}NaCl/mylar source and the sample-source sandwich was placed in a dry nitrogen atmosphere inside a temperature-controlled chamber. OrthoPositronium pickoff annihilation characteristics (τ_{oPs}, I_{oPs}) were measured. A source correction was used based on the oPs source component for control samples of annealed pure aluminium. Error bars represent the population standard deviation for five spectra. Conductance measurements have been described elsewhere [4]. Briefly, a locally designed multi-sample conductance cell with cylindrical sample compartments was employed. During the conductivity run, the temperature was ramped up at a steady rate of 0.2°C/min under the control of a Shimaden Digital Temperature controller. Conductivity was obtained by measuring the complex impedance of the cell between 20 Hz and 1 MHz using a HP 4284A Impedance Meter.

Results and discussion

Calculation of defect size and concentration from the oPs annihilation characteristics (τ_{oPs}, I_{oPs}) is described elsewhere [9, 10]. The oPs lifetime is related to the radius of the defect by:

$$\tau = \frac{1}{2}\left(1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\frac{2\pi R}{R+\Delta R}\right)^{-1} \quad (1)$$

where τ is the oPs lifetime (in ns) and ΔR has been found empirically to be 0.166 nm [12]. From the calculated defect radius, the average defect volume, V_h, is obtained from:

$$V_h = \frac{4}{3}\pi R^3 \quad (2)$$

assuming spherical defects.

Using the Nernst-Einstein equation in the Cohen-Turnbull framework [13], the ionic conductivity may be described as:

$$\sigma = CT^{-1/2}\exp\left(-\frac{\gamma V^*}{V_f}\right) \quad (3)$$

where γ is an overlap factor in the hard sphere model of volume available for transport, V^* is the minimum critical volume needed for diffusion to occur, C is a fitting parameter which includes the charge carrier number, and V_f is the average free volume per molecule at the measurement temperature T. If the average free volume (V_f) is equal or proportional to the defect volume as measured by PALS (V_h), a semi-logarithmic plot of $\sigma T^{1/2}$ versus the inverse of average free volume should give a linear function with a slope of $-\gamma V^*$.

Figure 1 shows the relationship of conductivity to the inverse of defect volume as measured by PALS (V_h in cm^3 mol^{-1}) as a function of temperature in three phases of the organic ionic plastic crystal N,N'methyl, ethyl pyrrolidinium TFSA. Previous work [3] on this OIPC has shown that a solid-solid transition from phase III to phase II appears at 14°C. Another broad transition from phase II to phase I begins at about 20°C, reaching a peak at 45°C. These transitions are evident in Figure 1 as changes in slope. This remarkable result indicates that defect volume is very important in mediating ionic transport. This result also suggests that the types of defect and/or the ionic species participating in transport vary depending on the phase of the OIPC. Both point and extended lattice defects are known to occur in N,N'methyl, ethyl pyrrolidinium TFSA [7].

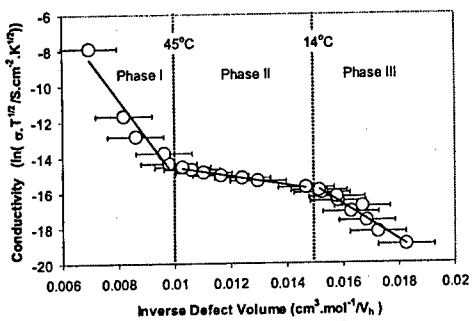


Figure 1 Semi–logarithmic plot of $\sigma T^{1/2}$ versus the inverse of defect volume (or free volume) as measured by PALS, V_h. Lines are best-fit for each phase, with linear regression coefficient $R^2 > 0.93$.

References

[1] EI Cooper, CA Angell, *Solid State Ionics* **18/19** (1986) 570.

[2] M Tansho, Y Furukawa, D Nakamura, R Ikeda, *Ber Bunsenges Phys Chem* **96** (1992) 550.

[3] DR MacFarlane, J Huang, M Forsyth, *Nature* **402** (1999) 792.

[4] DR MacFarlane, M Forsyth, *Advanced Materials* **13** (2001) 957.

[5] AJ Seeber, M Forsyth, CM Forsyth, SA Forsyth, G Annat, DR MacFarlane *Phys Chem Chem Phys* **5** (2003) 2692.

[6] J Efthimiadis, M Forsyth, DR MacFarlane *J Mat Sci* **38** (2003) 2393.

[7] AJ Hill, J Huang, J Efthimiadis, P Meakin M Forsyth, DR MacFarlane *Solid State Ionics* **154** (2002) 119.

[8] AM Cooper, G Deblonde, BG Hogg *Phys Lett* **29A** (1969) 275.

[9] M Eldrup D Lightbody, JN Sherwood *Chem Phys* **63** (1981) 51.

[10] M Eldrup NJ Pedersen, JN Sherwood *Phys Rev Lett* **43** (1979) 1407.

[11] PJ Aalarco, Y Abu-Lebdeh, M Armand, *Angew Chemie Intl Ed* **43** (2004) 141.

[12] YC Jean, *Microchem J* **42** (1990) 72.

[13] M Ratner, in Polymer Electrolyte Reviews, Eds. JR MacCallum, CA Vincent, (Elsevier: London, 1987) 18.

Improved lithium ion transport in polyelectrolytes

Maria Forsyth[1], Nolene Byrne[1], Churat Tiyapiboonchaiya[2], Patrick Howlett[2] and Douglas R.Macfarlane[2]

School of Physics and Materials Engineering and School of Chemistry
Australian Centre for Nanostructured Electromaterials
Monash University, Wellington Rd., Clayton, Victoria Australia 3800

High lithium ion transport numbers are critical in the quest for the high rate capability and long cycle life lithium batteries. The combination of high Li^+ transport and good mechanical properties, as found in polymers or polymer gel materials, would be the ideal combination. Single ion conducting polyelectrolyte systems have been studied by a number of workers in recent years, however typically these materials are hampered by poor dissociation of the lithium ion from the anionic backbone. In the present work improved materials have been developed whereby the lithium ion diffusivity (and hence conductivity) is enhanced through the use of dissociation enhancers such as nano-particulate oxide fillers, ionic liquids and zwitterionic compounds. Combinations of these dissociating additives results in even higher lithium ion diffusivity, with more than an order of magnitude improvement in conductivity observed, although an optimum concentration of these is apparent. The use of mixtures of ionic liquids and zwitterions as solvents has also been found to lead to improvements in the electrochemical behaviour of the Li/Li+ redox couple including improved rate characteristics and stability on cycling. The mechanism by which these additives enhance lithium ion conductivity and electrochemical properties is being investigated through the use of multinuclear NMR spectroscopy.

Synthesis, molecular structure, microphase stability and conduction mechanism in solvent-free low-dimensional copolymer – Li salt systems with high ambient conductivity

J. Liu, Y Zheng†, Y-P. Liao, G. Ungar and P. V. Wright
Dept. of Engineering Materials, University of Sheffield, Mappin St. Sheffield, S1 3JD UK
e-mail:p.v.wright@sheffield.ac.uk; tel (+) 44 0114 2225499, fax (+)44 0114 2225943

Introduction

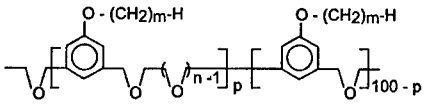
Recent work [1-3] has shown that systems of lithium salts in self-organised lamellae of amphiphilic polymers **I** (CmOn) with interphases of block copolymer **II** -{-[$(CH_2)_4$-O-]$_{-23}$-$(CH_2)_{12}$-O-}- give films having ambient conductivities $\sigma \sim 10^{-3}$ S cm^{-1} in impedance and extended DC polarisations between Li electrodes.

Experimental

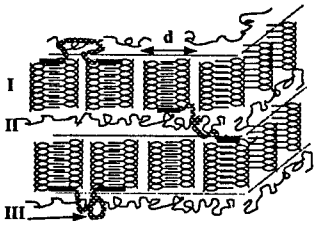
Two synthetic 'Williamson' procedures for **I** in which the halogen functions were *either* borne by the tetraethoxy monomer (Method X) *or* by the sidechain-bearing monomer (Method Y) have been compared. ^{1}H NMR was performed using a Bruker AC250. GPC was carried out using a Hewlett-Packard 1090. DCS was performed on a Du Pont 910. FTIR was carried out using a Perkin-Elmer spectrum 2000. Simultaneous SAXS and WAXS measurements over ambient to 50°C were carried out using a MAR Research Image plate with 5 or 10 minute exposure times. Impedance measurements over the range 1-1MHz with an amplitude of 0.1V were carried out with Solartron 1287A ECI / 1250 FRA using ITO coated glass electrodes with a cellulose acetate or polyethylene spacer. Molecular dynamics modelling was performed with Cerius^2 molecular dynamics software.

Results and discussion

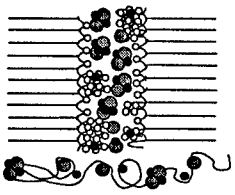
Extensive ^{1}H NMR studies have shown that optimum conductivities are obtained when **I** is a copolymer of CmO5-CmO1 where p, the mol% of C16O5 units may be as low as 20%. The side groups lengths, m, are typically 16 or 18 but optimum sub-ambient conductivities have been observed with mixed side



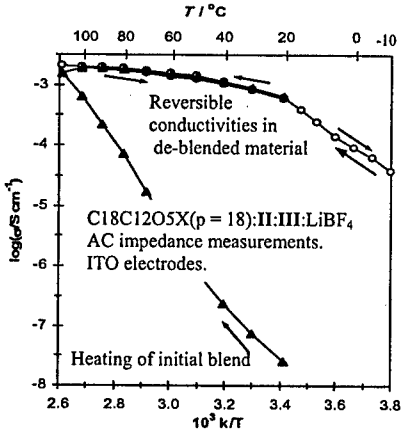
chain copolymers, m = 12 / 18 (50%/50%). The amphiphilic monomers and product promote self-condensation of side chain-bearing monomers in a heterogeneous reaction forming CmO1 units. However, Method X gave polyether and ester links whereas Method Y gave pure polyether as shown.



The stabilisation of the **I** / **II** interface ('wetting') is essential for ion transfer. Excellent reproducibility of conductivities have been obtained by incorporation of ABA block copolymer **III** H$(CH_2)_{18}$ [$(CH_2)_4$-O-]$_{-50}$-$(CH_2)_{18}$H in small proportion (~20% of **II**). SAXS and molecular dynamics modelling suggest that, in



ionophobic CmO1 segments, salt exists mainly as quadrupoles, essentially *decoupled* from the polyether and in the copolymer separated ions occur in the (minor proportion) of helical CmO5 segments. We propose low activation energy conduction in an applied field could proceed by a Li^+



hopping process between uncoupled aggregates,.

.....Li_2A_2 $Li_3A_2^+$ ⇀ Li_2A_2 → Li_2A_2 Li_2A_2 $Li_3A_2^+$ ..

Similar conductivity plots are observed from either Method X or Method Y mixtures.

Acknowledgments We are grateful to EPSRC and ESA for supporting this work.

References

[1] F.Chia, Y.Zheng, J.Liu, N.Reeves, G.Ungar, P.V.Wright, Electrochim. Acta, 2003, **48**, 1939-1951.

[2] Y. Zheng, J.Liu,Y-P. Liao, G.Ungar, P.V. Wright, J. Chem. Soc. Dalton Trans., in press.

[3] J.Liu, Y.Zheng, Y-P.Liao, G.Ungar, P.V.Wright, J. Chem. Soc. Faraday Trans., in press.

Polymer-in-Salt Electrolytes Based on Acrylonitrile and Butyl Acrylate Copolymers

E. Zygadło-Monikowska, Z. Florjańczyk, W. Wieczorek, N. Langwald, A. Tomaszewska
Warsaw University of Technology, Faculty of Chemistry, ul. Noakowskiego 3, 00-664 Warsaw, Poland
e-mail: **ewazyga@ch.pw.edu.pl**, tel. (+48-22) 660-5582, fax (+48-22) 660-7279

Introduction

There is great interest in the development of highly efficient energy sources for applications such as cellular phones, mobile computers, and also vehicles with electrical propulsion. Among them considerable attention is put on the development of lithium and lithium-ionic batteries. The application in lithium batteries of polymeric electrolytes instead of liquid ones provides a possibility of designing devices of large surfaces and any shape. The high share of anions in the electric charge transfer, which is connected with a drop in the cell power, is a considerable problem.

Electrolytes with high salt content are one of the ideas for obtaining electrolytes of relatively high anion immobilization. Such electrolytes, called polymer-in-salt-electrolytes (PISE) were first described by Angell et al. [1] and then many works were presented, concerning mainly polyacrylonitrile (PAN) based systems [2]. For these electrolytes it is assumed that the ion mobility is not directly connected with the segmental relaxation of the polymer matrix chains and results from the high degree of ion aggregation.

In this work we present the results of studies on the conductivity of a number of PISE as a function of salt concentration, type of lithium salt anion and chemical structure of the polymer matrix.

Experimental

The membranes of electrolytes were obtained by film casting from a solution in acetonitrile of the polymer and following lithium salts: LiI, $LiN(CF_3SO_2)_2$, $LiClO_4$, $LiAlCl_4$, $LiCF_3SO_3$, $LiPF_6$ and $LiBF_4$. Acrylonitrile (AN) and butyl acrylate (BuA) copolymers [poly(AN-*co*-BuA)], poly(butyl acrylate) and poly(methyl methacrylate) (PMMA) were used as polymer matrixes. The salt concentration varied from 10 to 80 mol% with respect to the number of AN, BuA or MMA monomeric units in the copolymer/polymer. Samples were investigated by DSC, FTIR and impedance spectroscopy. Impedance spectra were obtained over a frequency range of $10^{-2} - 10^5$ Hz.

Results

Due to the fact that PAN shows solubility in a small number of aprotic solvents such as DMSO and DMF, which are very difficult to remove during the membrane preparation, we propose the use of poly(AN-*co*-BuA) as the matrix. These polymers are well soluble in acetonitrile, a volatile solvent easily removable.

The studies carried out show that the conductivity of the electrolytes investigated increases with an increase in the salt concentration until reaching a maximum. The location of the maximum is characteristic for a given type of salt and polymeric matrix. Recently, we reported ionic conductivity for the system containing $LiN(CF_3SO_2)_2$ and poly(AN-*co*-BuA) [3].

Figure 1 shows the differences in the conduction ability of systems containing poly(AN-*co*-BuA) (2:1) and various lithium salts.

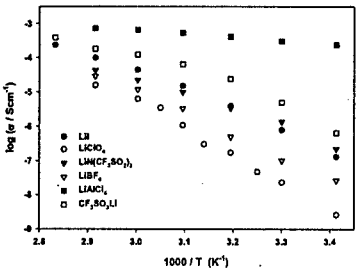


Figure 1. Ionic conductivity of electrolytes based on poly(AN-*co*-BuA) (2:1) with different lithium salts (1.2 moles of Li^+ per 1 mole of AN monomeric units in the copolymer).

DSC studies show that in a majority of composites studied, the introduction of a salt to the polymer causes a considerable decrease in the glass transition T_g value indicating its strong plasticizing effect. Figure 2 presents the dependence of T_g on the salt concentration for the poly(AN-*co*-BuA) and LiI system.

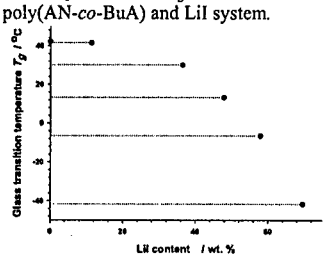


Figure 2. Glass transition temperature T_g of electrolytes comprising poly(AN-*co*-BuA) and LiI depending on the salt concentration.

References

[1] C.A.Angell, C.Liu, E. Sanchez Nature **362** (1993), p. 137
[2] A.Ferry, L.Edman, M.Forsyth, D.R.MacFarlane, J.Sun Electrochim. Acta, **45** (2000), p. 1237
[3] Z.Florjańczyk, E.Zygadło-Monikowska, A. Affek, A. Tomaszewska, A. Łasińska, M.Marzantowicz, J.R.Dygas, F.Krok, submitted to Solid State Ionics.

Acknowledgements

This presentation is based upon work in part supported by the US European Office of Aerospace Research and Development, Air Force Office of Scientific Research, Air Force Research Laboratory, under Contract No. F61775-01-WE01.

Monday, August 23
18:10 - 18:40

New Insights Into Structural and Electrochemical Properties of Anisotropic Polymer Electrolytes

D. Golodnitsky[1,2], E. Livshits[1], R. Kovarsky[1], E. Peled[1]
[1]School of Chemistry, Tel Aviv University,
[2]Wolfson Applied Materials Research Center, Tel Aviv 69978, Israel
S.H. Chung[3], S. Suarez[3], S. Greenbaum[3]
[3]Physics Department, Hunter College of CUNY, New York, NY 10021, USA
[1]School of Chemistry, Tel Aviv University,
[2]Wolfson Applied Materials Research Center, Tel Aviv 69978, Israel

Introduction

The classical polymer electrolyte consists of organic macromolecules (usually polyether polymer) that are doped with inorganic salts. The salt-solvent mixing entropy consists mainly of two components: translational and configurational. The incorporation of salts into the polymer inevitably reduces the freedom of polymer-chain motion, thus causing a reduction in translational entropy. The configurational entropy of mixing depends mainly on the available coordination sites in the polymer, which are affected by the spacing between sequential coordination sites and by steric effects. In polymer electrolytes, the conduction sites are not fixed; instead, the solvent site positions appropriate for cation bonding vary with time. The segmental movement of the polymer chain creates new sites and removes old ones. Therefore, the conductivity, which is coupled to the micro-Brownian motion of segments of the polymer chains above the glass- or melting-transition temperature, rises significantly with increasing amorphousness of the polymer electrolyte. On the basis of these observations, the ionic conductivity has been thought to be closely connected with increased flexibility of the chains and rapid relaxation of the host polymer.

In contrast to this, we have recently demonstrated experimentally the preferential ion transport along the ordered helical axis in LiX-PEO polymer electrolytes, where X is an anion, such as iodide, trifluoromethanesulfonate, hexafluoroarsenate, bis(oxalato)borate and trifluoromethanesulfonimide. It is fundamental to our understanding of transport processes in solid-state materials that enhaned conductivity comes about as a result of permanent conducting pathways for the movement of ions. This study is directed toward the demonstration of the possibility of making a rational design of novel polymer materials with extraordinary electrical properties on the basis of structural ordering.

Experimental

The electrolytes were prepared from poly(ethylene oxide) (P(EO)) with incorporation of different lithium salts by casting from acetonitrile solution on a teflon tray. All handling of PEs took place under an argon atmosphere in a VAC glove box with water content < 10 ppm. Ordered PEs were prepared either by stretching or casting under a magnetic field (MF).

Results and discussion

The relationship between the alignment of polymer helices and improvement of ion conduction properties of polymer electrolytes has been determined by scanning electron microscopy, XRD, NMR spectroscopy and electrochemical means. It was found that solution casting and drying under an applied magnetic field enhances both intra- and interchain ion mobility by about one order of magnitude in the direction perpendicular to the film plane. The magnetic -field effect is even more pronounced in polymer electrolytes with incorporated diamagnetic and paramagnetic nano-fillers. The lithium transference number increases from 0.2 to 0.6 in MF-oriented polymer electrolytes. The resistance of the solid-electrolyte interphase decreases by more than one order of magnitude in the lithium cells comprising these MF-oriented polymer electrolytes. We believe that the ability to create anisotropic shape-persistent, but flexible materials with preferred orientation is promising not only for getting higher power in lithium batteries but for many other nanoscale technological applications.

Polymer Electrolytes Based on Poly(N-Ethylethylenimine) and Poly(N-Methylethylenimine)

Roger Frech, Guinevere A. Giffin, Rebecca Sanders, Jördis Eisenblätter, Daniel T. Glatzhofer
Department of Chemistry and Biochemistry, University of Oklahoma
Norman, OK 73019-0370 USA
e-mail: **rfrech@ou.edu.** tel (+) 405 325 3831 fax (+) 405 525 6111

Introduction

The low room temperature conductivities of poly(ethylene oxide)-based polymer electrolytes, originating in the cyrstallinity of these materials, has driven a search for alternative polymer-salt systems. Poly(ethylenimine), PEI, is structurally similar to poly(ethylene oxide) but with the backbone oxygen atom replaced with an NH group. However, polymer polymer electrolytes based on PEI also yield low conductivities [1]. The highly crystalline nature of poly(ethylenimine), due in part to hydrogen bonding interactions, can be reduced or completely eliminated by the substitution of side chains on the backbone nitrogen atom. Tanaka et al. have described conductivity and thermal data of poly(N-methylethylenimine), PMEI, containing dissolved $LiClO_4$ and $LiCF_3SO_3$ [2]. A comparative thermal, vibrational, and conductivity study of PMEI with $NaCF_3SO_3$ and $LiCF_3SO_3$ has also been reported [3]. The recent synthesis of poly(N-ethylethylenimine), PEEI, affords an excellent opportunity to investigate the effect of substituent alkyl chain length on relevant properties of an ethylenimine-based family of polymer electrolytes. This paper will discuss a comparative study of PEEI, and PMEI complexed with $LiCF_3SO_3$, $NaCF_3SO_3$ and $LiBF_4$ using FTIR, DSC, and impedance techniques.

Experimental

PMEI was synthesized following a procedure previously reported [3]. PEI was converted to PEEI by reductive amination using $NaBH_4$/acetic acid. FTIR spectra were collected on a Bruker IFS66V system under vacuum at a 1 wavenumber spectral resolution. Thermal data were measured with a Mettler DSC 820 calorimeter by cycling the samples between –150 and 25°C. An HP 4192A impedance analyzer was used to collect impedance data over the range 5 Hz to 10 MHz. Samples for conductivity measurements were contained between stainless steel electrodes.

Results and discussion

The onset of the glass transition temperature of PEEI occurs at –102°C (-97°C midpoint), measured in a heating cycle. In contrast, the onset of Tg in PMEI is at –95°C (-91°C midpoint). This result is expected because the ethyl group attached to the nitrogen atom of the PEEI backbone "sweeps out" a slightly larger volume than does the substituted methyl group of PMEI. Therefore, there is a slight increase in the flexibility of the PEEI backbone relative to PMEI which is reflected in the slightly lower Tg of the former.

Vibrational spectroscopic studies show that the region 800-900 cm^{-1} contains modes that are dominated by C-N stretching and backbone CH_2 rocking motions; the frequencies and intensities of these bands are sensitive to the coordinative interactions of the lithium ions with the nitrogen atoms. Modes in the region from 1000 to 1200 cm^{-1} consist of a complex mixture of backbone stretching motions and CH_3CH_2 or CH_3 substituent motions; these modes reflect the difference in the side chain substituents. The ionically associated species in both systems are dominated by $Li^+CF_3SO_3^-$ contact ion pairs, with no striking differences between the two polymer hosts.

Preliminary conductivity data of the 10:1 (N:Li molar ratio) PEEI-$LiCF_3SO_3$ complex shows slightly lower values compared with the conductivity of a 10:1 PMEI-$LiCF_3SO_3$ complex over the same temperature range. A more detailed comparative study at a number of salt compositions will be reported at the conference.

Conclusions

The presence of an ethyl group in PEEI as compared to the methyl group in PMEI appears to have only a slight effect on the thermal behavior of the two materials. The addition of $LiCF_3SO_3$ raises the Tg in both PEEI and PMEI, in accordance with behavior observed in other polymer-salt systems. The similarity of ionic association in both systems is expected because there should be little or no change of basicity in the backbone nitrogen atom.

References

[1] C. K. Chiang, G. T. Davis, C. A. Harding, Solid State Ionics **18 & 19** (1986) 300.
[2] R. Tanaka, T. Fujuta, H. Nishibayashi, S. Saito, Solid State Ionics **60** (1993) 119.
[3] R. A. Sanders, A. G. Snow, R. Frech, D. T. Glatzhofer, Electrochim. Acta **48** (2003) 2247.

Lithium Migration Property of Phase-separated Polymer Gel Electrolyte

[1]Yuria Saito, [1]Kenichi Hirai, [1]Tetsuo Sakai, [2]Shuuhei Murata, [2]Keisuke Kii
[1]*National Institute of Advanced Industrial Science and Technology*
1-8-31, Midorigaka, Ikeda, Osaka 563-8577 Japan
e-mail: yuria-saitou@aist.go.jp, tel (+81) 72 751 9618, fax (+81) 72 751 9714
[2]*Nitto Denko Corporation*
1-1-2, Shimohozumi, Ibaraki, Osaka 567-8680 Japan

Introduction

Many types of polymer gel electrolytes for lithium secondary batteries have been developed recently. They can be categorized into two types of form: a homogeneously swollen gel and a phase-separated gel. In the swollen gel, an electrolyte solution is dispersed into the polymer network on a molecular level. Ionic species randomly migrate in the homogeneous network influenced chemically and physically by the polymer chains. The phase-separated gel, on the other hand, is composed of a framework of porous polymer and an electrolyte solution which occupies the interconnected pores. Ionic species of carriers migrate in the solution in the linked pore pathways without the polymer effect on the molecular level.

When the phase separation occurs in the gel electrolyte composed of urea-containing polymer, we found anomalous high diffusivity of ionic species which surpasses that of the original electrolyte solution. This indicates the significance of phase condition control of the gel to obtain high ionic conductivity and structural stability. In this research, we elucidated the diffusion behavior of the polymer gel electrolyte associated with the phase condition by the observation of NMR echo signal behavior.

Experimental

1,2-cyclohexylene-bis[(methacryloyloxy)ethylureido] (CBMEU, $C_6H_{10}(NHCONHC_2H_4OCOC(CH_3)=CH_2)_2$, prepared by Itoh Oil Chemicals Co., Ltd) of an urea group-containing polymer were used as the starting polymer material. The lithium electrolyte solutions of 1.4 M $LiPF_6$ dissolved in the mixed solvents of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with 1:1 and 3:1, in mono solvents of propylene carbonate (PC) and EMC were mixed with the polymer with several mixing ratio to prepare the gel of different phase conditions. Diffusion behavior of ionic species was observed using the pulsed gradient spin-echo (PGSE) NMR technique with the probed nuclei of ^7Li (116.8 MHz) for the cation, ^{19}F (282.7 MHz) for the anion and ^1H (300.5 MHz) for the solvent species using a JBM-ECP300W spectrometer [1].

The echo signal changes reflect the morphological feature of the space for carrier migration. In case of linear change in log-plot of intensity as a function of $\delta^2\Delta$ (δ: pulse width of the gradient pulse, Δ: diffusion time), the diffusion coefficient of each species (D_{Li}, D_F, D_H) was estimated from the slope. When the echo attenuation deviates from the linear behavior, restricted diffusion model was considered to elucidate the morphological feature of the gel.

Results and discussion

Figure 1 represents the diffusion coefficient change of the gel, CBMEU-$LiPF_6$-EC/EMC(1:1) with changing the polymer fraction in the gel. With increasing the polymer concentration, the diffusion value first decreased due to the viscosity increase of the gel. However, D_{Li} abruptly increased at 10 wt% of polymer. D_F and D_H were also enhanced at 13 wt% of polymer. These increases reflect the phase separation of the gel. It is amazing that the enhanced D_{Li} and D_F were greater than those of the original electrolyte solution. We speculate that the solution component was separated out from the swollen gel with changing the solvent composition or solution concentration during the phase separation process. In case of the gel with a different solvent, restricted diffusion behavior observed which implies the existence of domain structures in the gel. This would be intermediate condition between the homogeneous and phase-separated gels.

Acknowledgement

This research is supported by Hayashi Memorial Foundation for Female Natural Scientists.

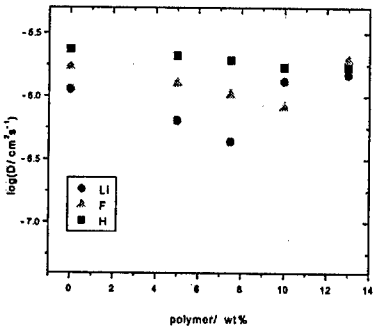


Figure 1 Diffusion coefficient change of gel of CBMEU-$LiPF_6$-EC/EMC(1:1) as a function of polymer concentration.

References

[1] Y. Saito et al., *J. Phys. Chem. B*, **107**, 8805 (2003).

Ionic Liquids as New Salts for Polymer Electrolytes The Scope and Prospects

Masayoshi Watanabe
Department of Chemistry & Biotechnology, Yokohama National University
Yokohama 240-8501, Japan
e-mail: **mwatanab@ynu.ac.jp**, tel +81-45-339-3955, fax +81-45-339-3955

Introduction

Ionic liquids are room temperature molten salts and of great interest as new electrolyte materials.[1] We have directed our attention to the combination of ionic liquids and polymers as new polymer electrolytes.[2] *In situ* radical polymerization of common vinyl monomers in these ionic liquids affords compatible combinations of the ionic liquids and the resulting network polymers[2] (Fig. 1). Completely compatible combinations are new polymer electrolytes and named "ion gels", which exhibit high ionic conductivities (typical room temperature conductivity: 10^{-2} Scm^{-1}). The high conductivities are caused by self-dissociating and ion-transporting abilities of the ionic liquids and by the decoupling of the ion transport and polymer segmental motion. If task-oriented properties, such as lithium ion conduction and proton conduction, are molecularly designed in the ionic liquids, the scope of the utility of ionic liquids and ion gels may greatly expand,.[3-5] In this talk, I will focus on the research on the design of task-oriented ionic liquids and ion gels, and the recent progress in our research group will be presented (Table 1).

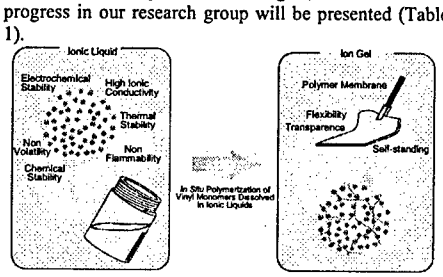


Fig. 1 Ion gels obtained by *in situ* polymerization of vinyl monomers dissolved in ionic liquids.

Results and Discussion

Conventional lithium salts have high melting points, mainly due to the strong electrostatic interactions. The introduction of Lewis basic ether ligands into super-weak anion structures remarkably reduces melting points of the lithium salts to give self-dissociating lithium ionic liquids.[3] Electrolyte properties of the resulting lithium ionic liquids and the ion gels are characterized.

We have recently found[4] that novel Brønsted acid-base ionic liquids, derived from a simple combination of a wide variety of organic amines with bis(trifluoromethane sulfonyl)imide, are anhydrous proton conductors and electroactive for H_2 oxidation and O_2 reduction at a Pt electrode under a non-humidifying condition, which shows the prospect of the use of protic ionic liquids as new materials for proton conductors at elevated temperatures.

Table 1 Important Chemistry and Application of Ionic Liquids and Ion Gels

Application Field	Properties to be Utilized	Chemistry to be Pursued
Lithium Polymer Battery	High ionic conductivity, Non-flammability, Non-volatility	Lithium-ionic conductivity
Double Layer Capacitor	Large double layer capacitance, High temperature stability	Capacity retention at low temperature
Fuel Cell	New media of proton conduction instead of water	Anhydrous proton-conducting membrane above 100 °C
Solar Cell	Non-volatility, Stability	Ion/electron mixed conduction
Actuator	Solidification of electrolytes, Non-volatility	Motility by electrochemical reactions
Electrochromics	Non-volatility, Stability	Reversible and durable electrochromic reactions

Electrons are also mobile in ionic liquids when a redox couples is dissolved in them at a high concentration. We have revealed that charge transport of an I^- / I_3^- redox couple in an ionic liquid nonlinearly increases with increasing the concentration by using microelectrode technique.[5] This anomaly of the charge transport at high concentrations of the redox couple with comparable $[I^-]$ and $[I_3^-]$ can be attributed to the exchange reaction of $I^- + I_3^- \rightarrow I_3^- + I^-$ and is quite suitable for an electrolyte in dye-sensitized solar cells.

A final example of applications of ion gels is an actuator. It is recently found that an electric double layer capacitor using an ion gel as an electrolyte exhibits bending displacement upon the electric polarization. The actuator can be operated under open atmosphere and a low applied voltage.

References

[1] A. Noda, K. Hayamizu, M. Watanabe, *J. Phys. Chem., B*, **105**, 4603 (2001).
[2] A. Noda, M. Watanabe, *Electrochim. Acta*, **45**, 1265 (2000).
[3] H. Shobukawa, H. Tokuda, M. Watanabe, *Electrochim. Acta*, in press (2004).
[4] (a) A. Noda, M.A.B.H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu, M. Watanabe, *J. Phys. Chem., B*, **107**, 4024 (2003). (b) M.A.B.H. Susan, A. Noda, S. Mitsushima, M. Watanabe, *Chem. Commun.*, **2003**, 938.
[5] R. Kawano, M. Watanabe, *Chem. Commun.*, **2003**, 330.

Ionic solids - a new class of fast ion conductors

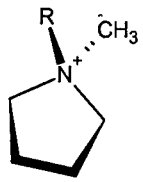
J. Adebahr[1*], D. R. MacFarlane[2] and M. Forsyth[1]
[1]School of Physics and Materials Engineering, and [2]School of Chemistry
Monash University, Clayton 3800, Victoria, Australia.
email: josefina.adebahr@spme.monash.edu.au

Abstract:
Solid state conductors are of interest in the growing area of electrolytes for electrochemical devices such as batteries, fuel cells, sensors and actuators. Ion conducting ceramics, polymer electrolytes, gels and glasses are materials that have been extensively investigated. Recently, the observation of fast-ion conduction in organic salts exhibiting rotator phases has led to an increased interest in these materials.[1]

The crystalline state of these materials is typically fully ordered at low temperatures, but as the temperature is increased they exhibit one or more solid-solid phase transitions, often due to the onset of different rotational motions. These transitions are usually associated with a large enthalpy and entropy increase. Some of these materials exhibit, in their highest temperature phase, plastic properties. In the plastic phase, the crystalline material flows readily under relatively low forces and can deform without fracture under stress.

Organic-based materials with multiple phase transitions and rotator phases include families of quaternary-ammonium-cations, imidazolium-cations and pyrrolidinium-cations.[3]

Salts based on N-alkyl-N-methyl-pyrrolidinium cations have been extensively explored in terms of phase behaviour, conductivity *etc.* The chemical structure of the salts, such as the choice of anion and/or the length of the alkyl chains, has been shown to greatly influence the properties of the materials. The iodide salts, for example, are usually solid at room temperature, exhibit fewer phase transitions and have a higher melting point, compared to salts based on anions with a more delocalised charge such as PF_6^-, BF_4^- or $N(SO_2CF_3)_2^-$. The melting point of the material decreases as the length of the alkyl group increases, up to a certain length (which is dependent on the choice of anion.



Doping these materials with a lithium salt has given more than 2 orders of magnitude increase in conductivity, and ^{7}Li NMR measurements reveal linewidths approaching those seen for liquids.[1] This suggests that these materials exhibits fast-ion-conduction properties, where the lithium ions are transported fast throughout the ionic matrix.

References:

1. D. R. MacFarlane, J. H. Huang, and M. Forsyth, Nature **402** (6763), 792 (1999).
2. J. Timmermans, J. Phys. Chem. Solids **18**, 1 (1961).
3. D. R. MacFarlane, P. Meakin, J. Sun, N. Amini, and M. Forsyth, Journal of Physical Chemistry B **103** (20), 4164 (1999).

Development of Polymeric Gel Electrolytes Containing Magnesium Salt and Ionic Liquid

Nobuko Yoshimoto, Takahiro Shirai and Masayuki Morita
Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering,
Yamaguchi University, 2-16-1 Tokiwadai, Ube 755-8611, Japan
e-mail:nobuko@yamaguchi-u.ac.jp, tel (+) 81-836-85-9213, fax (+) 81-836-85-9200

Introduction

Polymeric electrolyte that conducts magnesium ion (Mg^{2+}) is the key material for developing an all-solid rechargeable magnesium battery. We have recently proposed some polymeric gel electrolyte systems conducting Mg^{2+} at ambient temperature [1, 2]. Up to the present, it is generally accepted that such plasticizing materials as organic solvents are required to obtain high ionic conductivity at and below the ambient temperature [1-3]. In this paper, we report on a novel ionic gel system that consists of a polymer matrix dissolving magnesium salts and ionic liquids without any volatile organic solvents.

Experimental

Poly(ethylene oxide) monomethacrylate (PEM) and poly(ethylene oxide) dimethacrylate (PED) (Scheme 1 (a), PEM:PED = 3:1 by molar ratio) were used as prepolymers for the polymer matrix formation. The ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Scheme 1 (b), EMITFSI) or diethylmethyl(2-methoxyethyl) ammonium bis(trifluoromethylsulfonyl)imide (Scheme 1 (c), DEMETFSI), was used as a plastisizing reagent. $Mg[(CF_3SO_2)_2N]_2$ ($Mg(TFSI)_2$) as the electrolytic salt was dissolved in the ionic liquid. The mixture of the prepolymers and the ionic liquid was developed on an Al plate in a dry Ar atmosphere and solidified by photo-induced radical polymerization to yield cross-linked polymer matrix, poly(ethylene oxide)-modified poly(methacrylate) (PEO-PMA), containing ionic liquid dissolving $Mg(TFSI)_2$. The composition of the polymeric gel electrolyte is formulated as (PEO-PMA)-*a* mol % $Mg(TFSI)_2$/EMITFSI or DEMETFSI (*x*-*y*). The temperature dependence of the ionic conductivity was measured by an *ac* impedance technique (100 kHz to 1 Hz) in a temperature range of 20 – 60 °C.

Results and discussion

The obtained gel film was flexible and with proper mechanical strength. The results of thermal analysis (DSC) showed that the obtained gel film is stable in the temperature range of -150 °C to 150 °C. The ionic conductivity of the polymeric gel electrolyte depended on the content of the ionic liquid containing $Mg(TFSI)_2$. The composition of 80 wt. % of EMITFSI containing 20 mol % $Mg(TFSI)_2$ gave high conductivity of *ca.* 3.5 mS cm^{-1} at 60 °C.

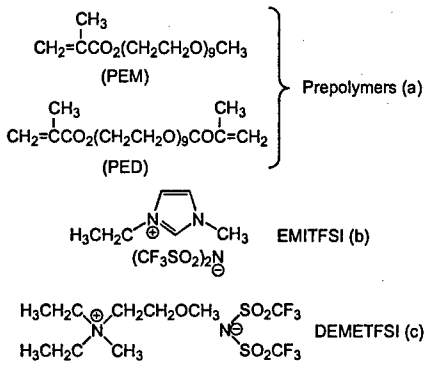
The mobile species in the polymeric gel sysytem was examined by a *dc* polarization method using Pt/Pt blocking and Mg/Mg non-blocking cells. The *dc* polarization of an Mg/Mg cell using the polymeric gel electrolyte proved that Mg^{2+} is mobile in the present polymeric system.

Acknowledgements

This work was financially supported by the Grants-in-Aid for Scientific Research (No. 15550164) from JSPS.

References

[1] M. Morita, N. Yoshimoto, S. Yakushiji, M. Ishikawa Electrochem. Solid-Stare Lett. **4** (2001), p. A177.
[2] N. Yoshimoto, S. Yakushiji, M. Ishikawa, M. Morita Electrochim. Acta **48** (2003), p. 2317.
[3] G. G. Kumar, N. Munichandraiah J. Power Sources **102** (2001), p. 46.



Scheme 1 Chemical structure of the prepolymers (a) and ionic liquid (b), (c).

Ion Transport Properties of Lithium Ionic Liquids and Ion Gels

Hitoshi Shobukawa, Hiroyuki Tokuda, and Masayoshi Watanabe

Department of Chemistry & Biotechnology
Yokohama National University and CREST-JST
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
e-mail: **d03ga116@ynu.ac.jp**, tel (+) 81 45 339 3955, fax (+)81 45 339 3955

Introduction

A wide variety of ionic liquids, also known as room temperature molten salts, have been investigated as new electrolyte materials for electrochemical systems. Since the first report on the air and water stable ionic liquids, there have been numerous attempts to find new ionic liquids by combining a wide variety of organic cations and anions. It is well known that ionic liquids, obtained by coupling imidazolium cation with fluorinated anions, have low melting points and high ionic conductivity. In this study, with a view to developing advanced electrochemical systems, we report the synthesis of ionic liquids having only lithium ion as the cationic species. We have also directed our attention to the combination of lithium ionic liquids and polymers and prepared a new polymer electrolyte for rechargeable lithium battery application. An insight into the relationship between the composition and ionic conductivity will be presented.

Experimental

Conventional lithium salts have high melting points, mainly due to the strong electrostatic interactions. However, a lithium salt of a large and super-weak aluminate anion[1] still have a much higher melting point than room temperature, and the ionic conductivity is very low even in the molten state. Strong Lewis acidic nature of Li^+ favors ion-pairing even in the molten state. The introduction of Lewis basic ether ligands groups into the weak anion structures remarkably reduces melting points of the lithium salts to yield self-dissociating lithium ionic liquids. Based on the concept, we recently reported the physicochemical properties of a series of lithium ionic liquids[2].

The new ion gels were comprised of lithium ionic liquids and tri-acrylate macromonomer (TA, mol. wt. = 8160, Dai-ichi Kogyo Seiyaku Co. Ltd). The ion gels were prepared by photo-initiated polymerization using 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator. Lithium ionic liquid concentrations in the polymer electrolytes were [lithium] / [ether oxygen] = 0.04-0.14, and thickness of the polymer electrolyte films was 200 μm.

Differential scanning calorimetry (DSC) measurements were performed on a Seiko Instruments DSC 220C in N_2 atmosphere. Glass transition temperatures were determined from DSC thermograms during the heating scans.

Temperature dependence of ionic conductivity was determined by the complex impedance method, using a computer-controlled impedance analyzer (Hewlett Packard 4192A) over a frequency range from 5 Hz to 13 MHz, under a 10 mV ac amplitude. The measurements were carried out with cooling from 353 K to 273 K at the intervals of 10 K, and the samples were thermally equilibrated at each temperature for at least 1.5 h prior to the measurements.

Results and discussion

The apparent degree of ionic dissociation[3] is relatively high, which indicates that the large number of ionic carrier contributes to the ionic ionic conduction in the lithium ionic liquids. Namely, the lithium ionic liquids have relatively high ionic activities.

DSC thermograms of the TA-lithium ionic liquid polymer electrolytes exhibit only one glass transition temperature (T_g). In the DSC thermograms of polymer electrolyte, the endothermic transitions were observed when the lithium ionic liquid concentrations were low. However the enthalpy change in the endotherms decreased with increasing in the lithium ionic liquid concentration. When [lithium] / [ether oxygen] was higher than 0.06, the polymer electrolytes became completely amorphous. With increasing in the concentration of the dissolved lithium ionic liquids, the T_g of polymer electrolytes are raised.

To accomplish the object of the study, we focus on the structure-property relationship for different combination of a polymer and a lithium ionic liquid. The unique propery of the system has been compared with the conventional polyether-base polymer electrolyte system, which is a typical example of a 'coupling system' between the structure and conduction relaxation times.

References

1) H. Tokuda, M. Watanabe, *Electrochim. Acta*, **48**, 2085, (2003)
2) H. Shobukawa, H, Tokuda, M.Watanabe, *Electrochim. Acta*, in press (2004)
3) A. Noda, K. Hayamizu, and M. Watanabe, *J. Phys. Chem. B*, **105**, 4603 (2001)

NMR Studies on Diffusion of Individual Ions of Lithium-salt doped Room Temperature Ionic Liquids correlating with the Ionic Conductivity

Kikuko Hayamizu[1] and Hiroe Nakagawa[2]
[1]National Institute of Advanced Industrial Science and Technology and [2]Yuasa Corporation
e-mail: **hayamizu.k@aist.go.jp**, tel (+)81-29-861-6295, fax (+)81-29-861-6295

Introduction

Room temperature ionic liquid (RTIL) is one of the important materials to use as an electrolyte for practical purposes from their attractive properties and many studies have been made from various viewpoints. Since the electrochemical studies have been devoted to the solution electrolytes where neutral solvents are included, we often encounter the difficulties to interpret various phenomena of the concentrated material where all the species are ions like RTILs. Previously we have applied NMR diffusion measuring methods to polymer electrolytes and find that the similar approach can be applied to RTILs, especially to the RTILs doping with the lithium salt. In this study five popular ionic liquids with doping lithium salt are studied. The cation is 1-ethyl-3-methyl imidazolium [emim] with anions of $[BF_4]$, $[(CF_3SO_2)_2N]$ and $[(C_2F_5SO_2)_2N]$ and the cation is 1-butyl-3-methyl imidazolium [bmim] with anions of $[BF_4]$ and $[PF_6]$ doped by the individual lithium salts like $LiBF_4$, $LiN(CF_3SO_2)_2$, $LiN(C_2F_5SO_2)_2$ and $LiPF_6$.

Experimental

The purity of the RTILs were checked by the NMR spectra. 1 M of the individual lithium salt was added, dissolved by stirring, pored into an NMR sample tube with the height 5 mm and flame-sealed.

NMR diffusion measurements were made by the modified Hahn sequence by using a 4.7T wide-wore super conducting magnet with a JEOL diffusion measuring attachment. The maximum pulsed-field gradient was 22 T/m to measure the slow diffusion (small self-diffusion coefficient). The ^1H, ^{19}F and ^7Li NMR measurements were carried out to obtain the 5 self-diffusion coefficients of the organic cations, anions and lithium ion, respectively. The temperature was changed in the wide range through the ambient temperature. The ionic conductivity was measured by the usual ac method.

Results and discussion

Generally, in the neat RTILs, the organic cation diffuses a little faster than the anions in the wide temperature range. With doping the lithium salt, the organic cation diffuses the fastest, next is the anion and the lithium ion of the smallest size diffuses the slowest. These features are similar to polymer gel and solution electrolytes where the lithium ion always diffuses the slowest. The temperature dependences of the diffusion coefficients were well fit on the VTF equation and each ion has the different fitting parameters within the same system. In addition the diffusion behaviors of the three ions in the same sample vary depending on the species included. For example, the doping of $LiBF_4$ in the $[emim][BF_4]$ brought the reduction of the diffusion coefficients of all the ions in the $[Li][emim][BF_4]$ system, while in the $[Li][bmim][PF_6]$ system, the diffusion coefficients of the [bmim] and $[PF_6]$ were almost unchanged after adding the lithium salt. Just after the sample preparation, the lithium diffusion plots were not straight lines at the lower temperatures and had the similarity to the lithium ion behaviors in the polymer electrolytes [1], but the structure relaxation brought the straight line plots after a long time. It looks certain that the salt-doped RTILs have some microstructures which change in structure gradually in long time intervals. The temperature dependence of the ionic conductivity of the lithium-salt doped RTILs studied was also fitted by the VTF equation. From the correlations with the ion diffusion and ion conduction, the interactions between the organic cation, lithium ion and anion are discussed.

Conclusions

The NMR measurements reveal the diffusion behaviors of the individual ions in the lithium-salt doped RTILs. Although the lithium ion is the smallest in its size, the diffusion is the slowest. This suggests the lithium ion always interacts with anions. The organic cations showed the fastest diffusion. The number of the unpaired ions would be the largest in the organic cations ([emim] or [bmim]), even though the total number of the anions in the paired and unpaired states is the largest.

References

[1] K. Hayamizu,et al, *Macromolecules* **36**, 2785(2003).

Bringing Light to Polymer Electrolytes: The Light-Emitting Electrochemical Cell

Ludvig Edman
Department of Physics, Umeå University, SE-901 87 Umeå, Sweden
e-mail: ludvig.edman@physics.umu.se, tel +46-90-7865034, fax +46-90-7866673

Introduction

Conjugated polymers (CPs), i.e. polymers with a single-double bond alternation along the backbone, are typically semiconductors with band gaps of 1-3 eV in the pristine state. They can, however, be transformed into *excellent electronic conductors*, with conductivities approaching that of copper, via doping. The addition of electron acceptor dopants, such as Br_2, produces a *p*-type material with hole conductivity, while electron donor dopants, such Li, produces an *n*-type material with electron conductivity.[1]

A significant number of today's CPs are in addition *highly luminescent*, and emission colors spanning the entire visible spectrum have been demonstrated. When a thin film of a pristine luminescent CP is sandwiched between appropriate cathode and anode materials (with Fermi levels matching the conduction band edge and valence band edge of the CP, respectively) a polymer light-emitting diode (pLED) is attained, which emits bright light when electrically stimulated.[2] Currently, pLEDs are beginning to be introduced commercially in display applications, primarily because they, in comparison to conventional liquid crystal displays and inorganic LEDs, are relatively easy to produce, allow for a flexible device configuration and exhibit high power efficiencies.[3]

An interesting alternative to the pLED is the polymer light-emitting electrochemical cell (LEC). It typically consists of phase-separated mixture of a CP and a polymer electrolyte as the active material positioned between two electrodes. When a voltage less than the band gap of the CP is applied ($V < E_g/e$), dissolved ions redistribute toward the electrode interfaces to screen the electric field from the bulk of the active material. When $V \geq E_g/e$, charge injection into the CP begins, with holes being injected at the anode and electrons at the cathode. The injected electronic charge carriers are compensated by counterions, which move from the polymer electrolyte into the CP, and electrochemical *p*-type doping at the anode and *n*-type doping at the cathode take place. After this turn-on time, a *p-i-n* junction is formed in the CP (*i* represents a thin insulating region separating the doped regions). Subsequently injected electrons and holes migrate through high-conductivity doped regions before recombining radiatively in the thin *i*-region.[4]

Since the operation of LECs, in contrast to pLEDs, includes doping of the CP, the requirements on electrode material selection and active material thickness are much less stringent. In fact, functional LECs with identical Au electrodes separating a 50 μm thick active material have been demonstrated.[4] In contrast, a functional pLED requires a low-work-function, and thus reactive, cathode (e.g. Ca) and a high-work-function anode (e.g. indium-tin-oxide, ITO) sandwiching a very thin film of CP (~ 100 nm).[2] Unfortunately, these intrinsic and important advantages of the LEC concept are currently offset by two problems: (i) a slow turn-on time, and (ii) a relatively short operational lifetime.

In this abstract, we very briefly present results obtained from two different LEC systems containing: (i) a traditional three-component active material; and (ii) a novel single-component active material. The former system elucidates the direct connection between the morphology of the polymer electrolyte and the turn-on time; while the latter system offers a straightforward probe of non-desired electrochemical side-reactions, an insight into the basic requirements for electrochemical doping and an unparalleled simple and appealing device fabrication.

Experimental

The molecular structure of superyellow (SY), obtained from Covion, is presented in the inset of Fig. 1. SY, poly(ethylene oxide) (PEO) and LiX [= $LiCF_3SO_3$ (LiTf) and/or $LiN(CF_3SO_2)_2$ (LiTFSI)] in a (10:3:2) mass ratio were dissolved in cyclohexanone in an approximately 10 mg solute per mL solvent ratio. The solutions were spin cast onto ITO covered glass substrates to form 400 nm thick films. Thereafter, Al top contacts (≈ 100 nm) were thermally evaporated through a shadow mask. A more detailed experimental description is provided in Ref. [5].

The molecular structure of poly[9,9'-bis(6''-(*N,N,N*-trimethylammonium)hexyl) fluorene-*alt-co*-phenylene]bromide (PFN^+Br^-) is presented in the inset of Fig. 2. LEC devices were produced by spin casting a 10 mg/mL methanol solution of PFN^+Br^- onto ITO covered glass substrates to form a 270 nm thick film, and then thermally evaporate Al top contacts. A more detailed experimental description is provided in Ref. [6].

Results and discussion

Fig. 1 presents the turn-on time for yellow emission at V = 4.0 V and room temperature (RT) for ITO/SY-PEO-LiX/Al LECs; X = Tf (open circles), X = TFSI (solid squares) and X = Tf-TFSI (stars).

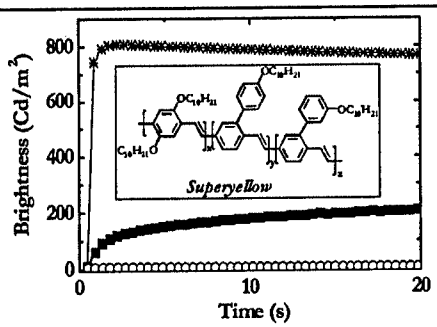


Figure 1.

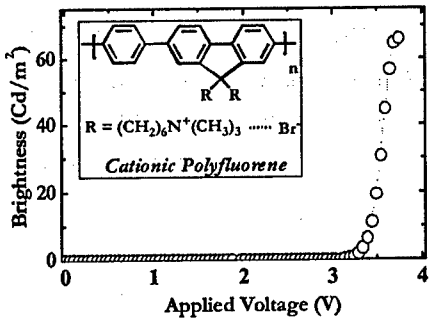


Figure 2.

The turn-on time of an LEC is directly related to the formation of the *p-i-n* junction, i.e. the redistribution of ions and the initial injection and transport of electronic charge carriers. Considering that ion mobilities are significantly lower than mobilities of electronic charge carriers and that the electronic injection is ohmic, it is clear that the ion mobility in principle dictates the turn-on time. Berthier et al. have demonstrated that the morphology of a polymer electrolyte strongly influences the ion mobility;[7] a static crystalline or glassy morphology exhibits negligible ionic mobility whereas a dynamic amorphous morphology can exhibit significant ion mobility.

We suggest that the observed variations of the turn-on time in Fig. 1 can be attributed to the morphology (and thus the ion mobility) of the PEO-LiX electrolytes at RT: PEO-LiTf is largely crystalline,[8] with a corresponding limited ion mobility, and the LEC with PEO-LiTf as the polymer electrolyte is accordingly extremely slow to turn on (of the order of hours). PEO-LiTf-TFSI, on the other hand, is expected to be amorphous with a high ion mobility, and its LEC also exhibits a fast turn-on-time of <0.4 s. Heat-treated PEO-LiTFSI, finally, is partially amorphous at RT,[9] and its LEC consequently exhibits an intermediate turn-on time.

Unfortunately, we also find an apparent trade-off between turn-on times and lifetimes in that the fast devices have shorter lifetimes than the slow devices.[5] It is highly plausible that facile ion transport in addition allows for a (too) fast transport of potential reactants, e.g. molecular anions, to side-reaction sites, with an obvious negative consequence for the device lifetime. A straightforward evaluation of this issue is, however, cumbersome due to the number of different potentially electroactive species in a three-component LEC.

In this context, recently initiated work on novel single-component LECs might be potentially of interest. Fig. 2 presents the brightness as a function of applied voltage for an ITO/PFN$^+$Br$^-$/Al LEC. The only electroactive species in this LEC (besides the cationic polymer and the electrodes) is the Br$^-$ anion, and its electrochemical oxidation potential is well defined.

Moreover, the fact that we can demonstrate efficient LEC operation (with blue light-emission at $V = E_g/e \approx 3$V; see Fig. 2) with a single-ion conductor as the active material is educational, since it demonstrates that a *p-i-n* junction is formed even though only one ionic species is mobile. More specifically, it shows that uncompensated and immobile cationic polyfluorene chains, which are left behind at the cathode when mobile Br$^-$ ions migrate to the anode, are capable of performing *n*-type doping with injected electrons.

Finally, from an application standpoint the single-component LEC concept is appealing, since it allows for *the* simple device fabrication, with a one-component (instead of the commonly employed three-component) active material deposited from a benign solvent (such as water or methanol) onto air-stable electrodes (such as Au or ITO).

References

[1] A.J. Heeger, J. Phys. Chem. B **105** (2001) p.8475.
[2] R.H. Friend, et al. Nature **397** (1999) p.121.
[3] O. Gelsen, Chemistry & Industry **17** (2003) p.19.
[4] Q. Pei, et al. Science **269** (1995) p.1086.
[5] L. Edman, et al. Synth. Met. **138** (2003) p. 441.
[6] L. Edman, et al. Appl. Phys. Lett. **82** (2003) p. 3961.
[7] C. Berthier, et al. Solid State Ionics **11** (1983) p.91.
[8] C. D. Robitaille and D. Fateux, J. Electrochem. Soc. **133** (1986) p.315.
[9] L. Edman, et al. J. Mater. Res. **15** (2000) p.1954.

Tuesday, August 24
12:05 - 12:35

Electrochromism in Visors and Goggles, Electrolytes for Electrochromic Applications

Jim Stevens
Department of Physics, University of Guelph
Guelph, Ontario, N1G 2W1
Canada

Electrochromism can be defined as a reversible and persistent colour change caused by an electric field; a variable transparency can result. This occurs in an electrochemical cell configuration and involves the insertion of electrons and small ions into an electrochromic material and the subsequent extraction of the same charges upon reversal of the process. Electrochromic materials such a transition metal oxides are normally coated (sputtered) on a substrate such as glass or a transparent polyester foil which has previously been coated with a transparent conducting thin film such as tin doped indium oxide (ITO). The ITO is the source of electrons and an electrolyte containing small ions is required to complete an electrochemical cell configuration.

Motorcycle riders often use helmets with dark visors. These visors may be dangerous after sunset. A solution would be a visor, which becomes transparent at the push of a button of by a voice command. The same idea could be applied to goggles for skiers. Visors and goggles such as these are being developed and should be available shortly.

Electrolytes suitable for such applications will be discussed. These include polyether-PMMA-lithium salt-aprotic solvent systems and copolymers of either 2-acrylamide-2-methyl-1-propane sulfonic acid and ethylene glycol methacrylate phosphate with methyl methacrylate, glycidyl methacrylate or 2-hydroxy ethyl methacrylate in polar aprotic solvents.

Polymer Electrolyte with Large Temperature-Dependent Conductivity for Novel Electrochromic Imaging

Norihisa KOBAYASHI, Mami NISHIMURA and Hirosada OHTOMO
Department of Information and Image Sciences, Chiba Univeristy, Chiba 263-8522, JAPAN
e-mail: **koban@faculty.chiba-u.jp**, tel (+) 81-43-290-3458, fax (+) 81-43-290-3490

Introduction

Electrochromism is one of the most successful ways to obtain multi-color images on an electrode due to its color variation, larger viewing angle, memory effects and so on. Many electrochromic materials, such as inorganic compounds, conducting polymers and functional molecules-pendant polymers, coated on an electrode were studied to analyze its electrochemical and spectroscopical properties. Common electrochromism is based on an electrochemical reaction, therefore requiring ion-conductors. However, the image space-selectively generated on a plane electrode by electrochromism has a disadvantage that the image may be spreading by the employment of highly conductive ion-conductor. This is due to a cell formation between the colored part and uncolored part through an ion-conductor.

In the present paper, we prepared thermally responsive polymer electrolyte to restrict the spreading of electrochromic images at room temperature. The polymer electrolyte showed good ion-conductivity at high temperature, but its conductivity dramatically decreased at room temperature. This polymer electrolyte should enable the electrochromic reaction leading to image formation at high temperature, but any electrochemical reaction should not proceed at room temperature.

.Experimental

The solution for the polymer electrolyte was prepared by mixing polyvinylbutyral (PVB) and suitable amount of TBAP and PEG in chloroform. TBAP and PEG were purchased from Kanto Chemical Co. Ltd. and were used as received. The mixture was cast on a Teflon plate and was allowed to stand for 5hr at 56°C under N_2 flow and further dried at 70°C for 12hr in vacuo. The resulting film was kept in vacuo before use. The thermal properties of the polymer electrolyte and chemicals were studied by Mac-Science DSC system. The melting point was determined as the top of the endothermic peak. The sample for the ionic conductivity measurement had a disk shape with 1 cm diameter and 200 ~ 500 μm thickness. The sample was sandwiched between stainless steel electrodes and was kept at constant temperature. Ionic conductivity measurement (ac 10 mV) were carried out with Solartron 1260 impedance gain phase analyzer (LCR meter) over the frequency range 10^0-10^7 Hz. The ac ionic conductivity was calculated from a complex impedance plot (Cole-Cole plot) with computer curve fitting. The temperature dependence of conductivity was determined by temperature-controlled ac measurement over the range 30-100°C.

Results and discussion

The resulting polymer electrolyte showed the conductivity of 10^{-5} S/cm at 100°C. However, it was difficult for us to determine the conductivity at the temperature less than 50°C because the complex impedance plots were not semi-circle in shape but scattered. The conductivity at around room temperature was estimated by direct-current method. The conductivity at 20°C was estimated to be 10^{-11} S/cm, indicating that the polymer electrolyte clearly showed the designed properties. The ion-conductive properties of the polymer electrolyte and the electrochromic characteristics of the device containing the polymer electrolyte will be discussed.

Polyacrylonitrile-Molybdenum Disulfide Polymer Electrolyte Nanocomposites

Guillermo González[1*], Eglantina Benavente[2], María Angélica Santa Ana[1]
[1] Departamento de Química, Facultad de Ciencias, Universidad de Chile, Las Palmeras 3425, Santiago, Chile.
[2]Departamento de Química, Universidad Tecnológica Metropolitana, Av. José Pedro Alessandri 1242, Santiago, Chile
e-mail: **ggonzale@uchile.cl**, tel (+562) 678 7255, fax (+562) 271 3888

Introduction

There is increasing interest in the chemistry of organic-inorganic nanocomposites arising from the insertion of organic species into low dimensional spaces defined in solid matrices. Fundamental questions related among others to the chemical recognition and self assembling associated to these composites, the potentially interesting properties of these products as materials and, more recently, the use of this kind of hybrids as precursors of tubular nanostructures justify the enthusiasm for this chemistry. A relevant potential application of some of these nanocomposites arises from its behavior as mixed ionic-electronic conducting solids able to be used in the design of electrode materials. Examples of these compounds are the intercalates arising from the insertion of poly(ethylene oxide) (PEO) based polyelectrolites into molybdenum disulfide in which the inorganic host and the interlaminar phase are the responsible of the electron and ion conductivity respectively. Considering that polyacrylonitrile (PAN) like PEO has been successfully used in the fabrication of solid polyelectrolites and that the its intercalation chemistry is still scarce we have decided to investigate the synthesis of layered PAN-based nanocomposites. In this work, we describe the co-intercalation of lithium and polyacrylonitrile into molybdenum disulfide discussing both, the effect of the intercalation on the lithium redox potential and the diffusion of the lithium ion in the interlaminar spaces of the nanocomposite.

Experimental

A suspension in benzene of Li_xMoS_2 ($x \geq 1$), prepared by reaction of MoS_2 (Aldrich) with n-butyl lithium (Merck), was treated under argon atmosphere with two equivalents of polyacrylonitrile (Aldrich, Mw 140.000) in the same solvent at room temperature. After stirring during 24 h the product was separated by centrifugation, washed three times with benzene and dried under vacuum. Purity and composition were determined by powder X-ray diffraction and elemental analysis respectively. Electrical conductivity and lithium diffusion coefficients were determined by ac impedance analysis and galvanostatic pulse-relaxation techniques respectively.

Results and discussion

The treatment of molybdenum disulfide (activated by lithium intercalation) with a colloidal suspension of polyacrylontrile in benzene, thermally or assisted by microwave dielectric heating, leads to the compound $Lo_{0.8}MoS_2(PAN)_{1.0}$. The laminar nature of the product is confirmed by both Scanning Electron Microscopy and powder X-ray diffraction analysis. The latter with well defined *001* reflections points to a repeat distance of 11.5 A.

Table 1. Interlaminar distance (Δc), Electrical conductivity (σ), and Li Chemical Diffusion Coefficients of PEO and PAN Nanocomposites Li_xMoS_2(Polymer).

Compound	Δc, Å	σ(298), S cm-1 (x)	D(298), cm2s-1 (x)
$Li_xMoS_2(PEO)_{1.0}$	16.0	$6.6 \cdot 10^{-3}$ (0.1)	$4.5 \cdot 10^{-13}$ (0.4)
$Li_xMoS_2(PAN)_{1.1}$	11.5	$1.1 \cdot 10^{-4}$ (0.8)	$5.9 \cdot 10^{-12}$ (0.4)

As observed in the Table, the MoS_2-PAN nanocomposite is a mixed ionic-electronic conductor with an electrical conductivity (10^{-4} Scm^{-1}) which is about 10^3 higher than the pristine MoS_2. The electrochemical deintercalation-intercalation process occurs with in an average pseudo equilibrium potential range of 2.8 V. According to lithium ion diffusion coefficients determined by galvasnostatic relaxation experiments at room temperature the product is a fast ionic conductor.

Structural features as well as electrochemical properties of the product are discussed by comparing the behavior of the product with those of poly(ethylene oxide) and dialkylamine molybdenum disulfide nanocomposites.

Conclusions

Direct reaction of polyacrylonitrile with molybdenum disulfide activated by the intercalation of lithium followed by electrochemical lithium deintercalation-intercalation experiments leads to a series of new polymer electrolytes based the cointercalation of lithium and PAN in the interlaminar spaces of MoS_2, displaying properties as mixed ionic-electronic conductors.

Acknowledgments

Reasearch partially financed by CONICYT (grant 1010924), Universidad de Chile and Universidad Tecnológica Metropolitana.

References

[1] B.Huang, G.B.Appetecchi, B. Scrosatti, J. Electrochem Soc. **142** (1995) L1.
[2] J.J.Hwang and H.J.Liu, Macromolecules **35** (2002) 7314.
[3] E. Benavente, M.A. Santa Ana, F. Mendizábal, G. González, Coord. Chem. Reviews **224** (2002) 87.

Influence of the plasticizer contents on the properties of HEC based solid polymeric electrolytes

G.O. Machado, H.C.A. Ferreira, **A. Pawlicka***
Departamento de Físico-Química, Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780, CEP 13560-970 São Carlos – SP, Brazil
E-mail: Agnieszka@iqsc.usp.br, tel (+55) 16 2739919, fax (+55) 16 2739952

Introduction

The development of new materials that can be applied as solid electrolytes led to the creation of modern systems of energy generation and storage [1]. Among these materials, solid polymer electrolytes (SPE), generally elastomeric materials containing ions, represent a promising alternative for the substitution of liquid electrolytes and inorganic crystals used in batteries, sensors and eletrochromic devices [2]. Solid polymeric electrolytes can be constituted by different systems where plasticized natural polymers can been found. Osman *et al.* [3] presented the results of ethylene carbonate plasticized chitosan acetate that exhibit the conductivity values of about 10^{-5} Scm^{-1}. Also the authors' recent studies have been directed to show that natural polymers based on glycerol plasticized amylopectin rich starch can be modified to obtain solid polymeric electrolytes [4]. These samples in the transparent film form showed not only very good ionic conductivity of about 10^{-4} Scm^{-1}, but also very good adherence to the glass and steel surface. Also the SPE of glycerol plasticized starch was tested in electrochromic device showing very promissory performance [5].

Experimental

Solid polymeric electrolytes were obtained by plastization process of hydroxyethyl cellulose (HEC) with different quantities of glycerol and addition of lithium salt ($Li(CF_3SO_3)$). The samples were obtained in the transparent film form with very good adhesion properties. These films were characterized by X-ray diffraction, thermal analysis (DSC) and UV-NIR spectroscopy. The ionic conductivity measurements were obtained by impedance complex spectroscopy as a function of salt contents and as a function of temperature.

Results and discussion

As it can be observed by X-ray diffraction measurements the semi-crystalline structure of HEC is evidenced by large band centered at Bragg angle $2\Theta=20^{o}$. The same band but a little more sharp is observed for the cellulose samples [6]. The addition of plasticizer, like glycerol in different quantities, modifies the structure of the samples. The diffractogramms became more large but still centered at $2\Theta=20^{o}$ indicating that the structure seems to be more amorphous. The presence of lithium salt in the samples is not observed in these diffractogramms suggesting that all $Li(CF_3SO_3)$ was totally dissolved by the system. From ionic conductivity measurements it can be observed that the conductivity values increases with the increasing of the plasticizer quantity up to 48% then the conductivity return to decrease. So it can be stated that the sample with 12% of glycerol and containing 6[O]/[Li] exhibit the ionic conductivity value of about $1.26\cdot10^{-6}$ S/cm at 30°C and this value increase up to $1.07\cdot10^{-5}$ S/cm for the sample with 48% of glycerol and the same quantity of salt. The sample with 60% of glycerol and the smaller Tg exhibit the conductivity of $2.11\cdot10^{-6}$ S/cm. This decrease in the conductivity values can be due to the large quantity of plasticizant that probably promotes the polymer/plasticizant phase separation [7]. The conductivity values of the sample containing 48% of glycerol was in the range of other solid polymeric electrolytes based on polysaccharides plasticized systems like for example starch plasticized with glycerol

Conclusions

It was observed that the increase of quantity of glycerol in the samples up to 48% promote the increase of the conductivity values reaching $1.07\cdot10^{-5}$ S/cm at 30°C and $1.06\ 10^{-4}$ S/cm at 83°C for the sample with [O]/[Li] = 6. These results show that plasticized HEC is very good material to be used for preparation of new solid polymeric electrolytes.

References

[1] R.A.Zoppi, S.P.Nunes. Polímeros: Ciência e Tecnologia 4 (1997), p. 27.
[2] J.F.LeNest, A.Gandini, H.Cheradame. British Polymer Journal 20 (1988), p. 253.
[3] Z.Osman, Z.A.Ibrahim, A.K.Arof, Carbohydrate Polym. 44 (2001), p.167.
[4] D.C.Dragunski, A.Pawlicka. Mol. Cryst. Liq. Cryst. 374 (2002), p. 561.
[5] D.C.Dragunski, C.O.Avellaneda, A.Pawlicka, NATO Science Series, Vol.59, pp. 255-258, Kluver Academic Publishers, Dordrecht, 2002.
[6] D.Fengel and G.Wegener, "Wood – Chemistry Ultrastruccture Reactions"Walter de Gruyter, Berlin (1984).
[7] D.Lourdin, L.Coignard, H.Bizot, P.Colonna. Polymer, 38 (1997), p. 5401.

* Author to whom all correspondence should be addressed

Solid polymer electrolytes prepared from a hyper-branched graft polymer using atom transfer radical polymerization

Mitsuru Higa, Yukiko Fujino, Taihei Koumoto, Ryousuke Kitani and Satsuki Egashira
Applied Medical Engineering Science,
Graduate School of Medicine, Yamaguchi University
Tokiwadai, 2-16-1, Ube City, 755-8611, Japan
e-mail: mhiga@yamaguchi-u.ac.jp tel:+81-836-85-9203, fax:+81-836-85-9201

Introduction

Solid polymer electrolytes (SPEs) have potential applications in many solid electrochemical devices such as solid state lithium-polymer-batteries [1-3]. The ideal solid polymer electrolyte material for these devices would not only have relatively high ionic conductivity in the solid state but also have characteristic properties such as high mechanical strength, processability and flexibility. To satisfy these rigorous performance requirements researchers have explored the design of solid electrolytes from block copolymers [4-16], which consist of covalently-bonded two chemically dissimilar polymer segments. A polymer having a high glass trasission temperature (*Tg*) is chosen as one of the polymer segments because it gives high mechanical strength to SPE. The other segment should have low *Tg* and high Li salt solubility because it gives high ionic conductivity to SPE.

In this study, we propose a solid polymer electrolyte prepared from a hyper-branched graft copolymer synthesized by atom transfer radical polymerization (ATRP) as one of strategies for preparation of a high performance SPE having high ionic conductivity as well as high mechanical strength. A macroinitiator of poly(MMA-co-CMS) for ATRP is prepared by copolymerization of methyl methacrylate (MMA) and chloromethylstyrene (CMS). A hyper-branched graft copolymer of PMMA-g-POEM$_x$ (x=5 or 9), which chemical structure is shown in Figure 1, is synthesized using ATRP by grafting POEM$_x$ side chains on the macro-initiator. SPEs are prepared from the polymer, $LiClO_4$ and PEG changing PEG content. The dependence of PEG content on the mechanical strength and ionic conductivity of the SPEs is investigated.

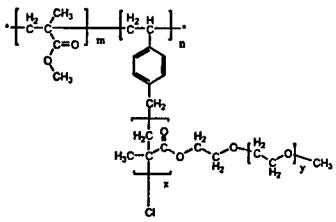


Fig. 1 Chemical structure of the hyper-branched graft copolymer synthesized in this study.

Experimental

A macroinitiator of poly(MMA-co-CMS) for ATRP was prepared by co-polymerization of MMA and CMS by a conventional radical polymerization. The synthesis was performed as follows: Initially, as-received MMA and CMS monomers (MMA:CMS ratio = x:1 on a molar basis, x=25, 50, 100, 200) were dissolved into toluene. The system was purged for 30 min with argon, and then the initiator, 2,2'-azobisisobutyronitrile, was injected with a monomer:initiator ratio of 2000:1 on a molar basis. The synthesis was conducted at 70°C. After the reaction, the polymer was precipitated in methanol and was dried in vacuum to constant weight.

The poly(MMA-co-CMS) copolymer was dissolved in 1-methyl-2-pyrrolidinone (Aldrich) solvent and poly(ethylene glycol) methyl ether methacrylate, referred to herein as poly[(oxyethylene)$_x$ methacrylate] (POEM$_x$) macromonomer was added to the solution. We used two types of POEM (POEM$_5$, *Mn*= 300g/mol: Aldrich) and (POEM$_9$, *Mn*= 475g/mol: Aldrich). The system was purged for 30 min with argon, and then copper chloride (Kanto Chem. Co. Inc.) and 4,4'-dimethyl-2,2'-dipyridyl (Aldrich) were added. The reaction was carried out at 90°C. The resulting hyper-branched graft copolymer was precipitated in petroleum ether/ethanol solvent and was dried in vacuum to constant weight.

Gel permeation chromatography (GPC) of the macroinitiator: poly(MMA-co-CMS) was conducted at 30°C in THF at a flow rate of 1mL/min, using a HPLC pump (JASCO PU-980), GPC columns (Shodex KD-804 and KD-805) and a refractive index detector (JASCO RI-2031 plus) with an auto sampler (JASCO AS-2055 plus). The data were analyzed by a personal computer running commercially available software (System Instrument Co. 480II data station) to estimate the molecular weight and molecular weight distribution of the macroinitiators.

Nuclear magnetic resonance (NMR) spectra were performed on the macroinitiators and the graft copolymers using a spectrometer for ^{1}H (JEOL JNM-EX270 FT NMR system). $CDCl_3$ was used as the solvent and tetramethylsilane as an internal standard. The data were analyzed using commercially available software (JEOL DATUM LTD. ALICE2) to estimate the CMS content in the macroinitiators and POEM content in the graft copolymers.

A solid polymer electrolyte (SPE) was made by casting a tetrafydrofuran solution of the hyper branched graft copolymers, $LiClO_4$ (Wako Pure Chemicals Ind., Ltd.) and poly(ethylenglycol dimethylether) [Mn=250, PEG, MERCK] on Teflon sheet and by drying it at 30°C for 24h. Li^+:[EO] ratio in all the SPEs is 1:10.

The electrical conductivity at 23°C was determined by impedance spectroscopy using a chemical impedance meter (HIOKI 3532-80) controlled by a personal computer.

The mechanical strength of the SPEs was determined with a table model-testing machine (SHIMAZU, EZ-Test500N). In

the static stress-strain curves, specimens with a nominal 20-mm-gauge length and 0.2-mm thickness were deformed in tension at a constant strain rate of 10mm/min at 25°C, and stress-strain data were determined to failure.

Results and discussion

We synthesized a copolymer of poly(MMA-co -CMS) as a macroinitiator of ATRP changing their MMA/CMS composition. The NMR spectrum of one of the copolymers has signals at 3.6 and 4.5 ppm corresponding to the methoxy group of the PMMA segment and the benzyl chloride groups, respectively. We calculated CMS composition in the macroinitiator using the ratio of the integrated areas of the methoxy group to that of the benzyl chloride groups. The CMS composition in the macroinitiators has a good correlation with CMS composition in feed. This means that the average length between the graft chains in the proposed structure of the graft copolymer can be controlled by changing the MMA/CMS ratio in the copolymerization of the macroinitiator. The GPC data show that the molecular weight and molecular weight distribution of the macroinitiators are Mn=19,000 and Mw/Mn=2.46, respectively.

The copolymers contain functional benzyl chloride groups, which are able to initiate the ATRP of POEM. The ^{1}H NMR spectroscopic analysis of one of the hyper branched graft-polymer confirms the proposed structure of the graft copolymer: Grafting of POEM to the poly(MMA-co-CMS) macroinitiator resulted in the appearance of peaks in the region of 3.2-4.3 ppm due to the O-CH_x bonding environments in the methacrylate and PEO moieties of POEM. We calculated POEM composition in the graft copolymer using the ratio of the integrated areas of the methoxy group to that of PEO moieties of POEM. In the ^{1}H NMR spectra of the graft copolymer, the signal at 4.5 ppm corresponding to the initial benzyl chloride groups of the macroinitiators disappeared. Therefore, it is assumed that the efficiency of the macroinitiator was close to 100%.

Solid polymer electrolytes (SPEs) were made from the hyper branched graft-polymers containing $POEM_5$ or $POEM_9$, $LiClO_4$ and poly ethylene glycol dimethylether (PEG), changing PEG content. The tensile strength and Young's modulus of the SPEs using the $POEM_5$ graft-polymer decrease with increasing PEG content. The SPE containing 20wt% of PEG has 0.5MPa of tensile strength. The mechanical strength of the SPE prepared from the $POEM_9$ graft-polymer has almost same values as that from the $POEM_5$ graft-polymer. These results indicate that the SPEs have enough mechanical strength for solid state polymer batteries.

The ionic conductivity of SPEs at 23°C as a function of PEG content. The ionic conductivity of the two SPEs increases with increasing PEG content. The ionic conductivity of the SPE made from $POEM_5$ has higher values than that from $POEM_9$ because of the high POEM content. The value of the ionic conductivity of the SPE made from $POEM_5$ is 6.0×10^{-5} S/cm at 23°C.

Conclusions

We synthesized a hyper-branched graft polymer synthesized by graft polymerization of poly(MMA-co-CMS) macroinitiator on POEM macromonomer using ATRP. The ^{1}H NMR spectroscopic analysis of the hyper branched graft copolymer confirms the proposed structure of the graft copolymer. Solid polymer electrolytes were prepared from the polymer obtained, $LiClO_4$ and polyethylene glycol dimethylether (PEG), changing PEG content. Although both the tensile strength and Young's modulus decrease with increasing PEG content, the tensile strength has 0.5MPa even when PEG content is 20wt%. The ionic conductivity of the SPEs increasing with PEG content is 6.0×10^{-5} S/cm at room temperatures. These results indicate that a SPE prepared from the hyper-branched graft copolymer has potential to be applied to a solid polymer electrolyte.

Acknowledgment

This work was supported by Electric Technology Research Foundation of Chugoku, No. 89, Tateisi Science and Technology Foundation, No. 1031017, JFE 21st Century Foundation and the Salt Science Research Foundation, No.0212.

References

[1]J.R. MacCallum, C.A. Vincent, *Polymer Electrolyte Reviews 1 and 2, Elsevier: London* (1987, 1989).

[2]F.M. Gray, *Solid Polymer Electrolytes, VCH Publishers: New York*, 1991.

[3] B. Scrosati, *Applications of Electroactive Polymers, Chapman and Hall, London*, 1993.

[4]P.P. Soo, B. Huang, Y.-I. Jang, Y.-M. Chiang, D.R. Sadoway, and A.M. Mayes, *J. Electrochem. Soc.*, 146, 32 (1999).

[5]M. Watanabe, S.-I. Oohashi, K. Sanui, N. Ogata, T. Kobayashi and Z. Ohtaki, *Macromokecules*, 18, 1945 (1985).

[6]J.R.M. Giles, F.M. Gray, J.R. MacCallum and C.A. Vincent, *Polymer*, 28, 1977 (1987).

[7]F.M. Gray, J.R. MacCallum, C.A. Vincent and J. R.M. Giles, *Macromolecules*, 21, 392 (1988).

[8]I. Khan, D. Fish, Y. Delaviz and J. Smid, *Makromol. Chem.*, 190, 1069 (1989).

[9]J. Li and I. Khan, *Makromol. Chem.*, 192, 3043 (1991).

[10]S. Kohjiya and Y. Ikeda, *Mater. Sci. Res. Int.*, 4, 73 (1998).

[11]H.R. Allcock, R.Prange and T.J. Hartle, *Macromolecules*, 34, 5463 (2001).

[12]D.R. Sadoway, A.M. Mayes, B. Huang, S.Mui, P.P. Soo, D.H. Saelin and C. Cook, *J. Power Sources*, 97-98, 621 (2001).

[13]A.-V.G. Ruzette, P.P. Soo, D.R. Sadoway and A.M. Mayes, *J. Electrochem. Soc.*, 148, A537 (2001).

[14]J. Saunier, F. Alloin and J.-Y. Sanchez, *Electrochim. Acta*, 45, 1255 (2000).

[15]P.E. Trapa, B. Huang, Y-Y. Won, D.R. Sadoway and A.M. Mayes, Electrochem. *Solid-state Let.*, 5 A85 (2002).

[16]J.F. Hester, P. Banerjee, Y.-Y. Won, A. Akthakul, M.H. Acar and A.M. Mayes, *Macromolecules*, 35, 7652 (2002).

Synthesis and Electrochemical Characterization of Novel Nanocomposite Polymeric Membranes

[1]Giselle Sandí*, [2]Riza Kizilel, [1]Kathleen A. Carrado, and [1]Norma Castagnola
[1]Chemistry Division, Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439
[2]Chemical and Environmental Engineering Department, Illinois Institute of Technology, Chicago, IL 60616
e-mail: gsandi@anl.gov, tel (+) 630 251 1903, fax (+) 630 252 9288

Introduction

The modification of polymer properties by the addition of another material, that is, a filler, have been studied for many years. Common fillers such as glass fibers, carbon fibers and carbon black, pigments and minerals, including silicates, are used to modify the macroscopic properties of the polymer. In recent years, a new class of materials have been developed by dispersing layered silicates with polymers at the nanoscale level. These new materials have attracted wide interest because they often exhibit chemical and physical characteristics that are very different from the starting material [1, 2]. In some cases, the silicates and polymers exist as alternating layers of inorganic and organic [3]. The possibility of improved mechanical, rheological, electrical, and optical properties and the ability to exercise control over existing physical and chemical behavior have led to a large number of studies of these materials, including composites of layer silicate clays with polyethylene oxide (PEO), epoxy resin, polystyrene, and a range of other thermoplastics and elastomers.

It is known that polymer electrolytes exhibit high conductivity only in the absence of a crystalline phase, which impedes the transport of ions, and only at temperatures well above the glass-transition temperature (Tg). A number of methods have been used to prepare totally amorphous polymers of high conductivity, including random copolymers or branched block copolymers. However, the mechanical strength of these polymers is often poor because of their low transition temperatures. Mechanical strength can be maintained by crosslinking of the polymer chains, but this comes at the expense of reduced conductivity. Another approach to increasing conductivity is to incorporate low molecular weight plasticizers into the polymer.

Nanocomposite materials of PEO and phyllosilicates were first suggested by Ruiz-Hitzky and Aranda [4] as candidates for polymer electrolytes. Within these materials, the polymer chains are intercalated between the silicate layers. The polymer chains then provide a mobile matrix in which cations are able to move. A considerable amount of interest has been shown in nanocomposites of PEO and montmorillonite, a layered aluminosilicate clay. When this composite contains $LiBF_4$, it displays conductivities up to 2 orders of magnitude larger than that of PEO itself at ambient temperatures. However, the addition of lithium salts, which is needed to obtain such conductivity values, is not desirable for two reasons; the first one relates to a more complicated synthetic route and the second relates to the fact that transference numbers are not unity since in this case both cations and anions move.

We have prepared a series of nanocomposites containing PEO intercalated in the layers of hectorite clays. These clays, also called phyllosilicates, belong to the family of smectite clay minerals. They are composed of two tetrahedral silicate layers sandwiching a central octahedral layer in a so-called 2:1 arrangement. In hectorite, isomorphous substitutions in the lattice of Li(I) for Mg (II) in the octahedral layers cause an overall negative charge that is compensated by the presence of interlayer, or gallery, cations. A significant amount of interlayer water is also present and the cations are easily exchangeable. A large degree of preferential orientation in films prepared by natural occurring clays tends to occur, however, due to their large platelet size (up to 1 μm). This can lead to non-conducting planes being perpendicular to the current path and thus reduce the conductivity. To avoid this problem, we followed a method developed by Carrado et al. [1] which involves direct hydrothermal synthesis and crystallization of hectorite with smaller platelet size, termed synthetic lithium hectorite (SLH). Organic molecules can be either incorporated directly from the gel or by subsequent intercalation. Figure 1 shows a schematic structure of intercalated PEO in a SLH. The circles in the gallery represent Li ions.

Experimental

Preparation of the SLH clay via hydrothermal crystallization at 100 ℃ of silica sol, magnesium hydroxide, and lithium fluoride can be found in detail in reference 1. In brief, precursor clay gels are of the composition: 1.32 LiF, 5.3 $Mg(OH)_2$, 8 SiO_2, n H_2O, to correlate with the ideal hectorite composition of $Li_{0.66}[Li_{0.66}Mg_{5.34}Si_8O_{20}(OH,F)_4]$. A typical reaction begins by suspending the LiF with stirring in water. Separately, $MgCl_2.6H_2O$ is dissolved in water and mixed with 2 N NH_4OH to crystallize fresh $Mg(OH)_2$. Prior to use, this brucite source must be washed several times with water to remove excess ions. It is then added wet to the LiF solution. This slurry is stirred for 15-30 min before addition of silica sol (ludox HS-30, Na^+-stabilized, 30%). The total volume is increased to afford a 2 wt% solids suspension, and is stirred and refluxed for 40-48 hours. Solids are isolated by centrifugation, washed, and air-dried.

Colloidal suspensions of 1 g SLH/100 ml de-ionized water were stirred for one-half hour. The

desired amount of PEO (100 000 average molecular weight, from Aldrich) was then added, and the mixture stirred for 24 hours. Mixtures contained 0.6, 0.8, 1.0, and 1.2 g of PEO/g of clay. Films were prepared by puddle-casting the slurries onto Teflon-coated glass plates and air-drying. Further drying was carried out at 120 °C under an inert atmosphere for at least 48 hours. The typical thickness of the films is about 40 μm.

X-ray powder diffraction (XRD) patterns of SLH and PEO powders were determined using a Rigaku Miniflex, with Cu Kα radiation and a NaI detector at a scan rate of 0.5° 2Θ/min and step size of 0.05.

AC impedance measurements as a function of temperature were obtained on films in sealed cells with lithium foil as the counter and working electrode, using a Solartron SI 1256 electrochemical interface and 1254 frequency response analyzer. A Tenney Junior Environmental Test Chamber was used to control the temperature of the cell with a precision of ± 0.5℃.

Transmission electron microscopy (TEM) was performed in a JEOL 100CXII Transmission Electron Microscope operating at 100kV. Approximately 0.2 mL of 1:1 PEO/SLH slurry was placed into a vial and sonicated for 30 seconds. Copper grids were then dipped into the resulting slurry. The Cu grids were allowed to dry for 2 hours in a vacuum oven at 100℃. Once dry, the grids were inserted into non-tilt holders and loaded into the instrument. Scale markers placed on the micrographs are accurate to within three percent.

Results and Discussion

Figure 1 shows a TEM of a film made of synthetic lithium hectorite (SLH) and PEO 1:1 mass ratio. The silica precursor is a Ludox solution (HS-30). Spheres of SiO_2 are clearly seen throughout the background. The average sphere diameter is about 12-15 nm (see scale bar on the bottom left). The chemical, physical, and electrochemical properties of this membrane have been published elsewhere (1, 2).

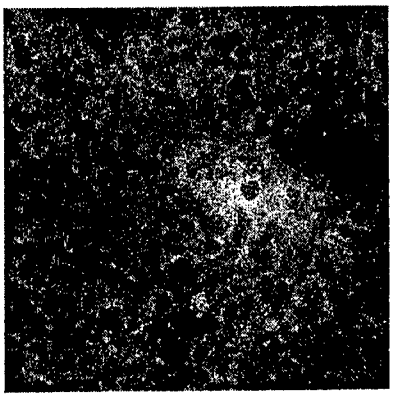


Figure 1: TEM of a SLH:PEO 1:1 ratio nanocomposite film.

Figure 2 shows the cole-cole impedance plot of a nanocomposite membrane prepared with a Ludox TM-40 solution in water. The conductivity measurements were performed using lithium electrolytes and the bulk resistance was obtained from the high frequency semicircle. As indicated in the Figure 2a, the charge transfer resistance decreases as the film is heated, but the bulk resistance remains almost constant (Figure 2b).

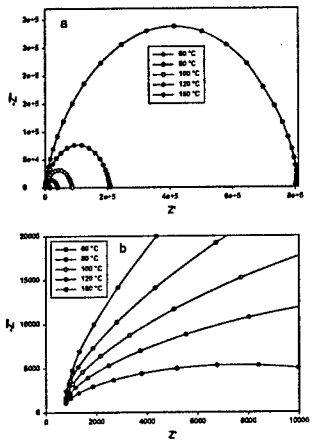


Figure 2: Cole-cole impedance plots of a film made of SLH:PEO 1:1 ratio nanocomposite film (Ludox TM-40 in water was the silica precursor).

Conclusions

From the Arrhenius conductivity plots (not shown), it is observed that for all the clay to polymer ratios, the higher conductivity is obtained for those membranes made with TM-40 as the precursor. The diameter of the SiO_2 for this precursor is about 25 nm by TEM. Membranes made with TEOS as the Si precursor, exhibited a conductivity two orders of magnitude lower than other Si precursor. It is clear by TEM that there are no SiO_2 spheres present. It is clear that the SiO_2 plays an important role in the conductivity of these materials.

References

[1] K. A. Carrado. *Appl. Clay Sci.* **17**, 1, 2000.
[2] G. Sandí, H. Joachin, R. Kizilel, S. Seifert, and K.A. Carrado. *Chemistry of Materials* **15** (4), 838, 2003.
[3] G. Sandí, K. A. Carrado, H. Joachin, W. Lu, and J. Prakash. *Journal of Power Sources.* **119-121**, 492, 2003.
[4]E. Ruiz-Hitzky, P. Aranda. *Adv. Mater.* **2**, 545, 1990.

Acknowledgments

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

Modeling of conductivity in composites with Random Resistor Networks

M.Siekierski*, K.Nadara
Warsaw University of Technology, Chemical Faculty, Polymer Ionics Research Group
ul. Noakowskiego 3, 00-664 Warsaw, POLAND
*corresponding author e-mail: **alex@soliton.ch.pw.edu.pl**, tel (+) 48 601 26 26 00,
fax (+) 48 22 628 27 41

Introduction

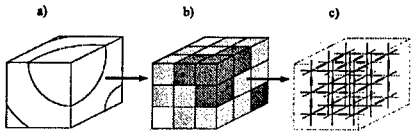
To predict the conductivity value of the composite system one can take into consideration the assumption of the oversimplified filler-matrix interaction mechanism and obtain the concentration - conductivity dependence consisting of three different regions. In the small filler concentration range almost no change of the conductivity is observed in comparison with the pristine system as the point of the percolation threshold is not yet achieved. At some point the conductivity of the system raises dramatically (a few orders of magnitude). The second area corresponds to the slow conductivity drop due to the dilution effect of the filler. Finally an abrupt decay is observed at the point in which the polymer matrix loses its continuity and the conductivity paths are blocked by the inert filler grains. This dependency can be easily obtained by the means of the Effective Medium Theory. This model has some disadvantages which limit its applicability:

1. Assumption that all grains are identical in respect to their shape and size.
2. A lack of mixing rule for grain shapes different form spherical.
3. A need of percolation threshold determination for each particular grain shape.
4. Assumption that the t/R ratio is constant.
5. Assumption of shell uniformity and no conductivity distribution is observed within it.
6. Assumption of ideally even distribution of composite grains.

To overcome these limitations a Random Resistor Network can be applied to simulate the electrical behavior of the composite.

Random Resistor Network (RRN) approach to modelling the sample properties is very versatile[1-3]. When applied to the electrical properties of matter the method is based on converting first the sample into its virtual image and later the image into two or three dimensional network of resistivities. The values of the elementary units correspond to the properties of the particular components of the composite. Most published research [4-6] works with so-called binary systems which are mixtures of two types of units, one being the insulator and the other being the conductor. The branches can be treated either as a resistor (path) or an insulator (break). In the results generated by this type of models an abrupt conductivity increase due to the percolation threshold can be observed for a particular contents of the conductive elements. Conductivity of inorganic composite electrolytes based on LiI/Al_2O_3 and $CuCl/Al_2O_3$ was simulated [4] assuming network geometry based on restrictions similar to those valid also for the polymeric electrolytes. The highly conductive layer here is also built on the grain-matrix border. Nodes of the network can be attributed to one of the two possible states. The resistivity of the branch between nodes is calculated taking into consideration the type of both end nodes. If both are occupied the current flow is closed if both are empty the branch represents a conductor and finally the branch with ends of different types is attributed to the element of high conductivity (shell).

The model proposed by us for the composite polymeric electrolyte is much more complicated. Firstly the thickness of the shell varies and is larger than the single network cell. It depends on the grain filler type, size and sample composition. Secondly one must also assume that the highly conductive shell is non-isotropic. First (Fig. 1a) the continuous model is generated by the insertion of virtual grains into the matrix. Random insertion is continued until the assumed volume fraction of the filler is achieved. In the second step (Fig. 1b) the virtual sample is divided into cells which are later treated as filled with uniform material. Finally, (c) a three-dimensional network of elementary resistances R_x is created.



The network nodes are localized in the centers of all units. In the second stage the algorithm finds the overall value of sample electrical parameters using a modification of the method introduced by Kirkpatrick [6]. The rules of energy and charge preservation lead to two basic equations (1) and (2):

$$j(r) = \sigma(r)\mathrm{grad}V(r) \qquad (1)$$

$$\mathrm{grad}j(r) = 0 \qquad (2)$$

where j(r) is current density, V(r) is electrical potential and σ (r) is electrical conductivity or admittance of cell number r. An iteration algorithm is used to solve the network. In each step the potentials of the nodes are changed to achieve a situation when for each node incoming current is equal to the outgoing (preservation of the Kirchoff's laws).

To calculate the effective resistivity one must find the overall current coming through the sample and thus the current coming through any of the perpendicular layers

of nodes in the sample. This value can be obtained by the addition of all elementary currents in branch resistors connecting all the nodes of two neighboring layers. In the stationary condition the first Kirchoff's law must me obeyed for each node (3).

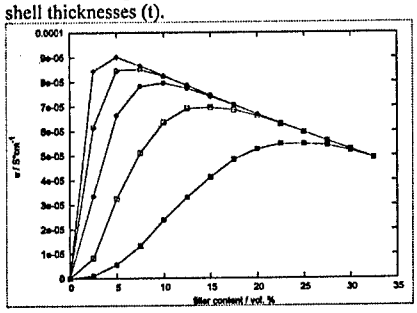
$$\sum_i I_i = 0 \qquad (3)$$

Experimental

The calculations were performed on an Intel® Pentium™ 4 PC computer with a Slackware GNU/Linux system installed. C++ was used for code generation. GNU C compiler was used to obtain the executables. The calculation times were in the range of two-three days for a set of data starting form 5 v/v% up to about 40 v/v% of the nonconductive additive. For most calculations the matrix size was equal to 100x100x100 and was limited by the calculation times. The conductivity of the pure polymer was equal to $1x10^{-8}$ Scm^{-1}, grain $1x10^{-12}$ Scm^{-1}, while the maximal conductivity of the shell was $1x10^{-4}Scm^{-1}$.

Results

Fig 2 shows conductivity dependencies observed for the constant filler grain diameter d=5 σm and for different shell thicknesses (t).



■- t=3.0μm, □- t=5.0μm, ●- t=7.0μm, O- t=9.0μm, υ- t=11.0μm.

The increase of t leads to an increase of maximum conductivity value together with shifting the maximum to lower filler amounts. Also the shape of the curve changes and becomes sharper. Interesting phenomenon can be observed for filler amounts much higher than the ones corresponding to the maximal conductivity value. In this region curves overlay one another. This can attributed to the observation that here there is no more unmodified matrix present and the sample is filled only with grains and shells. The phase composition and thus conductivity of the sample is independent of the t parameter and related only to the amount of the filler added.

The sample conductivity first raises with the increase of the filler amount. Above the filler concentration characteristic for the conductivity maximum a linear decrease is observed due to the dilution effect. The larger the grain is the smaller the conductivity values are. The maximum is also flater and is located at higher grain concentrations. For really large grains d = 11 and small t=3 values the maximum can not be observed in the studied concentration range.

Conclusions

The Random Resistor Network approach was successfully applied to conductivity calculation for composite polymeric electrolytes. The calculated value of conductivity in general follows the phase content changes in the sample. For small amounts of filler the value of conductivity increases with the increase of highly conductive shells contents. The maximum of conductivity is reached when the whole sample volume disregarding the part attributed to the grains is filled with the shells. The following decrease is related to the dilution of shell material with the grains and eventually with deterioration of conductivity in the shells according to the spatial distribution. The smaller are the grains (for constant thickness of the layer) the higher conductivity maximum is achieved for lower filler amounts. Analogically, for the constant grain diameter the increase of shell thickness leads to a conductivity increase. The proposed approach can be easily extended by the introduction of the non-spherical grain shapes, conductivity distribution within the layer and by the exchange of the direct current conductivity to the complex impedance to simulate the dielectric response of the composite.

References

[1] C.Xu, P.M.Hui, Z.Y.Li J. App. Phys. **90** (2001), p. 365

[2] M.Acharyya, B.K. Chakrabarti J. Phys. (Paris) **15** (1995), p. 153

[3] M.Acharyya, B.K. Chakrabarti Physica A **224** (1996), p. 254

[4] S. Jiang and J. J. Bruce Wagner J. Phys. Chem. Solids **56** (1995), p. 1113

[5] E. C. Yeh, M. Chiou, and K. Y. Hsu Thin Solid Films **297** (1997), p. 88

[6] S. Kirkpatrick Reviews of Modern Physics **45** (1973), p. 57

Nanocomposite polymer electrolytes based on poly(oxyethylene) and Cellulose Nanocrystals

F. Alloin,* M. A. S. Azizi Samir,* W. Gorecki,[§] A. Dufresne,[⊥] J-Y Sanchez*
**LEPMI-INPG, BP 75, F38402 St Martin d'Hères Cedex, France, [§]LSP, Université Joseph Fourier, BP 87, 38402 Saint-Martin d'Hères cedex, [⊥]EFPG-INPG, BP 65, F38402, St Martin d'Hères Cedex, France*
e-mail: **Fannie.alloin@inpg.fr**, tel (+) 04-76-82-65-60, fax (+) 04-76-82-66-70

Introduction

Many studies have focused on the enhancement of ionic conductivities of polymer electrolytes, most of them, due to their strong solvating ability, performed on poly(oxyethylene) (POE) and its copolymers. For safety and performances reasons, polymer electrolytes must exhibit high mechanical performances. It was early assumed that ionic conductivity requires an amorphous character of polymer electrolytes[1], which unfortunately leads to poor mechanical properties. An improvement in mechanical behavior can be usually achieved using cross-linked polymers. However obtaining suitable mechanical properties requires a high cross-linking density which results in a clear conductivity decrease. Alternatively, gain in mechanical properties, using α-Al_2O_2 fillers has also been reported[2].

In the present work tunicin whiskers were used as reinforcing phase in an amorphous POE cross-linked polycondensate[3]. The performances of the nanocomposite electrolyte were analyzed in terms of both conductivity and mechanical behavior. These performances were compared to those obtained for unfilled cross-linked polyethers matrices exhibiting several cross-linking densities.

Experimental

An unsaturated polyether was synthesized by reaction of α,ω-dihydroxyoligopoly(oxyethylene) with a dihalide isobutenyl compound according to the reaction previously described[4]. The nanocomposite was prepared by UV radiation curing in argon atmosphere. A homogenous suspension was obtained in Dimethylformamide by mixing the polymer and the suspension of whiskers. The lithium salt, LiTFSI was added by swelling the cross-linked films with a concentrated solution of salt in acetonitrile.

Results and discussion

Spectacular improvement of the tensile modulus was observed at high temperature with 6 wt% of whiskers (Figure 1) with a value of 22 MPa, up to, at least, 150°C, for the nanocomposite electrolyte. We compare the mechanical reinforcing effect provides by either the cross-linking of the polymer or the loading with tunicin whiskers. The tensile modulus obtained with filled electrolyte is more than one order of magnitude higher (22 MPa vs 2 MPa) than that obtained for the highly cross-linked, but unfilled, electrolyte.

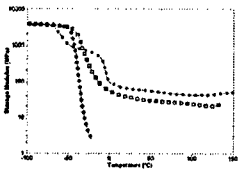


Figure 1: Storage tensile modulus E' vs. temperature at 1 Hz: unfilled electrolyte (O/Li = 12) (τ), salt-free filled polymer with 6 wt% tunicin whiskers (λ) and electrolyte (O/Li=12) filled with 6 wt% tunicin whiskers (♦).

The conductivity performances are not affected by the incorporation of a low amount of whiskers (Figure 2). The conductivity of the unfilled electrolyte with a high cross-linking density is lower, in relation to the decrease in the polymer chain mobility.

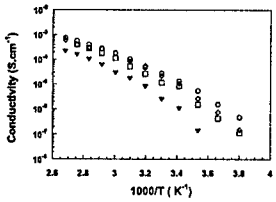


Figure 2: Ionic conductivity for composite (O/Li = 12) electrolytes filled with 0 (◊), 6 (ϒ) and 10 wt% (♦) of tunicin whiskers and the highly cross-linked unfilled electrolyte (▼).

Conclusions

The use of nanocomposite polymer electrolytes allows, for the first time since the discovery of polymer electrolytes[1], high ionic conductivities and very high mechanical strength to be conciliated.

References

[1] P.V. Wright, Br. Polym. J. **7** (1975) p 319
[2] W. Wieczorek, A. Zalewska, D. Raducha, Z. Florjanczyk, J.R. Stevens, J. Phy. Chem. B, **102** (1998) p 352
[3] MAS Azizi Samir, F. Alloin, J-Y Sanchez, N. El Kissi, A. Dufresne, Macromolecules **37** (2004) p 1386
[4] F. Alloin, J-Y Sanchez, M. Armand, J. Electrochem. Soc. **141** (1994) p 1915

Effect of high pressure CO_2 on the structural and electrical properties of ORMOCERS-APE systems based on Zr and Al

Vito Di Noto[1*], K. Vezzù[2], M. Vittadello[1], S. Lavina[1], A. Bertucco[2].
[1]Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, I-35131 Padova, Italy
[2]Dipartimento di Principi e Impianti di Ingegneria Chimica "I. Sorgato",
Università di Padova, Via marzolo 9, *I-35131 Padova, Italy*
E-mail: *vito.dinoto@unipd.it*

Introduction

The increasingly important role of supercritical fluids (SCFs) in polymer science is well known. Compressed gas based techniques are revealing their great potential in the field of polymer processing to modulate the physical-chemical properties of macromolecular materials. The liquid-like density and gas-like low viscosity of SCFs are at the basis of many high pressure solvent-free processes for versatile synthesis and modification of polymers. CO_2 is usually the candidate of choice among the SCFs for its easily accessible critical point (T_c= 31.8 °C, P_c= 74 bar). Some remarkable effects of compressed gases in a polymer matrix were observed such as swelling, plasticization and lowering of the glass transition temperature (T_g). Kwak *et al.* [2] have proposed an interesting crossover between the area of SCFs and the field of polymer electrolytes (PEs). These authors have reported that the conductivity of amorphous PEs of the ($PMEO_x$-$LiCF_3SO_3$) type is improved by treatment with supercritical CO_2, of about one order of magnitude. This finding come along a huge research effort undertaken to find alternative paths to increase the conductivity in PEs. In this contribution we bring together the promising results obtained from the investigation of hybrid inorganic-organic PEs and the effect of CO_2 on the structure and the conductivity of electrolytic complexes. We focus on the comparison between the CO_2 activity in two series (eleven complexes each) of hybrid inorganic-organic PEs of the ORMOCERs-APE (ORgannically MOdified CERamics As Polymer Electrolytes) type, with general formula: $[Al[(CH_2CH_2O)_{8.671}]_\rho/(LiClO_4)_z]_n$ ($1.85 \le \rho \le 2.24$, $0 \le z \le 1.06$) and $[Zr[(CH_2CH_2O)_{8.671}]_\rho/(LiClO_4)_z]_n$ ($1.80 \le \rho \le 1.99$, $0 \le z \le 0.90$).

Experimental

The investigated PEs were synthesized as previously reported and treated with high pressure CO_2 for 1.5 hours under 20°C and 5 MPa. The samples thus obtained were studied by differential scanning calorimetry (DSC) in the range –80-120 °C and Broad Band Dielectric Spectroscopy between 40Hz and 10Mz. The effects of CO_2 treatment on the PEs were investigated by impedance spectroscopy in the 40 Hz – 1 MHz range from –80° to 120°C. A detailed vibrational study (FT-IR and FT-Raman) was also carried out before and after the treatment.

Results and discussion

Both complexes $[Al[(CH_2CH_2O)_{8.671}]_\rho/(LiClO_4)_z]_n$ and $[Zr[(CH_2CH_2O)_{8.671}]_\rho/(LiClO_4)_z]_n$ after CO_2 treatment exhibit a change in the α-relaxation with respect to the untreated samples. This phenomenon has been interpreted in terms of a change in the polymeric conformation as confirmed by vibrational spectroscopy. The CO_2 treatment lower the conductivity of $[Al[(CH_2CH_2O)_{8.671}]_\rho/(LiClO_4)_z]_n$ complexes of about one order of magnitude, as opposed to $[Zr[(CH_2CH_2O)_{8.671}]_\rho/(LiClO_4)_z]_n$ complexes, where an increment by two orders of magnitude is observed. In both cases the conductivity of the untreated materials versus the reciprocal absolute temperature presents the typical Vogel-Tamman-Fulcher (VTF) behavior. On the other hand the treated samples show more complex profiles that require interpolation with both VTF and Arrhenius equations. The different effect on the conductivities of the treated complexes is explained in terms of the modified anion-trapping ability of Al and Zr centers and in terms of structural rearrangements produced by supercritical CO_2.

Conclusions

The CO_2 treatment on inorganic-organic polymer electrolytes of the ORMOCERs-APE type containing Al and Zr has a dramatic effect on conductivity. An increase is observed in the case of Zr and a decrease in the case of Al. The specific Lewis character of the inorganic elements in the materials and the structural modifications induced by the treatment determines the sign of the CO_2 effect.

References

[1] V. Di Noto, M. Furlani, S. Lavina *Polym. Adv. Technol.* 7 (1996), 759.
[2] G. H. Kwak, Y. Tominaga, S. Asai, M. Sumita *Electrochim. Acta* **48**, (2003), 1991.
[3] V. Di Noto, V. Zago *J. Electrochem. Soc.* **151**, (2004), *A216*.

Increasing lithium ion in electrolyte materials through the use of additives

N. Byrne[#], J.M. Pringle[*], C. Tiyapiboonchaiya[*], D. R. MacFarlane[*] and M. Forsyth[#]
[#]School of Physics and Materials Engineering and [*]School of Chemistry
Monash University, Wellington Rd, Clayton 3800 Australia.

Introduction

Gel electrolytes are an attractive alternative for many applications especially lithium ion batteries [1]. They reduce the risk of leakage and have the ability to maintain interfacial contact during charging and discharging.

The ionic conductivities of gels, however, is still not ideal for general practical application [2]. The use of ion dissociating additives has been shown to further enhance the ionic conductivity and the mobility of the lithium ion into the realm of practical application. Previous work has shown that ionic liquids act as good dissociators in polyelectrolyte [3], however ionic liquids some limiting characteristics steaming from the component ions migrating with the potential gradient leading to a less than unity transport of target ions. This equates to a reduced current density and hence rate capability of the device [4]. Zwitterioic compounds are "neutral" molecules as the cation and an anion are covalently tethered together therefore migration is minimized making these compounds excellent solvents for electrochemical applications[5].

Experimental

This work investigates the use of additives such as nano-particulate filler and zwitterionic compounds in a range of electrolytes for use in electrochemical devices. Ionic conductivity, ^{7}Li and ^{1}H diffusion have been used to investigate the effect these ion dissociators have on the ionic transport properties of the electrolyte. Cyclic voltammetry and cycling efficiency experiments were also preformed to assess the materials performance under cell conditions.

Results and discussion

Figure 1 shows an enhancement in the ionic conductivity of the well studied polyelectrolyte system poly(Li-AMPS) with the addition of both TiO_2 and zwitterion. It can be seen from this figure that both dissociators are capable of ionic conductivity enhancements with complementary behaviour being observed when both dissociators are present in the system.

Conclusions

The data presented shows how the addition of both zwitterion and filler to a PC based system has a clear additive effect with the ionic conductivity being increased by a factor of six.

References:

[1] G.B Appetecchi, P.Romagnoli & B. Scrosati. "Composite gel membranes: a new class of improved polymer electrolyte for lithium batteries" Electrochem Comm 3 (2001) 281-284.

[2] J. Adebahr, N.Byrne, M.Forsyth, D.R. MacFarlane & P. Jacobsson "Enhancement of ion Dynamics in PMMA-based gels with addition of TiO_2 nano-particles" Electrochim.Acta (2003)

[3] Sun, J., MacFarlane D. R. and Forsyth. M., *Lithium polyelectrolyte–ionic liquid systems.* Solid State Ionics, 2002. 147(3-4): p. 333-339.

[4] Howlett. P "Room temperature ionic liquids as electrolytes for use with the lithium metal electrodes" Thesis Feb 2004 Monash University.

[5] M. Yoshizawa, M. Hirao, A. Ito, H. Ohno "Ion conduction in zwitterionic-type molten salts and their polymers" Journal of Mat Chem 11 (2001) 1057-1062

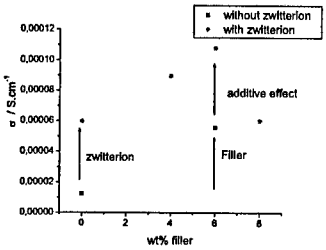


Figure 1: Ionic conductivity showing effect of both dissociators.

Determination of the lithium transference number in PEO-DME-$LiClO_4$ modified with alumina powder of different surface acidity.

Marcin Ciosek*, Maciej Siekierski
Warsaw University of Technology, Faculty of Chemistry, ul. Noakowskiego 3 room 348,
00-664 Warsaw, POLAND
*tel (+) 48 602 611 970, fax (+) 48 22 628 27 41, e-mail: **admin@soliton.ch.pw.edu.pl**

Introduction

Composite polymer electrolytes have been under wide investigation[1], due to the interest in their application in ambient and moderate temperature lithium or lithium ion batteries[2]. The cell efficiency is strictly related to the ion transport rate. It is therefore important to have knowledge of the ion transference number and salt diffusion coefficient, as well as the ionic conductivity while measurement of these parameters has been hindered by the lack of a simple technique.

In most systems based on polymer solvent the salt is usually not completely dissociated which is caused by a combination of low electrical permittivity of the solvent and the relatively high salt concentration.

If the salt isn't fully dissociated a series of equilibria exist and some associated species as ion-pairs, triplets and higher aggregates are formed. All of them may be mobile in the electrolyte and affect summary charge transport. In lithium batteries the electrodes are active only towards one of the ion constituents and blocking towards the others. So the assumption is that the cation is the electrode active specie.

Composite polymer electrolyte can be conceived as a system composed of three components: a polymer matrix, for example, polyethylene oxide (PEO); a source of lithium cation like LiX salts ($LiClO_4$, $LiBF_4$, $LiPF_6$ or others) and a filler, TiO_2, SiO_2, Al_2O_3 etc. Small amount of microsize powder in polymer electrolyte may lead to enhancement in system conductivity[3][4][5]. It has been also shown that the achieved conductivity enhancement depends on the type of surface Lewis acid groups of the aluminum oxide additives[6].

In the case when ion association appear it is impossible to distinguish between simple ions and other charged species. Instead, total material transfer or total current is determined. Therefore, an observable quantity relies on the transfer of an ion constituent and not free ion. The quantity is called the transference number. Because the transference number is based on the transport of the gram-equivalent one faraday of matter with one Faraday of charge flow. Thus the sum of the transference numbers for all possible charge carriers must be equal to unity:

$$\sum_i t_i = 1$$

Several methods have been employed for measuring the transference number. Ideally the obtained values of the transference number should be independent of the measurement method but each measurement is based on different assumptions and dependent on the electrolyte system thus will yield different values. The discrepancies can be explained by invalid assumptions made in the analyzes, including not accounting for the concentration dependence of transport properties or the assumption of an ideal solution.

Newman's the idea of the method [8] is to measure a complete set of transport properties like conductivity, the salt diffusion coefficient and cation transference number.

The advantage of the method is that it does not require that the solution be dilute and ideal.

To determine individual transport properties following measurements were performed:

conductivity - standard impedance measurement;

salt diffusion coefficient - restricted diffusion measurement;

cation transference number – concentration cell OCV measurements and symmetric cell polarization

Because of non-ideal solution to measure transference number it is necessary to set two independent experiments.

First the OCV of the concentration cell:

$$M|PEO_xMX|PEO_yMX|M$$

was measured and then symmetric cell:

$$M|PEO_yMX|M$$

was polarized and OCV registered.

Combining all measurements gives ability to determine complete transport properties set.

Results

In the present work a range of transport properties such as conductivity, diffusion coefficient and cation transference number of sample series of different filler type addition is determined.

The studied system was based on low molecular weight poly(ethylene oxide) – the PEO-DME (M_w=500)-$LiClO_4$. It was choosen because it is liquid which makes synthesis and further operation easear and it is chemical analoge to high molecular weight polyethers.

Salt concentration varies from $1e^{-3}$ to 1.5 $mol*kg^{-1}$ while alumina addition remains constant (10% mass) respectively to poly(ethylene oxide) quantity.

Conductivity studies are coupled to viscosity experiments, which helps to determine ionic associations on the basis of the Fuoss-Krauss formalism.

Changes in transference number values correspond with changes of free ions and ion triplets formation while changes in conductivity are coupled with diffusion coefficient. Cation transference number (t_+) strongly depends on number of free ions and ion

triplets in system. The t_+ value is positive in wide concentration range and decreases with increasing salt concentration without a maximum value. The t_+ value is negative for the highest salt concentration.

[1] E. Quartarone, P. Mustarelli, A. Magistris, Solid State Ion. 110 (1998) 1.
[2] B. Scrosati (Ed.), Applications of Electroactive Polymers, Chapman and Hall, London, 1993.
[3] F.M. Gray, Solid Polymer Electrolytes — Fundamentals and Technological Applications, VCH, Weinheim, Germany, 1991.
[4] W. Wieczorek, Z. Florjanczyk, J.R. Stevens, Electrochim. Acta 40 (1995) 2251.
[5] B. Scrosati, R. Neat, in: B. Scrosati (Ed.), Applications of Electroactive Polymers, Chapman and Hall, London, 1993, Chapter 6.
[6] W. Wieczorek, P. Lipka, G. Zukowska, H.Wycislik, J. Phys. Chem. B 102 (1998) 6968.
[7] M.J.Spiro Chem.Education 33,464 (1956)
[8] J.Newman, Y.Ma, M.Doyle, J.Electrochem.Soc.142 (1995), 1859-1868

Properties of highly pigmented electrolytes with large porosity for rechargeable Li-polymer batteries

Jochen Schulz, Michael Popall, Birke Olsowski, Carola Cronauer
Fraunhofer-Institut fuer Silicatforschung, Neunerplatz 2, 97082 Wuerzburg, Germany
e-mail: **schulz@isc.fhg.de**, tel (+) 49 931 4100 551, fax (+) 49 931 4100 559

Introduction

In the last decades, there were strong efforts in developing rechargeable lithium batteries with polymeric binders and electrolytes. These battery types have great advantages in safety and shaping aspects as compared to lithium ion batteries. Most of the concepts therefore are based on the extraction of plasticizers by solvents in the formed stack and adding the conducting salt solution afterwards (Bellcore-technique, e.g., [1]).

In this abstract, the addition of highly porous pigments on silica basis to an inorganic-organic hybrid polymer as a binder is described. The porous electrolyte formed by this procedure can be filled without any extraction step with the conducting salt solution. The influence of pigment pretreatment on the particle surfaces, the degree of filling of the binder, and the electrochemical properties are described.

Experimental

Silica-based particles with a specific surface of about 300 m^2/g and particle size of about 5 (Merck: LiChrospher®) and 10 µm (Merck: Pharmprep®) were used. These particles were coated with hydrolyzed / polycondensated dimethyldiethoxysilane (DMDS), 3-glycidoxypropyltrimethoxysilane (GLYMO), and a polyethersilane (PES) (silane A1230, GE silicone), respectively. The ratio between the pigments and the coating material was varied and the effect on the particle surface investigated by BET. The coated and uncoated pigments were mixed into an inorganic-organic hybrid polymer based on GLYMO and trivinylethoxysilane [2]. The pigmented binders were pressed into pellets and cured at temperatures between 100 and 150 °C. These pellets were investigated by BET and SEM and saturated with $LiPF_6$ dissolved in ethyl- / dimethylcarbonate solution (LP 50, Merck). The conductivities of these saturated pellets were measured by impedance spectroscopy (Solartron SI 1260).

Results and discussion

The specific surface of the coated pigments show only a slight decrease of about 20 % at molar ratios between 25 and 5 of pigment to coating silane. At lower ratios, the specific surface decreases drastically. Therefore, further investigations were performed at a molar ratio of 9. SEM investigations show no significant morphological differences between the three different types of coatings applied. Significant changes of the chemical behavior are observed between DMDS (hydrophobic) on the one side, and the GLYMO (hydro-philic plus reactive coating) and PES (hydrophilic) on the other side: The DMDS coated pigments showed a reduced bulk density as compared to the other ones due to reduced particle-particle interactions. This is also reflected in the behavior upon incorporation into the inorganic-organic polymer and addition of the conducting salt solution. Only 40 mass-% of hydrophobized pigments can be added to the binder, whereas about 90 mass-% are possible with the other, more hydrophilic ones. The pellets fabricated are saturated with the Li salt solutions. The take-up of salt solutions by the hydrophobized pellets is only about 30 mass-%, the pellets containing GLYMO-coated pigments can take up 45 mass-%, and the ones containing silane PES-coated pigments about 55 mass-%. This behavior clearly reflects the degree of hydrophobicity (PES < GLYMO < DMDS). The conductivity also show a dependency on the hydrophobicity and on the content of the conducting salt solution uptake. Pellets containing DMDS coated pigments have a conductivity < 10^{-7} S/cm. At comparable salt solution concentrations below 40 mass-%, the conductivities of systems containing PES-coated pigments are a about a factor of one thousand higher than that of the GLYMO-coated pigments. At a level of about 45 mass-% and above (PES) both systems show similar conductivities slightly below 10^{-3} S/cm.

Conclusions

The possibility to form highly porous separators for rechargeable lithium polymer batteries is demonstrated. The pigments involved have to be coated to show high hydrophilicity in order to increase the amount of conductive Li salt solution. The incorporation of the salt solution into the porous separator is due to capillary forces of the porous separator. Conductivities up to 10^{-3} S/cm can be achieved. This process of formation of Li conducting separators does not involve any extraction processes which is technologically very relevant.

References

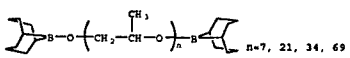
[1] T. Michot, A. Nishimoto, M. Watanabe, Electrochim. Acta 45 (2000), 1347.
[2] M. Popall, R. Buestrich, G. Semrau, G. Eichinger, M. Andrei, W. O. Parker, S. Skaarup und K. West, Electrochim. Acta 46 (2001), 1499.

Facile Preparation of Organoboron-based Ion Conductive Polymers

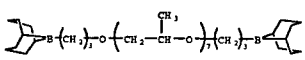
Tomonobu MIZUMO, Kenji SAKAMOTO, Noriyoshi MATSUMI, and Hiroyuki OHNO*
Department of Biotechnology, Tokyo University of Agriculture and Technology,
Koganei, Tokyo 184-8588, JAPAN
e-mail: **mizmo@cc.tuat.ac.jp**, Tel & FAX +81-(42)-388-7024

Introduction

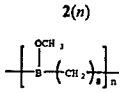
During recent few years, boron containing polymer electrolytes have drawn a great deal of attention as a new class of lithium ion conductor. Several researchers have reported the anion trapping nature of Lewis acidic borons [1], and the excellently high dissociation constant of borates [2]. In the present work, we examined facile preparations of organoboron based anion trapping polymer electrolytes using 9-borabicyclo[3.3.1]nonane (9-BBN), or monobromoborane-dimethyl sulfide complex (BH_2Br-DMS) (Figure 1). Both of them are common hydroborating reagent in the field of organoboron synthesis.



1(*n*)



2(*n*)



3

Figure 1. PPO oligomers having organoboron unit on the chain ends (**1**(*n*) ,**2**(*n*)), and poly(boric ester) (**3**).

Experimental

To α,ω-dihydroxyl PPO or α,ω-diallyl PPO oligomers, 0.5 mol cm^{-3} THF solution of 9-BBN (Aldrich) equimolar to the PPO chain ends was added dropwise at room temperature, and the resulting mixture was stirred for 5 h. This reaction gave the corresponding PPO having boric ester (**1**(*n*); *n* stands for number of the repeating unit of PPO), or alkylborane (**2**(*n*)) structure, respectively without generation of water. Then equimolar amount of lithium salt toward the organoboron unit was added to the solution.

We have also prepared poly(boric ester) according to *Chujo*'s method [3]. To a small excess amount of 1.0 mol cm^{-3} dichloromethan solution of BH_2Br-DMS (Aldrich), 1,7-octadiene was added dropwise at 0 °C, and stirred for several hours. The obtained solution of the poly(organoboron halide) was treated with dry methanol to give the corresponding poly(boric ester) (**3**). The polymer was purified by reprecipitation in dry methanol. Then lithium bis (trifulotromethylsulfonyl)imide (LiTFSI) was added to the THF/methanol solution of **3**.

In each case (**1**(*n*), **2**(*n*), and **3**), after removing solvents, the sample was dried *in vacuo* for 48 h before subjected to the measurements. The bulk ionic conductivity of each sample was measured by complex impedance method over frequencey range from 10^1 to 10^6 Hz.

Results and discussion

PPOs having 9-BBN structure on chain ends

The ionic conductivity of **1**(*7*)/$LiSO_3CF_3$ and **2**(*7*)/$LiSO_3CF_3$ was 4.57×10^{-6} S cm^{-1} and 2.83×10^{-6} S cm^{-1} at 50 °C, respectively (Figure 2). These values were lower than that of a typical PPO/$LiSO_3CF_3$ system (1.26×10^{-5} S cm^{-1}). This relatively low ionic conductivity is attributable to the decreased contribution of anion migration. The lithium ion transference number for **1**(*7*)/$LiSO_3CF_3$ and **2**(*7*)/$LiSO_3CF_3$ was 0.67 and 0.57, respectively. Similarly, **1**(*7*)/$LiCO_2CF_3$ showed high lithium ion transference number of 0.63. These values were comparable to that of polyethers having covalently bonded salt groups [4]. On the other hand, **1**(*7*)/LiTFSI showed higher ionic conductivity. However, the lithium ion transference number was 0.28.

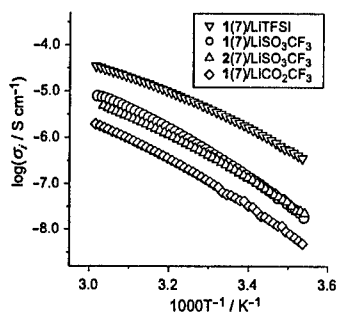


Figure 2. Temperature dependence of the ionic conductivity for **1**(*n*) and **2**(*n*) containing various lithium salts.

Poly(boric ester)s

The poly(boric ester) **3** was obtained as amorphous polymer. However, after adding LiTFSI (the molar ratio of Li^+ to boron atom was 10 - 30 %), an endothermic peak was observed for each sample in the DSC measurement. These peaks are attributable to the polymer/salt complex formation. The **3**/LiTFSI under a salt concentration of 20 % showed ionic conductivity of 4.34×10^{-6} S cm^{-1} at 50 °C during a cooling scan. It should be noted that polymer **3** showed considerable ionic conductivity even in the absence of polyether segments.

Conclusions

Organoboron based ion conductive polymers were readily prepared using common hydroborating reagents such as 9-BBN and BH_2Br-DMS. Obtained polymers showed characteristics as a new class of Lewis acidic polymer electrolytes.

References

[1] a) M. A. Mehta and T. Fujinami, *Solid State Ionics*, **113-115**, 187 (1998). b) W. Xu, X. Sun, and C. A. Angell, *Electrochim. Acta*, **48**, 2255 (2003). c) S. Tabata, T. Hirakimoto, M. Nishiura, and M. Watanabe, *Electrochim. Acta*, **48**, 2105 (2003). d) N. Matsumi, K. Sugai, and H. Ohno, *Macromolecules*, **36**, 2321 (2003).

[2] a) W. Xu, and C. A. Angell, *Electrochem. Solid State Lett.*, **4**, E1 (2001). b) W. Xu, D. Williams, and C. A. Angell, *Chem. Mater.* **14**, 401 (2002). c) H. Yamaguchi, H. Takahashi, M. Kano, and J. Arai, *J. Electrochem. Soc.*, **150**, A312 (2003).

[3] Y. Chujo, N. Takizawa, and T. Sakurai, *J. Chem. Soc., Chem. Commun.*, **1994**, 227.

[4] a) K. Ito and H. Ohno, *Electrochim. Acta*, **43**, 1247 (1998). b) Y. Tominaga, T. Mizumo, and H. Ohno, *Polym. Adv. Technol.*, **11**, 524 (2000). c) T. Fujinami, Y. Buzoujima, *J. Power Sources*, **119-121**, 438 (2003). d) T. Mizumo and H. Ohno, *Polymer*, **45**, 861 (2004).

Model composite polymer electrolytes containing tripenylborane

Marcinek M., Żukowska Z. and Wieczorek W.
Warsaw University of Technology
ul. Noakowskiego 3, 00-664 Warsaw, POLAND
e-mail: **marekmar@soliton.ch.pw.edu.pl** tel (+) 4822 6605739

Introduction

It seemed that the next step in the development of composite polymer electrolytes will be to obtain a highly single cation conductive systems. The idea is based on the use of anion-trapping compounds as additives. In the literature studies of the use of cation receptors such as crown ethers, cryptands and calixarenes in low molecular weight non-aqueous solutions [1-4] as well as polymer electrolytes are more widely described. Anion receptors based on boron compounds were applied to the solutions of lithium salts in aprotic (inert) electrolyte based on low molecular weight solvents [5,6] as well as in gel polyelectrolytes.[7] Boron based aza ether compounds (borane, borate complexes) have been studied by McBreen and coworkers [8-11] using mainly Near edge x-ray absorption fine structure spectroscopy (NEXAFS). These studies showed that the degree of complexation of Cl^- or I^- anions strongly depends on the structure of the boron compounds. Also the dramatic enhancement in ionic conductivity upon the addition of boron compounds has been noticed in these electrolytes.

This paper describes the physico chemical properties of composite electrolytes based on PEODME M_w=500 triphenylborane complexes with different salts LiI, $LiCF_3SO_3$, LiNTFSI, $LiBF_4$ and $LiClO_4$ (0,2 mol/g of polymer).

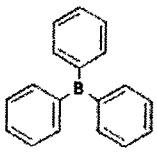


Figure 1. Structure of triphenyl borane

As a compound the triphenylborane is a relatively stable Lewis acid.

Studies on the use of anion receptors in polymer electrolytes are very limited. Papers dealing with this subject are based on either theoretical predictions [12] or studies on addition of boron family compounds, as well as cyclic or linear aza-ether structures with electron-withdrawing groups to oligoethers. [9-11, 13] The unique features of the new type of ionic conducting polymers with grafting anion receptors based on aza-ether structures are also described in literature.

Experimental

Impedance spectroscopy, FTIR

Results and discussion

Upon addition of the triphenylborane to the PEODME based model polymer electrolytes the increase in the conductivity in lower temperature range (e. g. below 0°C).

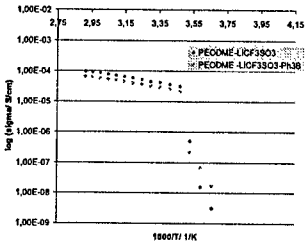


Figure 2

In higher temperature range upon anion complexation in some cases (PEODME $LiClO_4$, $LiCF_3SO_3$ electrolytes) the overall conductivity decreases proving that in this concentration (0,2 mol/kg PEODME) and temperature range the ion transport occurs mainly via anions.

The types of interactions between polymer salt and triphenylborane are discussed on the basis of FTIR spectroscopy.

Conclusions

The new model composite electrolytes has been synthetized and analysed in order to verify the use of triphenylborane as an anion receptor polymer ionic conductive systems

References

1. Y. Matsuda, H. Hayashida, M Morita M. *J. Electrochem. Soc.* **134** (1987), p. 2107.
2. A.F. Danil de Namor, M.A. Llosa Tanco, M. Salomon., J.C.Y. Ng. *J. Phys. Chem.* **98** (1994), p. 11796.
3. A.F. Danil de Namor, M.A. Llosa Tanco, M.Salomon, J.C.Y. Ng. *J. Phys. Chem.* **100** (1996), p. 14485.
4. A.F. Danil de Namor, L.E. Pulcha Salazar, M.A. Llosa Tanco, D. Kowalska, J. V. Salas, R. A Schulz *J. Chem. Soc. Faraday Trans.* **94** (1998), p. 3111.
5. A.F. Danil de Namor, R. G. Hutcherson, F. J. S. Verlade, M. L. Z. Ormachera, L. E. P Salazar, I. A. Jammaz, N. A. Rawi *Pure & Appl. Chem.* **70** (1998), p. 769.
6. H. S. Lee, X. Q. Yang, C. L. Xiang, J. McBreen, L. S. Choi. *J. Electrochem. Soc.*, **145**, (8)(1998), p. 2813.

7. X. Sun, H. S. Lee, S. Lee, X. Q.Yang, J. McBreen *J. Electrochemical & Solid State Letters* **1** **(6)**(1998), p.239.
8. F. Zhou, D. R. MacFarlane, M. Forsyth *Electrochim. Acta* **48** **(12)**(2003), p.1749.
9. J. McBreen, H. S. Lee, X. Q. Yang, X. Sun *J. of Power Sources* **89**(2000), p. 163.
10. H. S Lee, X. Q. Yang, X. Sun, J. McBreen *J. of Power Sources* **97-98**(2001), p. 566.
11. H. S. Lee, X. Q. Yang, J. McBreen, L S.Choi , Y. Okamoto, *Electrochimica Acta*, , **40** **(13-14)**(1995), p.2353.
12. P. Johansson, *Electrochim. Acta*, **48** **(14-16)**(2003), p. 2291.
13. H. S. Lee, X. Q. Yang, J. McBreen, L. S. Choi, Y. Okamoto Y. *J. Electrochem. Soc.*, **143** **(12)**(1996), p. 3825.

NMR Studies of Mass Transport in Polymer Electrolytes for Batteries and Fuel Cells

Steve G. Greenbaum
Physics Department, Hunter College of the City University of New York, USA
e-mail:steve.greenbaum@hunter.cuny.edu, tel (001) 212 772 4973, fax (001) 212 772 5390

Introduction

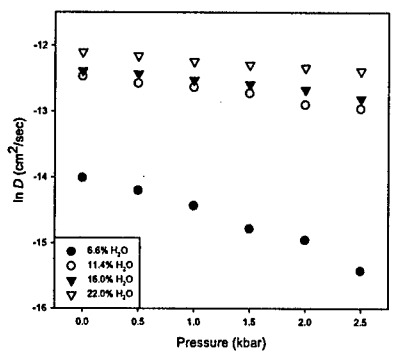
Nuclear Magnetic Resonance (NMR) remains one of the premier analytical methods to investigate structure and dynamics of disordered media. Two classes of materials germane to electrochemical conversion and storage technology are polyether-based solid electrolytes for lithium battery applications, and proton conducting membranes for fuel cells. The NMR techniques brought to bear in these studies range from spin-lattice relaxation probes of short-range phenomena to pulsed field gradient spin-echo determination of ion and molecular self-diffusion coefficients, the latter method more directly related to ionic conductivity and, in the case of fuel cells, fuel crossover phenomena. This talk will review recent experiments on superacid solutions as a model for proton conduction in sulfonated polymers. In a collaboration with T. Zawodzinski (Case Western Reserve U.), we explore the relationships between solution viscosity, ionic and molecular diffusivity, and electrical conductivity in these systems, and conclude that the presence of ordered ion/solvent structures at certain concentrations can facilitate proton transport. These studies are now being extended to the phosphoric acid/water system and, in collaboration with B. Benicewicz (Rensselaer Polytechnic Inst.), phosphoric acid immobilized in membranes. We have also implemented the use of pressure as a thermodynamic variable in diffusion measurements on NAFION. Results of the first such measurement on any composite material (to our knowledge) are given. On the lithium battery side, we will present ion and host mobility data on the diglyme: $LiCF_3SO_3$ system, a low molecular mass analogue of PEO-based polymer electrolytes, which have been extensively studied via vibrational spectroscopy by our collaborator, R. Frech. (University of Oklahoma). Finally, in collaboration with E. Peled and D. Golodnitzky (Tel Aviv University), we will show conductivity enhancement effects observed in magnetically oriented PEO-based polymer electrolytes, providing additional evidence for ion transport along the direction of the PEO helices

Experimental

One of the topics to be presented involves the first known pressure-dependent measurement of water self-diffusion in a membrane; NAFION-117 was chosen for this investigation. The measurements were conducted in the fringe (inhomogeneous) field region of a 7 T NMR magnet, with a central field value of 1.7 T and a gradient strength ($G = dB_z/dz$) of 0.253 T/cm. A standard NMR probe was fitted with a Cu/Be high pressure bomb containing the rf coil and sample.

Results and discussion

The proton NMR self-diffusion coefficients were extracted from spin-echo decays in the presence of the static field gradient. NAFION membranes containing four different water contents were investigated and the results are shown below.[1]



Activation volumes extracted from the data, according to $\Delta v = -kT\left(\frac{\partial \ln D}{\partial P}\right)_T$ increase with decreasing water content, suggesting that polymer pendant group motions are involved in water and proton transport at low water content.[1]

References

[1] J. R.P. Jayakody, P.E. Stallworth, E. Mananga, J. Zapata-Farrington, *Journal of Physical Chemistry B* 108, 4260 (2004).

This research was supported by grants from the U.S. Office of Naval Research, Air Force Office of Scientific Research, and the Department of Energy.

Quantitative Infrared Studies of PEO Based Electrolytes

J. E. Furneaux*, Allison M. McCoy*, Varuni Seneviratne*, and Roger Frech**
*Department of Physics and Astronomy, University of Oklahoma, Norman OK 73019, USA
**Department of Chemistry and Biochemistry, University of Oklahoma, Norman OK 73019, USA
e-mail: **furneaux@mail.nhn.ou.edu**, tel (+) 01(405)325-3961 x 36103, fax (+) 01(405)325-7557.

Introduction

Polymer electrolytes are ionically conducting solid phases formed by dissolving salts in ion-coordinating macromolecules. Poly(ethylene oxide), PEO complexed with lithium salts are the most often studied examples of polymer electrolytes. Here, we extend previous work [1-8] focusing on PEO with $LiCF_3SO_3$, lithium triflate.

The molecular-level understanding of the ionic conductivity mechanism in polymer electrolytes is poor, although it is known that ionic association, cation-polymer interactions, and polymer segmental motion play critical roles. Local structures identified by X-ray diffraction and vibrational spectroscopy have provided valuable insight about ionically associated species and cation-polymer interactions. Here, we extend vibrational spectroscopic studies to give a foundation for quantitative studies of ionic association and polymer configurations.

Quantitative comparisons of vibrational spectra of polymer electrolytes have been hampered by the lack of standards. We have addressed two important issues toward the development of standards. First, we have identified an effective trace marker for these systems, SbF_6^-, which has a strong unvarying signature ν_1 line at 658 cm^{-1}. Second, we have carefully studied changes in ionic association via the $\delta_s(CF_3)$ modes and confirmed that the intensity of this mode is independent of ionic association.

Experimental

PEO of various molecular weights (100,000, 10,000, 2,000 Da) was dried for 48 h at 10^{-2} mBarr and 45-50°C. We prepared a samples by dissolving $LiSbF_6$ in acetonitrile with PEO in the correct amounts to give desired ether oxygen to SbF_6^- ratios of 500:1. The solvent was then extracted and weighed amounts of the resulting solid were dissolved in acetonitrile with appropriate amounts of $LiCF_3SO_3$ to give ratios of 500:x:1. This procedure insures that all samples have a known ratio between PEO SbF_6^- so that the intensity of the SbF_6^- absorption can be used to quantitatively compare spectra. The resulting viscous solutions were cast on ZnSe windows. We then recorded temperature dependant IR spectra using a Bruker IFS66V spectrometer over the range of 400 cm^{-1} to 4000 cm^{-1}.

Results and discussion

For PEO:$CF_3SO_3^-$ ratio of 40:1, we find striking changes in spectral intensities of the $CF_3SO_3^-$ bands as the PEO melts (see attached Fig.) $LiSbF_6$ in. By normalizing these spectra using the SbF_6^- ν_1 intensity, we directly compared the total $\delta_s(CF_3)$ intensity as the temperature changed. Within the uncertainties of our fitting, we find this total intensity unchanged even as the sharp line at 760.5 cm^{-1}, associated with the aggregate species, is almost totally converted into lines associated with free and pair species. Thus we have confirmed that the absorption intensity is independent of association for $\delta_s(CF_3)$ modes in PEO:$LiCF_3SO_3$. We are in the process of further analyzing our data to extract quantitative comparisons of the other $CF_3SO_3^-$ modes. We are also examining PEO modes that are especially sensitive to conformation, the CH2 rocking and CO stretching modes between 800 and 1000 cm^{-1}. These analyses will be presented at the meeting.

Conclusions

We have studied vibrational spectra from PEO with dissolved salts to obtain relative absorption strengths for modes of the triflate anion associated with Li. We found that by adding a trace of $LiSbF_6$ to the PEO before actual sample preparation we could quantitatively compare samples with different salt concentrations and different polymer configurations. These quantitative comparisons are making possible detailed pictures of polymer-salt systems, even mixed phase systems and amorphous systems. Such pictures are a step toward a clear understanding of the interactions between the polymer and dissolved salt.

References

[1] S.Schantz, J. Sandahl, L. Borjesson, L. M. Torell, J. R. Stevens, J. Chem. Phys., **28-30** (1988) 1047.
[2] R. Frech, W. Huang, Polymer, **35** (1994), p. 235
[3] R. Frech, W. Huang, Macromolecules, **28** (1995), p. 1246.
[4]V. Seneviratne, J. E. Furneaux, R. Frech, Macromolecules, **35**, (2002), p. 6392.
[5] V. Seneviratne, R. Frech, J. E. Furneaux, Electrochimica Acta, **48** (2003), p. 2221.
[6] C. P. Rhodes, R. Frech, Macromolecules, **34** (2001), p. 2660.
[7] V. Seneveratne, R. Frech, J. E. Furneaux, M. Khan, J. Phys. Chem B, (2004) in press.
[8] V. Seneveratne, R. Frech, J. E. Furneaux, M. Khan, J. Phys. Chem B, (2004) in press.

Thursday, August 26
10:05 - 10:25

Radiotracer Diffusion and Ionic Conduction in the Polymer Electrolyte $PEO_{30}NaI$

Sh. Obeidi, B. Zazoum, and N.A. Stolwijk
Institute of Materials Physics, University of Muenster,
Wilhelm-Klemm-Str. 10, 48149 Muenster, Germany
e-mail: **stolwij@uni-muenster.de**, tel (+) 49 251 8339009, fax (+) 49 251 8338346

Introduction

Despite numerous studies related to ionic transport in polymer electrolytes the understanding of the underlying mechanisms is still far from being complete. A major reason for this unsatisfactory state-of-the-art may be that most studies on ion motion relied on dc conductivity measurements, which only yield the net macroscopic effect of all charged mobile species. Only few publications in this field report the use of ion-specific techniques by which the diffusion properties of cations and anions can be determined individually. One such technique is pulsed-field-gradient NMR. Another powerful ion-specific method, i.e., radiotracer diffusion, was only employed on a very small number of polymer-salt systems so far [1,2]. In this paper we compare for $PEO_{30}NaI$ the diffusivity of ^{22}Na and ^{125}I with the overall ionic conductivity over a wide temperature range.

Experimental

Depth profiles of ^{22}Na and ^{125}I were measured by means of microtome sectioning after isothermal diffusion annealing in the temperature range from 67 to 180 °C, in which $PEO_{30}NaI$ is fully amorphous. Additional information was obtained by measurements of the dc electrical conductivity using impedance spectroscopy. To this aim the frequency-dependent impedance of cylindrical $PEO_{30}NaI$ samples was recorded as a function of temperature using stainless steel electrodes

Results and discussion

Tracer self-diffusion coefficients resulting from Gaussian or erfc fits show near-linear behaviour in an Arrhenius plot, both for Na and I. It is found that I diffuses faster than Na by a factor of 2 to 5 upon going from high to low temperatures. This is reflected by the circumstance that the apparent activation energy of I (0.29 eV) is distinctly lower than that of Na (0.39 eV). In contrast to both tracer diffusivities, the dc conductivity exhibits a pronounced Vogel-Tamann-Fulcher behaviour reflected by a downward curvature in the Arrhenius plot. As a consequence, the overall conductivity increasingly falls below the sum of the Na and I tracer diffusivity with increasing temperature. This phenomenon can be explained by the formation of neutral Na-I ion pairs, which contribute to mass transport but not to charge transport. Evaluating simultaneously the different types of experimental data within a combined ion-pair/single-ion diffusion model yields besides the diffusivities of all individual species also the ion-pairing reaction constant as a function of temperature.

Conclusions

This work contributes to the understanding of ion transport in polymer electrolytes. For the $PEO_{30}NaI$ system the results can be summarized as follows:

(i) Neutral cation-anion pairs contribute to mass transport but not to charge transport.

(ii) The fraction of ion pairs increases with increasing temperature according to a pair formation enthalpy of 0.2 eV.

(iii) The diffusivities of the ion pair and the two single ions obey the same VTF temperature dependence.

(iv) The magnitude of the diffusivity increases in the order cation, anion, ion pair, which reflects their decreasing degree of coupling to the polymer matrix.

(v) The cation transference number of 0.1 is independent of temperature and lower than the T-dependent values estimated from the ionic tracer diffusion coefficients.

(vi) Cation transport largely takes place in the highly mobile ion-pair configuration

References

[1] A.V. Chadwick, J.H. Strange, and M.R. Worboys, Solid State Ionics 9-10, 1155 (1983)

[2] D. Fauteux, M.D. Lupien, and C.D. Robitaille, J. Electrochem. Soc. 134, 2761 (1987)

Relaxation of Ions and Dipoles in LiTFSI Salt-in-Polymer and Polymer-in-Salt Electrolytes

J.R. Dygas[1], M. Marzantowicz[1], F. Krok[1], A. Łasińska[1], Z. Florjańczyk[2], A. Affek[2], E. Zygadło-Monikowska[2]

[1]Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warszawa, Poland
[2]Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warszawa, Poland
e-mail: **jrdygas@mech.pw.edu.pl**, tel (+48) 22 6608213, fax (+48) 22 6282171

Introduction

Lithium bis(trifluoromethanesulfone)imide (LiTFSI), salt with large and flexible anion, is an attractive component of polymer electrolytes. LiTFSI dissolved in PEO inhibits crystallization and the polymer electrolyte can be amorphous or semi-crystalline [1]. Recently, we reported high ionic conductivity in amorphous mixtures of acrylonitrile – butyl acrylate copolymer and LiTFSI at high content of the salt [2]. Here we analyze impedance spectra of the two systems, representing salt-in-polymer and polymer-in-salt electrolytes, in order to explore relaxation of ions and dipoles.

Experimental

Random copolymers of acrylonitrile and butyl acrylate, poly(AN-co-BuA), were prepared by radical polymerization. Foils of poly(AN-co-BuA) or high molecular weight PEO with various amounts of LiTFSI were obtained from acetonitrile solutions.

Impedance of polymer foils, placed between gold plated stainless steel electrodes in chamber filled with argon, was measured in frequency range from 10 MHz to 0.01 Hz at temperature between -60°C and 100°C. Automated analyzers allowed measurement of impedance of absolute value up to 100 TΩ.

Results

Impedance spectra were analyzed by fitting equivalent circuit, which modeled phenomena affecting the ac response of polymer electrolyte: high frequency dielectric constant, dipolar relaxation, flat dielectric loss, ionic conductivity with dispersion caused by relaxation of mobile ions and polarization at electrodes, see inset of Fig.1.

At low temperature relaxation of bond dipoles within macromolecules is seen as dielectric loss peak at high frequency. Increase of the real part of conductivity above the dc value, accompanied by a finite decrease of the dielectric constant $\Delta\varepsilon$, follows power law frequency dependence with exponent $n \cong 0.45$. Flat dielectric loss at high frequencies obeys power law frequency dependence with exponent $m \cong 0.77$. The relaxation frequency of local ionic charge displacement, the onset frequency of conductivity dispersion and the frequency of crossover to flat dielectric loss provide information on various time scales of ionic motion. The characteristic frequencies follow similar temperature dependence as the dc conductivity, see Fig.1. The relaxation strength $\Delta\varepsilon$ can be used to estimate the spatial extent of non-random displacements of mobile ions. Despite observed universality of the ac response, quantitative differences between the two studied systems exist. Variation with the salt content of the characteristic quantities, derived from impedance spectra to describe the relaxation of ions and dipoles, will be discussed.

References

[1] J.R.Dygas, B.Misztal-Faraj, Z.Florjańczyk, F.Krok, M.Marzantowicz, E.Zygadło-Monikowska, Solid State Ionics **157** (2002) p. 249.

[2] Z.Florjańczyk, E.Zygadło-Monikowska, A.Affek, A.Tomaszewska, A.Łasińska, M.Marzantowicz, J.R.Dygas, F.Krok, submitted to Solid State Ionics.

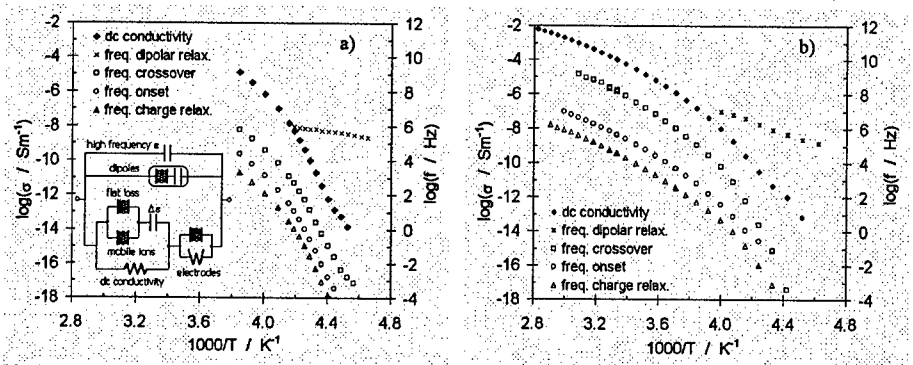


Fig.1. Temperature dependence of the dc conductivity and characteristic frequencies: for: a) PEO_{10}:LiTFSI; b) poly(AN-co-BuA):LiTFSI of molar ratio 2AN m.u.:1BuA m.u.:1.5LiTFSI. Equivalent circuit is shown as inset.

Free Volume and Conductivity in Polymer Electrolytes: A temperature and pressure dependent study

Steven J. Pas,[a,b,c] Malcolm D. Ingram,[c,d] Klaus Funke[a,c] and Anita J. Hill[e,f]
[a]Institute for Physical Chemistry, [b]The International Graduate School of Chemisty and [c]Sonderforschungsbereich 458, Westfälische Wilhelms-Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany.
[d]Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen, Scotland, UK AB24 3UE
[e]CSIRO Manufacturing Infrastructure and Technology and [f]School of Chemistry, Monash University, Private Bag 33, Clayton South MDC, VIC, Australia
e-mail: **stpas@uni-muenster.de**, tel (+49) 251 83 23433

Introduction

The non-Arrhenius behaviour of the temperature dependence of the DC conductivity typically measured in polymer electrolytes is the hallmark of ionic motion being coupled with the host polymer matrix. Due to this coupled nature ionic motion is most often described by considering only the properties of the host matrix, without regard to the ions themselves. One of the most common approaches for describing ionic conductivity is with free volume theory.[1]

Positron annihilation lifetime spectroscopy (PALS) is a technique used to determine the size and concentration of free volume elements (holes) in polymer electrolytes.[2] To determine if free volume can be used exclusively to describe mobile ions we studied the pressure and temperature dependence of both the conductivity and free volume of a representative polymer electrolyte.

Experimental

Polymer electrolytes were obtained by dissolving the appropriate amount of dried $NaPF_6$ into a purified and dried liquid polyether triol of a random co-polymer of ethylene oxide and propylene oxide (molecular weight of 3600 $g.mol^{-1}$, 80% ethylene oxide) to form an ether oxygen to cation ratio of 20:1. The polyol-salt complex was crosslinked with a stoichiometic amount of hexamethylene diisocyanate over a mercury catalyst.

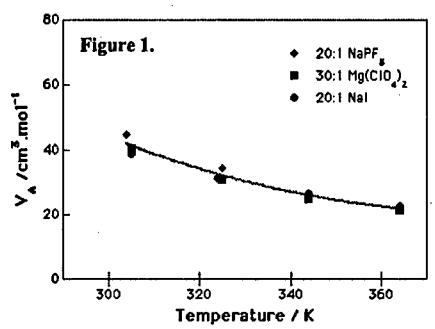
AC impedance spectroscopy at ambient pressure was carried out using a broadband dielectric analyser with samples cast into a locally built cell with stainless steel blocking electrodes. Variable pressure conductivity was performed in a high-pressure autoclave with samples sandwiched between gold electrodes.

PALS experiments were performed using an EG&G Ortec fast-fast coincidence system with a ^{22}Na source. Temperature dependent measurements were made using a Peltier temperature control system. High pressure measurements were made in a locally designed cell. Lifetimes were determined using the PFPOSFIT program with the shortest lifetime fixed to 125 ps.

Results and discussion

The DC conductivity of the 20:1 $NaPF_6$ electrolyte displayed a characteristic non-Arrhenius temperature dependence which yielded acceptable values from a VTF fit. The temperature dependence of the mean hole volume, V_h, (as measured by PALS) showed a linear increase of 0.53 $cm^3.mol^{-1}.K^{-1}$. When extrapolating the temperature dependence of V_h to zero free volume a temperature very close to T_0 from the VTF fit was found. A linear relationship of $\ln(\sigma)$ on the inverse of V_h as a function of temperature was also found. Without relying on any particular model these two observations imply that free volume is very important in mediating ion transport.

Considering the theory of Cohen and Turnbull[1] a critical volume for ionic motion of 840 $cm^3.mol^{-1}$ was calculated. This corresponds to roughly the volume of 20 ethylene oxide units. This is surprising considering the PF_6^- anion is most likely the dominant conductor (V_m=72 $cm^3.mol^{-1}$) and dynamic light scattering studies[3] have previously shown that ion motion involves the cooperative movement of around only 6 to 7 ethylene oxide units.

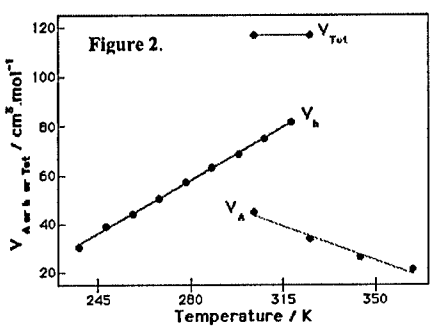


Conductivity was measured as a function of pressure at many temperatures for electrolytes consisting of several salts (NaI, $NaPF_6$ and $Mg(ClO_4)_2$) with differing concentrations. The electrolytes showed a characteristic decrease in conductivity with pressure. The activation volumes calculated from these measurements ranged from 45 $cm^3.mol^{-1}$ to 20 $cm^3.mol^{-1}$ over the temperature range 304 K to 365 K. Each of the electrolytes showed similar values and trends (Figure 1) suggesting that the volume required for ionic conducitivity depends only on the polymer matrix.

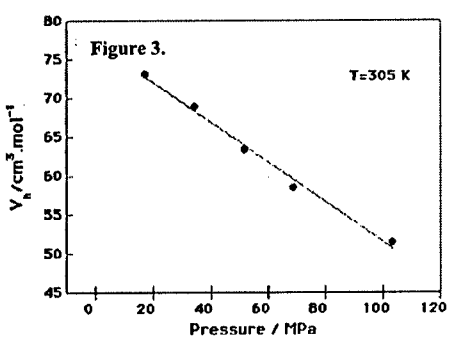
Duclot and co-workers[4] calculated critical volumes for a series of polyelectrolytes by assuming the

dependence of free volume on temperature and pressure can be taken from kinetic gas theory. Using this method a rather small critical volume of 15 $cm^3.mol^{-1}$ was calculated. This value is surprising as it is less than the molar volume of the PF_6^- anion and less than a single ethylene oxide unit.

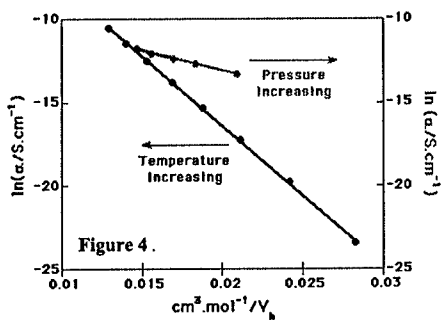
We propose that the total volume required for ionic motion can be estimated from the available free volume (V_h), as measured by PALS, plus the extra volume required for ionic motion to occur (i.e. the measured activation volume). Using this approach a constant total volume of 117 $cm^3.mol^{-1}$ has been obtained for the $NaPF_6$ electrolyte (Figure 2). This value equates to roughly 3 to 4 ethylene oxide units.



The pressure dependence of the free volume of a polymer electrolyte has been measured for the first time. In a similar way to reducing temperature, the effect of pressure is to reduce hole volume (Figure 3). A linear dependence of ln(σ), resulting from the application of different pressures, on the inverse of V_h has also been found. This linearity again suggests that free volume is important in mediating ionic transport.



From the above discussion of the hole volume, including its dependence on temperature and pressure, as well as its influence on the value of the conductivity, one might be tempted to assume that the DC conductivity, σ, is eventually determined by $V_h(p,T)$ alone. In that case, ln(σ), would have to be proportinal to $\exp(-V^*/V_h(p,T))$, where V^* is a constant. Our present reults do, however, prove that such a treatment is not appropriate. This is shown in Figure 4. Evidently, the variation of V_h with temperature and the variation of V_h with pressure affect the measured conductivity in very different ways. A proper understanding of the origin of the different slopes of the two lines in Figure 4 requires consideration of the dynamics of the mobile ions.



Conclusions

A linear dependence of ln(σ) on the inverse of V_h (both as a function of temperature and pressure), and zero hole volume being close to T_0 obtained from a fit to the VTF equation suggests free volume is very important in mediating ionic transport. Activation volume measurements of several electrolytes (of differing concentrations) suggest that the volume required for ion motion depends on the polymer matrix. Critical volumes required for ionic motion calculated on the basis of certain models were found to be unrealistic. The addition of the activation volume to the mean hole volume, however, provides a more realisitic and model-free alternative. By comparing the relationship of ln(σ) on the inverse of V_h, as a function of temperature and pressure, it was found that free volume alone cannot be used to explain the non-Arrhenius behaviour of the temperature dependence of the DC conductivity. Therefore, the practice of describing ionic motion by considering only the properties of the polymer matrix may be inappropriate.

References

[1] M.H. Cohen and D. Turnbull. *J. Chem. Phys.*, **31** (1959), p1164.

[2] D. Bamford, G. Dublek, A. Reiche et.al. *J. Chem. Phys.* **115** (2001), p. 7260

[3] L .Torrell and C.A. Angell. *Brit Poly J.* **20** (1988), p. 173

[4] M. Duclot., F. Alloin, O. Brylev et. al. *Solid State Ionics* **136-7** (2000), p. 1153

Thursday, August 26
11:25 – 12:10

Overcoming Performance Limitations of Membrane-Electrode Assemblies for Direct Methanol Fuel Cells

Piotr Zelenay
Los Alamos National Laboratory, Materials Science and Technology Division
Los Alamos, New Mexico 97545, U.S.A.
E-mail: zelenay@lanl.gov; *Phone:* (+) 505-667-0197; *Fax*: (+) 505-665-4292

Thanks to the high energy content of liquid methanol (6.1 kWh kg^{-1} at 25°C), already demonstrated potential for the integration into a compact system and convenience of use, the polymer-electrolyte direct methanol fuel cell (DMFC), is viewed as a promising power source for portable civilian and military applications. When compared with other power sources, a typical "reference" 20 W DMFC system easily outperforms its market competitors, Li-ion batteries in particular, at operating times longer than approximately 10 hours. This is because, for a net stored energy higher than 200 Wh (= ten-hour operation of a 20 W system), the fuel cell based system becomes lighter than an equivalent battery pack.

Key Performance Factors. –DMFC research and development effort at Los Alamos National Laboratory focuses on several potential applications of direct methanol fuel cells, including portable power source for the military (20-100 W power level), consumer electronics (*e.g.*, laptop computers, cellular phones), and auxiliary power for automotive transportation. Depending on the specific system requirements, the temperature and pressure of cell operation, catalyst loading and cell design may differ, sometimes quite significantly, however, the key factors impacting DMFC performance remain the same, regardless of application. These factors are: *(i)* anode and cathode electrocatalysis, *(ii)* membrane performance, in particular conductivity and methanol/water permeability, *(iii)* structure and durability of the membrane-electrode assembly (MEA), including optimization of the gas-diffusion layers, and *(iv)* single cell and stack hardware. In this presentation, we will provide an overview of the most recent accomplishments in the fundamental electrode and membrane research, aimed specifically at improving the performance and performance durability of today's MEAs.

Electrocatalysis. –In this part of the talk we will analyze the effect of atomic composition of Pt-Ru catalysts on the DMFC anode performance. We will also present the latest results from the cathode catalyst effort that focuses on improving the performance by lowering the average size of nanopraticles of platinum and other platinum-based catalysts.

Performance Durability. –We will further present the latest data on performance durability, possibly the single most important issue for the future of DMFCs. Among several factors identified at Los Alamos as directly impacting the long-term DMFC stability, we will focus on *(i)* surface oxidation of the platinum cathode, *(ii)* ruthenium permeation through the membrane, *(iii)* anode operation under extreme conditions, and *(iv)* changes in the hydrophilic and hydrophobic properties of the cathode.

Novel DMFC MEAs. –Finally, we will introduce a new MEA fabrication process designed to minimize unrecoverable performance loss of Nafion®-based DMFCs. Novel MEAs are made using recently developed alternative catalyst/ionomer suspensions and high-temperature processing routes, which include an acid boil. The new fabrication process results in improved long-term MEA stability. For example, at life-test times longer than 1400 hours, performance of the novel MEA is up to 20% higher than that of the standard MEA. After 3000 hours of the life test (the end of the longest novel MEA life test), the unrecoverable performance loss of the novel MEA is only 15 mA cm^{-2} at 0.5 V, whereas that of a standard Los Alamos MEA is 37 mA cm^{-2} after merely 1000 hours.

Different rates of performance degradation are accompanied by different changes in the high frequency resistance (HFR) of the MEAs. The HFR gain is much higher for the standard MEA than for the MEA obtained by the new process. Since under well-controlled humidification conditions changes to membrane conductivity over time are expected to be very small, the HFR increase is likely to be caused by rising resistance at the membrane/electrode(s) interface(s) – much faster for the standard MEA than the novel one. This process appears to occur much faster for the

standard MEA, suggesting significantly more robust membrane-electrode interface of the novel MEA.

Electrochemically active surface area of the anode and the cathode can be determined at various life test times using carbon monoxide stripping charge. Loss in that charge is found to be much lower for the novel than standard MEA. This may be due to improved networking of the Nafion® polymer within the electrode, leading to better catalyst layer integrity.

Further analysis of CO stripping voltammetry for the two MEAs reveal the impact of high-temperature and pre-leaching of the Pt-Ru anode catalyst in acid boil on ruthenium crossover and subsequent contamination of the cathode by Ru. As also observed earlier with other systems, the high-temperature treatment and pre-leaching involved in the novel fabrication process help to greatly reduce ruthenium crossover.

NMR Studies of Mass Transport in High Acid Content Fuel Cell Membranes Based on PBI/Phosphoric Acid

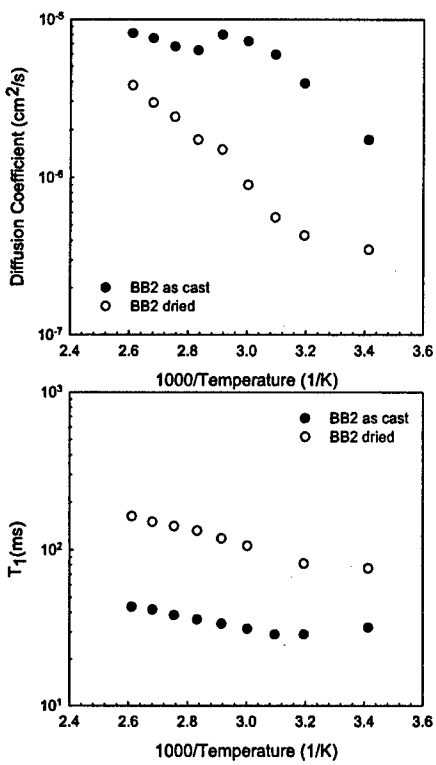
S.H. Chung[#], Lisa Durantino[#], J.R.P. Jayakody*,
H. Zhang[‡], L. Xiao[‡], B. Benicewicz[‡], and S.G. Greenbaum*
[#] William Paterson University of New Jersey,
Wayne, NJ 07470 USA
*Hunter College of CUNY
New York, NY 10021 USA
[‡]Rensselaer Polytechnic Institute,
Troy, NY 12180 USA

Acid doped polybenzimidazole (PBI) has emerged as a promising candidate for a low-cost and high performance fuel cell membrane material. It has been shown that this polymer electrolyte membrane exhibits high ionic conductivity at temperatures up to 200°C.[1] However, additional progress is still needed for the large-scale application of PBI in fuel cells. Furthermore, the conventional method to prepare acid doped PBI membranes involves a multi-step process while the mechanical properties of the resulting membranes are largely limited by the low molecular weight of PBI used in previous studies. A novel process, previously reported and termed as the PPA process, has been developed to prepare pyridine-based PBI (PPBI) membranes loaded with high levels of phosphoric acid by direct casting of the PPA polymerization solution without isolation or redissolution of the polymers, followed by a sol-gel transition induced by the hydrolysis of PPA into phosphoric acid.[2]

In an attempt to understand the ion dynamics in these membranes, two samples of this material prepared in a different manner have been examined by using nuclear magnetic resonance (NMR) techniques over a range of temperatures from 290 to 383 K. The first sample BB1 was prepared by soaking the PBI films in phosphoric acid solutions whereas the second sample BB2 was produced by the new sol-gel process which allows for greater levels of phosphoric acid loading. Using experimental techniques described elsewhere[3], ^{1}H (I=½) and ^{31}P (I=½) NMR linewidths, spin-lattice relaxation times T_1, and self-diffusion coefficients D for these materials are reported. To obtain consistent and reproducible data, the samples were dried at 423K for 90 minutes. Significant differences in the diffusion coefficients and relaxations times before and after drying are noted. For all samples a single ^{31}P peak centered close to the reference signal from 85% H_3PO_4 was observed. There were no spectral indications of condensed phosphates. In BB1 the linewidths and relaxation times show weak temperature dependence in contrast to the data for BB2 where there were indications of motional narrowing and a well-defined T_1 minimum. The diffusion data show that protons diffuse faster than the phosphorus carrying species, which means that the inter-phosphate proton transfer is important in these materials. Proton NMR diffusion and T_1 data for BB2 are shown at right.

This work was supported, in part by the U.S. Office of Naval Research (Hunter College), and A.R.T. program (William Paterson University).

Proton NMR Self Diffusion and Spin-lattice Relaxation



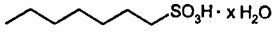
1.Wang J. T., Savinell R. F., Wainright J., Litt M. and Yu H., *Electrochim. Acta*, **1996**, 41(2), 193.
2. Krishnamurthy B., Zhang H., Ramanathan L. S., Xiao L., Scanlon E., Choe E. W., and Benicewicz B. C., 202nd ECS meeting abstract, Salt Lake City, Oct. 2002.
3. Chung, S.H., Bajue, S. and S.G. Greenbaum, S.G., *J. Chem. Phys.* 2000, 112(19), 8515.

Proton Conductors for Low Humidity Conditions

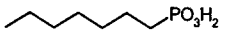
Timo Rager*, Michael Schuster, Akihiro Noda, Klaus-Dieter Kreuer, Joachim Maier
MPI for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany
*Current address: Syngenta Crop Protection AG, Im Breitenloh 5, 4333 Münchwilen, Switzerland
e-mail: **timo.rager@syngenta.com**, phone (+)41 62 868 53 01, fax (+)41 62 868 56 05

Introduction

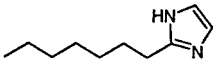
An important challenge in polymer electrolyte fuel cell research is to find proton conducting materials that require less humidification and show reduced swelling in water and water/methanol as compared to state of the art membranes. Mainly three functional groups have been considered as proton solvents for fuel cell membranes: sulfonic acid groups [1], phosphonic acid groups [2,3], and nitrogen heterocycles [4]. In order to evaluate the suitability of these functional groups for fuel cell applications at low hydration, we have prepared the model compounds **S-C$_7$**, **P-C$_7$**, **I-C$_7$** and characterized these with respect to proton conductivity in the water-free state, proton diffusion coefficients, thermo-oxidative stability, water uptake, and electrochemical stability.



S-C$_7$
mp ≤ 37 °C



P-C$_7$
mp 104-106 °C



I-C$_7$
mp 46-48 °C
bp 125 °C/10^{-2} mbar

Experimental

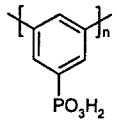
Proton conductivity was measured by impedance spectroscopy, diffusion coefficients were determined by frequency-resolved pulsed field gradient (PFG) NMR, thermal stability was investigated by TGA-MS under 20% oxygen atmosphere, water uptake was investigated by TGA under saturated water vapor, and electrochemical stability by cyclic voltammetry.

Results and discussion

S-C$_7$ is by far the most hygroscopic of all compounds and could only be prepared in the form of hydrates with a minimum water content of 0.1 H_2O per sulfonic acid group. Its conductivity, thermal stability and electrochemical stability decrease rapidly with decreasing water content. **I-C$_7$** is readily obtained in the anhydrous state and has essentially no disposition for taking up water. Its conductivity is even below the conductivity of **S-C$_7$** with the lowest water content. The compound shows good electrochemical stability, but at the same time strongly inhibits the H_2 oxidation and O_2 reduction reactions at the Pt electrodes. The best combination of properties is given for **P-C$_7$**. High degrees of self-dissociation and high mobility of the acidic protons lead to reasonably high proton conductivities in the fully anhydrous state, the water uptake from the gas phase is clearly reduced as compared to **S-C$_7$**, whereas the thermo-oxidative stability is significantly higher than for the two other compounds. The electrochemical properties are intermediate between those of **S-C$_7$** and **I-C$_7$**.

From these observations we conclude that the phosphonic acid group has the highest potential to meet the requirements for a proton conductor at low hydration.

As the next step toward a chemically stable fuel cell membrane, we have prepared a fully aromatic polymer with a high density in phosphonic acid groups.



References

[1] O. Savadogo J. New. Mat. Electrochem. Systems **1** (1998), p. 47
[2] X. Xu, I. Cabasso PMSE (Am. Chem. Soc. Polym. Mat. Sci. Eng. Div.) **68** (1993), p. 120
[3] S.V. Kotov, S.D. Pedersen, W. Qiu, Z.-M. Qiu, D.J. Burton J. Fluorine Chem. **82** (1997) p. 13
[4] K.D. Kreuer, A. Fuchs, M. Ise, M. Spaeth, J. Maier Electrochim. Acta **43** (1998), p. 1281

Brønsted Acid-Base Ionic Liquids and Ion Gels as Proton Conducting Nonaqueous Electrolytes

Md. Abu Bin Hasan Susan, Akihiro Noda, Masayoshi Watanabe
Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
e-mail: **susan@ynu.ac.jp**, tel (+) 81-45-339-3955 fax (+)81-45-339-3955

Introduction

The recognition of the polymer electrolyte fuel cells (PEFC) as the most prospective environmentally benign power sources has resulted in an upsurge of interest on the development of polymer electrolytes for such devices. This has led to the exploration of constraints associated with the use of water at temperatures higher than 100 °C and pointed eyes on the ubiquitous ionic liquids for alternatively efficient, highly proton conducting polymer electrolytes with high operational temperatures. Ionic liquids, possessing the wealth of desirable electrochemical and materials properties are very promising, but need to act as proton solvents or themselves be capable of proton conduction for their true use as proton conductors. Recently, we have reported that Brønsted acid-base ionic liquids are proton conducting and can serve as fuel cell electrolytes under nonhumidifying conditions at elevated temperatures.[1-2]

In this study, we aim at innovating protic ionic liquid systems capable of fast proton conduction and preparing ion gels by incorporating ionic liquids in network polymers. We characterize the ionic liquids and ion gels in terms of their physicochemical properties and proton conduction behavior for their potential use as proton conducting nonaqueous electrolytes.

Experimental

Appropriate amounts of bis(trifluoromethanesulfon) imide (HTFSI) and a wide variety of organic amines, maintaining defined molar ratios were mixed and heated above the respective melting points in an Ar atmosphere glove box to have a novel series of protic ionic liquids. The ion gels were prepared by *in situ* radical polymerization of a neutral hydrophobic monomer, methyl methacrylate (MMA) in the ionic liquids at 60 °C for 12 h by addition of 2 mol% of a cross linking monomer, ethyleneglycol dimethacrylate (EGDMA) and 1 mole% 2,2'-azobisisobutyronitrile (AIBN).

The thermal properties were studied using thermogravimetry (TG) and differential scanning calorimetry (DSC), while ionic conductivities were determined by complex impedance methods. The ^{1}H-NMR spectra of the ionic liquids were taken by using a double tube. Self-diffusion coefficients were determined by pulsed-gradient spin-echo (PGSE) NMR measurements. The electrochemical activity and proton transport behavior of the ionic liquids were analyzed at the three-phase boundary of the ionic liquids/Pt/N_2, H_2 or O_2 by electrochemical polarization experiments.

Results and discussion

Most of the amines formed neutral salts, which showed high thermal stability as an ionic liquid, for instance, the commenment of decomposition for the salt of 4,4'-trimethylene dipiperidine with HTFSI could be observed at temperatures >400 °C. Notably, the neutral salts of 1,2,4-triazole, triethylamine, and butylamine with HTFSI are liquid at room temperature. The melting point (T_m) of the systems changes with change in compositions. The equimolar salt for imidazole (Im)/HTFSI melts at 73 °C and the T_ms of other compositions are lower than those of the equimolar salt and Im or HTFSI, giving eutectics between the equimolar salt and Im or HTFSI. Some compositions with certain molar ratios of Im and HTFSI are liquid at ambient temperature.

The equimolar salts exhibited high conductivity ($\gtrsim 10^{-2}$ scm^{-1}). The ionic conductivity (σ) has been found to depend strongly on temperature and composition of the systems. For the Im/HTFSI system, the σ increases with increasing Im mole fraction with a sharp decrease for neat Im. The σ for [Im]/[HTFSI] = 9/1 attains the value of ca. 0.1 Scm^{-1} at 130 °C.

The analyses of the conductivity, ^{1}H NMR chemical shift, self-diffusion coefficient and electrochemical polarization results indicate that proton conduction in the representative amine-HTFSI systems depends on the composition, and in base-rich compositions, it follows a combination of Grotthuss and vehicle type mechanisms. Some of the systems studied are electroactive for H_2 oxidation and O_2 reduction at a Pt electrode under nonhumidifying condition and provide clear evidences for electric power generation by a H_2/O_2 fuel cell at elevated temperatures.

We have finally focused our attention on the construction of solid-state proton conductors. Our preliminary results show the compatibility of MMA with some of the protic ionic liquids both at the equimolar and base-rich compositions. We succeeded to preapare ion gels by radical polymerization of the compatible vinyl monomer. The obtained polymer electrolytes were self-standing, transparent, and exhibited moderately high ionic conductivity. Studies on the proper modification of this approach to obtain highly proton conducting polymer electrolytes with sufficient mechanical strength and electrochemical stability are now underway.

References

[1] M.A.B.H. Susan, A. Noda, S. Mitsushima, M. Watanabe Chem. Commun. **2003**, p. 938.
[2] A. Noda, M.A.B.H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu and M. Watanabe J. Phys. Chem. B. **107** (2003), p. 4024.

Inorganic-organic hybrid protonic polymeric materials for fuel cells based on polycondensed and organically cross-linked sulfonyl- and styrene functionalized alkoxysilanes

Stéphane Jacob [a,b], Christiane Poinsignon [b], Michael Popall [a,*]
[a] Fraunhofer Institut für Silicatforschung, Neunerplatz 2, D-97082 Würzburg, Germany
[b] Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces, ENSEEG Domaine universitaire, 1130, rue de la piscine, F-38402 St Martin d'Hères Cédex, France
e-mail: **popall@isc.fhg.de**, tel (+49) 9314100522, fax (+49) 9314100559

Introduction

A new class of proton conducting inorganic-organic polymer (ORMOCER®) electrolytes for fuel cells based on polycondensed and organically cross-linked sulfonyl- and styrene functionalized alkoxysilanes has been developed [1].

Experimental

Different synthesis processes are used. ***System-I*** is based on two polycondensates. In the first one, an alkoxysilane containing a sulfonated group and a styrene derivative functionalized alkoxysilane are hydrolyzed and co-condensed. In the other one, an alkoxysilane containing at least a nitrogen heterocycle, an amine group or a sulfonamide group and a styrene derivative functionalized alkoxysilane are reacted. The two polycondensates are then mixed. After evaporation of the solvent, the resins are shaped into thin films and organically cross-linked via UV and/or thermal curing.

System-II: the sulfonated functionalized alkoxysilane is first hydrolyzed and condensed, then the two other alkoxysilanes are added for co-condensation.

System-III: the three alkoxysilanes used for system-I are hydrolyzed and co-condensed without any partial hydrolysis of one of the component.

Results and discussion

Thermal stability of the three systems up to 180 °C (< 5 % weight loss, heating rate: 10K/min) was measured by thermo-gravimetric analysis. The conductivity of the materials shows an Arrhenius behavior in the temperature range 25 - 110 °C. Anhydrous system-I / imidazole membranes exhibited conductivities up to 5.0×10^{-3} Scm^{-1} at 110 °C.

By modifying the polycondensate synthesis process, the material properties were optimized. A 1.0×10^{-2} Scm^{-1} conductivity value was measured for system-II/imidazole membranes at 110 °C under an inert gas atmosphere. Activation energies of 0.45 up to 0.78 eV were determined depending on imidazole content in the temperature range 25 - 110 °C. The conductivity of system-III / imidazole membranes was measured from room temperature up to 140 °C. The materials have conductivities up to 9.1×10^{-3} Scm^{-1} at 100 °C. Above 100 °C, the conductivity even increases more and is as high as $2.0 \times 10^{-2} \pm 1.5 \times 10^{-3}$ Scm^{-1} at 140 °C.

Conclusions

Anhydrous proton conducting inorganic-organic polymer electrolytes with improved electrochemical and mechanical properties were synthesized. Conductivity of these ORMOCER®/imidazole membranes reach up to 2.0×10^{-2} Scm^{-1} at 140 °C.

References

[1] S. Jacob, S. Cochet, C. Poinsignon, M. Popall Electrochim. Acta 48 (2003), p. 2181

Prediction of Methanol and Water Fluxes Through a Direct Methanol Fuel Cell Polymer Electrolyte Membrane

S.S. Sandhu, R.O. Crowther, **J.P. Fellner**
Department of Chemical and Materials Engineering, University of Dayton,
300 College Park, Dayton, OH 45469-0246
e-mail: **sarwan.sandhu@notes.udayton.edu**, tel (+1) 937.229.2648, fax (+1) 937.229.2756

Abstract
The transport theory based, explicit mathematical equations are presented to predict the fluid phase superficial velocity, methanol and water molar fluxes, and the chemical species (methanol and water) dimensionless concentration profiles in the polymer electrolyte membrane, Nafion™117, of a direct methanol fuel cell. Implementation of these equations is illustrated to generate the numerical data as functions of the variables such as the pressure difference across the membrane, methanol concentration at the cell anode, temperature, and position in the membrane.

Results and Discussion

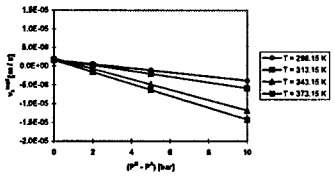


Figure 3. Fluid phase superficial velocity as a function of pressure difference for Nafion™117 membrane, current density of 100 mA / sq cm, and the assumed membrane anode-side methanol concentration of 0.1 mol / L.

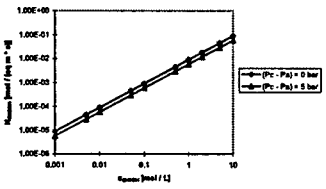


Figure 4. Methanol molar flux through the membrane as a function of the assumed membrane anode-side methanol concentration for Nafion®117 membrane, current density of 100 mA / sq cm, and cell temperature of 343.15 K.

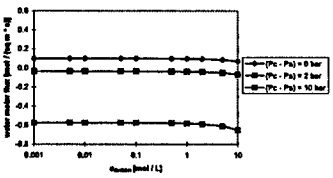


Figure 5. Water molar flux through the membrane as a function of the assumed membrane anode-side methanol concentration for Nafion™117 membrane, current density of 100 mA / sq cm, and cell temperature of 343.15 K.

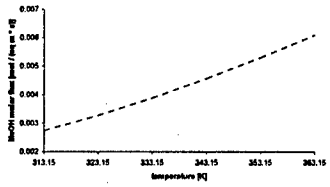


Figure 6. Methanol molar flux through the membrane as a function of temperature for Nafion™117 membrane, current density of 100 mA / sq cm, and membrane anode-side methanol concentration of 500 mol / cu m.

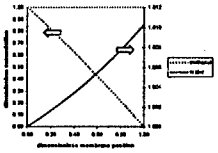


Figure 7. Dimensionless methanol and water concentration profiles for Nafion™117 membrane, current density of 100 mA / sq cm, and cell temperature of 353.15 K, and membrane-anode-side methanol concentration of 500 mol / cu m.

Conclusions

Explicit mathematical equations to predict the fluid phase superficial velocity, methanol and water molar fluxes, and their dimensionless concentration profiles in the PEM of a DMFC were presented in this paper and their implementation was illustrated to generate the data. Methanol crossover from the anode catalyst layer to the cathode catalyst layer of a DMFC can be reduced by increasing the cathode-channel flow pressure relative to the anode-channel flow pressure. Also, methanol crossover flux decreases with a decrease in the methanol concentration in the anode-side of the PEM. This decrease in the methanol concentration in the anode-side of the PEM can result from a low concentration of methanol in the feed to the anode channel of a DMFC or higher reaction rate at a higher temperature resulting in a high current density. The fluid phase superficial velocity can be directed from the anode to cathode side of the PEM, vice versa, or be zero by selecting carefully the cathode side pressure relative to the anode side pressure at the fixed values of other DMFC operational parameters such as temperature, current density, etc.

A spectroscopic study of proton conducting polymer membranes based on PVdF/PAN blends.

A.Martinelli[a], A.Matic[a], P.Jacobsson[a], L.Börjesson[a]
M.A.Navarra[b], S.Panero[b], B.Scrosati[b]
[a]Department of Applied Physics, Chalmers University of Technology, 412 96 Göteborg, Sweden
[b]Department of Chemistry, University of Rome "La Sapienza", P.le Aldo Moro 5, 00185 Rome, Italy
e-mail: **annamart@fy.chalmers.se**, tel +46 (0)31 772 3635, fax +46 (0)31 772 2090

Introduction

Within the intensive search for new suitable proton conducting materials a novel type of polymer membranes has recently gained considerable attention as promising alternative to the commercial perfluorinated membranes (Nafion®)[1,2]. These membranes are applicable to both PEMFC and DMFC, having the dual functionality of electrolyte as well as separator.

In this contribution we present a spectroscopic study on the functionality of new membranes based on a polyvinylidenefluoride (PVdF)/polyacrylonitrile (PAN) blend mixed with plasticizers, propylene carbonate and cyclopentanone (PC and CP). The porous polymer matrix has good thermal and chemical stability as well as a good ability to absorb the liquid protonic component, a 6M sulfuric acid aqueous solution. The conductivity of an optimised membrane composition, combining PVdF/PAN polymer and Al_2O_3 ceramic filler, reaches values of $\sim 10^{-1}$ Scm^{-1}.[4] We have performed infra-red (IR) and Raman experiments on membranes with varying compositions in order to investigate the functionality and the microscopic interactions in this system.

Experimental

For the synthesis of the membranes and the electrochemical characterization of them we refer to ref [3] and [4].

IR spectra were recorded using a Bruker IFS 66S instrument, with the possibility to measure ATR in the multiple reflection mode, as well as in the single-touch mode. This Bruker instrument is equipped with a FRA 106 module, used here to record FT-Raman spectra.

Results and discussion

The proton conducting property of the membrane is obtained by soaking a precursor membrane in an acidic soulution. Thus, the fucntionality of these membranes depend strongly on the acid absorbing ability. This process can readily be followed by vibrational spectroscopy where the solvents (CP and PC) and the acid have distinctly different vibrational bands. In figure 1 the IR spectrum of a precusor membrane is compared to a membrane soaked in the acidic solution. It is evident that a phase inversion occurs in the soaking process, i.e. the solvents are completely replaced by the acidic aqueous solution. The results clearly show that a pure PVdF membrane does not have the ability to absorb the acid solution, which is in agreement with the insulating property of this membrane. The absorbing ability is dramatically increased by the addition of PAN or ceramic filler and an optimised composition can be found in the ternary system PVdF-PAN-Al_2O_3.

From the vibrational spectra we can also obtain structural information on the polymer matrix. The results from the Raman experiments show that the PVdF component undergoes a conformational change during the preparation procedure.

To further investigate the functionality of the different components of the membrane we can also investigate acid interactions when it is entrapped in the polymer matrix. By vibrational spectroscopy we can monitor the dissociation degree. We observe that the acid (H_2SO_4) behaves differently inside the polymer matrix than as a free aq. solution. By fitting the recorded spectra of the soaked membranes and calculating the ratio SO_4^{2-}/HSO_4^- we find that this value is lower for the acid entrapped in the membrane. We also see that the presence of dispersed Al_2O_3 particles slightly increases the value of the ratio.

Conclusions

We have performed infra-red and Raman spectroscopy on a new family of proton conducting membranes based on PVdF/PAN-blends. The results reveal the role of the PAN component as well as the ceramic filler in providing the absorbing ability of the acidic solution. We are also able to follow conformational changes of the polymer matrix due to the preparation procedure. Furthermore we observe that the dissociation degree of the acid solution is decreased when entrapped in the polymer matrix, influencing the number of charge carriers in the system.

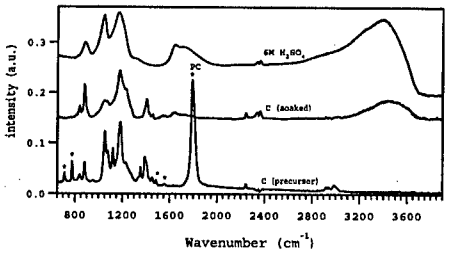


Figure 1 FT-IR spectra of a PVdF/PAN membrane before and after soaking in 6M aqueous H_2SO_4 solution. Characteristic PC bands are marked with stars (*).

References
[1] E.Peled, T.Duvdevani, A.Melman, Electrochem. and Solid State Letters **1** (1998), p. 210-211
[2] E.Peled, T.Duvdevani, A.Aharon and A.Melman, Electrocem. and Solid State Letters **3** (2000), p. 525-528
[3] M.A.Navarra, S.Materazzi, S.Panero and B.Scrosati J. Electrochem. Soc. **150** (2003), p. A1528-A1532
[4] M.A.Navarra, S.Panero and B.Scrosati, submitted to J. Solid State Electrochem.

Stability study of PEMFC ionomers through model molecules mimicking polymer repeat units

M. Maréchal, J. Guindet, J.-Y. Sanchez
LEPMI Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces de Grenoble
1130 rue de la Piscine, BP 75, Domaine Universitaire
38402 SAINT MARTIN D'HERES CEDEX, FRANCE
e-mail: **manuel.marechal@inpg.fr**, tel (+33) (0)4 76 82 65 62, fax (+33) (0)4 76 82 66 70

Introduction

PEMFC membranes are clearly identified as a technological bolt. A rather broad range of proton-conducting ionomers may fulfil the conductivity requirements but not the lifetime ones [1]. Among the ionomeric materials free of fluorine, thermoplastics based on polyaromatic skeleton e.g. polyethersulfone [2] or polyetheretherketone are often selected [3]. The properties of these polymers and to a lesser extent their sulfonated forms are rather well known [4] but few studies deal with their electrochemical stability [5]. In order to accelerate or to detect the potential electrochemical instability, we selected to focus a cyclic voltammetry study on model molecules. The latters mimic the polymer repeat units, e.g. of UDEL® and RADEL® polysulfones from SOLVAY and polyetheretherketone (PEEK) as well as their sulfonated forms. After their synthesis, their characterization was performed by ^{1}H NMR and ^{13}C NMR. Their thermal and electrochemical properties were thereafter evaluated.

Experimental

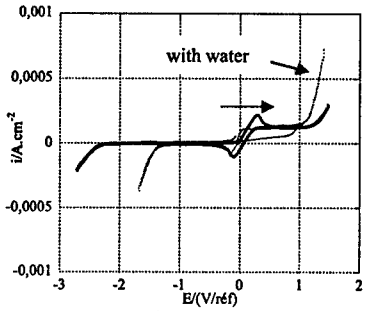
Thermogravimetric analysis (TGA) was performed on the materials in order to appreciate their thermal stabilities. Melting points and glass transition temperatures were measured using DSC and modulated DSC. The electrochemical study plan follows gradual complexation logic to reach the closest conditions the polymer meets in a PEMFC. The molecules are studied at 30°C then 80°C successively under argon, oxygen and hydrogen.

Results

These molecules enable to begin a data base when comparing their characteristic temperatures (glass transition, fusion, start of degradation) with the associated polymers ones.

The sulfolane is a well adapted solvent to our study since (i) its electrochemical stability window is much wider than that of water (ii) it dissolves both the neutral model molecules and their ionic forms (iii) as its very high boiling point enables high temperature analyses. These following cyclic voltammetries are typical of those obtained for the model molecules. It shows their stability in the sulfolane electrochemical window and, therefore in water. The molecule electrochemical stability is thus known on the open operation range of a PEMFC. If polysulfone, polyethersulfone repeat monomer units and their sulfonated forms appear absolutely stable within the electrochemical window of sulfolane, PEEK and sulfonated PEEK models molecules show an electrochemical instability, in reduction, but out of the water electrochemical window.

As for diphenylsulfide, repeat monomer unit of polyphenylene sulphide, it shows instability in oxidation.



Sulfolane + TEAP 0,1 molL^{-1} + ferrocene degassed with argon at 80°C with BAES, work electrode: platinum (2 mm in diameter), auxiliary electrode: platinum, reference: Ag/Ag^{+} 10mmol in acetonitrile scan rate: 100 mV.s^{-1}

However, these preliminary studies were performed in conditions far away from those met in a fuel cell. Obviously the model molecule instability does not necessarily induce a dramatic decrease of the membrane lifetime. On the contrary, an electrochemical stability of the model molecules is a warrant of the associated polymer one.

Conclusions

The beginning data basis purpose is to create a correlation between the model molecules and their associated polymers. This tool allows circumventing the study difficulties of polymers electrochemical stability, e.g. insolubility, especially when a molecule mimicking the associated polymer is easy to obtain.

References

[1] J. Rozières, D. J. Jones, Annu. Rev. Mater. Res., 33, **2003**, 503-555

[2] B. Baradie, C. Poinsignon, J-Y Sanchez, Y. Piffard, G. Vitter, N. Bestaoui, D. Foscallo, A. Denoyelle, D. Delabouglise, M. Vaujany, J. Power Sources, 74, **1998**, 8-16

[3] J. Kerres, W. Cui, G. Eigenberger, D. Bevers, W. Schnurnberger; A. Fischer, H. Wendt, Hydrogen Energy Progress XI, Proceedings of the World Hydrogen Energy Conference 11th, Stuttgart, June 23-28, **1996**, 1951-1956

[4] M. Rikukawa, K. Sanui, Prog. Polym. Sci. 25, **2000**, 1463-1502

[5] S.-Y. Park, J.-W. Lee, S.-H. Jang, L.-H. Jang, D.-K. Kim, D.-K. Choi, Y.-I. Joe, J. Power Sources, 83, **1999**, 217-222

Synthesis and structural characterization of two new siloxanic proton conducting membranes

Vito Di Noto*, Michele Vittadello, Sandra Lavina.
Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, I-35131 Padova, Italy
e-mail: **vito.dinoto@unipd.it**

Introduction

The dawn of hydrogen economics, called upon to counterbalance the looming peak of oil production, is still delayed because of stringent scientific issues that still need to be addressed in fuel cell research. Nowadays, the investigation in this field is focused on one hand on improving the efficiency of electrodes and on the other hand on increasing the performances of proton conducting materials. The preparation of polymeric membranes based on hybrid inorganic-organic systems, such as ORMOCERs-APPE (ORganically MOdified CERamics As Proton Polymer Electrolytes), [1,2] certainly represent a promising approach to the latter aspect of the problem. An innovative supramolecular design for these systems is represented by three-dimensional networks consisting of Si, Zr or Ti knots bridged together by macromolecular moieties like $-(SiR_1R_2O)_n-$. R_1 and R_2 are functional groups that provide the desired sulphonic or phosphonic acidity. This report presents a synthesis of two new siloxanic protonic membranes of the ORMOCERs-APPE type.

These systems are fully characterized by means of vibrational spectroscopy (FT-IR and FT-Raman), morphological measurements (ESEM) and thermal analysis (TG and DSC).

Experimental

Two membranes, **A** and **B**, were obtained via a two stage procedure: the preparation of the precursor P and then the preparation of the membranes. The first stage was carried out under inert atmosphere and is illustrated in the Scheme. Membrane **A** was prepared by suitable hydrolysis and activation in H_2SO_4 0.1 M. Membrane **B** was obtained by a similar procedure, but also adding some α,ω-bis(hydroxi)-poly(dimethylsiloxane) to the precursor water solution. Both membranes were obtained as pellets under pressure at 80 °C.

Results and discussion

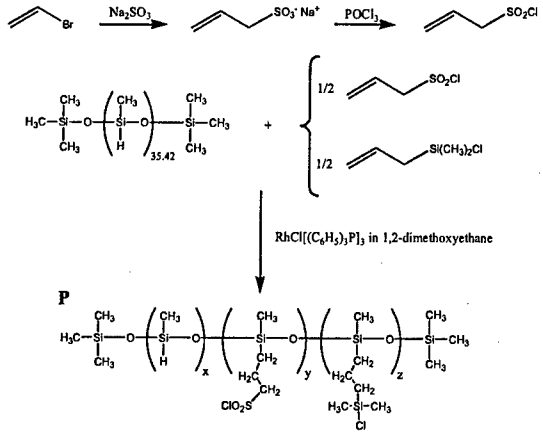
Membranes **A** and **B** are transparent and homogeneous as shown by ESEM and EDAX, respectively. Vibrational investigation (FT-IR e FT-Raman) allowed us to determine the network structure, the conformation of the macromolecular bridges and the dipole-dipole and proton-dipole interactions in the bulk of the membranes. Membrane (A) is thermally stable up to 198 °C, while the second (**B**) up to 200 °C. Both do not decompose up to 190 °C in flux of oxygen. These protonic materials are chemically stable, very easily filmable and can be used in a fuel cell operating within the range 5 °C ≤ T ≤ 145 °C. Ionic exchange capacity is of 0.33 meq/g for membrane **A** and 0.15 meq/g for membrane **B**. FT-IR and FT-Raman confirmed that these materials are reticulated with pendant acid functionalities $-SO_3H$. The suggested formulas for the membranes are (**A**) $\{Si(CH_3)_3[Si(CH_3)HO]_{21.26}-[Si(CH_3)((CH_2)_3SO_3H)O]_{1.8}-[Si(CH_3)((CH_2)_3Si(CH_3)_2O-)-O]_{14}-Si(CH_3)_3\}_n$ and (**B**) $\{Si(CH_3)_3[Si(CH_3)HO]_{21.26}-[Si(CH_3)((CH_2)_3SO_3H)O]_{1.8}-[Si(CH_3)((CH_2)_3(Si(CH_3)_2O-)_w)-O]_v[Si(CH_3)((CH_2)_3Si(CH_3)_2O-)-O]_{14-v}Si(CH_3)_3\}_n$.

Conclusions

In this study two new siloxanic protonic membranes of the ORMOCERs-APPE type were investigated. The promising results are encouraging with respect to the possibility of preparing membranes with performances comparable to Nafion®.

References

[1] V. Di Noto, M. Furlani, S. Lavina *Polym. Adv. Technol.* 7 (1996), 759.
[2] M. Popall, M. Andrei, J. Kappel, J. Kron, K. Olma, B. Olsowski, *Electrochim. Acta* **43** (1998), 1155.



Scheme: Synthesis of the membrane precursor P.

Thursday, August 26
18:40 - 19:00

The influence of the solvent composition on the viscosity, glass temperature and vibrational spectra in PC-H_3PO_4 anhydrous electrolytes

Grażyna Z. Żukowska[1*], Katarzyna Nadara[1], Kenneth R. Jeffrey[2], James R. Stevens[2]
[1] Warsaw University of Technology, Department of Chemistry
Noakowskiego 3, 00-664 Warsaw, Poland
[2] The Guelph Waterloo Physics Institute, Department of Physics
University of Guelph, Guelph, Ontario, Canada N1G 2W1
• e-mail zosia@chemix.ch.pw.edu.pl

Solutions of acids in polar, aprotic solvents are of great interest for their application in fuel cells or electrochromic materials. Their electrochemical and chemical stability, compatibility with polymers and conductivity are the most intensively studied properties. The knowledge of acid-solvent interaction is essential for understanding of conductivity mechanism.

Cyclic carbonates are widely used as solvents for gel electrolytes because of their high dielectric constant leading to high conductivity values, and the wide electrochemical stability window of their solutions of variety lithium salts. Among them, propylene carbonate is particularly interesting thanks to its unique properties: high dielectric constant (65 at 25°C), low viscosity (2.5 cP at 25°C)[1] and lack of crystallinity of salt solutions.

Vibrational spectra of propylene carbonate were analysed in details by Janz et al (Raman spectra)[2] and Pethrick et al (Raman and IR spectra)[3]. Raman and IR spectroscopy are widely used to study ionic solvation in liquid or solid electrolytes. Ionic association in PC doped with various lithium salts were studied by many authors. For example, Battisti et al found splitting or shift of the maximum of several bands of PC in PC-$LiClO_4$ solutions.[4] However, these authors did not observe major changes in the peak of the carbonyl band. Barthel et al studied changes in the position and shape of the carbonyl stretching mode in PC –$LiClO_4$ solutions.[5] They observed the decrease of the intensity of the band at 1780 cm^{-1} and increases of the intensity of new spectral feature at 1753 cm^{-1} with rise in the salt concentration. Cation solvation in PC-nitromethane was studied by Yaeger et al. who noticed presence of new band for PC-salt complex within the carbonyl stretching vibration, peaking at 1773 cm^{-1}.[6]

PC was also used as a solvent for proton conducting electrolytes, alone or in mixtures with other solvents.[7-9] Ion-solvent and ion-ion interactions in these complex systems were explained with the help of FT-ir or Raman spectra analysis. However, in contrast to the PC-lithium salt systems, spectra of acid doped systems based on PC were not completely described. Additionally all of the so far available data concern the studies at ambient or above ambient temperatures. In the present study we undertook an attempt to explain the interactions in the H_3PO_4-PC mixtures by means of vibrational spectroscopy, viscosity and conductivity results. We explained the solvation of an acid in PC solution on the basis of low-temperature FT-ir spectra, compared with viscosity and DSC data.

References:

[1] Barthel, J.; Goves, H.-J.; Schmerr, G.; Wachter, R. In *Topics in Current Chemistry: Physical and Inorganic Chemistry*; Boschke, F. L., Ed.; Springer-Verlag: Heilderberg, 1983; pp 33-145.
[2] Janz, G. I.; Ambrose, J.; Coutts, J. W.; Downey, J. R. Jr *Spectrochim. Acta* 35 (1977) 175
[3] Pethrick, R. A.; Wilson, A. D. *Spectrochim. Acta* 1974, 30A, 1073
[4] Barthel, J.; Buchner, R.; Wismeth, E. *J. Solution Chem.* **2000**, *29*, 937
[5] Battisti, D.; Nazri, G. A.; Klassen, B.; Aroca, R. *J. Phys. Chem.* **1993**, *97*, 5826
[6] Yeager, H. L.; Fedyk, J. D.; Parker, R. J. *J. Phys. Chem.* **1973** *77* 2407
[7] Stevens, J. R.; Wieczorek, W.; Raducha, D., Jeffrey, K. R. *Solid State Ionics* **1997**, *97*, 347
[8] Ericson, H.; Svanberg, C.; Brodin, A.; Grillone, A. M., Panero ,S.; Scrosati, B.; Jacobsson, P. *Electrochim. Acta* **2000**, *45*, 1409
Wieczorek, W.; Zukowska, G.; Borkowska, R.; Chung, S. H.; Greenbaum, S. *Electrochim. Acta* **2001**, *46*, 1427

From plastic Li-ion to plastic Li metal cells operating at room temperature

L. Sannier[1], R. Bouchet[2], M. Chami[3], S. Grugeon[1], J-M. Tarascon[1]
[1] Laboratoire de Réactivité et Chimie des Solides, Université de Picardie Jules Verne, 33 Rue Saint Leu 80039 AMIENS Cedex, France
e-mail: lucas.sannier@u-picardie.fr, tel :+ 33 (0) 3 22 82 75 87, fax :+ 33 (0) 3 22 82 75 90
[2] Laboratoire MADIREL, Université de Provence, Centre Saint Jérôme, 13397 MARSEILLE Cedex 20 France
[3] Laboratoire de Physico-Chimie Moléculaire, Université de Bordeaux I, 351 cours de la libération 33405 TALENCE Cedex

Introduction

To face the rapid increase in the portable device market, the improvement of today's accumulator becomes urgent. While providing great safety benefits, Li-ion batteries are reaching their intrinsic limits in term of energy and power density. To circumvent such a limitation, a possible solution could be the use of metallic lithium systems. Nevertheless, this kind of accumulators, well-known for ages due to their huge potential, presents safety problems relative to the irregular lithium deposition on the lithium metal electrode surface upon subsequent charges, which leads to dendrites formation. Such dendrites enhance the risk of short-circuit, which could promote a thermal runaway of the batteries, and cannot be prevented by the use of a classical separator based on a classical polyethylene membrane (Fig. 1a). To circumvent this issue, *Armand* suggested the use of a dry solid polymer electrolyte consisting of poly(ethylene oxide) (PEO) and a lithium salt (Fig. 1b) [1]. While limiting the dendrites progression in the separator, the main drawback of such a system is that batteries have to operate above 60°C in order to reach a sufficient ionic conductivity. In 1994, Bellcore developed a porous polymer membrane mainly based upon poly(vinylidene fluorine-co-hexafluoropropylene) (PVdF-HFP) (Fig. 1c) [2].

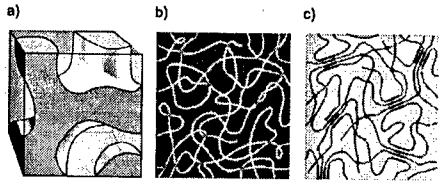


Figure 1: Schematic representations of polymer Electrolyte. a) A poly-olefin membrane in which the liquid electrolyte is held by capillaries. b) Solid (dry) polymer electrolyte consisting of entangled chains, through which the Li ions (points) move assisted by the motion of polymer chains. c) A hybrid (plasticized) network consisting of a semicrystalline polymer, whose amorphous regions are swollen in a liquid electrolyte, while the crystalline regions enhance the mechanical stability.

Once soaked in liquid electrolyte, such membrane system merges the merits of both technologies, that is to say a good ionic conductivity together with the ability to prepare flexible flat configuration membranes, which prevent from liquid electrolyte leakages. Such separator membranes are being used in some of today's plastic Li-ion cells. Nevertheless, even if this system gathers the required qualities to be used as a separator in lithium metal batteries, the polymer composing the membrane does not seem to be stable versus lithium due to the presence of fluorine atoms.

To bypass the above issues, within this work, we tried to combine the advantages of the liquid electrolyte solvated PEO, which ensures a good interface with the lithium, and the PVdF-HFP, which enables the fabrication of free-standing gel polymer electrolyte (GPE). To reach this goal, two different routes have been pursued (Fig. 2). The first one, similar to that of *Nishimura et al.*[3], consists in solvating both polymers separately prior to mixing them together in the presence of a plasticizer to finally obtain a unique membrane (denoted hereafter BM). The second way consists in placing a PEO high molecular weight thin film, acting as a buffer, between the lithium and an industrially made PVdF-HFP membrane to produce a bi-layer separator (denoted hereafter BLS) [4].

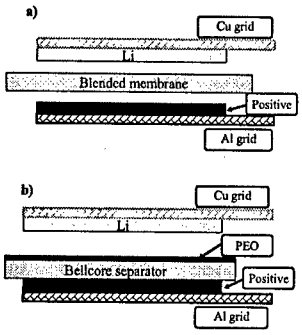


Figure 2: a) Configuration of batteries using the blended membrane and b) the bilayer separator.

In this presentation, we will describe the lithium ion technology developed by Bellcore before focusing on the improvement realized in order to use the lithium metal as negative electrode.

Membranes characterizations

The electrolyte weight uptake has been studied by dipping the two different membranes in a liquid electrolyte solution. It has been shown that for BM, whatever the composition in PEO, a maximum was reached after about 35 minutes. For the BLS the needed

time was only 5 minutes. Over these times, whatever type of membrane, the PEO started to diffuse into the dipping solution. The ionic conductivity was measured by means of impedance spectroscopy. For BM, a linearly increase, depending on the PEO content included on the membrane until 40%, was found. Above this proportion, even if the conductivity is more promising, the swelling of the film becomes too important to obtain a free-standing sample. Our study was particularly focused on the membrane containing 30% of PEO, which exhibits an ionic conductivity around 1.7 10^{-3} S/cm. For BLS, this value is equal to the one of the only Bellcore separator (i.e. 10^{-3} S/cm).

The physical and electrochemical properties of these two polymer membranes configurations were studied by various analytical techniques such as X-ray diffraction (XRD), differential scanning calorimetry (DSC), before and after soaking in liquid electrolyte. For both systems, after the swelling, only the peaks of PVdF-HFP were recovered, evidencing the complete swelling of the PEO.

Investigation on the Li/GPE interface

Electrochemical impedance spectroscopy (EIS) was performed on Li/GPE/Li symmetric cells. While the electrolytic resistance remained stable even during aging at 70°C over days, the interfacial resistance exhibited a continuous increase by a factor equal to the square root of time typical of the expansion of a passivation layer.

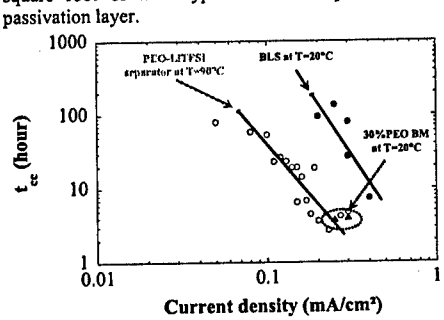


Figure 3: Representation of the time needed to short-circuit a symmetric cell (tcc) versus current density for the different types of separator.

However, it was proved, that under polarization, this resistance underwent a huge decrease meaning the modification of the passivation layer for both types of separator.

To evaluate the performances of the GPE, symmetric cells were polarized at different current densities until a short-circuit appearance (Fig. 3). Such experiments, developed by *Rosso et al.*[5], showed that short-circuit occurs in BM at RT after a time of polarization (denoted t_{cc}) similar to the one obtained with a solid PEO-LiTFSI membrane separator at 90°C. Meanwhile, t_{cc} of BLS were 10 times higher indicating the ability for the membrane to avoid the dendritic growth inside the separator.

Cycling performances

Rechargeable Li/GPE/$Li_4Ti_5O_{12}$ lithium flat batteries were assembled and cycled at a C/2 rate in discharge and at a C/10 rate in charge. Most of the batteries based on the BLS underwent a random short-circuit before reaching 100 cycles confirming the drawback of such a separator under polarization. On the opposite, all the batteries containing BLS sustained a reversible capacity still exceeding 80% of the initial capacity for 300 cycles at room temperature. Nevertheless, even if the BLS seems to prevent short-circuits, it has been shown, by post-mortem investigations on cycled batteries, that it was not able to avoid irregular lithium deposition along the operation of the batteries. SEM pictures realized on a battery cross section have revealed the formation of a lithium moss upon cycling. It has been found that after less than 400 cycles, the initial 100μm lithium foil was consumed to produce approximately 300μm of lithium moss (Fig. 4).

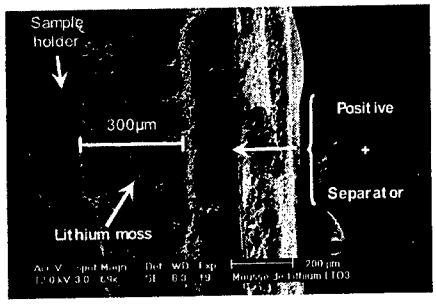


Figure 4: SEM picture of the cross section of a battery cycled about 400 times at C/2-C/10 rates.

This mossy lithium deposition was then investigated by IR and co-focal Raman spectroscopy.

References

[1]. M. Armand, J.M. Chabagno, M. J. Duclot, in *Fast Transport in Solids*. **1979**, P. Vashista, J. N. Mundy, G. K.. Shenoy Eds: North-Holland, New York. p. 131.

[2]. J.-M. Tarascon, A. S. Gozdz, C. Schmutz, F. Shokoohi, P. C. Warren, *Solid State Ionics*, **86-88** (1), 49, (1996)

[3]. K. Nishimura, US **6,165,645**, (2000)

[4]. L. Sannier, R. Bouchet, L. Santinacci, S. Grugeon, J.-M. Tarascon, *J. Electrochem. Soc*, **151** (6), A873, (2004)

[5]. M. Rosso, T. Gobron, C. Brissot, J.-N. Chazalviel, S. Lascaud, *J. Power Sources*, **97-98**, 804, (2001)

P40 Friday, August 27 9:45 - 10:05

Proposal of a new actuator using ion gel driven at low voltage under atmospheric condition

Sayaka NANJO, Masayoshi WATANABE
Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, Japan.
e-mail: **d03ga123@ynu.ac.jp**, tel & fax (+) 81-45-339-3955

Introduction

Current electroactive polymer (EAP) actuators[1], which directly respond to external electrical simulation by displaying a significant shape or size displacement, can be driven only at a high voltage or in aqueous media, therefore they have safety defects or long-term stability problems, which result in restrictions in the operating conditions. In this research, to complement these defects, we have proposed and realized the application of an electric double layer capacitor (EDLC) using an ion gel[2], which is made by radical polymerization of vinyl monomers in a non-volatile ionic liquid, to a new EAP actuator that can be driven at a low voltage under an atmospheric condition. From the specific bending displacement that the actuator shows to the external applied voltage, we investigate the principle of the applicability of the EDLC using the ion gels to the new actuator, and approach to the elucidation of operating mechanism.

Experimental

The ion gel was obtained by *in situ* radical polymerization of methyl methacrylate (MMA) in an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)imide ([emim][$N(SO_2CF_3)_2$]; EMITFSI) as the polymerization solvent. Then, an EDLC was made by adhering carbon powder to both sides of the ion gel and cutting it into a ribbon. The EDLC was supported by clamping the one end and displacement of the free end of the EDLC was measured by a laser displacement meter. The displacement responses in the air were stimulated by applying rectangular wave form voltage (± 1.5 V) at a cycle of 20s or 120s, and triangular wave form voltage (± 1.5 V) at a scan rate of 0.01V s^{-1} to 9 Vs^{-1}.

Results and discussion

The displacement responses of the EDLC to the applied voltage were always bends to the anodic side, and the applicability to a new actuator driven at ± 1.5 V in the air could be found. Firstly, on applying rectangular voltage, the displacement increased with increasing the charging of the electric double layer. Secondly, on applying triangular voltage, the displacement respose reversibly followed the forwarded and backwarded volatege change. According to these responses, it was considered that the actuator could convert a part of the electric energy that was stored at the electric double layer into the dynamic energy that was used for the deformation, and the charging and discharging was associated with the reversible deformation.

Conclusions

It became clear that it was possible to apply the EDLC using the ion gel as a polymer electrolyte to EAP actuators, and we succeeded in the invention of the new actuator driven at low voltage under atmospheric condition.

References

[1] (a) R. Pelrine, R. Kombluh, Q. Pei, J. Joseph, *Science*, **287**, 836 (2000). (b) M. Shahinpoor, *Electrochim. Acta*, **48**, 2343 (2003). (c) E. Smela, *Advanced Materials*, **15**, 481 (2003).
[2] (a) A. Noda, M.Watanabe, *Electrochim. Acta*, 45, 1265 (2000). (b) T. Kaneko, A. Noda, M. Watanabe, *Polym Prepr., Jpn.*, 49, 754 (2000).

Recent development of ENEA lithium metal battery project

W.H. Henderson, J.-H. Shin, G.B. Appetecchi, F. Alessandrini and **S. Passerini***
ENEA (Agency for New Technology, Energy and the Environment)
IDROCOMB, Via Anguillarese 30, 00060 Rome, Italy
e-mail: **passerini@casaccia.enea.it**, tel. (+) 39 06 3048 4985, fax (+)39 06 3048 6357

Introduction

Lithium-ion batteries are currently or soon will be the battery of choice for high-energy applications such as portable electronics, telecommunications and hybrid electric vehicles. The next generation lithium metal batteries require different, preferably solid-state, electrolytes. Polymer electrolytes appear to be the most promising, but their ionic conductivity at ambient-moderate temperatures is much too low. New methodologies are required to improve the performance of such electrolytes [1].

Ionic liquids (ILs) – salts which are liquids at or near room temperature – are revolutionizing many technologies resulting in more environmentally friendly 'greener' chemistry. Here it is shown that the incorporation of room-temperature ILs into conventional PEO-lithium salt electrolytes dramatically improves the performance (i.e., specific energy and power) of solid-state lithium metal batteries at low temperatures. These are true 'dry' polymer electrolyte consisting only of commercial PEO and two salts (with Li^+ and organic cations and common anion).

Experimental

PEO, avg. M_v *ca.* $4x10^6$ (Union Carbide), LiTFSI (3M), V_2O_5 (Pechiney) and carbon (Ketjen Black, Akzo Nobel) were dried under vacuum for 48 hrs at 50 °C the first and at 150 °C the others. $PYR_{13}TFSI$ was prepared as described previously [2]. The salt is a clear liquid at room temperature. The materials were stored and handled in a dry room (< 1% relative humidity, 20 °C). Polymer electrolytes and composite cathodes were prepared by mixing the desired amounts of PEO, LiTFSI and $PYR_{13}TFSI$ and V_2O_5 and carbon for the latter. The mixtures were vacuum sealed in coffee bags and annealed at 60 °C and 90°C, respectively, for 24 hrs. Thin polymer electrolyte films were prepared by hot-pressing the mixtures at 110 °C between two Mylar sheets. Composite cathode films were made by calendering the mixture at room temperature. No solvent was used in the electrolyte and cathode preparations. Thin layer cells were prepared by sandwiching the appropriate components (lithium foil, electrolyte film, cathode film). The cells were vacuum sealed in coffee bag envelopes and then laminated by hot-rolling at 100 °C to optimize the contact between the cell components. The measurements were performed using a Solartron Electrochemical Interface (ECI 1287), a Solartron Frequency Response Analyzer (FRA 1260) and a Maccor Battery Cycler (Series 4000). All cells were thermally equilibrated for at least 1 hr at the selected temperature prior to measurements.

Results and discussion

The ionic liquid containing polymer electrolytes and cathodes have been subjected to an extensive electrochemical characterization that will be presented at the meeting. The overall behavior is well represent in Figure 1 where is reported the cycling behavior of a Li/V_2O_5 battery operating at 40°C. In spite of the relatively low temperature for a dry polymer electrolyte, the battery was able to deliver more than 250 $mAhg^{-1}$ at C/20 rate. Except for the first cycle, the cycle efficiency approaches the unity while the fading shown by the battery is obviously due to the intrinsic irreversibility of the lithium insertion/extraction process in crystalline V_2O_5 cathode.

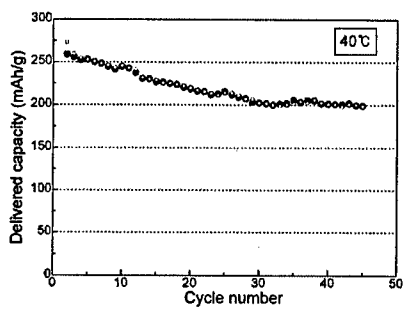


Figure 1. Cycle performance of a $Li/P(EO)_{20}LiTFSI+x\ PYR_{13}TFSI$ (x= 1.73)/V_2O_5 cell at 40°C. The discharge and charge were performed at C/20 rate. Empty marker: discharge capacity, solid marker: charge capacity.

Conclusions

It is important to emphasize that the solid polymer electrolyte membranes proposed here were actually utilized and tested in flexible, thin solid-state Li metal batteries (with no volatile components) at low temperatures. The batteries were able to deliver about 200$mAhg^{-1}$ after 40 deep discharges at 40°C. To our knowledge this is the best performance obtained for 'dry' polymer electrolyte-lithium metal batteries at such a moderate temperature. A further optimization (or selection) of the ionic liquid is expected to allow room temperature operation.

References

[1] J.-M. Tarascon, M. Armand, *Nature* **414** (2001), p.359.
[2] J.-H. Shin, W.A. Henderson, S. Passerini, *Electrochem. Comm.* **5** (2003) p.1016

Friday, August 27
10:35 – 10:55

Research and Development of All-Solid-State Lithium Polymer Batteries -Degradation analysis and fabrication of high-voltage, high-capacity batteries-

Shiro Seki, Yo Kobayashi, Hajime Miyashiro, Atsushi Yamanaka, Yuichi Mita and Toru Iwahori
Materials Science Research Laboratory, Central Research Institute of Electric Power Industry (CRIEPI), Tokyo, Japan
E-mail: s-seki@criepi.denken.or.jp, Tel +81-3-3480-2111, Fax +81-3-3488-6697

Introduction

Research and development of all-solid-state lithium polymer batteries (LPBs) have been carried out with the goal of the realization of an electric power load leveling system for customer use. Since LPBs don't contain organic electrolyte solution, their safety has been improved markedly. Moreover, the scale-up of the battery system is expected to be realized by multicell stacking in a single external package. The suitable management of each cell is required through the utilization of cathode materials with high voltages, to achieve a simple and low cost battery system. The conventional solid polymer electrolytes (SPEs) used in the LPBs are poly(ethylene)oxide (PEO) and its derivative. However, the oxidation decomposition of the SPE takes place at over 4 (V vs. Li/Li^+). Therefore, the most commonly reported cathode materials for the LPB were 3V-class ones (*e.g*, V_2O_5), and the R&D of the 4V-class (*e.g*, $LiCoO_2$ and $LiMn_2O_4$) LPB systems is now in progress.

We have so far advocated the '*Concept of a polymer–ceramic composite*' as a guiding principle in the design of a battery with the capacity for high-voltage operation. By having an oxidation resistance inorganic electrolyte intervene between the cathode active material and the SPE, we hope to achieve battery operation in a voltage region higher than the potential window of SPEs (**Figure 1**). To date, we have conducted experiments using the thin-film cathode, in order to examine the principle described above [1]. However, when the utilization of LPB is considered, it is essential to examine the application powder cathode sheet of the cathode active material, SPE, and electronically conductive additive [2]. In this research, after preparing the LPB using the application cathode sheet, the degradation factor of the 4V-class LPB was estimated by means of electrochemical analysis. Then the protection of SPE from oxidation was proposed by its combination with inorganic electrolyte. Furthermore, high-voltage and high-capacity LPBs [3] were demonstrated.

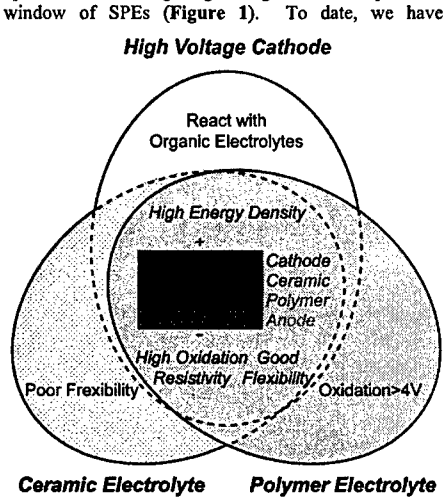


Fig. 1 Conceptual figure of the 'Concept of a polymer-ceramic composite'.

Experimental

The matrix polymer used for the SPE sheet was P(EO/MEEGE/AGE)=82/18/1.7 (*Daiso*). The ratio of the LiTFSI ($LiN(SO_2CF_3)_2$) in the polymer was [Li]/[ether oxygen]=0.06, and the thickness of the SPE film was approximately 50 μm. The cathode sheet consisted of $LiCoO_2$ as a cathode active material, acetylene black as an electronically conductive additive, and the P(EO/MEEGE)-LiBETI ($LiN(SO_2CF_2CF_3)_2$) complex as an ionically conductive binder. The SPE sheet was cut into disks which were then sandwiched between lithium metal and a cathode sheet, and finally encapsulated in the 2032 type coin cell.

For the electrochemical analysis of battery degradation, 'constant voltage impedance measurement method' was applied. The cell was charged up to 4.2 (V vs. Li/Li^+). Then the complex impedance measurements were performed at intervals of one hour, while the cell potential was maintained at 4.2 (V vs. Li/Li^+) (200 kHz – 50 mHz, under 10 mV ac amplitude; PAR VMP 2/Z). The time dependence of the impedance spectrums, which were obtained from the fitting program of ZSimpWin, was discussed.

For high-voltage LPBs, application cathode sheets using the Li_3PO_4-coated $LiCoO_2$ powder ($Li_3PO_4/LiCoO_2$=3/97 by weight) and Li_3PO_4-mixed $LiCoO_2$ powder ($Li_3PO_4/LiCoO_2$=5/95 by weight) were fabricated. After preparing the LPBs (see above), the charge-discharge tests were performed at 3.0-4.6 (V vs. Li/Li^+) with the current density of 0.05 ($mAcm^{-2}$). All measurements were performed at 333 (K).

Results and discussion

Figure 2 shows the time dependence of the impedance spectrum for the $LiCoO_2$ cathode/SPE/Li cell at 333 (K) and 4.2 (V vs. Li/Li^+). Two semicircles were observed in the impedance spectrum and it can be separated into three components, the SPE bulk (R_b), the

SPE/Lithium interface ($R_{Lithium}$) and the SPE/$LiCoO_2$ cathode interface ($R_{Cathode}$), from high frequency. At the time that the high voltage was applied, the increase in $R_{Cathode}$ was dominant compared with that of R_b or $R_{Lithium}$. It is considered that the oxidation decomposition of SPE has taken place at the SPE/$LiCoO_2$ interface. When aiming at LPBs which can operate at high voltages, it is concluded that the protection of the cathode interface is necessary.

Figure 3 shows the charge-discharge curves of the Li/SPE/$LiCoO_2$ cells, namely, those which are without Li_3PO_4, Li_3PO_4-coated and Li_3PO_4-mixed $LiCoO_2$. Although the ionic conductivity of Li_3PO_4 was low ($\sigma = 10^{-8}$ (Scm^{-1}) at room temperature), it was adopted according to the result in Ref [1]. Even charging to 4.6 (V vs. Li/Li^+) was impossible for the cell using a normal $LiCoO_2$ cathode sheet. However, reversible charge-discharge to 4.6 (V vs. Li/Li^+) was made possible by coating and the addition of Li_3PO_4, and the discharge capacity was approximately 200 ($mAhg^{-1}$), respectively. These values are quite high values, being about 1.4 times the capacity reported conventionally (3.0-4.2 (V vs. Li/Li^+) charge-discharge; approximately 140 ($mAhg^{-1}$)). As mentioned above, it was confirmed that the '*Concept of a polymer-ceramic composite*' is effective in LPBs.

Furthermore, not only the Li_3PO_4-coated system but also the Li_3PO_4-mixed system was excellent in the characteristic. In a future presentation, these topics will be discussed in greater detail by using 'constant voltage impedance measurement method'.

Acknowledgments

The authors are grateful to *Daiso Co., Ltd.*, for supplying us with valuable chemicals (P(EO/MEEGE/AGE), P(EO/MEEGE)) for our research.

References

[1] Y. Kobayashi *et al.*, *J. Electrochem. Soc.*, **150**, 1586 (2003).
[2] S. Matsui *et al.*, *J. Power Sources*, **97-98**, 772, (2001).
[3] Y. Kobayashi *et al.*, *Abstract of IMLB-12*, Abstract No.371 (2004).

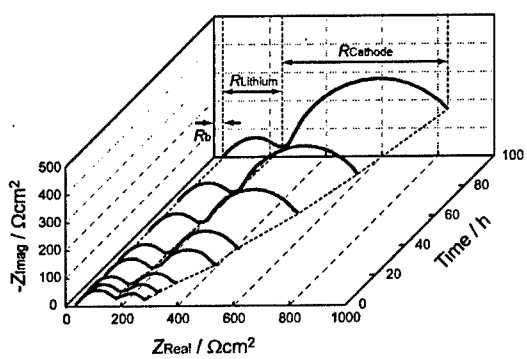


Fig. 2 Impedance spectra of a LiCoO2/SPE/ Li cell at 333 (K) and 4.2 (V vs. Li/Li+).

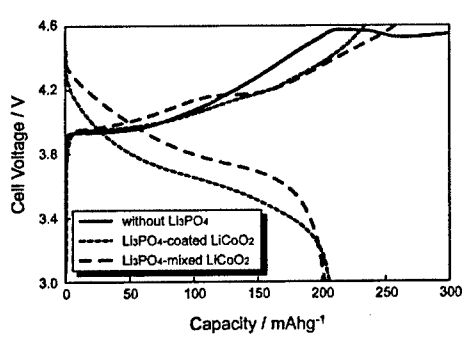


Fig. 3 Charge-discharge curves of the Li/SPE/LiCoO2 cathode cathode cells, without Li3PO4, Li3PO4-coated and Li3PO4-mixed.

Dip-Coating of Battery Materials by Deposition of Nanoparticles on Polymer-Conditioned Surfaces

J.O. Besenhard, A. Basch, B. Gollas, J.-H. Han, K. Leitner, K.-C. Möller, M. Winter
Institute for Chemistry and Technology of Inorganic Materials, Graz University of Technology,
Stremayrgasse 16, A-8010 Graz, AUSTRIA
e-mail: besenhard@tugraz.at, tel (+) 43 316 873 8260, fax (+) 43 316 873 8272

Introduction

Surface-coating of active battery materials and also of current collectors is commonly used e.g. for decreasing contact resistances or improving self-discharge, corrosion and safety characteristics. We have developed a dip-coating process (Substrate Induced Coagulation, SIC) resulting in self-assembling of nanoparticles on preconditioned surfaces. SIC is a method for coating surfaces uniformly with layers of nano-dispersed particles. It uses intermolecular forces between a surface pre-treated with a polymer and particles dispersed in aqueous or non-aqueous solutions [1]. The stability of the dispersion can be adjusted to a point where the interaction with the polymer-modified surface leads to coagulation of the particles, forming a layer on the surface (see Fig. 1).

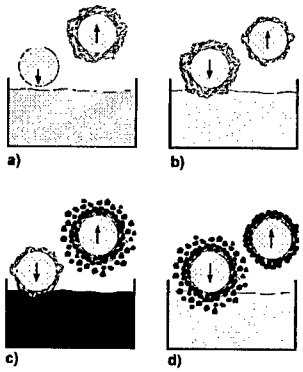


Figure 1: Substrate induced coagulation (SIC). a) The substrate is conditioned by dipping into a polymer solution. b) rinsing to remove unbound polymer. c) dipping into a dispersion of carbon black. d) rinsing to remove unbound particles.

A typical application of the SIC process is coating of particles of $LiCoO_2$ (the most common cathode material for lithium ion cells) with carbon black (to improve conductivity or with Al_2O_3 (to reduce oxidative electrolyte decomposition). Core-shell materials of this kind have been presented recently [2, 3]. Following the coating-process an elevated temperature treatment can remove undesired traces of conditioner or surfactants required to stabilize the dispersions.

Experimental, results and discussion

The effect of polymer pre-conditioning on the amount of adsorbed carbon black particles may be illustrated by Fig. 2, showing electron micrographs of a mica surface (a) conditioned with polyvinyl alcohol (PVA, ca. 40 nm) and (b) non-conditioned after dipping in a solution of carbon black in *N*-Methyl-2-pyrolidinone.

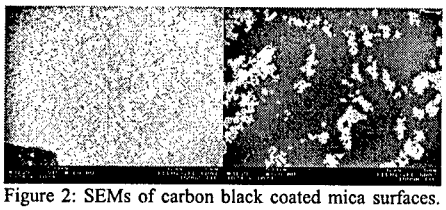


Figure 2: SEMs of carbon black coated mica surfaces. PVA-conditioned (left), un-conditioned (right).

Conclusions

SIC is a simple, cheap and versatile coating method, in particular for powder substrates. It is unique in its general applicability: virtually all kinds of substrates can be coated with any kind of fine materials. The restriction that the SIC process can only be performed in aqueous solutions has now been overcome by the development of a non-aqueous process.

Acknowlegement

Support by the Austrian Science Fund in the Special Research Program "Electroactive Materials" is gratefully acknowledged.

References

[1] J. O. Besenhard, S. Hanna, C. Hagg, D. A. Fiedler, M. Bele, S. Pejovnik, The 1997 Joint International Meeting of the Electrochemical Society and the International Society of electrochemistry, Paris, 1997.

[2] J. O. Besenhard, K.-C. Möller, M. R. Wagner, H. J. Santner, C. Veit, E. A. Lanzer, P. Raimann, C. Korepp, A. Trifonova, A.Basch, W. Kohs, K. W. Leitner, J.-H. Han, M. Winter, 12th International Meeting on Lithium Batteries, Nara 2004, Abstract 37.

[3] A. Basch, B. Schaffer, R. Horn, J. Albering, M. Winter, J. O. Besenhard, 12th International Meeting on Lithium Batteries, Nara 2004, Abstract 133.

Cellulose Derivatives as Lithium Ion Conductor

Marcin Chelmecki, Wolfgang H. Meyer, Gerhard Wegner
Max Planck Institute for Polymer Research Mainz
e-mail: **marcin.chelmecki@mpip-mainz.mpg.de**, tel (+) 49 6131 379 223, fax (+) 49 6131 379 100

Introduction

The separator membrane in batteries and fuel cells is of crucial importance for the function of these devices. In lithium ion batteries the separator membrane as well as the polymer matrix of the electrodes consists of polymer electrolytes which are lithium ion conductors.

To overcome the disadvantage of currently used polymer electrolytes which are highly swollen with liquids and thus mechanically and electrochemically unstable, the goal of this work is a new generation of solid polymer electrolytes with a rigid backbone and a soft side chain structure. Moreover the novel material should be based on cheap substrates and its synthesis should not be complicated aiming at low overall costs.

Experimental

The new materials are based on hydroxypropylcellulose and oligoethyleneoxide derivatives as starting materials. The grafting of the oligoethyleneoxide side chains onto the cellulose was carried out following two synthetic methods. One is based on a bromide derivative and another based on p-toluolsulfonyl as a leaving group. The side chain reagents were prepared form tri(ethylene glycol) monoethyl ether. In order to improve the mechanical properties the materials were crosslinked. Two different conceptions have been engaged based on either urethane chemistry or photosensitive dimethylmaleinimide derivatives. PEO - graft - cellulose derivatives with a high degree of substitution between 2,9 and 3,0 were blended with lithium trifluoromethanesulfonate, lithium bis(trifluorosulfone)imide and lithium tetrafluoroborate. The molar ratios were in the range from 0,02 to 0,2 [Li]/[O]. The products have been characterized with nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS), laserlight scattering (LS) and x-ray diffraction (XRD) with respect to their degree of substitution, molecular weight and chemical structure. The effect of salt concentration on ionic conductivity, thermal behaviour and morphology has been investigated with impedance spectroscopy, differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The crosslinking reactions were controlled with dynamic mechanical analysis (DMS).

Results and discussion

The degree of substitution of our products is varying between 2,8 and 3,0 as determined by NMR. PEO - graft - cellulose derivatives are highly viscous liquids at room temperature with glass transition temperatures around 215 K. The glass transition temperature for the Lithium salt complexes of PEO - graft - cellulose derivatives increase with increasing salt content. The maximum conductivity at room temperature is about 10^{-4} and at 100°C around 10^{-3} Scm^{-1}. The presence of lithium salt decreases the thermal stability of the complexes in comparison to pure PEO - graft - cellulose derivatives. Complexes heated over 140 – 150°C completely lose their ionic conductivity. The temperature dependence of the conductivity presented as Arrhenius-type plots for all samples is similar in shape and follows a VTF behaviour. This proofs that the ionic transport is closely related to the segmental motions of the polymer chains.

Conclusions

Novel cellulose derivatives with grafted oligoethylenoxide side chains with well-defined chemical structure and high side chain grafting density have been synthesized. Cellulose was chosen as stiff, rod like macromolecule for the backbone while oligoethylenoxides are chosen as flexible side chains. A maximum grafting density of 3.0 have been obtained. The best conductivity reaches 10^{-3} Scm^{-1} at 100°C for a Li-triflate salt complex with a [Li]/[O] ratio of 0.8. The cross-linked complexes containing the lithium salts form elastomeric films with convenient mechanical stability. Our method of cellulose modification is based on relatively cheap and commercially available substrates and as such appears to be a promising alternative for industrial applications.

References

[1] Lauter U., Meyer W.H., Wegner G., Macromolecules 1997, **30**, 2092-2101;
[2] Nishaburi A., Dissertation, Johannes Gutenberg University of Mainz, 2000;
[3] Yue Z., McEwen I.J., Cowie J.M.G., Solid State Ionic 2003,**156**, 155-162;
[4] Xiao Y., Ritcey A.M., Langmuir 2000, **16(9)**, 4252-4258.

Friday, August 27
12:05 - 12:35

Electroanalytical characterization of nonaqueous proton conducting gel containing dodecatungstophosphoric redox centers

Pawel J. Kulesza[a], Adam Lewera[a], Grażyna Żukowska[b], Władysław Wieczorek[b] Malgorzata Chojak[a], Krzysztof Miecznikowski[a]
[a]*Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland*
[b]*Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, PL-00-664 Warsaw, Poland*

During recent years, there has been growing interest in electrochemical measurements of solid or semisolid systems performed in the absence of liquid electrolyte phase [1-3]. Representative examples of applicable materials include polymer-attached redox molecules and redox ions that are exchanged into ionomer polymers, ionically conducting mixed-valence inorganic solids, redox melts, systems consisting of redox species dissolved in ionic polymer solvent or solid electrolyte, and systems prepared by sol-gel chemistry. The systems are considered for such technologies as charge storage in batteries and redox capacitors, electrochromism, electrosynthesis, microelectrochemical electronics, analytical determinations and amperometric sensing.

The presence of mobile charge-compensating ions and the existence of mixed-valence redox centers are among the main requirements for a material to show electroactivity in solid, rigid or semirigid (nonfluid) state with no contact with external liquid electrolyte. The population of charged species (mobile ions and electrons) must be fairly large in the system in order to avoid problems with migration and ohmic resistance. A robust proton conducting polymeric electrolyte which contains electroactive centers is an interesting possibility in this context. It is noteworthy that proton conductors are generally characterized by potentially higher dynamics (diffusion coefficients) of ionic transport in comparison to alkali metal electrolytes at ambient and moderate peratures. We explore here recent achievements in the area of proton-conducting polymer gels based on polyacrylates or polymethacrylates [4-6]. The respective gel electrolytes are typically two- or three-component systems consisting of polymer matrix swollen with a solution of proton donor in a polar solvent. In the present work, we continue our initial study in this area, and we propose a novel dodecatungstophosphoric acid doped polymer gel that is bifunctional in nature: $H_3PW_{12}O_{40}$ acts as both proton donor and as electroactive species. Further, the polyoxometallate based proton conducting gel functions as redox conducting material because it contains large population of mobile protons in addition to mixed-valent polytungstate redox centers between which fast electron transfers are feasible.

We demonstrate here the possibility of preparation of nonaqueous proton conducting gels containing mixed valent heteropolytungstate (dodecatungstophosphoric) redox centers. The materials are physicochemically very stable, and dodecatungstophosphoric acid serves both as strong acid, i.e. source of mobile protons, and as a well-behaved mixed-valent redox system.

Electrochemical properties have been assessed from ultramicroelectrode based solid state voltammetric experiments performed in the absence of external liquid electrolyte on bulk gel blocks. By analogy to the behavior of phosphotungstic acid single crystal, the results are consistent with the view that the material is characterized by well-defined redox reactions.

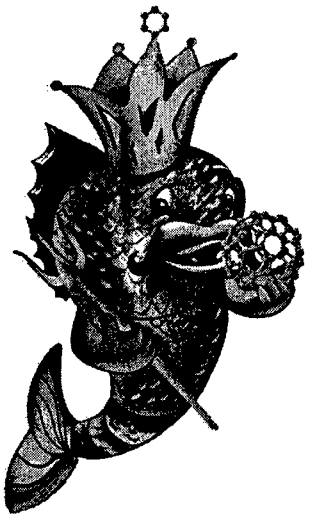
The room temperature ionic (protonic) conductivity of the bulk gel has been found to be equal to 1.64×10^{-3} S cm^{-1}. The following parameters have been determined from the combination of potential step experiments performed in two limiting diffusional regimes (radial and linear): the concentration of heteropolytungstate redox centers, 6×10^{-2} mol dm^{-3}; and the apparent diffusion coefficient, 5×10^{-7} cm^2 s^{-1}. The charge propagation mechanism is interpreted as reflecting primarily physical diffusion of heteropolytungstate in the gel pores rather than electron hopping (self-exchange).

[1] P. J. Kulesza, M.A. Malik, in „Interfacial Electrochemistry, Theory, Experiment, and

Applications" (A. Wieckowski), Chapter 37, Marcel Dekker, New York, 1999.
[2] P. J. Kulesza, J. A. Cox, Electroanalysis, 10, 73 (1998).
[3] A. Lewera, K. Miecznikowski, M. Chojak, O. Makowski, J. Golimowski, P.J. Kulesza, Anal. Chem., 76, 2694 (2004).
[4] J. R. Stevens, W. Wieczorek, D. Raducha, K. R. Jeffrey, Solid State Ionics, 97, 105 (1997).
[5] D. Raducha, W. Wieczorek, Z. Florjanczyk, J. R. Stevens, J. Phys. Chem., 100, 20126 (1996).
[6] K. Checkiewicz, G. Zukowska, W. Wieczorek, Chem. Mater., 13, 379, (2001).

9th International Symposium on Polymer Electrolytes

Poster Abstracts



P O S T E R

P1

A Fully Polymeric Proton Conductor Based on Benzimidazole-Functionalized Polysiloxanes

Christian Persson and Patric Jannasch
Polymer Science and Engineering, Lund University, P.O. Box 124,
SE-22100 Lund, Sweden, www.polymer.lth.se
e-mail: **christian.persson@polymer.lth.se**, tel (+) 46 46 222 8267 fax (+) 46 46 222 4115

Introduction

Proton-conducting polymers are important materials due to their key function in applications such as polymer electrolyte fuel cells (PEMFCs), electrochemical sensors, and electrochromic devices [1, 2]. However, most of these materials are dependent on water or other small molecules to facilitate proton conduction [3]. Because losses of these compounds are practically unavoidable during PEMFC operation, there is a need to develop new polymeric materials that are capable of fast proton conduction in the absence of any volatile compounds. The proton transport in these materials should not rely on proton vehicles such as water, but rather on intrinsically conducting polymers with a fast proton transfer from proton donor to proton acceptor sites. This is similar to the so-called "Grotthuss" mechanism, which is well known for water [4, 5]. Nitrogen-containing heterocycles have shown to be interesting compounds in this context. Heterocycles such as imidazole, benzimidazole, and pyrazole are in many aspects similar to water in relation to their respectively melting point [5]. They can also be covalently tethered to polymer backbones which prevents the proton conducting phase from being leached out of the membrane. In these systems, a high local mobility of the heterocycles are of major importance for the conductivity [4, 6].

We have developed a series of fully polymeric model compounds where benzimidazole units are tethered to a polysiloxane backbone via short, flexible thioether chains. Polysiloxanes are known for their outstanding chain flexibility and are therefore expected to facilitate a high segmental mobility in the materials. Fundamental knowledge about the performance of these model compounds may be of considerable interest when designing the next generation of fuel cells which might operate without the need of humidification. The synthesis, thermal properties, and the intrinsic properties with respect to proton conductivity are discussed for these materials.

Experimental

1,3,5,7-Tetramethyl-1,3,5,7-tetravinylcyclosiloxane (V4), and 1,3,5-hexamethylcyclosiloxane (D3) were copolymerized in different compositions to form poly(methylvinylsiloxane-co-dimethylsiloxane) (PVMS). According to Figure 1, the vinyl groups of the copolymers were then reacted with benzimidazole-functionalized thiols via a free radical thiol-ene reaction in THF, with AIBN as the radical source. The samples are designated bimiPVMSx, were x is the molar percentage of vinylsiloxane groups in the PVMS. The reaction was monitored by ^{1}H NMR and FTIR-spectroscopy. Thermal properties and stability were studied by differential scanning calorimetry (DSC), and thermograviometric analysis (TGA). Proton conductivities were determined by impedance spectroscopy in the temperature range 20-150 °C. All samples were carefully dried under vacuum at 65 °C for several days before characterization. All further sample handling was done in an argon filled glove-box.

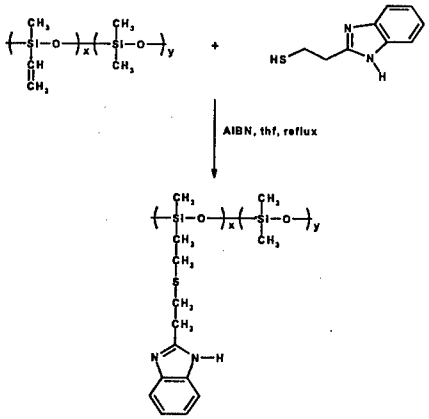


Figure 1. Preparation of benzimidazole-grafted polydimethylsiloxane.

Results and discussion

The composition of the copolymers was determined by using ^{1}H NMR-spectroscopy, and comparing the integrated signal originating from the protons of the vinyl groups between 5.7-6.1 ppm with that arising from the Si-CH_3 protons at 0.1 ppm. The modification of the PVMS was followed by observing the gradual disappearance of the shift from the vinyl protons. Simultaneously, shifts originating from the protons of the thioether spacer, and the benzimidazole unit emerged as the reaction proceeded. After 40 hours, all vinyl groups were converted into thioether bridges. It was also possible to follow the reaction by monitoring the disappearance of the CH_2 wag vibration of the vinyl group at 960 cm^{-1} using FTIR-spectroscopy. Furthermore, IR bands from the N-H deformation and

C=N in the imidazole ring of the product was observed at 1540 cm^{-1} and 1623 cm^{-1} respectively.

All polymers were fully amorphous materials, and showed single glass transition temperatures (T_g). As expected, the T_g's of the modified PVMS's were dramatically increased as compared to the neat PVMS. The T_g's ranged from -125 °C for the unmodified PVMS to 59 °C for bimiPVMS57, as measured by DSC (Figure 2). All samples were stable up to 165 °C according to the TGA measurements.

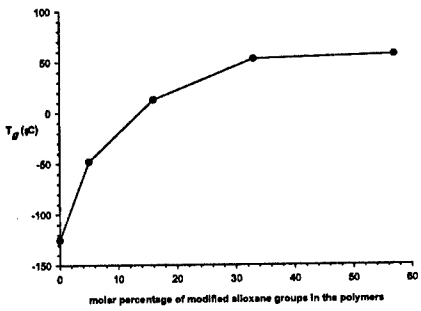


Figure 2. The effect of the benzimidazole content on T_g.

Proton conductivities just above 10 µS/cm were measured for bimiPVMS57 at 150 °C under anhydrous conditions. The conductivity can most probably be greatly improved by adding a suitable acid as dopant. The temperature dependence of the conductivity was more pronounced in the materials with a higher concentration of benzimidazole in the temperature range studied. This is a consequence of the higher T_g in these materials. However, as the temperature was increased, the conductivity of the samples with high concentrations of benzimidazole increased sharply. The Arrhenius conductivity curves were convexly shaped, an indication that the conductivity was promoted by segmental mobility.

Conclusions

We have synthesized model compounds based on polysiloxanes grafted with benzimidazole units via short thioether spacers. The modifications resulted in materials showing a maximum conductivity above 10 µS/cm at 150 °C for the best performing sample under anhydrous conditions. However, adding a polymeric acid to the system is expected to increase the conductivity by an order of magnitude. Obviously, the thermal stability of the materials has to be improved if the materials are to be used under harsh conditions, such as in a fuel cell.

References

[1] K.D. Kreuer, *Journal of Membrane Science* **185** (2001), 29.
[2] K.D. Kreuer, *Chemistry of Materials* **8** (1996), 610.
[3] B.C.H. Steele, A .Heinzel, *Nature* **414** (2001), 345.
[4] M. Schuster, W.H. Meyer, G . Wegner, HG. Herz, M. Ise, M. Schuster, K.D. Kreuer, J. Maier, *Solid State Ionics* **145**, (2001), 85.
[5] W. Munch, K.D. Kreuer, W. Silvestri, J. Maier, G. Seifert, *Solid State Ionics* **145** (2001), 437.
[6] J.C. Persson, P. Jannasch, *Chemistry of Materials* **15** (2003), 3044.

P O S T E R

P2

A Spectroscopic, Thermal, and Conductivity Study of Branched Poly(ethylenimine) – Sodium Triflate complexes.

Nathalie M. Rocher, Roger Frech
Department of Chemistry and Biochemistry, University of Oklahoma
Norman, OK 73019-0370 USA
e-mail: **natrocher@ou.edu**, tel (+) 405 325 0102 fax (+) 405 325 6111

Introduction

The crystallinity of PEO-based polymer electrolytes results in low ionic conductivities and has led to a search for alternative polymer hosts that are amorphous. In an early publication, Harris *et al.* [1] studied the ionic conductivity of branched poly(ethylenimine), BPEI, complexed with sodium trifluoromethanesulfonate (NaTf) based electrolytes for potential application in high energy density batteries. That work indicated a maximum conductivity of 2×10^{-6} S cm^{-1} at 40°C for the N:Na=20 (molar ratio) complex. The present research examines BPEI:NaTf complexes whose compositions range from 20:1 to 2:1, using FT-IR spectroscopy, calorimetry and ac conductivity measurements.

Experimental

BPEI, (number average molecular weight=10,000) was obtained from Aldrich. BPEI-NaTf samples were prepared in an argon atmosphere glove box by dissolving weighed amounts of BPEI and NaTf in dry methanol. The BPEI-NaTf solutions were stirred over night before casting as films. Infrared data at a resolution of 1 cm^{-1} were recorded using a Bruker IFS66V spectrometer with a KBr beam splitter over a range of 500-400 cm^{-1}. DSC data were collected using a Mettler DSC 820 calorimeter under a dry nitrogen purge at heating and cooling rates of 5°C/min. After drying 24 h in the glove box, and 24 h under vacuum, the 20-30 mg samples were sealed in 40 μL aluminum pans. Conductivity measurements were made over the frequency range 0.005-10000 kHz using a Hewlett-Packard 4192A LF impedance analyzer. The samples were cast directly onto a stainless steel electrode in an argon atmosphere. The samples were allowed to dry 24 h in the glove box and 24 h under vacuum before testing. Powder X-ray diffractograms were recorded using a Scintag XTRA diffractometer with CuKα radiation over the range $8 \leq 2\theta \leq 50°$ in 2θ steps of 0.100° with scan rate of 0.75° min^{-1}.

Results and discussion

A spectral study of the NH stretching and NH bending regions in BPEI shows that the primary amines dominate these regions of the spectrum. In the IR spectrum, the primary amine groups give rise to two N-H stretching modes; $\nu_s(NH_2)$ at 3279 cm^{-1} and $\nu_{as}(NH_2)$ at 3352 cm^{-1}. The vibrational frequency of the secondary amine group in BPEI, ν(NH), overlaps with $\nu_s(NH_2)$ at 3279 cm^{-1}. Upon addition of NaTf to bring the solution to a 3:1 composition, both $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ bands become sharper and shift to higher frequencies. The asymmetric band shifts by 26 wavenumbers to 3378 cm^{-1}, and the symmetric band shifts by 30 wavenumbers to 3311 cm^{-1}. For comparison, in the 3:1 BPEI-LiTf system, $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ bands are shifted only to 3305 cm^{-1} and 3370 cm^{-1} respectively, confirming that the Na–N interaction is weaker than the Li–N interaction [2].

At a 4:1 N:Na ratio, two bands abruptly appear at approximately at 3469 cm^{-1} and 3454 cm^{-1}. The intensity of these two bands increases with addition of salt, however their frequencies do not shift. The appearance of these bands is probably related to the formation of a crystalline phase at high salt concentration.

BPEI is an amorphous polymer with a glass transition temperature T_g=-55°C. Upon addition of NaTf, T_g increases regularly and reaches 5°C at a 5:1 composition, but then decreases to about -10°C at a 3:1 composition. Furthermore, for salt compositions of 4:1, 3:1, and 2:1, the existence of a crystalline phase is indicated by an endotherm peak of melting at 63°C. The presence of a crystalline phase has been confirmed by the observation of sharp peaks in the X-ray powder diffractograms of the 3:1 materials. These peaks are unrelated to the peaks of pure NaTf. The ionic conductivity of the BPEI:NaTf complexes was also studied at several compositions from 20:1 to 2:1 in a temperature range from room temperature to 80°C. Additionally, the effect of salt concentration on the ionic association in the BPEI:NaTf complexes was also examined.

Conclusions

A general trend towards structural order in BPEI:NaTf systems was noted with increasing salt concentration. Spectroscopically, this is shown by a sharpening of the bands, especially in the NH stretching region. Thermally, the increase in T_g upon addition of salt and the appearance of a T_m above a 4:1 concentration confirms this structural order. Finally, the strong and sharp peaks in the X-ray powder diffractograms are unambiguous evidence for long range structural order rather than local order in the BPEI:NaTf complexes.

References

[1] Harris, C. S.; Ratner, M. A.; Shriver, D. F., J. Am. Chem. Soc. 2220 (1987) 1778.
[2] Paul, J.-L.; Jegat, C.; Lassegues, J.-C., Electrochim. Acta 37 (1992) 1623.

Activating Effect of Boron Trifluoride on the Ionic Conductivity of Lithium Carboxylates

Aneta Affek*, Anna Tomaszewska, Ewa Zygadło-Monikowska, Zbigniew Florjańczyk
Warsaw University of Technology, Faculty of Chemistry, ul. Noakowskiego 3, 00-664 Warsaw, Poland
*corresponding author: e-mail: **amolenda@ch.pw.edu.pl**, tel. (+48-22) 660-7114, fax (+48-22) 660-7279

Introduction

Recently it has been discovered that certain compounds containing boron, oxygen, carbon and hydrogen can serve as improved electrolyte additives in rechargeable lithium batteries. Angell et al. prepared electrolytes where the solvent of the electrolyte consists predominantly of a borate ester ring compound [1]. The electrolytes showed a wider electrochemical stability window than other conventional systems. The fluorinated boron-based compounds bearing different fluorinated groups are described as an anion trapping moiety enhancing the ionic conductivity and cation transference number of electrolytes [2].

In this work we describe the preparation and properties of fluoroborate molecules obtained in the reaction of lithium salts of carboxylic acids with boron trifluoride etherate. These compounds are used as additives for the polymer-in-salt electrolytes for enhancing ion dissociation and promoting a predominance of cation conduction.

Experimental

The fluoroborate compounds were prepared by mixing a solution or dispersion of lithium carboxylate in acetonitrile and a molar excess of boron trifluoride etherate. To prepare the electrolyte, the fluoroborate compound, lithium salt and polymer matrix were dissolved in acetonitrile. An acrylonitrile (AN) and butyl acrylate (BuA) copolymer was used as the matrix. The solution was cast on a flat Teflon disc and dried in a vacuum oven. The impedance measurements were carried out on an Atlas 98HI impedance analyzer in the temperature range from 20 to 80°C.

Results and discussion

The insertion of BF_3 to the "polymer-in-salt" system comprising a carboxylate lithium salt causes a significant effect on ionic conductivity. Figure 1 shows the temperature dependence of the ionic conductivity for electrolytes based on pristine lithium acetate and lithium acetate with the addition of BF_3. FTIR analysis shows a weak interaction of lithium ions and CN groups present in the polymer matrix [poly(AN–*co*–BuA 2:1].

The spectral and X-ray analysis of the product of the reaction of lithium laurylate and BF_3 shows that in such systems fluoroborate esters can be obtained (Fig. 2). The presence of the fluoroborate esters in the electrolyte has an advantageous effect on the lithium ion mobility. At the same time the formation of $LiBF_4$ is observed.

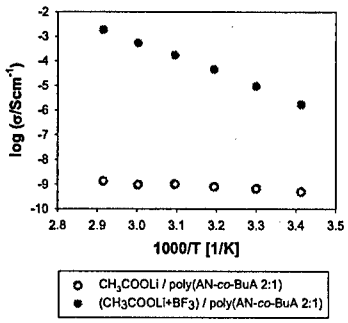


Figure 1. Changes of conductivity as a function of inverse temperature for the ($CH_3COOLi+BF_3$) / poly(AN-*co*-BuA 2:1)[1.2:1] electrolyte.

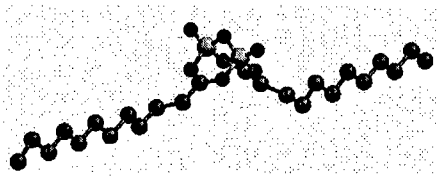


Figure 2. Molecular structure of $C_{12}H_{46}B_2O_4F_3$. The carbon, oxygen, boron and fluorine atoms are shown in gray, red, green and blue, respectively. The hydrogen atoms are omitted.

Acknowledgements

This presentation is based upon work in part supported by the US European Office of Aerospace Research and Development, Air Force Office of Scientific Research, Air Force Research Laboratory, under Contract No. F61775-01-WE019.

References

[1] S.S.Zhang, C.A.Angell Electrochem. Soc. **143** (1996), p. 4047
[2] US Patent 6,022,643

Brønsted Acid-Base and -Polybase Complexes as Electrolytes for Fuel Cells

Hideyuki Matsuoka, Hirofumi Nakamoto, and Masayoshi Watanabe
Department of Chemistry and Biotechnology, Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
e-mail: **d04ga129@ynu.ac.jp**, tel (+) 81-45-339-3955, fax (+) 81-45-339-3955

Introduction

Polymer electrolyte fuel cells (PEFC) have attracted significant attention for their highly power densities. Most of the PEFCs employ hydrated perfluorosulfonic polymer membranes, typically Nafion®, and, their operating temperature is limited by the boiling point of water, which causes several drawbacks such as low energy efficiency, catalyst poisoning by CO in the reform gas etc. Therefore, fuel cell operation at higher temperature is desirable.

We have directed our attention to ionic liquids, which have great thermal stability, and revealed that Brønsted acid-base protic ionic liquid system of imidazole (Im)-bis(trifluoromethanesulfonyl)imide (HTFSI) serves as fuel cell electrolytes at elevated temperatures and the fast proton conduction *via* proton exchange reactions (proton hopping) between the protonated Im cation and Im occurs in Im-rich compositions.[1] In this study, we chose 2,5-diphenyl-1,3,4-oxadiazole (DOD), which has higher thermal stability than Im as a Brønsted base and prepared DOD-HTFSI complexes with varying compositions. The properties of the complexes as fuel cell electrolytes at elevated temperatures were evaluated. Finally, we applied the concept of DOD-HTFSI complexes to a polybase, poly[*p*-phenylene-2,5-(1,3,4-oxadiazole)] (POD) and studied the thermal behavior, ionic conductivity and fuel cell characteristics of the complexes of POD neutralized by HTFSI. The ultimate goal is to realize solid-state proton conductors under entirely non-humidifying conditions with high operational temperatures.

Experimental

Appropriate amounts of bis(trifluoromethanesulfonyl)imide (HTFSI) and 2,5-diphenyl-1,3,4-oxadiazole (DOD) were mixed at various molar ratios to have DOD-HTFSI complexes. The POD-HTFSI complexes were, on the other hand, prepared by immersing POD films into an HTFSI/toluene solution, followed by vacuum drying, and were identified by FT-IR. The physicochemical properties and the proton transport behavior of the DOD-HTFSI and POD-HTFSI complexes were studied by thermogravimetry, differential scanning calorimetry, complex impedance method, and electrochemical polarization.

Results and discussion

The ionic conductivity for DOD-HTFSI complexes exhibited maximum at [DOD]/[HTFSI] = 8/2 composition. The activation energy for the ionic conduction decreased with increasing DOD mole fraction. Since the number of ion carriers, $HDOD^+$ and $TFSI^-$, is maximum at the equimolar composition, the increase in ionic conductivity with increasing DOD mole fraction indicates enhanced ionic mobility, which is also confirmed by the lower activation energy. The conductivity in DOD excess compositions therefore may be due not only to ionic species like $HDOD^+$ and $TFSI^-$, but also to proton hopping through free DODs.

To explore electrode reactions of the complexes at the three-phase boundary of the complex/Pt/H_2 or O_2, cyclic voltammetric measurements were conducted, using a two-compartment glass cell under dry N_2, H_2, or O_2 gas bubbling atmosphere. The complexes were found to exhibit electroactivity for both H_2 oxidation and O_2 reduction at a Pt electrode. Furthermore, when the working and counter electrodes were under O_2 and H_2 bubbling atmospheres, electric power generation was observed.

Since the DOD-HTFSI complexes work as fuel cell electrolytes, we focused our attention on constructing solid-state proton conductors using the polybase, POD, based on the concept of DOD-HTFSI complexes. FT-IR measurements were conducted to characterize the interactions between the polybase POD with the dopant acid HTFSI. The stretching vibration band of N-H^+ was observed around 2600 cm^{-1}. This indicates that POD is protonated with HTFSI to form the POD-HTFSI complex. After the thermal analyses and the ionic conductivity, the prospect of the POD-HTFSI complexes as fuel cell electrolytes was evaluated by using a single cell comprised of the membrane electrode assembly (MEA) with the POD-HTFSI complexes.

Reference

1) A. Noda *et al.*, *J. Phys. Chem. B*, **107**, 4024-4033 (2003).

P O S T E R

P5

Characterisation of new ormolytes for zinc Batteries

S. C. Nunes[1], V. de Zea Bermudez [1], **M. M. Silva**[2], S. C. Barros, M. J. Smith[2], R. A. Sá Ferreira[3], L. D. Carlos [3] J. Rocha[4]

[1]Department of Chemistry, University of Trás-os-Montes and Alto Douro, 5001-911 Vila Real, Portugal
[2]Department of Chemistry, University of Minho, Gualtar, 4710-057 Braga, Portugal
[3]Department of Physics and CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
[4]Department of Chemistry and CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
e-mail: **snunes@marao.utad.pt**, tel (+) +351259350253 , fax (+) +351259480

Introduction

Over the last few years the research, development and technology of zinc-based primary and secondary batteries has progressed significantly [1]. Zinc-containing systems present several advantages: low-toxicity, low cost, high stability, high volumetric and specific density and high availability of natural resources.

A few studies have been focused on the investigation of polymer electrolytes [2] and gel polymer electrolytes [3] doped with Zn^{2+} ions.

In the present work, the synthesis and characterisation of the morphological, structural, thermal and electrochemical properties of innovative sol-gel derived poly(oxyethylene) (POE)/siloxane hybrid electrolytes (di-ureasils) incorporating zinc triflate ($Zn(CF_3SO_3)_2$) are reported. The framework of the di-ureasils contains POE chains with about 40.5 repeat units bonded by means of urea linkages to the siliceous backbone. The materials prepared were identified by the notation d-$(2000)_nZn(CF_3SO_3)_2$, where d represents di, U the urea group, 2000 the average molecular weigh of the organic precursor and n (salt composition) is the molar ratio OCH_2CH_2/Zn^{2+}.

Experimental

A series of notation d-$(2000)_nZn(CF_3SO_3)_2$ di-ureasils samples with $n \geq 1$ were prepared according to a procedure described previously [4].

Results and discussion

The analysis of the diffractograms and the termograms of d-$U(2000)_nZn(CF_3SO_3)_2$ xerogels demonstrates that the addition of zinc salt inhibits the formation of crystalline phases at $n \geq 10$. The thermal decomposition of the ormolytes is initiated at approximately 300 °C. At 30 and 100 °C the most conducting ormolytes are d-$U(2000)_{60}Zn(CF_3SO_3)_2$ ($3x10^{-6}$ $\Omega^{-1}cm^{-1}$) and d-$U(2000)_{20}Zn(CF_3SO_3)_2$ ($7x10^{-5}$ $\Omega^{-1}cm^{-1}$), respectively.

Conclusions

Promising $Zn(CF_3SO_3)_2$-doped hybrid electrolyte materials with good thermal stability and encouraging ionic conductivity were produced by the sol-gel chemistry.

References

[1] G. C. Farrington, R. G. Linford, in *Polymer Electrolytes Reviews 2*, J. R. MacCallum and C. A. Vincent, , Elsevier Science Publishers Ltd, 1989, Cap. 8

[2] Å. Wendsjö, J. Lindren, C. Paluszkiewicz, Electrochimica Acta **37 (9)** (1992) p.1689

[3] G. G. Kumar, S. Sampath, Solid State Ionics **160** (2003) p.289

[4] S. C. Nunes, V. de Zea Bermudez, D. Ostrovskii, M. M. Silva, S. Barros, M. J. Smith, L. D. Carlos, J. Rocha and E: Morales, J. Electrochem. Soc. , submitted

Characterisation of Sulfonated Bisphenol-A-Polysulfone

P. Genova-Dimitrova[a], C. Iojoiu[a, b], M. Maréchal[a], C. Poinsignon[a], **J.-Y. Sanchez**[a]
[a]LEPMI Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces de Grenoble
1130 rue de la Piscine, BP 75, Domaine Universitaire
F-38402 SAINT MARTIN D'HERES CEDEX, FRANCE
[b]ERAS Labo, 222 RN 90
F-38330 SAINT NAZAIRE-LES-EYMES, FRANCE
e-mail: **Jean-Yves.Sanchez@inpg.fr**, tel (+33) (0)4 76 82 65 62, fax (+33) (0)4 76 82 66 70

Introduction

Years ago we have started working on bisphenol-A-polysulfone (PSF), known as Udel-1700, at that time from Amoco, and its sulfonated derivative PSS [1]. Some features on the sulfonation process, sulfonation agents, intrinsic viscosity variations were already investigated [2]. In this paper we focus our attention on the characterisation of PSS by different methods such as ^{1}H NMR, ^{13}C NMR, FT-IR-spectra, elemental and thermal analyses. In addition, a new way of sulfonation level assessment by ^{1}H NMR and an acid-base titration technique will be proposed. Up to now, a great deal of information on PSS has been published by some authors [3, 4]. However, there is no comparative data on different analytical methods, concerning a whole range of sulfonation degree of PSS. Most of the characterizations seem imprecise or (and) time-consuming. In membranes based on these unidimensional Ionomers, mechanical properties and lifetime, strongly depend on the chain lengths. It is therefore essential to dispose of accurate and rapid methods to characterize the Ionomers.

Experimental

Sulfonation with $[(CH_3)_3SiSO_3Cl]$ leads, after treatment with sodium methoxide, to the sodium sulfonate form (PSSNa which is dissolved in DMF and precipitated in the acidic form (PSS) with HCl. PSS and PSSNa are only soluble in polar solvents as DMF, DMSO (dimethyl sulfoxide), NMP, some hydrophilic solvents. Sulfonation leading to a cationic exchange capacity from 1 to 2.75 H^+/kg is carried out. PSF is an example of a polymer, converted to a polyelectrolyte via functionalisation in the post polymerisation step. The sulfonating agent trimethylsilylchlorsulfonate (TMSCS) is chosen because it does not damage the polymer chains [2]. Usually the sulfonation of PSF into PSS is conducted to a moderate sulfonation degree, based on the need of such kind of product for most applications. We went beyond these initial considerations taking into account the further chemical modification of some sulfonic groups of PSS. So that we have achieved a high sulfonation degree of 1.37 which means a partial sulfonation of the second benzene ring per monomer unit. More recently we have reported [2] that this chemical modification is well controllable under certain conditions.

Results and discussion

The importance of the sulfonation level in maximising the membrane performance determines our intention to summarise the data. It is evident that the plot of FT-IR /^{1}H NMR measurement coincides with that of the ionic exchange capacity by acid-base titration (adapted in our lab). Therefore, the titration method, introduced in this work, seems to be precise and comparative to the spectral methods. Also, the FT-IR-analysis and the new acid-base titration technique are calibrated to the ^{1}H NMR-method as an absolute one.

Conclusions

PSS is characterised by means of NMR-, FT-IR-spectra, acid-base titration, elementaly analysis, DSC and conductivity. It is proposed a new way of sulfonation degree calculation based on ^{1}H NMR data which is in agreement to the existing procedure and to a new acid-base titration technique, adapted by us. By elemental analysis it is confirmed that its results are not practicable in the case of PSS. It is confirmed that the T_g is rising with the sulfonation level, but in specific fashion, concerning the acid and the basic form of the ionomers.

References

[1] B.Baradie, thesis, INPG-Grenoble (1997)
[2] P. Genova-Dimitrova, B. Baradie, D. Foscallo, C. Poinsignon, J.-Y. Sanchez, J. Membrane Sci,, 185(1) (2001) 59
[3] R. Nolte, K. Ledjeff, M. Bauer, R. Mulhaupt, J. Membrane Sci., 83 (1993) 211.
[4] B. C. Johnson, I. Yilgar, C. Tran, M. Iqbal, J. P. Wightman, D. R. lloyd et J.E.Mcgrath, J.Polym. Science: Chem, 22 (1984) 721
[5]C.Poinsignon, J.-Y. Sanchez,Y. Piffard, G. Vitter, B. Baradie, Europ. Patent 97401613.1 /07.07.1997

Comparison between ab Initio results and crystallographic data in Ionomers.

C. Chauvin[1], I. Gautier-Luneau[2], C. Perez del Valle[2], F. Alloin[1], C.Iojoiu[1,3], J.Y. Sanchez[1]
1.LEPMI, BP.75, 2.LEDSS B.P.53, F-38402 St-Martin-d'Hères, 3.ERAS-Labo, 222 RN 90, F-38330 St Nazire les Eymes.
christophe.chauvin@lepmi.inpg.fr, tel (+33) 4 76 82 67 64, fax (+33) 04 76 82 66 70

Introduction

Ten years ago we started an *ab initio* study, at the HF level, on organic anions and their lithium salts, using Gaussian 92 programs. Thus this comparative study, performed on $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $(CF_3SO_2)_2CH^-$, allowed us (i) to put into evidence the higher extent of charge delocalization in imide anion (ii) to show that imide is also the hardest anion [1]. Then a comparative conformational study between $(CF_3SO_2)_2N^-$, $(CF_3SO_2)_2CH$ evidenced the higher flexibility of imide while the study of their lithium ion pairs shown that both anions form a bidentate ion-pair [2].

Now, Density Functional Theory (DFT) which takes into account all the electronic interactions is a useful method to calculate electronic structure [3]. DFT allows determining the electron density, the total energy and the bond lengths. Recently used to study salt solutions, i.e LiTFSI, $LiASF_6$ and lithium triflate dissolved in oligo(oxyethylene) OOE [4] it shown that OOE adopts an helix structure, 3 oxygens interacting with Li^+. From DFT studies [5] performed on solutions of lithium salts in various glymes, 5 has been suggested as an average coordination number. Other studies dealt with Li^+ coordination by solvents based on N, O and S heteroatoms [6]. We have synthesized various salts which an oligo(oxyethylene) tail $CH_3(OCH_2CH_2)_nOSO_3^-Li^+$ (called POEMSLi with n=2, 3, 7, 12, 16 and 42). Thus, these ionomers, in addition to their ionic function, have also solvating ability.

Experimental

The structure of POEMSLi (n=3) has been determined by X-ray diffraction. IR, ^{1}H-NMR and ^{13}C-NMR have been also performed. Ab initio calculations were carried out, using Gaussian 98 programs. Geometry were determined and optimized using DFT methods at the B3LYP/6-31+G* level of theory.

The electrochemical stability investigation was performed with a three-electrode configuration. Stainless-steel and two lithium metallic foils were respectively used as working, reference and auxiliary electrodes,.

Results and discussion The crystal structure of POEMSLi (n=3) is shown in figure 1. The cation lithium is coordinated to five oxygen atoms: three of oxyethylene unit, one of the sulfate group of the ligand and an other one (O2') of the sulfate group of an other POEMSLi ionomer which is not presented for clarity. The optimized geometry determined by DFT is quite similar.The optimized geometry determined by DFT is quite similar.

	O1-Li (Å)	O5-Li (Å)	O6-Li (Å)	O7-Li (Å)	O2-Li (Å)
RX	1.93	2.10	2.11	2.14	1.94
DFT	1.99	2.22	2.06	2.06	2.03

Table 1: Bond lengths

In the crystal O2 is coordinated with a lithium belonging to another ionomer, leading to a kind of polymeric chain.

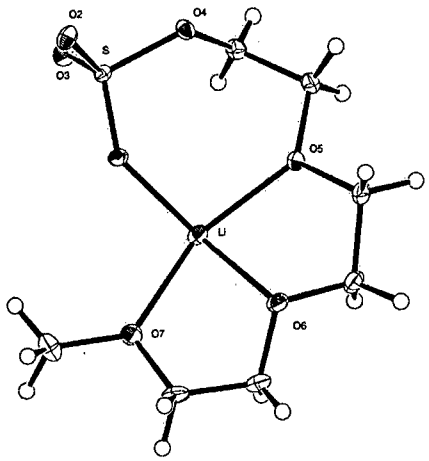


Figure 1: Crystallographic structure of POEMSLi (n=3)

We have modelised by DFT only one ionomer. In this case sulfate group rotate to allow the coordination of the cation lithium by O1 and O2. This can explain the difference between crystallographic structure and DFT one. Ab initio can also be useful to construct a NMR and IR spectrum. Those are in fair agreement with experiments. We also intended to calculate the HOMO value of the anion for different n in order to explain the variation of the potential of oxidation which increases from 4.4 to 4.6 V vs Li/Li^+ for n=2 to 7 and decreases from 4.6 to 4.1 V for n=7 to 42.

Conclusion

Modelisation may (i) predict lithium salt structures (ii) explain electrochemical results. But the salts studied reported here are oligomers making difficult the access to the conformations..

References

[1] D. Benrabah, R. Arnaud, J.Y. Sanchez, Electrochimica acta, 40, (1995), 2437.
[2] R.Arnaud, D.Benrabah, J-Y.Sanchez, J.Phys.Chem., 100, 26, (1996), 10882.
[3] R. M. NieminenH., Current opinion in solid state and materials science, 4, (1999), 493.
[4] I. Martin-Litas, Y. G. Andreev, P. G. Bruce, Chem. Mater.14, (2002), 2166
[5] P. Johansson, J. Tegenfeldt, J. Lindgren, Polymer, 40, (1999), 4399
[6] P. Johansson, Polymer, 42, (2001), 4367

P O S T E R

P8

Conductivity Studies on PMMA Based Proton Conducting Gel Electrolytes

S.L. Agrawal, Shilpa Pandey
Solid State Ionics Research Laboratory, Department of Physics,
A.P.S. University, Rewa (M.P) – 486003. India
E mail: shilpa_pandey20@rediffmail.com

Abstract
Polymeric gel electrolytes have gained prominence in Solid State Ionics research over the years on account of their increasing usages in various electrochemical devices and as well as its ease of fabrication. In the present work, an attempt has been made to synthesize PMMA based proton conducting gel electrolytes with two types of salts, namely, NH_4SCN and $[(NH_2CH_2CO_2)_2]$ and characterize them electrically. The ionic conductivity of as synthesized gels assessed from cole-cole plot reveal maximum conductivity of $2.8X10^{-2}$ Scm^{-1} and $7.7X10^{-3}$ Scm^{-1} for NH_4SCN and $(NH_4CH_2CO_2)_2$ liquid electrolyte systems respectively which drops in general on addition of PMMA in the matrix. Such a behavior has been correlated to increase in viscosity of the electrolyte. The slight enhancement of electrical conductivity observed at intermediate concentration (5-8wt %) has been attributed to dissociation of ion aggregates. The temperature dependence of gel electrolytes revealed VTF behavior indicating liquid like transport of mobile carriers. The present study suggests ammonium thiocyanate based proton conducting gel electrolyte to be a better electrolyte for usage in ECD and smart window applications.

Dependence of the proton conductivity and methanol permeability of a PVA based cation-exchange membrane on its water content

Mitsuru Higa, Satsuki Egashira, Kentaro Hatemura,
Nobutaka Endo and Koji Matsusaki
Applied Medical Engineering Science,
Graduate School of Medicine, Yamaguchi University
Tokiwadai, 2-16-1, Ube City, 755-8611, Japan
e-mail: mhiga@yamaguchi-u.ac.jp tel:+81-836-85-9203, fax:+81-836-85-9201

Introduction

A direct methanol fuel cells (DMFCs) using polymer electrolyte membranes are one of the most attractive power sources due to the stable operation at a rarely low temperature, the high energy generation yield and energy density, the simplicity of system [1-4]. Most DMFC research has concentrated on polymer electrolyte membrane fuel cells (PEMFC) fed directly with methanol [5]. The proton diffusion across the membrane is associated with water transport in the membrane and methanol is also transported to the cathode by electro-osmotic drag. The methanol transport, that is called as methanol crossover, decrease in cell performance [6,7]. Considerable effort has been developed in order to reduce methanol crossover as well as to reach high proton conductivity. Poly(vinyl alcohol) (PVA) membrane has been used in ethanol dehydration to break the ethanol-water azeotrope because it selectively passes water molecule over ethanol or methanol [8-10]. The diffusion coefficient of water soluble solutes and the ionic conductivity through PVA membrane depends on membrane water content [11,12]. Hence, it is important to examine the relationship between the methanol permeability and proton conductivity of the membrane and its water content.

In this study, we have prepared a cation-exchange membrane by blending PVA and a polyanion changing polyanion content. The membranes are crosslinked physically in order to control their water content. The ionic conductivity, mechanical strength and methanol permeability of the membranes has been measured as a function of the water content.

Experimental

PVA based cation-exchange membranes were prepred by casting aqueous solutions of a mixture of PVA[poly(vinyl alcohol), Aldrich] and a polyanion. The weight percent of polyanion in dried membranes was changed to control the charge densities of the cation-exchanage membranes. The membaranes were annealed at various temperatures for 20 min. to control their water content.

The water content was measured as follows: a membrane, weighted in the dry state, was immersed in an ion-exchanged water at 25°C for 3 days. The membrane was removed from the water, tapped with filter paper to remove excess water on the membrane surface, and was weighted in the wet state. The water content is given from the weights in the wet state, Ww, and in the dry state, Wd, as:

$$H \equiv \frac{(Ww-Wd)/1.0}{(Ww-Wd)/1.0+Wd/1.3} \qquad (1)$$

where 1.0 and 1.3 are the densities of water and PVA.

The ionic conductivity at 23°C was determined by impedance spectroscopy using a chemical impedance meter (HIOKI 3532-80) controlled by a personal computer.

The mechanical strength of the membranes was determined with a table model-testing machine (SHIMAZU, EZ-Test500N). In the static stress-strain curves, specimens with a nominal 20-mm-gauge length and 0.2-mm thickness were deformed in tension at a constant strain rate of 10mm/min at 25°C, and stress-strain data were determined to failure.

Results and discussion

The water content of the membranes increased with the polyanion content because osmotic pressure in the membranes increases with increasing the number of the charged groups. The water content decreased with increasing annealing temperature because the degree of crystalinity in the PVA matrix increase with increasing annealing temperature.

The ionic conductivity of the membranes increased with polyanion content,, and decreased with increasing annealing temperature because the water content increased with polyanion content, and decreased with increasing annealing temperature. To examine the ionic mobility in a gel membrane, many authors have replaced the ionic mobility, σ_i, in eqn (2) with the apparent one, $\bar{\sigma}_i$, which is a function of both σ_i and factors such as membrane geometry. The factors due to membrane geometry are related to the mobility ratio as [13,14]

$$\frac{\bar{\sigma}_i}{\sigma_i} = \varepsilon \frac{1}{\theta^2} \qquad (2)$$

where θ is the tortuosity defined as a mean increase in path length due to the obstruction of gel matrix; ε is the void fraction defined as the ratio of the sum of the cross sectional area of the paths to the membrane area. Mackie and Meares [14] derived stochastically the factor as a function of the water content, H, of a swollen gel:

$$\varepsilon = H, \ \theta = \frac{2-H}{H} \qquad (3)$$

Equations (2) and (3) give the ionic mobility in the

Design of Ion Conductive Ionic Liquid Domain using Phosphate Groups on DNA Strand

Naomi Nishimura, Yasuhiro Nomura and Hiroyuki Ohno
Department of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan
e-mail: **ohnoh@cc.tuat.ac.jp**, tel and fax (+) 81-42-388-7024

Introduction

DNA is known to have important roles in biological systems. Since DNA has superior characteristics besides the molecular memory, DNA has been studied as new functional materials. We first made ion conductive DNA films based on the ionic liquid chemistry.[1] Since nucleic acid bases were heteroaromatic rings, the bases were regarded as starting materials for ionic liquid. Adenine and cytosine became ionic liquid after neutralization with bis(trifloromethanesulfonyl)imide (HTFSI). Nucleic acid bases in DNA were also neutralized with HTFSI to prepare successive ionic liquid domain. In this study, ionic liquid domain was prepared along with DNA chains by using their phosphate groups.

Experimental

Phosphoric acid di-n-butyl ester (PDE) was used as a low molecular weight model. 1-Alkyl-3-methylimidazolium (C_nMI; n=2:C_2MI, 4:C_4MI, 8:C_8MI, and 12: $C_{12}MI$) bromide salts were prepared by ordinary procedure, and corresponding ionic liquids were obtained after anion exchange. Structure of these samples was confirmed by ^{1}H-NMR and FT-IR spectroscopy.

Na-DNA isolated from salmon milt was the gift from Daiwa Kasei Co. C_nMI-DNA was obtained by cation exchange of Na-DNA. The structure of these samples was confirmed by Raman and FT-IR spectroscopy. Ionic conductivity and thermal behavior of all the obtained samples were calculated from complex impedance plots with Solartron model 1260; Schlumberger and DSC-120; SEIKO Instrument Inc.

Results and discussion

All the low molecular weight model salts (C_nMI-PDEs) were obtained as clear liquid. Higher ionic conductivity was observed for these ionic liquids having shorter alkyl chains. The highest ionic conductivity of 2.91×10^{-4} S cm^{-1} at 30 °C was observed for C_2MI-PDE. However, longer alkyl chain of imidazolium cation was known to show lower melting point and higher viscosity,[2] this tendency was not found in our system.

Phosphate groups of DNA were then turned to imidazolium salts. All the C_nMI-DNAs were obtained as white powder after freeze drying. These C_nMI-DNAs are soluble in methanol, suggesting efficient cation exchange of DNAs. Flexible films were obtained when these C_nMI-DNAs methanol solutions were cast and dried. Double strand structure of C_nMI-DNA was confirmed by Raman spectroscopy. For FT-IR spectroscopy, the band at 1230 cm^{-1} due to P=O stretching vibrations shifted to higher frequencies. This strongly suggested that Na cation was substituted with bigger cation. However, high ionic conductivity was not found in the bulk. To realize higher ionic conductivity, 5 wt% of 1-ethyl-3-methyl imidazolium BF_4 ($EMIBF_4$) salt was added to C_nMI-DNAs. Temperature dependence on the ionic conductivity of C_nMI-DNA mixed with 5 wt% $EMIBF_4$ is shown in Figure 1. C_nMI-DNA with shorter alkyl chain of imidazolium cation showed higher ionic conductivity like model systems. Since the ionic conductivity in these cases was attributed to the migration of cations. This tendency was well comprehensible to reflect the cation structure. Furthermore, the ionic conductivity data were analyzed using the Vogel-Fulcher-Tamman (VFT) equation to confirm that the ion migration was decoupled with the segmental motion of DNA.

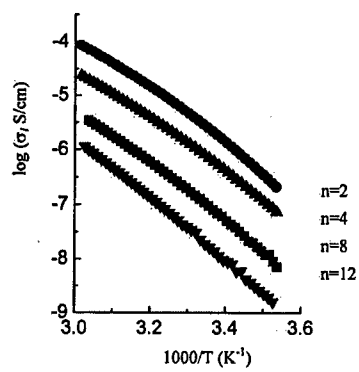


Fig.1 Temperature dependence on the ionic conductivity of C_nMI-DNA containing 5 wt% of $EMIBF_4$.

Conclusion

Imidazolium type ionic liquids were first prepared with phosphoric acid di-n-butyl ester as low molecular weight model compounds of DNA. The resulting salts were all obtained as liquid. The highest ionic conductivity of 2.91×10^{-4} S cm^{-1} at 30 °C was observed for C_2MI-PDE. Then imidazolium cations were introduced as the counter cations of the phosphate groups of DNA. The ionic conductivity of C_nMI-DNAs was greatly improved by adding 5 wt% of $EMIBF_4$.

References

[1] N. Nishimura and H. Ohno, *J. Mater. Chem.*, **12** (2002), 2299.
[2] S. V. Dzyuba and R. A. Bartsch, *Chemphyschem*, **3** (2002), 161.

P O S T E R

P11

Dielectric Study on the system PEG(400):LiTf and PEG(400):$Mg(Tf)_2$

M. Fredriksson, J. Carlsson, M. Furlani, I. Albinsson, B.-E. Mellander
Chalmers University of Technology and Göteborg University, Physics and Engineering Physics S-41296 Göteborg, Sweden

In this work the systems Poly(ethylene glycol) 400:Lithium trifalte (PEG400:LiTf) and PEG400:$MgTf_2$ have been investigated, in the concentration range 8<O/Li<526 with high frequency (1 MHz-1.8GHz) impedance analysis and Differential Scanning Calorimetry (DSC). The comparison of the two systems help to outline a few characteristic of the two electrolytes. The DSC measurements identifies the range of concentration where the plasticising effect of the salt prevents the crystalisation. The dielectric loss of the both systems is consistent with the presence of ion pairs and the value of the dielectric constant at the lower frequencies is higher for the magnesium system. This, in combination with the study of the ionic conductivty versus concentration suggests a different coordiantion for the magensium and lithium ions. A simple model, based on molecular modelling and molecular mechanics (MM2 force field), is proposed.

Effect of Lewis Acids on the Conductivity of Polymer-in-Salt Type Electrolytes

Anna Tomaszewska*, Aneta Affek, Ewa Zygadło-Monikowska, Zbigniew Florjańczyk
Warsaw University of Technology, Faculty of Chemistry, ul. Noakowskiego 3, 00-664 Warsaw, Poland
*corresponding author: e-mail: **anna.tomaszewska@ch.pw.edu.pl**, tel. (+48-22) 660-7114, fax (+48-22) 660-7279

Introduction

Attempts to develop novel polymer electrolytes for application in lithium and lithium-ionic batteries with high ionic conductivity and immobilizing anions were based on various strategies. One of the solutions, for the first time proposed by Angell et al. [1] are polymer-in-salt type systems, in which it is assumed that due to high ionic agglomeration the electric charge is transported mainly involving lithium cations. Promotion of a predominance of cation conduction can be achieved also by the introduction of compounds, which act as anion receptors [2]. In this work we studied the application of various Lewis acids as agents reducing the interionic interaction and mobility of the anions of weakly dissociating lithium salts of carboxylates in a polymer-in-salt system. An acrylonitrile (AN) and butyl acrylate (BuA) copolymer was applied as the polymeric matrix.

Experimental

Lithium carboxylates: CH_3COOLi, CF_3COOLi and $C_2O_4Li_2$ were obtained in the reaction of corresponding acids with *n*-butyllithium. The isolated salts were reacted with Lewis acids at an equimolar ratio. The salts obtained were characterized by means of FTIR spectroscopy and DSC analysis, and in the case of lithium trifluoroacetate and boron trifluoride also by ^{19}F NMR spectroscopy. The membranes of electrolytes were obtained by film casting from a solution in acetonitrile with the molar ratio of Li^+ to AN monomeric units in the poly(AN-*co*-BuA) matrix equal 1.2. Samples were investigated by DSC, FTIR and impedance spectroscopy. Impedance spectra were obtained over a frequency range of 10^{-2} – 10^5 Hz using an Atlas 98HI analyzer.

Results and discussion

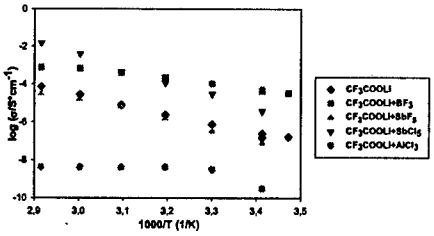


Figure 1. Conductivity changes versus inverse temperature of electrolytes comprising poly(AN-*co*-BuA) and CF_3CO_2Li as well as its complexes with various Lewis acids (Li^+ : CN mole ratio = 1.2:1)

A varying effect of the Lewis acid addition on the properties of the studied electrolytes depending on the type of acid has been observed. Figure 1 shows the conductivity of electrolytes comprising CF_3COOLi and such Lewis acids as: BF_3, $SbCl_5$, SbF_5 and $AlCl_3$.

Similarly as for other carboxylates (Fig. 2), the best results were obtained in the case of introducing BF_3 to the system. Moreover, the electrolytes containing this acid are characterized by high flexibility and adhesion to the electrodes.

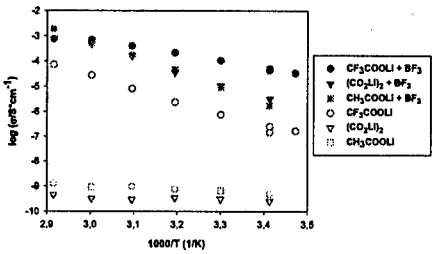


Figure 2. Effect of the BF_3 addition on the conducting properties of electrolytes containing lithium carboxylates and poly(AN-*co*-BuA 2:1).

Preliminary studies on the application of salts involving Lewis acids in the preparation of gel electrolytes have been carried out on the example of CF_3COOLi and BF_3, using the AN and BuA copolymer as matrix and propylene carbonate as solvent. A high-conducting electrolyte was obtained, characterized by a slight effect of temperature on ionic conductivity.

Acknowledgements

This presentation is based upon work in part supported by the US European Office of Aerospace Research and Development, Air Force Office of Scientific Research, Air Force Research Laboratory, under Contract No. F61775-01-WE019.

References

[1] W.Xu, L.Wang, C.A.Angell Electrochim. Acta **48** (2003), p. 2037

[2] S.S.Zhang, C.A.Angell J. Electrochem. Soc. **143** (1996), p. 4047

P O S T E R

P13

Effects of minimal water content in lithium and potassium triflate-PEG400 systems

Naffiseh Saei, Pia Siewert, Susanne Thernström, Maurizio Furlani, Ingvar Albinson and Bengt-Erik Mellander
Chalmers University of Technology and Göteborg University, Physics and Engineering Physics
S-41296 Göteborg, Sweden

The systems PEG 400- Li and K triflate (8<O/M<526) with different amount of water (up to 10% in weight) have been studied with DSC in the range –120 to 90 °C The plasticising anti-freezing and anti-crystalline effects of water were maximal for O/M ≤ 20, and for the potassium system.

These water palsticised systems perhaps not interesting lithium batteries can be important in electrochromic devices where a protic solvent and some proton conductivity is tolerate or even wanted.
Conductivity and dielectric properties in the range 1 MHz –1.8 GHz have been measured.

P O S T E R

P14

Electrochemical Synthesis of Polypyrrole in Ionic Liquida

Jennifer M. Pringle,[1] D. R. MacFarlane,[2] G. G. Wallace[3] and **M. Forsyth**[1]
(1) School of Physics and Materials Engineering (2) School of Chemistry, Monash University, Wellington Road, Clayton, Victoria 3800, Australia. (3) University of Wollongong, Intelligent Polymer Research Institute, Northfields Avenue, Wollongong, NSW 2522, Australia.
e-mail: **jenny.pringle@spme.monash.edu.au**, tel (+613) 9905 4535, fax (+613) 9905 4597

Introduction

Electrochemical polymerisation and cycling of conducting polymers is traditionally performed in an electrolyte/molecular solvent system. When the polymer is oxidised in an appropriate electrolytic medium, anions can enter the polymer from the solution to effect charge balance. Recent work has suggested that in some cases when conducting polymer films are oxidized and reduced in an ionic liquid, the intercalation/de-intercalation of cations rather than anions can occur.[1, 2] Use of ionic liquids in combination with conducting polymers has recently started to attract some attention, with promising results - films prepared in conventional solvents but cycled in an ionic liquid show improved actuator performance and significantly increased lifetimes, to up to one million cycles.[3]

Ionic liquids are a new class of solvent composed entirely of ions - typically a large organic cation and a smaller inorganic anion - which have a number of advantages over conventional solvents. They have a wide liquid range and negligible vapour pressure, which overcomes the problem of solvent evaporation that exists with the long-term use of volatile solvents in electrochemical applications. Of particular importance, ionic liquids possess good electrical stability, with electrochemical windows typically over 4V wide.

Experimental

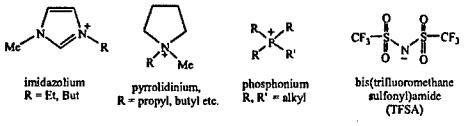
Polypyrrole films were grown at either constant potential (1V) or constant current (0.1 mA cm^{-2}), at room temperature, using a stainless steel working electrode, platinum gauze counter electrode and silver pseudo-reference electrode, from a 0.1M pyrrole in ionic liquid solution. The imidazolium and pyrrolidinium ionic liquids were prepared using published procedures. The phosphonium ionic liquids were kindly donated by Cytec. The polypyrrole films were ground with MgO and analysed in the solid state using ^{31}P MAS NMR and ^{13}C CPMAS NMR, using a Bruker AM-300 MHz spectrometer.

Results and discussion

Here we report the use of ionic liquids as the growth medium for the electrosynthesis of polypyrrole, as well as their use as the supporting electrolyte for the electrochemical cycling of the films. We also investigate the influence that the nature of the ionic liquid has on the growth and physical properties, such as morphology and conductivity, of the films produced.

Solid state NMR techniques have been used to study ion intercalation/de-intercalation from the ionic liquids into the polypyrrole films, both during growth and cycling, and to assess how this varies with different ionic liquids.

Polypyrrole has been successfully prepared in different ionic liquids utilising various combinations of cations and anions such as those shown below:



The nature of the ionic liquid used can have a significant influence on the morphology; the more viscous, less conductive *N,N*-butylmethylpyrrolidinium bis(trifluoromethanesulfonyl) amide ionic liquid gives smoother polypyrrole films than the 1-ethyl-3-methylimidazolium analogue, which is consistent with a slower growth rate.

Conclusions

Use of ionic liquids as the growth solvent for polypyrrole can result in significantly improved electrochemical activities and smoother film morphologies.

Preliminary solid state NMR analysis shows significant incorporation of the imidazolium cation into the polypyrrole films compared to negligible incorporation of the pyrrolidinium species. Further, the phosphonium cation appears to be incorporated into the film during growth and remains in the film even after extended oxidation or cycling in either the ionic lqiuid or a molecular solvent system.

References

[1] J. Ding, D. Zhou, G. Spinks, G. Wallace, S. Forsyth, M. Forsyth, D. MacFarlane. Chemistry of Materials 15 (2003) 2392-2398.

[2] H. Randriamahazaka, C. Plesse, D. Teyssié, C. Chevrot. Electrochemistry Communications 6 (2004) 299-305.

[3] W. Lu, A.G. Fadeev, B. Qi, E. Smela, B.R. Mattes, J. Ding, G.M. Spinks, J. Mazurkiewicz, D. Zhou, G.G. Wallace, D.R. MacFarlane, S.A. Forsyth, M. Forsyth, Science 297 (2002) 983-987.

P O S T E R

P15

Electrolytes based on PEO-boronate ester polymers for application in electrochromic windows

P.-Y. Pennarun and P. Jannasch
Department of Polymer Science & Engineering, Lund University
P.O. Box 124, SE-221 00 Lund, Sweden
e-mail: Patric.Jannasch@polymer.lth.se, tel (+46) 462229860, fax (+46) 462224115

S. Papaefthimiou and P. Yianoulis
Department of Physics, University of Patras, Patras 26500, Greece

Introduction

An electrochromic (EC) window is an active solar control device whose transmittance in the visible and near IR region of the spectrum can be reversibly modulated with the application of a low voltage (typically 3-5 Volt DC). Scientific research on these devices has been pursued during the last 20 years, as they can improve the comfort of people living or working in residential buildings, and reduce cooling, heating and ventilating loads.

A typical EC window is constituted by 5 different layers[1] : i) a transparent electronically conductive film deposited on glass (usually ITO), ii) an electrochromic film (generally WO_3[1]) in contact with iii) an ion conducting electrolyte containing a dissolved lithium salt, iv) an ion storage layer (optional), and v) a second transparent conductive film. Coloration is obtained by migration of Li^+ to the active layer by application of the voltage.

Most of research on electrolytes for EC windows has focused on optimising the ionic conductivity in order to facilitate a fast delivery of Li^+ to the active layer. However, in this study we have focused our efforts more on the interface stabilisation during the coloration process. We have developed electrolytes based on PEO-boronate ester polymers and different lithium salts. The presence of boron was expected to improve the dissociation of the salts and to stabilise the interface between electrolyte and WO_3 layer.

Experimental

Syntheses of PEO-boronate ester polymers (PBEP) were achieved under reflux of toluene with a mixture of poly(ethylene glycol) (PEG), boron trioxide, and either diethylene glycol monomethyl ether (DEGMME) or triethylene glycol monomethyl ether (TEGMME). In order to vary the structure of the polymer formed, PEG with different molecular weights were used. After reaction, toluene was removed by evaporation under high vacuum at 60°C during 12 hours. The polymers were then handled in a glove box under argon atmosphere (moisture content below 1.5 ppm).

Electrolytes were prepared by adding precise volumes of a 20 wt % anhydrous solution of $LiClO_4$ in dimethyl carbonate (DMC) to precise weights of each polymer in order to obtain the desired salt concentrations. DMC was subsequently removed by evaporation under high vacuum during 12 hours. The electrolytes were named in the following way: BXY-Z where B is boron, X is the molecular weight of PEG used for synthesis, Y=T or D for TEGMME or DEGMME, respectively, and Z represents the salt concentration expressed as the ratio [EO]:[Li]. Structural characterisation of the polymers was carried out by NMR (^1H and ^{13}C) and IR analysis.

Two electrolytes based on $LiClO_4$ (8.6 and 10.6 wt% respectively), poly(methyl methacrylate) (PMMA, 7 wt%) and propylene carbonate (PC) were prepared as reference material. Characterisation of polymers and their electrolytes based on $LiClO_4$ was carried out by DSC, thermal gravimetry and EIS measurements.

Results and discussion

Synthesis of PBEP from monohydroxy and dihydroxy functional poly(ethylene glycol) oligomers, and boron trioxide led to transparent, uncoloured, rubbery polymers. Due to the high density of branching of these polymers (see Figure 1), most of them were amorphous.

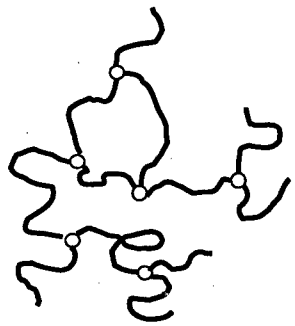


Figure 1: Schematic representation of the branched PBEP with boron (O) and PEO-like chains ( ).

It appeared that the electrolytes were stable up to at least 150°C and degradation due to the presence of ClO_4^- occurred above 280°C. Electrolytes prepared with PEGs having the highest molecular weights (>300 g/mol) presented the highest conductivities but were not suitable for use in EC device as they crystallised at low temperature. The electrolytes based on B300T were

selected as the most suitable ones because of their high conductivity and transparency. At room temperature, the conductivities of its electrolytes were at least 125 times lower than the one of the gel electrolyte based on PMMA (see Figure 2).

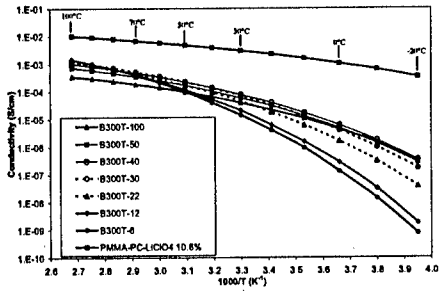


Figure 2: Arrhenius plots of the conductivity for electrolytes based on $LiClO_4$ and the B300T polymer. Also shown is the conductivity of the gel electrolyte containing 10.6 wt% salt.

The optical and electrochemical properties of EC devices prepared with electrolytes based on PEBP were compared with PMMA gel electrolytes. The EC devices incorporating the new boron-containing electrolytes were found to have excellent optical characteristics with extremely low luminous transmittance values in the coloured state (below 0.5%) and contrast ratios which reached 1:7700. This contrast ratio was 60 times higher than the one obtained with the gel electrolyte containing 10.6 wt% of LiClO4. The reason may be that a stabilisation of the interface occurred and played a major role in the coloration efficiency. Furthermore, the EC devices presented a high open circuit memory. The use of PC was found to play a dominant role in shortening the lifetime of the devices, and solvent-free systems were therefore chosen for further studies.

Conclusions

We have here presented a new approach to improve the overall performances of EC devices. We have shown that the ionic conductivity of electrolyte was not the most important parameter to reach fast and high coloration levels. Stabilisation, enhancement of salt dissociation and partition between electrolyte and WO_3 layer also played an important role. The inclusion of a Lewis acid in the electrolytes seemed to enhance these factors.

Acknowledgements

This work was supported under the EU FP5 project ELEVAG, contract N° ENK6-CT-2001-00547.

References

[1] U. O. Krasovec, A. S. Vuk, B. Orel, Solar Energy Mater. Solar Cells 73 (2002), 21.

[2] C.G. Granqvist, Solar Energy Mater. Solar Cells 60 (2000), 201.

[3] F. Zhou, D.R. MacFarlane, M. Forsyth, Electrochim. Acta 48 (2003), 1749.

[4] S. Papaefthimiou, G. Leftheriotis, P. Yianoulis, Electrochim. Acta 46, 13-14 (2001), 2145.

Electrorheological Fluids Based on Polymer Electrolytes

Anna Krztoń-Maziopa and Janusz Płocharski
Faculty of Chemistry, Warsaw University of Technology
ul. Noakowskiego 3, 00-664 Warszawa, Poland
e-mail: **amaziopa@hotmail.com**, tel (+)48 22 660 53 48, fax (+) 48 22 628 27 41

Introduction

Electrorheological (ER) fluids usually consist of dielectric particles suspended in a liquid of low electric permittivity. In response to the electric field the ER fluids solidify rapidly, or increase their viscosity. Such a millisecond response of these fluids is a subject of great interest because of many possible industrial applications, especially in the automotive and aerospace industries. It has been recognised that the drastic increase of the viscosity of ER fluids is due to the formation of particle chains that bridge the electrodes. This process is greatly affected by polarisation phenomena within the solid phase and at the surface of the grains and also by the mobility of charge carriers through the structure formed between electrodes in the electric field.

Experimental

In the present work, to examine relations between properties of dispersed solid particles (electric conductivity, type of mobile ion, grain size) of a set of ER fluids and resulting shear viscosity, we studied suspensions based on polyacrylonitrile doped with different salts (lithium, sodium and potassium thiocyanate, potassium perchlorate, lithium triflate and tetrabutylammonium iodide) as the solid phase and silicone oil (PDMS) as the liquid matrix. Polyacrylonitrile is a linear polymer that contains polar groups in the backbone and doping with salt conveniently modifies its electric properties, especially the ionic conductivity. The conductivities of solids were calculated from impedance spectra taken on pellets pressed out of powder samples and films made of initial solutions. In addition the samples were characterised by means of FTIR spectrometry to find the nature of the polymer - salt complex. The characterised powders were then suspended in PDMS and their flow curves at the presence of electric field were recorded.

Results and discussion

ER fluids contained polyacrylonitrile doped by different salts showed Bingham-like behaviour upon the application of electric field. The highest value of the yield stress exhibited suspensions based on polymer doped by thiocyanates. We also found that the suspensions containing polyelectrolytes as a dispersed phase exhibited low current densities in comparison to the ER fluids based on other conductive polymers.

Conclusions

We noted that controlling the concentration and type of salt permits to get materials of different electrorheological activity. The type of the counter ion and doping level of the polymer had strong influence on the electrorheological properties of the suspensions studied. We also stated a non-linear relation between concentration and the type of salt in the solid material and the magnitude of ER effect.

P O S T E R

P17

Electrorheological studies of polymer electrolytes in liquid crystalline matrix

Monika Ciszewska and Janusz Płocharski
Faculty of Chemistry
Warsaw University of Technology,
ul. Noakowskiego 3, 00 664 Warszawa, Poland
e-mail: **ciszko2001@yahoo.com**, tel (+48)22 6605348, fax (+48)22 6282741

Introduction

Typical electrorheological (ER) fluids comprise fine solid particles of high dielectric permittivity and moderate conductivity dispersed in an inert insulating liquid. Under external electric field the dispersed particles undergo polarisation and form larger structures contributing to rapid changes of rheological parameters of the system. In particular a significant increase of apparent viscosity is observed. The behaviour of an ER fluid is often approximated by the Bingham model with a clearly marked yield stress. There is also another group of ER fluids of homogeneous nature consisting of solutions of liquid crystalline polymers. In this case a strong increase of viscosity upon application of external electric field is also observed but the character of the fluids is Newtonian with no yield stress observed.

One of the most important factors hindering technical application of ER fluids is their low value of yield stress under electric field. We believe that a considerable improvement can be obtained by replacing the inert matrix of an ER suspension with a liquid crystalline solution. As the dispersed solid phase we chose powdered polymer electrolyte. For comparison we measured the ER behaviour of the polymer electrolyte powder dispersed in inert silicone oil as well as homogeneous solution of a polymer liquid crystal.

Experimental

The polymer electrolyte powders were obtained from polyacrylonitryle (PAN) doped with four different salts: potassium perchlorate, potassium thiocyanate, lithium triflate and tetrabutylammonium iodide, in concentration range of 5% - 20% m/m. The lyotropic liquid crystal – poly(hexyl isocyanate) (PHIC) dissolved in xylene was chosen as the active liquid matrix.

The prepared samples of the polymer electrolytes were first characterised by means of FTIR and impedance spectrometry. Then, rheological measurements under electric field were performed. First, the xylene solutions of PHIC at concentrations 3,5%-35% m/m were characterised without any suspended powder. In parallel the flow curves were recorded for 15% m/m suspensions of doped PAN samples in poly(dimethyl siloxane). Finally, the ER properties of the doped PAN powders dispersed in the xylene solutions of PHIC were studied.

Results and discussion

We have observed that the viscosity of the PAN powders in the PHIC solution increases considerably upon application of electric field exhibiting a strong ER effect. The obtained flow curves were of Bingham type. Comparison of these results with the data of PAN in silicone oil and pure PHIC solution shows that the viscosity increase of the hybrid fluid is bigger that the sum of the effects measured for the two latter fluids. In some experiments we recorded the fivefold increase of the viscosity as compared with the sum of the effects characteristic of the separately treated samples. The particularly high enhancement was recorded for the sample of PAN doped with 5% of lithium triflate at 2 kV/mm and the shear rate of 450 Hz. However, at low fields (about 0,3 kV/mm) some decrease of the ER fluid viscosity was observed resulting probably from instability of the polymer electrolytes in electric fields.

Conclusions

It was found that the hybrid ER fluids comprising doped PAN polymer electrolytes and PHIC based lyotropic liquid crystalline matrix exhibited a strong ER phenomenon whose magnitude was considerably enhanced in comparison with both ER active components measured separately. Therefore, a clear synergetic effect was observed.

Free Volume Studies of Polymer–Ionic Liquid Mixtures

Anita J Hill[1,2], Steven J Pas[3], Shiro Seki[4], Masayoshi Watanabe[4]

[1] CSIRO Manufacturing and Infrastructure Technology, Private Bag 33, South Clayton, MDC Victoria 3169, Australia

[2] Monash University, School of Chemistry, Wellington Rd, Clayton, Victoria 3800, Australia

[3]University of Münster, Institute of Physical Chemistry, Corrensstrasse 30, 48149 Münster, Germany

[4]Yokohama National University, Dept Chem & Biotechnol, Hodogaya Ku, 79-5 Tokiwadai, Yokohama, Kanagawa 2408501, Japan

e-mail: anita.hill@csiro.au, tel (+61) 3 9545-2777, fax (+61) 3 9544-1128

Introduction

In the past two decades, there have been several approaches to the development of flexible solid organic ionic electrolytes. The present work focuses on polymer ionic liquid mixtures [1], as this route offers flexibility of polymer choice to tailor mechanical and optical properties (outside the traditional range of polyetheroxides PEOs and other rubbery EO containing polymers) as well as the ability to tailor miscibility with the ionic liquid for maximum conductivity. In this work we examine mixtures of 1-ethyl-3methyl-imidazolium bis(trifluoromethylsulfonyl) imide (EMITFSI) with methylmethacrylate (MMA). EMITFSI is an ionic liquid at room temperature with conductivity of 10^{-2} S cm^{-1} and Tg of –87°C. Polymethylmethacrylate (PMMA) is a tough, transparent glassy polymer with a Tg of 120°C and a large sub-Tg secondary β transition region, in the temperature range -15°C to 60°C, that is regarded as responsible for its toughness.

The interaction (or miscibility) between the MMA groups and the ionic liquid may be important to both the mechancial as well as transport properties of these electrolytes. One method of studying the interaction between MMA and EMITFSI is via examination of the free volume that influences both the chain mobility and the ion mobility. In the present work we measured free volume using using positron annihilation lifetime spectroscopy (PALS) in order to investigate whether creation of accessible free volume via interaction of the ionic liquid and polymer phases could lead to improvement in electrolyte performance.

Measurement of the ortho-Positronium (oPs) accessible free volume in in polyurethane-lithium perchlorate electrolytes using PALS has established the correlation between the oPs accessible volume and ionic conductivity (σ). The relative free volume element size is calculated from the oPs lifetime (τ_{oPs}) and the relative number of free volume elements from the intensity (I_{oPs}). Concentration of salt and plasticizer [2] as well as variable temperature [3] have been used to vary the free volume and transport properties in these polymer electrolytes, and these results show a strong correlation between oPs accessible volume and log(σ), supporting the notion that free volume mitigates the mobility of ions in molecular solid electrolytes [4].

Experimental

Samples were prepared by in-situ radical polymerization of deoxidized MMA, ethylene glycol dimethacrylate (EGDMA, 2 mol% based on MMA) and benzoyl peroxide, (2 mol% based on MMA) as an initiator, dissolved in EMITFSI. The mixtures were heated between glass plates for 24 h at 80°C and post cured at 140°C. Salt concentration is given by the normalized ratio (EMITFSI/MMA=mol/mol). The PALS measurements were made at ambient temperature (22°C) in dry nitrogen.

Results and discussion

Figure 1 shows the increase in τ_{oPs} and free volume element size as a function of molar ratio EMITFSI:MMA. As this molar ratio increases, the free volume increases and the Tg decreases as PMMA becomes more plasticized. These results can be compared to the increase in conductivity of 2 orders of magnitude over this range.

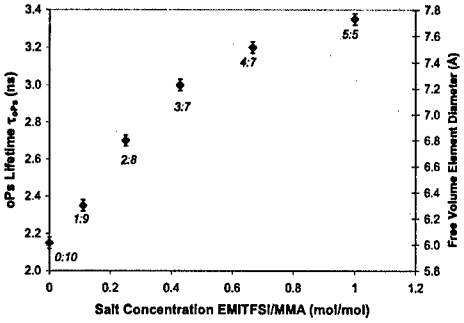


Figure 1 Lifetime of oPs (τ_{oPs}) and free volume element diameter as a function of salt concentration.

Conclusions

The free volume elements available to assist ion mobility increase in diameter by 1.7 Å as PMMA is plasticized by EMITFSI. Future work examines the effect of the sub-Tg mobility of the polymer on the ionic mobility of the ion gel.

References

[1] M Wantanabe, T Mizumura, *Solid State Ionics* **86-8** (1996) 353.

[2] M Forsyth, P Meakin, DR MacFarlane, AJ Hill, *J. Phys. Condens. Matter* **7** (1995), 7601.

[3] ZL Peng, B Wang, SQ Li, SJ Wang, *J. Appl. Phys.* **76** (1994) 1.

[4] M Ratner, in Polymer Electrolyte Reviews, Eds. JR MacCallum, CA Vincent, (Elsevier: London, 1987) 18.

High Frequency Dielectric Study on PEG400, PPG400 and the Statistical Copolymer P(EP)G 600

C. Stappen, M. Furlani, G. Niklasson
Chalmers University of Technology and Göteborg University, Physics and Engineering Physics
S-41296 Göteborg, Sweden

The aim of this study was the dielectric characterisation of pure polymers. Through the impedance spectroscopy measurement of the samples the real permittivity and imaginary permittivity development was observed.

The measurement on the pure polymers revealed interesting results about the dynamics of the polymers. The plot of real permittivity versus frequency showed that P(EG) has the highest value at all frequencies, suggesting that the two end-groups are dominant, where as the bulky P(PG) has a lower value, which can be explained by its randomly oriented polymer chain. The effect of the polarity of the end-groups is probably very important in the determination of the real permittivity at low frequencies. This effect becomes less important at higher frequencies, where the relaxation mechanism of the polymer are likely responsible for the drop in the value of ε'. Observing the curve of the semi-decapped copolymer P(EPG) this can be only underlined as this curves intersects the curve of P(PG), having a lower value below 100 MHz and a higher value above. So, the fact that the copolymer is semi-decapped dominates its behaviour at low frequencies but becomes – relatively – unimportant at higher frequencies. The plot of the imaginary permittivity of the three pure polymers showed that P(EG) and P(EPG) have very similar dynamics, both differing immensely from P(PG). The maximum of the dielectric loss, corresponding to the polymer relaxation, lies around 1 GHz for P(EG) and P(EPG), and around 200 MHz for P(PG). This can be attributed to the fact that the methyl groups of the P(PG) chain hinder the dynamics.

The fact that P(PG) systems are not as useful as the other two systems has been observed and explained. The copolymer P(EPG) and P(EG) show a similar behaviour and explanation for this was also provided. The copolymer has been tested to have a good performance and a high durability in electro-chromic devices and it can therefore be concluded that the use of the copolymer system in electro-chromic devices is recommended.

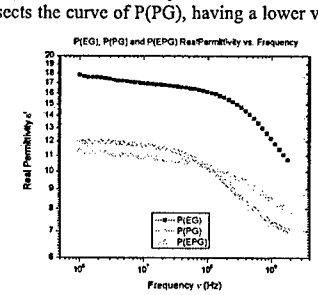


Figure Błąd! W dokumencie nie ma tekstu o podanym stylu.-**1 The real permittivity of the pure polymers plotted against frequency**

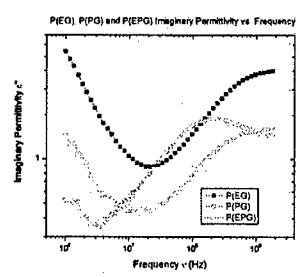


Figure Błąd! W dokumencie nie ma tekstu o podanym stylu.-**2 The imaginary permittivity of the pure polymers plotted against frequency**

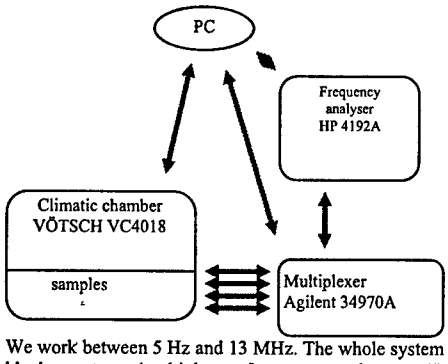
Improved conductivity measurements of fuel cell polymer electrolytes

M. Maréchal, J. Guindet, J.-P. Diard, J.-Y. Sanchez
LEPMI Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces de Grenoble
1130 rue de la Piscine, BP 75, Domaine Universitaire
38402 SAINT MARTIN D'HERES CEDEX, FRANCE
e-mail: **manuel.marechal@inpg.fr**, tel (+33) (0)4 76 82 65 62, fax (+33) (0)4 76 82 66 70

Introduction

During the PEMFC working, the cell temperature and the humidity membrane are prone to great variations [1]. The polyelectrolytes use is thus related to a precise knowledge of ionic conduction properties under these various conditions [2, 3]. It appeared fundamental to develop a study system. New conductivity measuring cells were designed in order to ensure an optimal control of the geometrical factors. These cells are placed in a climatic chamber allowing the work temperature control as well as relative humidity (RH). The membrane resistance measurements are free from the polarization phenomena by using electrochemical spectroscopy impedance [4]. Several samples are successively analyzed using a multiplexer and a homemade software. This automated measurements system allows many samples characterization under comparable and wide climatic conditions variationsExperimental

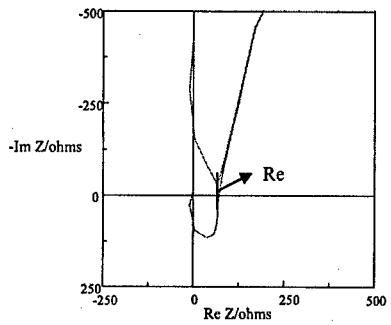
The following diagram represents the system synoptic view. The spectra are acquired automatically and the climatic conditions are programming simultaneously.



We work between 5 Hz and 13 MHz. The whole system blank spectrum (multiplexer, frequency analyzer, cell) is modelled by a resistance and an inductance in series, this is the blank. We can thus, with an experimental spectrum go up with the symmetrical system spectrum (blocking electrode/ membrane/ blocking electrode). This corrected spectrum in obtained by subtraction of the blank to the experimental spectrum. The resistance Re obtained to the imaginary part maximum (see in the following figure), in many cases, allows calculating the conductivity. This follow Re is obtained to 1,25 MHz. This is an intrinsic value of a system polyelectrolyte/membrane taking form/climatic conditions. The two gold electrodes with 2 millimetres diameter are aligned with a very good accuracy.

Results and discussion

This spectrum is obtained after the sample stabilization. Besides automation allows following this stabilization without constraint.



Corrected with the positive maximum (Max) and experimental spectra of Nafion® 117 at point (20°C; 98%RH)

Thus we have a well-adapted tool to this long measurements kind. Such a system is also justified by the very long settling times in particular with respect to the relative humidity. During a 10%RH decrease this time can reach several days for the complete stabilization! We made Nafion®117 measurements on the working square (10°C to 95°C, 10%RH to 100%RH).

Conclusions

The whole automated system allows (i) a great measuring accuracy, (ii) more significant campaigns in a broad climatic range and thus more supported comparisons. In addition, the polyelectrolytes are not compared at only one (T, RH) working point which might lead to hasty conclusions.

Despite our measurements have an error close to 20%; such a system enables precise comparative measurements between electrolytes.

References

[1] S. Miachon, P. Aldebert, J. Power Sources, 56 (1995) 31-36

[2] T. A. Zawodzinski, Jr., C. Derouin, S Radzinski, R. J. Sherman, V. T. Smith, T. E. Springer, S. Gottesfeld, J. Electrochem. Soc, 140-4 (1993) 1041-1047

[3] Y. Sone, P. Ekdunge, D. Simonsson, J. Electrochem. Soc., 143 (1996) 1254-1259

[4] C. A. Edmonson, P. E. Stallworth, M. E. Chapman, J. J. Fontanella, M. C. Wintersgill, S. H. Chung, S. G. Greenbaum, Solid States Ionics, 135 (2000) 419-423

In-Situ Impedance and Optical Study of Crystallization and Melting of PEO:LiTFSI Polymer Electrolytes

M. Marzantowicz[1], J.R. Dygas[1], F. Krok[1], A. Łasińska[1], Z. Florjańczyk[2], A. Affek[2]
[1]Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warszawa, Poland
[2]Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warszawa, Poland
e-mail: marzan@mech.pw.edu.pl, **tel (+48) 22 6608405, fax (+48) 22 6608419**

Introduction

It is well known that the degree of crystallinity of a polymer electrolyte has significant influence on ionic conductivity. Recently, we have studied the effects of inhomogeneity on impedance spectra, pointing out a possibility to relate elements of the equivalent circuit to different phases of the semi-crystalline polymer [1]. Melting and growth of crystalline structures in PEO based electrolytes is visible in a polarizing microscope. Here we present results of investigation combining in-situ polarizing microscope and impedance spectroscopy aimed at establishing direct relation between morphological features and electrical properties of a polymer electrolyte.

Experimental

A custom measurement cell and heating/cooling apparatus was build, allowing heating and cooling between –20°C and 150°C. The samples were placed between two ITO glasses in air-tight cell. Pristine polyethylene oxide and PEO with various amount of lithium salt $LiN(CF_3SO_2)_2$ were investigated. Impedance was measured with Novocontrol Alpha-N dielectric analyzer in frequency range 10^{-2} to 10^7 Hz. The spectra were fitted with an equivalent circuit, describing multi-phase electrolyte and electrodes.

Results

The study was focused on correlation between morphology and electrical properties (mainly ionic conductivity) of electrolytes with different polymer to salt ratio during crystallization and melting processes. Isothermal as well as non-isothermal experiments were carried out.

In Fig 1, time dependence of conductivity obtained from impedance spectra is presented for the sample of PEO:LiTFSI 6:1 isothermally crystallized from rapidly cooled melt at 20°C. For selected stages of crystallization, polarizing microscope photographs are shown. After initial phase of spherulite nucleation and growth (A, B), the growth of spherulites appears to be completed at stage C, after which no significant changes of optical picture were recorded (D). In the same period, electrical conductivity shows continuous decrease with time. It seems that closing of conductivity pathways through amorphous polymer in later stage of crystallization has much more impact on ionic conductivity than the growth of spherulites. During crystallization, the impedance spectra undergo significant changes. Inhomogeneity of the semi-crystalline electrolyte causes conductivity dispersion, which is, however, differently manifested between electrolytes with various polymer to salt ratios.

References

[1] J.R.Dygas, B.Misztal-Faraj, Z.Florjańczyk, F.Krok, M.Marzantowicz, E.Zygadło-Monikowska, Solid State Ionics **157** (2002) p. 249

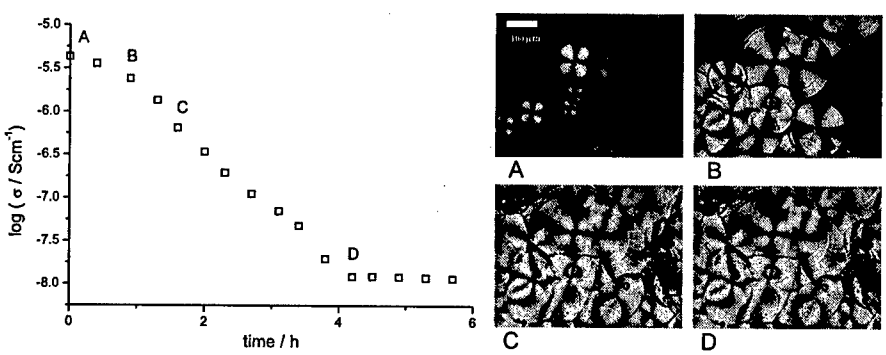


Fig 1. Conductivity of PEO:LiTFSI 6:1during isothermal crystallization at 20°C and corresponding micrographs.

Intercalation of Polyacrylonitrile into Bentonite

Eglantine Benavente[1*], María Angélica Santa Ana[2], **Guillermo González**[2]
[1] Departamento de Química, Universidad Tecnológica Metropolitana, Av. José Pedro Alessandri 1242, Santiago, Chile
[2] Departamento de Química, Facultad de Ciencias, Universidad de Chile, Las Palmeras 3425, Santiago, Chile.
e-mail: **eglantina.benavente@utem.cl**, tel (+562) 787 7109, fax (+562) 271 3888

Introduction

Organic-inorganic hybrids based on the intercalation of a polymer into layered inorganic matrices have receive much attention, among others because its potential as electrolyte or electrode materials in electrochemical devices. Properties of these products, like its mechanical stability and the possibility of forming robust films frequently with high anisotropy degree, are in generally much appreciated. Most studies in these field are related to poly(ethylene oxide). The preparation of well characterized products arising from the intercalation of other polymers, which are also relevant as polymers electrolytes like poly(acrilonitrile), has been rare until now. In this work we describe the synthesis and primary characterization of ther interclation of PAN into a montmorillonite clay, the bentonite.

Experimental

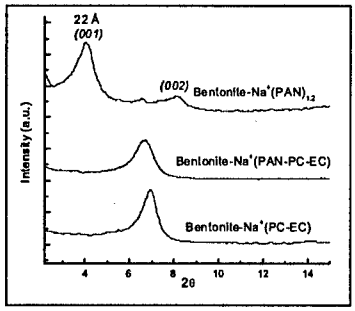
0.057 g polyacrylonitrile power (Aldrich, Mw 140.000), dissolved in 10 ml PC/EC (Aldrich) 1:1 (v/v) mixture by stirring vigorous during 3 h at 70 °C, was added to a suspension of Na-bentonite (Sigma, < 2μm, *cec* ca 100 meq/100) and stirred during 48 h at 70 °C in the same solvent. The product was separated by centrifugation and washed three times with PC and absolute ethanol, and finaly dried under vacuum. Analysis: exp. [calc. for $Na_{0.47}(Al_{1.58}Fe_{0.17}Mg_{0.25})(Al_{0.22}Si_{3.78}O_{10})(OH)_2$ $(PAN)_{1.25}$ $\cdot H_2O$]: C: 10.09 (10.2); N: 4.54 (3.97) ; H: 1.34 (1.30).

Results and discussion

The treatment of a suspension of the bentonite in mixture of ethylene carbonate (EC)-propylene carbonate (PC) with a solution of PAN in the same solvent leads to a single lamellar phase. As observed in the difractogramm reproduced in Figure 1, where two *001* brag reflections may be appreciated, the interlaminar distance is about 22 Å. The elemental analysis of the product indicates an intercalation degree of about 1.25 mol of the PAN monomer per $[Si,Al]_4$ unit of the clay. The amount of water intercalated in the product corresponds aproximately to two H_2O molecules per mol sodium ion.

In the synthesis, the selection of the solvent used in the intercalation is crucial. Indeed, when recognized, well PAN solvents like dimethylsulphoxide or dimethylformamide were used, not any PAN intercalation could be observed. Reactions taking benzene as solvent, used succesfully for intercalating PAN into molybdenum disulfide, also failed in the case of the clay. Apparently, this intercalation is only possible in solvents with moderate donor ability like the organic carbonates (DN about 15). In the intercalation mechanism the competence of the solvent and the polymer for solvating the clay interchangeable cations appear to be important.

Figure 1. X-ray diffraction patterns of intercalation



products of PAN in bentonite.

Observed stoichiometry indicates an intercalation degree which is lower than that corresponding to available interlaminar suface. That, in addition to the rather large interlaminar distance observed in the intercalate, 12 Å, suggests that PAN, together with intercalated water, is involved the coordination sphere of the Na^+ clay contraions.

Conclusions

The intercalation of polyacrylonitrile into bentonite is possible only using the polymer solution in a solvent with medium donor activity. This effect may be understand considering the role of PAN in the coordination of the exchangeable cations located in the interlaminar space of the clay.

Acknowledgements

Research partially financed by FONDECYT (Contract 1030102) and the Universidad Tecnológica Metropolitana.

References

[1] Y. S. Choi , I. J. Chung, Polymer **45** (2004) 3827.
[2] E. Benavente, M.A. Santa Ana, F. Mendizábal, G. González, Coordinati.on Chem. Reviews **224** (2002) 87.
[3] P Aranda, E. Ruiz-Hitzky. Applied Clay Science **15** (1999) 119.

Investigations on the ion transport mechanism in PVOH-based polymer gels

R. A. Vargas, I. Palacios and V. H. Zapata
Departamento de Física, Universidad del Valle, A. A. 25360, Cali, Colombia.
[1]e-mail: **rvargas@calima.univalle.edu.co**, tel (572) 339 2417, fax (572) 339 3237

Introduction

The change in the electrical properties of polymer membranes based on poly (vinyl alcohol) (PVOH) and potassium hydroxide (KOH) have been investigated as a function of the environment relative humidity (RH%) and temperature. The membranes have been characterized by electrical conductivity (using impedance spectroscopy) and thermal measurements (using differential scanning calorimetry (DSC) and thermogravimetric analysis). It has been found that the temperature dependence of the ionic conductivity (keeping constant the relative humidity) follows an Arrhenius–type behavior associated with the ion transport mechanism in water swollen polymer films. A treatment of the experimental data is used [1] to explain the conductivity trend as a function of RH% based on the Onsager equation valid for electrolytic solutions. The equation has been applied to the relevant parameters of the polymer membranes and it describes change in its conductivity as a function of its water content satisfactorily.

Experimental

A series of alkaline solid electrolyte membranes based on poly(vinyl alcohol) (PVOH), potassium hydroxide (KOH) and water (H_2O) have been prepared by the cast technique. The thermal analysis has been done with a modulated differential calorimeter, TA Instruments MDSC 292 and a microbalance TGA 2050; impedance spectroscopy has been done with a LCR meter HP 4174A. The measurements have also been done as a function of the relative humidity (RH%) .

Results and discussion

A sigmoidal shape has been obtained for the σ vs. RH% plots. To test this conductivity trend of the investigated system as a function of the environmental humidity, we have used the modified Onsager equation:

$$\sigma = \sigma_0 - \left[(a'\sigma_0/(CT)^{3/2} + (b'/(CT)^{1/2}\right] \quad (1)$$

whereby the capacity (**C**) of the material is viewed to depend on RH%. In Eq. (1) σ_0 is the limiting value of σ, **a'** and **b'** are constants which depend on the total mobile ion concentration and the material mechanical properties. For a sample with salt/polymer content of x = 0.14 and at 285 K, the best fitting parameters are $\sigma_0 = 1.8 \times 10^{-2}$ $(\Omega.cm)^{-1}$ that corresponds to 100 % of relative humidity, $a' = -2.05 \times 10^{-4}$ $(F\ K)^{3/2}$ and $b' = 1.86 \times 10^{-3}$ $(F\ K)^{1/2}(\Omega cm)^{-1}$. For other salt content in presence of environmental humidity and changing the temperature between 253 and 301 K, conductivities between approximately 10^{-3} and $10^{-1}(\Omega cm)^{-1}$ have been obtained.

The thermal and transport results are explained in terms of the plastification effects of water on the polymer and the presence of a separated phase KOH/H_2O in the polymer.

Conclusions

The results point to a separate liquid-like phase with KOH/H_2O composition from polymeric phase with composition $PVOH/KOH/H_2O$ phase. The plastification of PVOH by the water and salt content in the polymeric phase is clearly shown since the glass transition temperature (T_g) is greatly decreased. The liquid-like $PVOH/H_2O$ phase is primarily responsible for the ion migration in the blend. A treatment of the experimental data has been used in order to explain the ionic conductivity trend as a function of the environmental humidity, which is based on the Onsager model for the protonic conductivity in acid aqueous solutions. That is, the absorbed water by increasing the dielectric constant inside the polymer free volume, leads to the dissociation of the ion aggregates similar to that of aqueous solutions.

References

[1] R. A. Vargas, V. H. Zapata, M. I. Delgado and I. Palacios, Solid State Ionics (to be published).
[2] N. Camaioni, G. Casalbore-Miceli, Y. Li, C.M. Mari, M.-J. Yang, Solid State Ionics, 144 (2001) 355.

Ion-conductive Properties of Mesoporous Silica-filled Composite Polymer Electrolytes

Sumiko Igawa*, Yoichi Tominaga, Shigeo Asai, Masao Sumita
Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152- 8550, JAPAN
*e-mail: **sigawa@mbox.op.titech.ac.jp**, tel (+) 81- 3- 5734- 2431, fax (+) 81- 3- 5734- 2876

Introduction

It is well known that the ionic conduction in solid polymer electrolytes is improved by the addition of inorganic fillers such as particle SiO_2, Al_2O_3 and TiO_2. In this study, we used mesoporous silica as an inorganic additive for polymer electrolytes. The mesoporous silica has well-ordered hexagonal pores and a large specific surface area. We expect that the silica will act as a bypass for the fast ionic conduction.

Experimental

Mesoporous silica (SBA-15) was synthesized by the hydrothermal method. Nonionic triblock copolymer ($EO_{20}PO_{70}EO_{20}$) was dissolved in water with HCl. Tetraethyl-orthosilicate (TEOS) was dropped into the surfactant solution, and the mixture was stirred at 35 °C for 24h. The mixture was kept in the oven at 80 °C for 24h. As-synthesized SBA-15 was filtered, and calcined at 400 °C for 4h.

Oligo (oxyethylene methacrylate) (MEO), $LiCF_3SO_3$ ($[Li^+]/[OE]=1/10$) and inorganic filler (SBA-15 or particle silica: 0, 2.5, 5, 7.5, 10, 15, 20[wt%]) were dissolved in methanol for 24h. AIBN was added to the solution, and then the solvent was removed. The 0.5 mm-thick film was obtained by polymerizaion at 160 °C. The ac impedance and DSC mesurement were carried out.

Results and discussion

Fig.1 shows the relation between the ionic conductivity and filler content for PMEO-$LiCF_3SO_3$-filler composite electrolytes. The conductivity of SBA-15 filled samples was higher than that of the original PMEO electrolyte. In general, the carrier ions in polymer electrolytes transport through the segmental motion with oxyethylene chains, the conductivity decreases with the increase in T_g. However, by the addition of fillers, the conductivity of PMEO-Li salt composite was improved in spite of the increase in the T_g. This is due to the additional contribution to the ionic conduction, which is independent of the segmental motion of polymer, by the formation of the ion-conductive path on the filler surface [1]. Moreover, the conductivity of SBA-15-filled PMEO-Li salt electrolyte was higher than that of the sample filled with particle-type silica. This result suggests that the large surface of SBA-15 can be effective for ion-conductive paths. The conductivity of SBA-15 composite samples decreases with increasing the content higher than 2.5wt%. This is caused by the decrease of amorphous PMEO phase, which attributes to the ionic transport by the segmental motion.

References

[1] F.Croce, L.Perci, B.Scrosati, F.Serraino-Fiory, E.Plichta, Electrochimica Acta, 46 (2001) 2451.

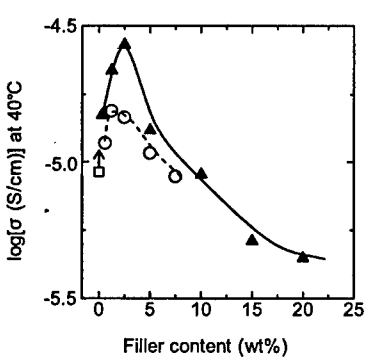


Fig.1 Relation between the ionic conductivity and filler content for PMEO-$LiCF_3SO_3$-filler composite electrolytes
(□:original, ▲:SBA-15, ○ :particle silica)

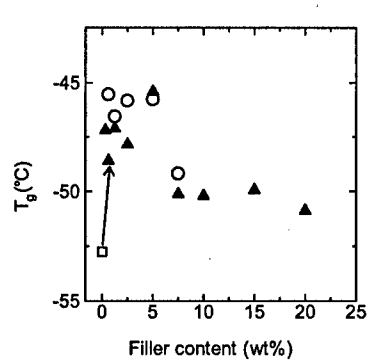


Fig.2 Relation between T_g and filler content for PMEO-$LiCF_3SO_3$-filler composite electrolytes
(□:original, ▲:SBA-15, ○ :particle silica)

Ion-Gels Prepared by Incorporation of Protic Ionic Liquids in Polymer Networks as Anhydrous Proton Conducting Non-aqueous Electrolytes

Nobuaki Ishibashi, Md. Abu Bin Hasan Susan, Hirofumi Nakamoto, Masayoshi Watanabe
Department of Chemistry and Biotechnology, Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
e-mail: **d04ga101@ynu.ac.jp**, tel +81-45-339-3955, fax 81-45-339-3955

Introduction

The efficacy of polymer electrolyte fuel cell (PEFC) as the most prospective power source has resulted in a tremendous surge of interest on polymer electrolytes for such devices. Most significant PEFCs use perfluorosulfonate ionomers, typically Nafion® as their electrolytes under humidifying conditions, which are associated with a number of constraints, such as water management, "flooding", catalyst poisoning by CO in the reform gas etc, originating from the low boiling point of water. This necessitates the innovation of alternatively efficient, highly proton conducting polymer electrolytes with high operational temperature. Ionic liquids, possessing the wealth of desirable electrochemical and materials properties, are very promising, but need to act as proton solvents or be capable of conducting protons for their true use in proton conductors. Recently, we have shown that Brønsted acid-base ionic liquids derived from a wide variety of organic amines with a super strong acid, bis(trifluoromethanesulfon) imide (HTFSI) can serve as fuel cell electrolytes at elevated temperatures under non-humidifying conditions and fast proton conduction has been revealed for such ionic liquid systems under base-rich conditions.[1-3]

This study aims at evaluating a new series of ionic liquids derived from the combination of 1,2,4-triazole (TZL) with HTFSI and their ion-gels as fuel cell electrolytes and provide an insight into the mechanism of proton conduction with eyes pointed on the number of proton acceptor sites for fast proton conduction.

Experimental

Appropriate amounts of HTFSI and TZL, maintaining defined molar ratios, were mixed and heated above the respective melting points. A commercially available porous poly(vinylidenefluoride) (PVdF) membrane filter was impregnated with TZL/HTFSI compositions for the incorporation of protic ionic liquids into polymer networks to obtain ion-gels. The thermal properties for the TZL/HTFSI compositions and the ion-gels were studied using thermogravimetry (TG) and differential scanning calorimetry (DSC), while ionic conductivities were determined by complex impedance methods. The proton transport behavior of the ionic liquids were analyzed at the three phase boundary of the ionic liquids/Pt/H_2 or O_2 by electrochemical polarization experiments. The fuel cell characteristics of the ion-gels were performed in a single cell with the membrane electrode assembly (MEA) comprised of Pt/C, Kyner Flex®, and the ionic liquid under non humidifying conditions at temperatures higher than 100 °C.

Results and discussion

The combination of TZL with HTFSI yielded protic ionic liquids, melting point (T_m) of which changes with change in composition. Interestingly, the neutral salt and some other compositions are liquid at room temperature. The neutral salt has thermal stability of >250 °C, which decreases with excess TZL in the system.

The TZL-HTFSI system exhibited high ionic condictivity. The ionic conductivity of [TZL]/[HTFSI] = 75/25 is higher than that of the equimolar salt, for instance, the values at 130 °C are 3.8×10^{-2} and 2.2×10^{-2} Scm^{-1} for the base rich composition and equimolar salt, respectively. Since the number of ion carriers, $HTZL^+$ $TFSI^-$ are maximum at the equimolar composition, the increase in the mole fraction of TZL indicates enhanced ionic mobility. The conductivity is therefore, due not only to ionic species like $HTZL^+$, $TFSI^-$, but also to intermolecular proton transfer.[1,3]

The electrochemical polrization results evidence protonic conduction in the neutral salts as well as the base-rich compositions of the TZL-HTFSI system. The TZL/HTFSI compositions are electroactive for H_2 oxidation and O_2 reduction at a Pt electrode under non-humidifying conditions, which shows the prospect of the use of the system for anhydrous proton conductors. The difference of the electrical power generated by the base-rich composition of TZL and the corresponding neutral salt is significantly higher compared to imidazole/HTFSI system, which indicates that the number of proton acceptor sites in the Brønsted base might play important role to govern proton conduction.

Preliminary results for a H_2/O_2 fuel cell with an ion-gel containg the neutral salt of TZL/HTFSI indicates that the proton conductivity in the liquid state retain in the ion-gels and the polymer electrolytes of this variety can serve as fuel cell electrolytes under entirely non-humidification conditions and elevated temperatures. The optimization of the experimental conditions for the PEFC performace test and the development of strategy to realize stable ion-gels for solid-state proton conductors are now underway.

Reference

1) A. Noda, M.A.B.H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu and M. Watanabe J. Phys. Chem. B. **107** (2003), p. 4024.
2) M.A.B.H. Susan, A. Noda, S. Mitsushima, M. Watanabe Chem. Commun. **2003**, p. 938.
3) M.A.B.H. Susan, M. Yoo, H. Nakamoto, M. Watanabe Chem. Lett. **32** (2003), p. 836.

Ionic Conduction of Polyether-Based Electrolytes Under High-Pressure CO_2

Yoichi Tominaga*, Shingo Hirahara, Shigeo Asai, Masao Sumita
Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, JAPAN
*e-mail: **ytominag@o.cc.titech.ac.jp**, tel (+) 81 3 5734 2431, fax (+)81 3 5734 2876

Introduction

We have previously studied the PEO [1,2] and PMEO-Li salt mixtures [3], using supercritical CO_2 treatment to improve the ionic conductivity. The PEO electrolyte clearly exhibited higher conductivity after CO_2 treatment. Here, we study the effect of CO_2 on the ionic conductivity of polyether electrolytes using an *in situ* complex impedance measurement system consisting of a supercritical fluid extraction equipment and a high-pressure reactor. By using this system, the direct influence of CO_2 on ionic conduction in polyethers will be observed [4,5]. Furthermore, in the near future, we can suggest that the use of CO_2 as solvent is effective for preparation of high ion-conducting polymeric materials. This paper reports the effect of CO_2 pressure on ionic conduction in polyether-based electrolytes possessing some kinds of Li salts under the subcritical and supercritical state.

Experiment

The PEO (M_w=5x10^5)-LiX (X=Br, I, NO_3, CF_3SO_3; BF_4, ClO_4, TFSI) mixtures were used as a crystalline electrolyte system. An amorphous system (PMEO-LiX) was prepared from oligo(oxyethylene glycol) methacrylate (MEO; CH_2=C(CH_3)-COO-($CH_2CH_2O)_8$-H) monomer. The ratio of a Li ion concentration to oxyethylene (OE) unit of both PEO and PMEO electrolytes was arranged to be 10 mol% ([Li^+]/[OE]=1/10).

The supercritical CO_2 extraction system which consists of a delivery pump, an automatic backpressure regulator, and a heater was used for measurement. A high-pressure original reactor (max. 30 MPa, 200 °C) was constructed from a retainer and a vessel (50 ml) with a PEEK seal. The reactor has six access ports on the surface of the retainer, and threaded fixtures on the flat surfaces. SUS tubes were used for the inflow and outflow of liquid CO_2. Pt wire (0.4 mm-diameter) insulated by a PEEK tube was fixed on the side of a SUS plate (15x15 mm, 0.5 mm-thick) for use as electrodes. A Teflon® plate (1.0 mm-thick) was used as a spacer between two SUS electrodes. The sample was sandwiched between the SUS electrodes with a spacer, and the cell surface was insulated by Polyimide tape. The ionic conductivity was measured by the complex impedance method using a Solartron 1260 Impedance Analyzer (Schlumberger) in the frequency range from 100 Hz to 20 MHz. The cell was loaded in the reactor, which was filled with neat CO_2 and vented to atmospheric pressure three times. The CO_2 pressure was then increased up to each measurement pressure, and maintained with a flow rate of 1 ml/min. After the pressure stabilized, the reactor was heated slowly from room temperature to 100 °C. The temperature was held constant, every 10 °C interval for 15 min, following which the impedance measurement was carried out.

Results and discussion

Pressure dependence of the ionic conductivity at 40 °C for PMEO electrolytes under CO_2 is shown in Figure 1. The conductivity of PMEO-based electrolytes increased with increasing pressure under CO_2. In particular, the conductivity of LiTFSI-based electrolyte increased by more than one order of magnitude upon pressurization, to a maximum at 15 MPa. Moreover, the conductivity of CF_3SO_3 and ClO_4 systems was also improved by the pressurization. The CO_2 pressurization also increases the Lewis acid-base interaction, simply because of the increase in CO_2 density. The large enhancement in ionic conductivity around room temperature is caused by the increase of carrier ions. An increase of pressure decreases T_g since the number of penetrating CO_2 molecules increases. It is therefore

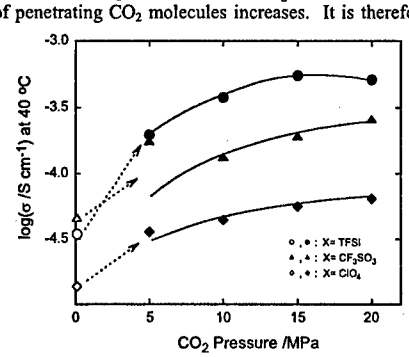


Fig.1 Pressure dependence of the conductivity for $PMEO_{10}LiX$ under atmospheric (open symbols) and under high-pressure CO_2 (close symbols).

expected that CO_2 penetration together with Lewis acid-base interaction between polyether or ions and CO_2 reduces T_g, and probably promotes the lithium salt dissociation.

References

1. Y. Tominaga *et al.*, Mater. Lett., **57**, 777 (2002).
2. Y. Tominaga *et al.*, Macromolecules, **36**, 8766 (2003).
3. G.-H. Kwak *et al.*, Electrochim. Acta, **48**, 1991 (2003).
4. Y. Tominaga *et al.*, Polymer, **44**, 4769 (2003).
5. G.-H. Kwak *et al.* Electrochim. Acta, **48**, 4069 (2003).

Ionic Conductivity in the Crystalline Polymer Electrolytes PEO_6:$LiXF_6$, X=P, As, Sb

Edward Staunton, A.M. Christie, Y. G. Andreev and P. G. Bruce
School of Chemistry, University of St. Andrews, Scotland, UK KY16 9ST
e-mail: **es36@st-andrews.ac.uk**, tel (+) 441334463814, fax (+) 441334463808

Elucidation of the crystal structures of poly(ethylene oxide)$_6$:$LiXF_6$, X=P, As, Sb from their powder diffraction patterns by 'Simulated Annealing' at St. Andrews led to the recent discovery that ionic conduction can occur in the crystalline phase of these materials.

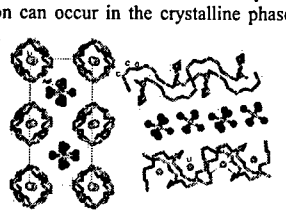


Fig. 1 Crystal structure of P(EO)$_6$:$LiAsF_6$

The structures of these materials are unique in that the lithium ions are co-ordinated by 5 ether oxygens and are arranged in rows, the rows located inside a cylindrical surface formed by two PEO chains. Each chain adopts a non-helical conformation that defines a half cylinder; the two half cylinders interlock on both sides. The lithium ions are completely dissociated from the anions (Fig. 1). As such it was proposed that this material may exhibit conductivity in the crystalline phase[1-3].

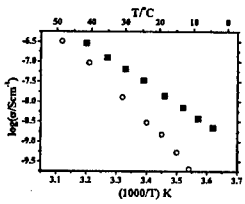


Fig. 2 Ionic conductivity, σ, of crystalline (squares) and fully amorphous (circles) phases of P(EO)$_6$:$LiSbF_6$

This challenges the established view that conduction occurs exclusively in amorphous materials above their glass transition temperature and that crystalline complexes are insulators! The three crystalline polymer electrolytes, referred to in the title, have been shown not only to conduct, but to do so better than the analogous amorphous phases (Fig. 2).

The conduction mechanism in amorphous polymer electrolytes relies on relatively slow local solvent reorganization (segmental motion), this limits the level of conductivity that can be achieved. Indeed, despite strenuous efforts, the maximum conductivity (10^{-4} Scm^{-1} at 25°C) in such amorphous polymer electrolytes has remained too low for many applications. If however the sites to which an ion migrates were already present and aligned in the structure (as they are in the crystalline phase), rather than relying on chain dynamics to generate such sites, ion hopping could take place as soon as sufficient energy were available for the ion to hop. Hence relatively higher conductivities may be possible for crystalline systems.

Further investigation of these materials has shown an increase in ionic conductivity with reduction of molecular weight of the crystalline polymer electrolyte which coincides with the increase in crystallite size on reducing molecular weight[4] (Fig. 3). The crystallite size decreases from 2500 Å (M_w = 1000) through 2300 Å (M_w = 1500) to 2000 Å (M_w = 2000).

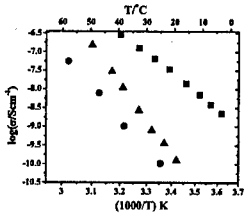


Fig 3. Comparison of σ of P(EO)$_6$:$LiSbF_6$ prepared from PEO M_w1000 (squares), 1500 (triangles) and 2000(circles)

Recently it has been witnessed that doping these complexes with other lithium salts can raise significantly the conductivity. Substitution of the Group 15 hexafluoride anions by larger anions has also succeeded in a significant increase in conductivity. Furthermore we have modified the polymer chains, resulting in further increases in levels of conductivity achieving 10^{-4} Scm^{-1} at 30°C (Fig. 4).

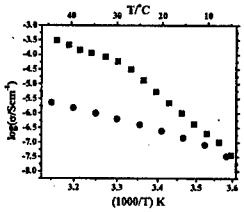


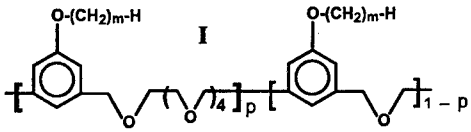
Fig. 4 Comparison of P(EO)$_6$:$LiPF_6$ materials. Prepared with 'standard' polymer (circles), prepared with 'modified' polymer (squares)

[1] MacGlashan, G.S., Andreev, Y.G. and Bruce P.G. *Nature* **398**, 792-794 (1999)
[2] Gadjourova, Z., Martin y Marero, D., Tunstall, D.P. and Bruce, P.G. *Chem. Mater.* **13**, 1282-1285 (2001)
[3] Gadjourova, Z., Andreev, Y.G., Tunstall, D.P. and Bruce P.G., *Nature* **412**, 520-523 (2001)
[4] Stoeva Z., Martin-Litas I., Staunton E., Andreev Y.G., and Bruce P.G., *JACS* **125**, 4619-4626 (2003)

Li^+ transport in amphiphilic copolymer mixtures - the influence of copolymer sequencing.

Y-P. Liao, Y. Zheng, J. Liu, G. Ungar and P.V. Wright
Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield, S1 3JD UK

High ambient conductivities have been observed in Li salt complexes of **I**, which are copolymers poly[2,5,8,11,14-pentaoxapentadecamethylene(5-alkyloxy-1,3-phenylene)] (abbrev. CmO5) and poly[2-oxapropylene(5-alkyloxy-1,3-phenylene)] (abbrev. CmO1). In these systems the side chain length, m = 16, 18 or mixed side chains with 12. **I** and Li salt is



blended with **II**, a linear amphiphilic copolymer - $[-(CH_2)_4\text{-}O\text{-}]_{23}\text{-}(CH_2)_{12}\text{-}O\text{-}$ and **III**, a block copolymer $C_{18}H_{37}\text{-}[-(CH_2)_4\text{-}O\text{-}]_{\sim 50}C_{18}H_{37}$ which is present in minor proportions to promote blending of **I** and **II**. Following heat treatment and deblending of the mixture **III** also stabilises the interface between of **I** and **II**, the latter forming an ion bridge or 'glue' between the lamellae of **I** through which decoupled ion transport apparently takes place to give AC (complex impedance) conductivities ~ 10^{-3} S cm^{-1} at ambient temperatures with low activation energies.

^{7}Li NMR shows that significant cation mobility is present down to -20°C. However, molecular dynamics modelling indicates that, while *ion separation with Li^+ coordination* occurs in CmO5 polymers, in CmO1 sequences the salt is present as *decoupled small aggregates* LiA and Li_2A_2 in a novel kind of complex in which the aggregates confer some degree of salt stabilisation on the polymer as evidenced by the formation of liquid crystal phases at 50°C, above the isotropic melting temperatures of the pure polymer (42°C for C16O1)

Optimum conductivities have been observed by complex impedance measurements with a major molar proportion of C16O1 (*i.e.* p = 0.15-0.25). This suggests a conduction mechanism taking place by Li^+ hopping between decoupled aggregates in C16O1 – rich regions of the structure, *e.g.* Li_2A_2 $Li_3A_2^+$ $Li_2A_2 \rightarrow Li_2A_2$ Li_2A_2 $Li_3A_2^+$ .The formation of channels in the structure which could incorporate such sequences in unimpeded rows might be most likely to be found if the CmO1 sequences occurred in *blocks* rather than in random arrangement with the CmO5. Blocks of CmO5 (*ion separation*) may then be found alongside the CmO1 channels (Li^+ *transport*) Such an arrangement, as well as providing unimpeded 'hopping trackways', could allow counterion charge compensation at each aggregate hopping site along CmO1-aggregate sequences by minor local ion redistribution in the CmO5 – separated ion sequences.

Conductivity data for systems in which copolymers **I** have been prepared by 'blocky' sequencing are compared with those from more random sequencing and are found to support these proposals.

References

[1] Y. Zheng, F. Chia, G. Ungar and P.V. Wright, *Chem. Commun.*, 2000, 1459-1460.
[2] Y. Zheng, F. Chia, G. Ungar, P.V. Wright, *J. Power Sources*, 2001, **97-98**, 641-643.
[3] Y. Zheng, F. Chia, G. Ungar, P.V. Wright, *Electrochim. Acta,* 2001, **46**, 1397-1405.
[4] F. Chia, Y. Zheng, J. Liu, G. Ungar, P.V. Wright, *Solid State Ionics*, 2002, **147**, 275-280.
[5] F. Chia, Y. Zheng, J. Liu, N. Reeves, G. Ungar, P.V. Wright, *Electrochim. Acta,*2003, **48**,1939-1951
[6] J. Liu, Y. Zheng, Y-P. Liao, X. Zeng, G. Ungar and P.V. Wright, to be published *J. Chem Soc. Faraday Transactions*
[7] Y. Zheng, J. Liu, Y-P. Liao, X. Zeng, G. Ungar and P.V. Wright, to be published *J. Chem Soc. Dalton Ttransactions.*

P O S T E R

P30

Molecular dynamics simulation of the layered vanadium pentoxide/PEO/lithium-salt system

Heiki Kasemägi, Alvo Aabloo
Institute of Technology, Tartu University, Tähe 4, 50101 Tartu, Estonia.
Bruce Dunn
Department of Materials Science and Engineering, University of California, Los Angeles, CA. 90095-1595, USA.
and Josh Thomas*
Department of Materials Chemistry, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden.
* *e-mail:* josh.thomas@mkem.uu.se; *tel:* (+46) 18 471 3763; *fax:* (+46) 18 513548

Introduction

The rechargeable lithium-ion polymer battery is a critical power source in a number of portable electronic devices. While our everyday electronic gadgets have batteries of visible dimensions, micro-scale devices - Micro-Electro-Mechanical Systems (MEMS), which integrate mechanical elements, sensors, actuators and electronics on a common chip - need a battery with micro-scale dimensions. Such dimensions require new approaches to battery design and architecture. Common thin-film 2-dimensional architecture will be replaced by 3-dimensional micro-batteries [1], which are currently undergoing intense development.

Vanadium pentoxide, $V_2O_5 \cdot nH_2O$, gel has been widely studied and has a great potential as an electrode material for rechargeable lithium-ion batteries. In its xerogel and, especially, its aerogel forms [2], it has already played an important role in 3-dimensional battery architecture by virtue of its high surface area, porosity and specific capacity.

A number of experimental studies of polymer intercalation into layered inorganic matrices show enhanced Li-ion conductivity at ambient temperature, along with a small temperature dependence [3]. The inorganic host can vary from layered silicates (montmorillonite, hectorite, etc.) [3] to vanadium [4] and molybdenum[5] oxides; intercalates are represented by poly(ethylene oxide)(PEO) [4], poly(dimethyl siloxane), polypyrrole [6], polyaniline [7], *etc.*

The calculations

Molecular Dynamics (MD) simulations have been made of the $V_2O_5 \cdot 1.5H_2O\text{-}LiBF_4(PEO)_{20}$ system, both for an infinite vanadium pentoxide gel layer surrounded by a PEO/lithium-salt complex along the z-axis, and for an infinite vanadium pentoxide rod along the x-axis surrounded by a PEO/lithium-salt complex in the y- and z-directions. The simulations use periodic boundary conditions and an Ewald summation for the long-range electrostatic forces. The systems were allowed to relax for at least 200ps under constant-volume conditions (NVT), followed by at least 1ns NpT simulation for data sampling every 1000 time-steps.

The effects of PEO intercalation into the vanadium pentoxide matrix have been analysed, along with the local environment at the PEO-vanadium pentoxide interface, salt-ion interactions with water and the vanadium pentoxide layers.

References

[1] R.W. Hart, H.S. White, B. Dunn and D. Rolinson, *Electrochem. Commun.*, **5**, 2003, 120.
[2] D.B. Le, S. Passerini, A.L. Tipton, B.B. Owens and W.H. Smyrl, *J. Electrochem. Soc.*, **142**, 1995, L102.
[3] S. Wong, R.A. Vaia, E.P. Giannelis and B. Zax, *Solid State Ionics*, **86-88**, 1996, 547.
[4] Y.-J. Liu, J.L. Schindler, D.C. DeGroot, C.R. Kannewurf, W. Hirpo and M.G. Kanatzidis, *Chem. Mater.*, **8**, 1996, 525.
[5] T.A. Kerr, H. Wu and L.F. Nazar, *Chem. Mater.*, **8**, 1996, 2005.
[6] J.H. Harreld, B. Dunn and L.F. Nazar, *Int. J. Inorg. Mater.*, **1**, 1999, 135.
[7] N.-G. Park, K.S. Ryu, Y.J. Park, M.G. Kang, D.-K. Kim, S.-G. Kang, K.M. Kim and S.-H. Chang, *J. Power Sources*, **103**, 2002, 273.

New Proton Conducting Composite Membranes for Polymer Fuek Cells

A. Magistris*, A. Carollo, S. Grandi, C. Tomasi, P. Mustarelli, E. Quartarone

Dept. of Physical Chemistry, University of Pavia, INFM, and IENI-CNR, V.le Taramelli 16, I-27100 Pavia, Italy.
e-mail: **Aldo.Magistris@unipv.it**, Tel: +39 0382 507573, Fax. +39 0382 507575

The polymer membrane is probably the most critical component in the optimization of the PEMFC design and operational requirements. As well known, an ideal proton membrane must guarantees thermal stability up to 200°C, an optimal proton transport, a reduced fuel cross-over and, last but not least, a low price.
Up to now, Nafion and derived perfluorinated polymers have been considered the standard materials for electrolyte in PEMFC, but they show considerable disadvantages, like high cost and mostly low operation conditions, limited to 100°C [1, 2], temperature at which the Pt catalyst poisoning due to CO traces in the fuel is favoured. In order to overcome these drawbacks, the current focus for research in this field is the replacement of Nafion with alternative and more efficient membranes, with high proton conductivity at temperatures exceeding 130°C.
Many new membranes for polymer fuel cells PEMFC have been developed in these last years [3]. However the more recent approaches seem to be directed towards the composite membranes, which can substantially be nano/macro composite or hybrid organic-inorganic membranes [4].
In this paper we present the synthesis of a new membrane as electrolyte for polymer fuel cells, that is a silica-based hybrid organic-inorganic composite, prepared by sol-gel route [5]. This polymer has been compared with another proton conducting membrane belonging to the polybenzoimidazole family, which we have prepared by condensation of 3,4-diamino benzoic acid monomers in polyphosphoric acid, as reported by Asensio and co. [6]. These membranes have been characterised by means of thermogravimetry and modulated differential scanning calorimetry in order to investigate their thermal properties.
After doping of the membranes respectively with phosphotungstic acid and phosphoric acid, we studied the proton conductivity behaviour, varying the temperature and the dopant concentration. These preliminary results have been analysed even by a comparison with other well-tested membranes, such as Nafion and sulphonated grafted-PVDF.

References:

[1] J.S. Wainright, J.T. Wang, D. Weng, R.F. Savinell, M. Litt, J. Electrochem. Soc., 142 L121 (**1995**)
[2] J. A. Asensio, S. Borros, P. Gomez-Romero, J. Electrochem. Soc. 151 (**2004**) A304.
[3] J. A. Kerres, J. Membr. Sci. 185 (**2001**) 3.
[4] O. Savadogo, J. Power Sources 127 (**2004**) 135.
[5] U.L. Stangar, N. Groselj, B. Orel, A. Schmitz, Ph. Colomban, Solid State Ionics 145 (**2001**) 109.
[6] J. A. Asensio, S. Borros, P. Gomez-Romero, J. Polym Sci. A, 40 (**2002**) 3703.

New Salts Based on Lithium Oligoether Sulfate Ester.

C. Chauvin, X. Ollivrin, F. Alloin, J-F.Le Nest, J.Y. Sanchez
LEPMI Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces de Grenoble
E-mail: **christophe.chauvin@lepmi.inpg.fr**, tel (+33) 04 76 82 67 64, fax (+33) 04 76 82 66 70

Introduction

In solid polymer electrolyte, the main contribution to ionic transport is insured by the anion as measured cationic transference numbers often range between 0.1-0.5 [1,2]. An improvement in the battery performance can be obtained by an increase of the cationic transference number or by using a single-cation polymer electrolyte [3,4]. With respect to inorganic lithium salts the use of organic ones makes possible the integration of extra functionalities [5] which allows for example solvatation property. Some authors have investigated the conductivities of sulfonated POE oligomers [6,8] and lithium oligoether ester sulfate [9,10]. In this study, we evaluated the properties of mono or di- lithium oligoether ester sulfate of various molecular weights.

Experimental

Thermal properties were determined with a modulated DSC for TA. TGA analysis was carried out using a Netzsch STA409 Thermal analyser. The transference number determination was performed by a combinaison of complex impedance and potentiostatic polarization measurements [11]. The investigation of the electrochemical stability range of the salts was performed with a three-electrodes configuration. Stainless-steel and two lithium metallic foils were used as working, reference and auxiliary electrodes, respectively. The experiments were carried out under vacuum at a scanning rate of $1 mV.s^{-1}$.

Results and discussion

The lithium salts were synthesized in two steps: the alcohol function esterification by $HClSO_3$ then a lithiation with LiOH. Four family of lithium salt were synthesized: $CH_3(OCH_2CH_2)_nOSO_3^-Li^+$ (called POEMSLi), $Li^+{}^-O_3SO(CH_2OCH_2)_nCH_2OSO_3^-Li^+$ (called POEDSLi). The structure of the resulting ionomers was confirmed by ^{1}H-NMR, ^{13}C-NMR and elemental analysis.

The incorporation of salt function increases the glass transition temperature due to salt/polymer interactions [12] and modifies slightly the melting temperature. The TGA analyses were performed in Helium and air flow: No differences in the degradation temperature were found between the two atmospheres at a temperature rate of 5°C/min. The thermal degradation starts at 160°C, up to 260°C a mass loss of 86% is observed. An influence of water was observed: the addition of 100 ppm of water in the salt decreases the thermal stability. The salt of highest molecular weight seems to be more stable: POEMS1900Li (O/Li=42) is stable up to 240°C. The complex POEMS350Li /POE (Mw= 300 000 g/mol), O/Li=30 is stable up to 220°C.

Ionomers exhibit good intrinsic ionic conductivities as they have a ionic function but also, due to their ethylene oxide units, a solvation ability.

The best conductivities reach 3.10^{-5} S/cm at 60°C for POEMS350Li, 6.10^{-5} S/cm at 60°C for POEDS1000Li. The cationic transference numbers were measured at 70°C.

	POEMSLi			POEDSLi		
Salts	350	550	750	400	600	1000
O/Li	7.2	11.8	16.3	3.8	6.1	10.7
t_{Li^+}	0.95	0.89	0.85	0.53	0.72	0.89

Cationic transference number of POEMSLi and POEDSLi

Due to the fixation of the sulfate anion on the polyether backbone, a cationic transference number close to unity are reached.

The electrochemical stabilities of the POEMS164Li and POEMS750Li dissolved in POE 300 000 were studied. The reversibility of the plating/stripping reaction of lithium was observed. The complexes are stable in oxidation up to 4.1 V vs Li/Li^+.

Conclusion

These salts based on oligoether-ester sulfate have sufficient thermal and electrochemical stabilities and, in addition, they have a cationic transference number close to unity. As they are not fluorinated they are environmentally friendly and non-expensive. Thus they are interesting properties as electrolyte for lithium batteries.

References

[1] H. Cheradame, J.F. Le Nest, A. Gandini, M. Leveque, Journal of Power Sources, 14, (1985), 27

[2] F. Alloin, D. Benrabah and J.Y. Sanchez, Journal of Power Sources, 68, (1997), 372

[3] M. Doyle, T.F. Fuller and J. Newman, Electrochimica Acta, 39, (1994), 2073

[4] K.E. Thomas, S.E. Sloop, J.B. Kerr and J. Newman, Journal of Power sources, 89, (2000), 132

[5] X. Ollivrin, F. Alloin, J-F.Le Nest, D.Benrabah, J-Y Sanchez.Electrochimica Acta, 48,(2003),1961

[6] T. Hamaide, C. Carré, A. Guyot, Second International Symposium on Polymer Electrolytes, Ed. B. Scrosati, Elseiver, (1989), 175

[7] D.H. Dong, T.E. Hogen-Esch, G.B. Zhou, J. Smid, Polym. Prepr., 34, (1993), 550

[8] K. Xu, C.A. Angell, Electrochimica Acta, 40, (1995), 240

[9] Y. Chen, G. Wan, Journal of macromolecular science pure and applied chemistry, A30(5), (1993), 365

[10] H. Chen, Z. Deng, Y. Zheng, W. Xu, G. Wan, Journal of macromolecular science pure and applied chemistry, A33(9), (1999), 1273

[11] J. Evans, C.A. Vincent, P.G. Bruce, Polymer, 28, 2324, (December 1987)

[12] Cheradame, J.F. Lenest, A. Gandini, British polymer journal, 20, (1988), 253

Novel composite polymer-in-salt electrolytes based on PVdF matrix obtained with a solvent free technique.

M.Malinowska, J.Piekarska, **M.Siekierski***, G.Żukowska
Warsaw University of Technology, Chemical Faculty, Polymer Ionics Research Group
ul. Noakowskiego 3, 00-664 Warsaw, POLAND
*corresponding author e-mail: **alex@soliton.ch.pw.edu.pl**,
tel (+) 48 601 26 26 00, fax (+) 48 22 628 27 41

Introduction

Polymer-in-salt electrolytes are extensively studied in several last years [1-4]. The mechanism of conductivity in those systems is intermediate between the composite polymeric electrolytes and inorganic ionic glasses. On one hand the highly conductive region is located on the salt grains boundaries due to their highly defective structure. On the other hand the polymeric material included in the composite acts mainly as a binding agent and a source of the grain surface defects thus it does not take an important part in the charge carrier transport process. A percolation between the salt grains must be observed to maintain the high mobility paths along the sample, thus a particular volume fraction of the salt in the composite is needed to obtain a high conductivity.

The poly(vindylidene difluoride) (PVdF) matrix (Kynar® copolymer) is widely used in gel electrolytes for lithium batteries. The material is known to be both chemically and thermically stable. On the other hand it is well known that if a solvent is incorporated into the PVdF structure it is almost impossible to have it fully removed. Thus the typical method of obtaining polymer-in-salt electrolytes based on the dissolving of the polymer and salt in the solvent, casting of the film and solvent evaporation is here unusable.

A thermal method based on subsequent homogenization of polymer and salt mixture, pressing of the pellet and thermal sintering was used to obtain the composites. During the process the temperature was elevated slightly above the PVdF melting temperature to allow the interaction between the salt and the matrix. Samples with different sintering time (0.5-12h) and with varying number of sintering cycles (1-3) were prepared for system compositions (salt to polymer molar ration 0.5:1 to 2:1) and for lithium salts including lithium tetrafluoroborate, lithium triflate and LiTFSi.

Experimental

All reagent were carefully dried under vacuum (10^{-5} Torr, 60 hours) prior to use. The drying temperature was in range 130-160°C. The homogenization process was performed in the nitrogen filled dry-box with humidity lower than 5ppm. The pressing process was performed in a steel made pan with working diameter equal to 13 mm. The used load varied with the salt used and was equal to 6000 kg for lithium triflate and 8000 kg for other two salts. For the sintering process a vacuum oven made of titanium was used to avoid the chemical interaction with the samples. The temperature of the process was equal to 175°C and was controlled by a PID regulator.

The sintered pellets were covered with thin gold film by vacuum evaporation to maintain good electrical contact for the impedance measurements. The a.c. impedance was registered for 1 Hz – 100 kHz range for varying temperatures (25-95 °C). The obtained data were analyzed with the Bernard Boukamp's EQ program to determine the d.c. conductivity of the samples and with authors program to analyze the activation energies according to the Almond-West Formalism.

Results

The typical thermal dependence of the conductivity for PVdF-$LiBF_4$ 1:1 samples with different sintering times is depicted below.

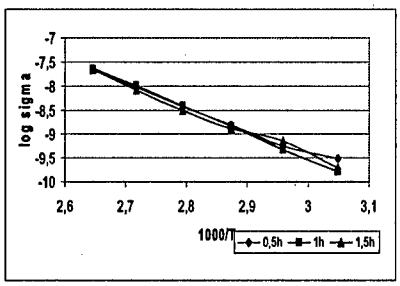


Figure 1 The thermal dependency of conductivity for PVdF-$LiBF_4$ samples 1:1 molar ratio for different sintering times.

The observed changes are generally small and better pronounced in low temperature range where the sample with the shortest sintering time exhibits the best conductivity. The Arrhenius character of the conducitivity dependence is observed for all samples studied in whole temperature range.

A comparison between the conductivities and activation energies of conduction for the same samples is collected in the table below.

Novel "Polymer in Salt" Electrolytes Based on Acrylonitrile – Butyl Acrylate Copolymers and LiTFSI

A. Łasińska[1], A. Affek[2], J.R. Dygas[1], Z. Florjańczyk[2], F. Krok[1], M. Marzantowicz[1], A. Tomaszewska[2], E. Zygadło-Monikowska[2*]

[1]Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warszawa, Poland
[2]Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warszawa, Poland
*corresponding author: **e-mail:** ewazyga@ch.pw.edu.pl, phone 48 22 6605582, fax: 48 22 6607279,

Introduction

"Polymer-in-salt" electrolytes proposed by Angell et al. [1] combine good mechanical properties of polymer and high conductivity of amorphous salt. They are attractive for prospective application in polymer lithium-ion batteries.

Electrolytes based on the polyacrylonitrile and acrylonitrile-butadiene copolymers have been studied because the interaction between Li^+ ions and nitrile groups is suitable for stabilization of amorphous ionic clusters. In this study a newly developed random copolymer of acrylonitrile and butyl acrylate is investigated with LiTFSI salt.

Experimental

The copolymer of acrylonitrile (AN) and butyl acrylate (BuA) was prepared by radical polymerization. The molar ratio of AN to BuA was 2:1. The $LiN(CF_3SO_2)_2$ salt was added in acetonitrile solution in an amount corresponding to the molar ratio of Li to AN monomeric units between 0:1 and 20:1. Samples were investigated by DSC (Perkin-Elmer Pyris 1) and impedance spectroscopy.

Impedance spectra in the frequency range from 10^7Hz to 10^{-2}Hz were recorded at constant temperature during heating, cooling and heating after fast cooling. Measurements were conducted by computer-controlled setups based either on Solartron 1260 analyzer and Keithley 428 current amplifier or on Novocontrol Alpha-N Dielectric Analyzer. Polymeric samples (thickness about 0.300 mm) were placed between gold plated stainless steel electrodes in argon atmosphere.

Results and discussion

The results of impedance and DSC measurements indicate that a change of the composition by increasing the salt content leads to an increase in ionic conductivity and decrease in glass transition temperature T_g. Temperature dependence of conductivity above T_g can be described by the Vogel-Tamman-Fulcher (VTF) function (Fig. 1). Such behavior, similar to that observed for inorganic glasses, is related to the high value of the decoupling index [1]:

$$\log(R_\tau) = \log(\tau_s/\tau_\sigma) \approx 14.3 + \log[\sigma(T_g)] \qquad (1)$$

where τ_s - structural relaxation time, τ_σ - electrical relaxation time, $\sigma(T_g)$ - conductivity at T_g [S/cm]. In the studied systems log R_τ^* is between 1.7 and 5.6, increasing with an increase in the salt content.

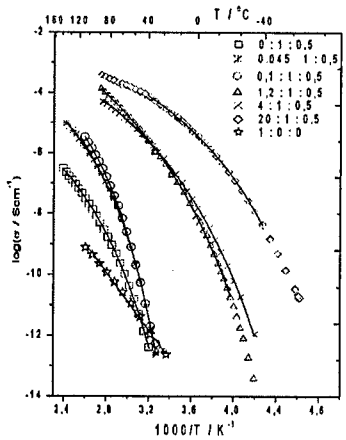


Fig.1. Conductivity in systems LiTFSI - poly(AN-co-BuA) of various molar ratios Li:AN:BuA. Continuous lines represent VTF function or Arrhenius function in case of pristine salt (1:0:0).

Conclusions

Values of the decoupling index $\log(R_\tau)$ for the studied system are higher than those obtained with the same salt in the traditional polymer matrix - PEO (about 1). The values of $\log(R_\tau)$ increase with increasing content of salt while the T_g values decrease. These observations suggest that ion transport in the studied system becomes significantly de-coupled from the polymer segments movement at high salt concentration.

References

[1] K. Xu, C.A. Angell, *Electrochim. Acta*, **40** (1995) p. 2401.

P O S T E R

P35

Novel Composite Proton-Exchange Membranes (C-PEM) for Fuel-Cell Applications

E. Peled, T. Duvdevani, **M. Philosoph**
School of Chemistry, Tel Aviv University,
Tel Aviv, Israel 69978.
M. Rakhman, T. Feiglin.
Israel Plastics & Rubber Center (IPRC)
Technion City, Haifa, Israel 32000.

Proton-exchange membranes (PEMs) are found in many electrochemical applications including fuel cells, electrolyzers, super-capacitors, sensors and batteries. Nafion is the most commonly used membrane in fuel cells operating at near-room temperature (up to 100°C). Nafion, a solid polymer electrolyte, has two major disadvantages; it is very expensive and it dries during fuel-cell operation as a result of water dragging by the proton. In recent years, there has been an intensive effort to develop a low-cost solid polymer electrolyte to replace Nafion. Our goal was to develop a novel family of nanocomposite PEMs. They are made of silica-anchored sulfonic acid (SASA) bound by a polymer. Aryl and alkyl sulfonic acids were chemically combined with high-surface-area silica and the resulting SASA powder was bound to a polymer to give a composite PEM. TGA-DTA measurements show that these SASA powders are stable up to 250oC. The room-temperature conductivity of SASA-based 50-70 μm thick C-PEM, is in the range 0.003-0.05 S/cm. Some preliminary performance tests were carried out in DMFC. So far, the cell resistance is too high (about 2 Ohm.cm2). The Cell OCV is 0.65V and its maximum power density at 70°C is 30mW/cm^2. Crossover-current density for 100 micron thick membrane at 1M methanol and at 70°C is 0.1A/cm^2.

P O S T E R

P36

Nuclear Magnetic Resonance study of plasticized HEC/Lithium salt polymer electrolytes

L.V.S. Lopes[2], G.O. Machado[1], **A. Pawlicka**[1], J.P. Donoso[2]
[1]IQSC, Universidade de São Paulo, PO Box 780; 13560-970 São Carlos, SP, Brazil
[2]IFSC, Universidade de São Paulo, PO Box 369; 13560-970 São Carlos, SP, Brazil
agnieszka@iqsc.usp.br Tel: 55-16-273 9919

Introduction

Solid polymer electrolytes (SPE) obtained from natural polymers have been the object of a great deal of research because of their mechanical and electrical properties [1,2]. The dynamics of ions and the polymer chains of these SPE constitute one of the most interesting problems in the field of solid state ionics and, among several spectroscopic techniques, nuclear magnetic resonance (NMR) have been especially useful to study these dynamics [2-6] . In prevoius papers, we reported the conductivity and NMR characterization of SPE formed by amylopectin rich starch plasticized with glycerol and containing lithium perchlorate [4] and those formed by hydroxyethylcellulose (HEC) grafted with poly (ethylene oxide) diisocyanate complexed with lithium salts [2,3]. In the present work, we report ^{1}H and ^{7}Li NMR line shapes and spin-lattice relaxation measurements as a function of temperature in a series of polymer electrolytes formed by HEC plasticized with glycerol and containing lithium salts ($LiClO_4$ and $LiBF_4$). The measured conductivity of the HEC/$LiClO_4$ system plasticized with 48 wt% of glycerol is 6×10^{-5} S/cm at room temperature.

Experimental

The polymer electrolytes were prepared by the procedure described in refs. [2,3]. The proton (^{1}H) NMR lineshapes and spin-lattice relaxation time measurements were carried out on a pulsed NMR spectrometer operating at 36 MHz in the temperature range 150-350 K. The ^{7}Li NMR measurements were performed in the same temperature range using a Varian-400 MHz NMR spectrometer (^{7}Li resonance frequency 155.4 MHz).

Results and discussion

The NMR results exhibit the qualitative features associated with the lithium and the proton dynamics, namely the presence of resonance line narrowing and well defined spin-lattice relaxation rate maxima, indicating that both, lithium and protons have a relatively high mobility in these polymer electrolytes. Above 150 K the proton motions induces a progressive cancellation of the dipolar interactions, which are the main source of line broadening of the ^{1}H spectral line at low temperature, producing a line narrowing. The onset of the ^{1}H line narrowing occurs below the T_g of the HEC/$LiClO_4$/glycerol electrolytes (T_g = 214 K for the sample with 48% of glycerol). The motional narrowing process was found to be independent of the lithium salt, indicating that the activation energy for the lithium ion motion is not affected by the different lithium salt used in the polymer electrolyte. A single ^{1}H relaxation rate maximum is observed at around 244 K. The mechanism responsible for the proton relaxation in these systems is the random fluctuations of the ^{1}H-^{1}H dipolar interactions between protons presented in the solvating medium (HEC and plasticizer). The relaxation rate T_1^{-1} maximum corresponds to a fluctuation rate of the order of the Larmor frequency (36 MHz). The relaxation curve has a asymmetric shape around the rate maxima. The activation energies obtained from the low- and the high-temperature side of the T_1^{-1} maximum, are 0.24 and 0.17 eV, respectively. The low temperature (183 K) ^{7}Li NMR absorption spectrum are characterized by a narrow main absorption (full width at half maximum $\Delta H \sim 10$ kHz) corresponding to the central $1/2 \leftrightarrow -1/2$ transition, superimposed on a broader baseline (ΔH ~30-40 kHz), which is due to the quadrupolar distribution of the satellite transitions $\pm3/2 \leftrightarrow \pm1/2$. Concerning the ^{7}Li spin-lattice relaxation, the data display a single relaxation rate maximum at 303 K. The ^{7}Li NMR relaxation in ionic solids are mainly governed by two mechanism: (i) quadrupolar relaxation due to the interactions between the nuclear quadrupole moment with the fluctuations of the surrounding electric-field gradients produced by the charge distribution at the site of the nucleus, and (ii) the dipolar relaxation which produced by random fluctuation of the lithium homonuclear and heteronuclear dipolar interactions. The analysis of the relaxation data yields activation energies in the range of 0.11 to 0.20 eV for the HEC/glycerol/$LiBF_4$ electrolytes.

Conclusions

The dynamical parameters obtained from the NMR data demonstrate that the Li^+ mobility in these systems is comparable to those found in others plasticized polymer electrolytes. Activation energies extracted from the ^{7}Li relaxation data are in the range 0.12 – 0.20 eV. The ^{1}H spin-lattice relaxation data, which is mainly governed by the ^{1}H-^{1}H dipolar interactions, suggests that the proton dynamics in these plasticizers electrolytes is greater than in the grafted systems.

References

[1] C. Schoenenberger et al, Electrochim. Acta 40 (1995) 2281
[2] A Regiani et al, Polymer Int. 49 (2000) 960
[3] C.E. Tambelli et al, Electrochim. Acta 46 (2001) 1665
[4] L.V.S. lopes et al, Electrochim. Acta 48 (2003) 2021
[5] S.H. Chung et al, Solid St Ionics 112 (1998) 153
[6] M. Forsyth et al, Solid St Ionics 85 (1996) 209.

PEO based nano-composite solid polymer electrolytes containing copper salts

M.A.K.L. Dissanayake[1], P.A.R.D. Jayathilaka[1], B.-E. Mellander[2] and I. Albinson[2]
[1]Postgraduate Institute of Science & Department of Physics, University of Peradeniya, Peradeniya, Sri Lanka
[2]Physics and Engineering Physics, Chalmers University of Technology, Gothenburg, Sweden
e-mail: **laxmand@pdn.ac.lk**

PEO based nano-composite solid polymer electrolytes containing copper salts exhibit interesting electrochemical properties. The polymer electrolyte PEO_9:$Cu(CF_3SO_3)_2$ made by complexing copper triflate ($CuTf_2$) with PEO appears to show scientifically intriguing transport properties. Although copper ion transport in these systems has been seen from plating stripping processes, the detailed mechanism of ionic transport and the species involved are yet to be established. In order to obtain enhanced ionic conductivities and also to contribute towards understanding the ionic transport process in Cu^{++} ion conducting, PEO based composite polymer electrolytes, we have studied the system PEO_9: $CuTf_2$: Al_2O_3 incorporating 10 wt % of alumina filler particles of grain size 10 μm, 37 nm, 10-20 nm and also particles of pore size 5.8 nm. Thermal and electrical measurements show that the system remains amorphous down to room temperature. The composite electrolyte is predominantly an ionic conductor with electronic conductivity less than 2 %. The triflate ($CF_3SO_3^-$) ions appear to be the dominant carriers. The presence of alumina grains has enhanced the conductivity significantly from room temperature up to 100 °C. The nano-porous grains with 5.8 nm pore size and 150 m^2/g specific surface area exhibited the maximum conductivity enhancement.

Nano-composite solid polymer electrolyte films of composition PEO_9 CuCNS + 10 wt% Al_2O_3 were prepared by solvent casting technique and characterized by the differential scanning calorimetry (DSC), ac impedence and DC polarization measurements. DSC traces show that the composite electrolyte exhibits a pronounced crystalline to amorphous phase transition around ~ 60°C similar to the filler-free electrolyte. The conductivity variation with temperature for both the filler free $(PEO)_9$CuCNS material and composite polymer electrolyte $(PEO)_9$ CuCNS + 10 wt% Al_2O_3 shows Arrhenius behaviour exhibiting two distinctive regions below and above ~ 60°C. There is about two-fold increase in the overall electrical conductivity of the composite polymer electrolyte compared to the filler free polymer electrolyte. DC Polarization measurements indicate that the charge transport in this electrolyte is predominantly due to ions, exhibiting high anionic transference numbers : $t_- = 0.86$ for $(PEO)_9$ CuCNS, and $t_- = 0.98$ for $(PEO)_9$CuCNS + 10 wt %, Al_2O_3. The anionic transference number has increased by about 10% due to the presence of the alumina filler.

The observed conductivity enhancement in both these systems has been attributed to Lewis acid-base type surface interactions of ionic species with O^{2-} and OH^- groups on the filler grain surface. These interactions are expected to give rise to the creation of additional sites and conducting pathways for the migrating anions.

Performance of ionic liquids and ion gels as electrolytes in dye-sensitized solar cells

Chizuru Matsuyama, Ryuji Kawano, Akihiro Sato, Masayoshi Watanabe
Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
e-mail: **d03ga129@ynu.ac.jp**, tel (+) 81-45-339-3955, fax (+)81-45-339-3955

Introduction

While dye-sensitized solar cells (DSSCs) have such advantages over other solar cells as the low cost, compared with silicon solar cells, they still have problems of the safety and durability, resulting from the use of liquid electrolytes. Ionic liquids have unique properties, such as non-volatility, non-flammability, thermal stability, chemical stability and high ionic conductivity. In this study, different ionic liquids were used to reveal the fundamental properties of I^-/I_3^- redox couples in ionic liquids, including the equilibrium potentials and the charge transport mechanism.

Furthermore, the ionic liquids were gelated to afford quasi-solid-state ion gels containing the iodine redox couple. The gel electrolyte is promising for the use in the DSSCs, since it can afford solid state DSSCs. The ion gel in the presence of an I^-/I_3^- redox couple was formed by using urethane-forming reaction in this study. Furthermore, gelation in the cell was made, and the photo-electron conversion characteristic was examined.

Experimental

Ionic liquids used in this study are EMImTFSI, $EMImBF_4$, $BMImPF_6$, EMImDCA and BPTFSI. A microelectrode technique was employed for the electrochemical measurements in order to simplify determination of the equilibrium potential and transport property of the redox couple from steady-state voltammetry. The ionic liquid was used for the solvent, and the iodine redox couple was used for the solute. All the samples were prepared in a N_2-filled glove box, and the electrochemical measurements were conducted under a N_2 atmosphere at room temperature. The molar ratios of $[I^-]$: $[I_2]$ were 1:1, 1.5:1, 4:1, 10:1, 1:0, and a series of samples were prepared, maintaining the total concentration of I^- and I_3^- in the range of 0.1 M-2 M for each molar ratio.

Photo-electrochemical measurements were performed using an AM 1.5 solar simulator, and the photo-intensity was 100 mW cm^{-2}. The measurements were made on open cells (seal-less cells), and the electrode size was 0.45 cm^2.

Results, discussion and Conclusions

It is revealed that two kinds of diffusion mechanisms contribute to the charge transport from cyclic voltammetry. They are the physical diffusion (D_{phys}) and the exchange-reaction-based diffusion (D_{ex}). D_{phys} was affected by the viscosity and D_{ex} showed different values in each ionic liquid. Although the ionic liquids have about 100 times higher viscosity, as compared with an organic solvent (acetonitrile), the diffusion coefficient (D_{app} ; $D_{app}= D_{phys}+ D_{ex}$) in the ionic liquids is retained at 1/10 of that of the organic solvent. It is suggested that contribution of the exchange reaction in an ionic liquid is large.

The electrochemical characteristics and performances of DSSCs with ionic liquids as their electrolytes have been explored. It is revealed that the exchange reaction between I^- and I_3^- occurs in the ionic liquids with quick diffusion of I_2. Furthermore, the rate of the exchange reaction in the ionic liquids reaches about 90%. The equilibrium potential (E_{eq}) and the open cercuit potential (V_{oc}) are reasonably correlated in the ionic liquids except for EMImDCA.

The photo-electron conversion characteristic of the ion gel DSSCs formed by using urethane reaction was examined. The performance of the cells reaches about 90% of that of the ionic liquid cells.

References

[1] R. Kawano and M. Watanabe, *Chem. Commun.* **2003**, 330.
[2]A. Noda, K. Hayamizu, and M. Watanabe, *J. Phys. Chem. B.* **2001**, *105*, 4603.
[3] D. R. MacFarlane, S. A. Forsyth, J. Golding and G. B. Deacon, *GreenChem.* **2002**, *4*, 444.
[4] W. Kubo, S. Kambe, S. Nakade, T. Kitamura, K. Hanabusa, Y. Wada, S. Yanagida, *J. Phys. Chem. B.* **2003**, *107*, 4374.
[5]A. Noda and M. Watanabe, *Electrochim.* Acta. **2000**, *45*, 1265.

P O S T E R

P39

Physicochemical Properties and Structures of Room Temperature Ionic Liquids

Hiroyuki Tokuda, Kikuko Hayamizu,
Md. Abu Bin Hasan Susan and Masayoshi Watanabe
Department of Chemistry and Biotechnology, Yokohama National University
79-5 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501, Japan
e-mail: **d02sa103@ynu.ac.jp**, Tel & Fax: (+)81-45-339-3955

Introduction

Room-temperature ionic liquids (RTILs) are comprised entirely of ions and are receiving an upsurge of interest in multidiscipinaly areas for their unique physicochemical properties, such as negligible vapor pressure, non-flammability, high ionic conductivity, and high thermal, chemical and electrochemical stability. Various efforts have been made to introduce them in practical applications, such as batteries, capacitors, fuel cells, solar cells and actuators. The formation of polymer electrolytes based on these RTILs has also been proposed, which may be able to play an important role in the field of solid state ionics for their potential application. However, the fudamental understanding of a relationship between microscopic dynamics of the ions and ionic structures requires increasing attention for molecular (ionic) design of RTILs to achieve desirble physical and chemical properties.

In this study, ion transport behaviors of common RTILs were investigated by changing the cationic and anionic structures. To determine ionic self-diffusion coefficients by PGSE-NMR method is one of the most effective strategies to explore the ion transport properties and the ion association/dissociation in the ionic liquids, which may be considered as the most important factor for the unique phenomena. Moreover, we present experimental results on the relationship between the ionic structures and ionicity by a combination of the PGSE-NMR diffusion method and UV-visible spectral polarity measurements.

Experimental

The RTILs with different geometries, based on several cationic and anionic structures, have been synthesized as shown in Figure 1. The physicochemical properties, such as thermal properties, density, viscosity, ionic conductivity and self-diffusion coefficients of cation and anion, have been correlated with the change in the anionic structure, for a fixed cationic species, and *vice versa* to provide a deep insight into the relationship with the ionic structure. The donor ability of anion and acceptor ability of cation were estimated by UV-visible spectral polarity measurements.

Results and discussion

The self-diffusion coefficients individually detected by PGSE-NMR for the cation and anion exhibits higher values for the cation compared to the anion over a wide temperature range. The summation of the cationic and anionic diffusion coefficients for the RTILs well contrasts to the viscosity data. The analysis

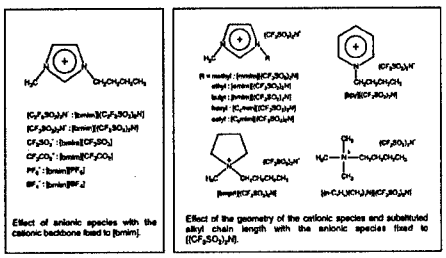


Figure 1 Molecular Structures of RTILs.

of the diffusivity and the fluidity by the use of the Stokes-Einstein equation and a comparison of the self-diffusion coefficients of each ionic species indicate that the ionic diffusion in the ionic liquids appear to have significant influence from factors like the ionic size, shape and the state of aggregation.

The influence of ionic association is further revealed from the ratio of molar conductivity obtained from impedance measurement (Λ_{imp}) and that calculated from the ionic diffusivity using Nernst-Einstein equation (Λ_{NMR}). The ratio, $\Lambda_{imp}/\Lambda_{NMR}$, provides quantitative information on the ions contributing to ionic conduction as the diffusion component. The ratio for the [bmim] based RTILs follows the order $[PF_6]$ > $[BF_4]$ > $[(C_2F_5SO_2)_2N]$ > $[(CF_3SO_2)_2N]$ > $[CF_3SO_3]$ > $[CF_3CO_2]$. In the case where the anionic structure is fixed as $[(CF_3SO_2)_2N]$ and the cationic structure is changed with maintaining the same butyl-substituents, the ratio follows the order [bmpy] > $[(n\text{-}C_4H_9)(CH_3)_3N]$ > [bpy] > [bmim]. The difference in the $\Lambda_{imp}/\Lambda_{NMR}$ represents the difference in ionic character; in other words, "ionicity" of the ionic liquids. The ionicity of RTILs is in good agreement with the polarity determined by solvatochromism and ^{1}H-NMR chemical shift. These results indicate that the ionicity of RTILs can be explained by the V. Gutmann's donor-acceptor concept. Moreover, the significant physical and chemical properties of RTILs can be explained by using this valuable parameter. In this presentation, we will also demonstrate the ionic diffusion behavior in novel polymer electrolytes based on the ionic liquids, "ion gels".

References

[1] A. Noda, K. Hayamizu, M. Watanabe *J. Phys. Chem. B* **105** (2001), p. 4603

Protic ion gels as proton conducting electrolyte under anhydrous condition

Hirofumi Nakamoto, Masayoshi Watanabe
Department of Chemistry and Biotechnology, Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501,Japan
e-mail: **d04sa105@ynu.ac.jp**, tel & fax(+) 81-45-339-3955

Polymer electrolyte fuel cells (PEFC) are promising for the realization of electric vehicles and portable power supplies. The PEFCs usually employs water swollen perfluorosulfonic acid polymer membranes as the electrolyte. Proton conductivity of the membranes is satisfactory only when they contain sufficient amount of water, and it is, therefore, nessesary in this system to carry out water management, and the operational temperature needs to be maintained below 80°C. On the contrary, the operation of the PEFC at elevated temperatures is a requisite to reduce the problem of catalyst poisoning by CO when reform gas is used, and to lower the quantity of the expensive catalyst. One way to solve these problems is to use proton carriers other than water. [1]

Ionic liquids consist only of ions and have many useful properties, such as nonflammability, nonvolatility, high ionic conductivity, thermal stability, and electrochemical stability, for the use as electrolytes. We have recently reported that protic ionic liquids derived from the combination of Brϕnsted acid and base at various compositions can be used for proton conductors and the system can be a novel replacement of water-containing electrolytes. [2]

In this study, we used benzimidazole (BIm) and bis(trifluoromethanesulfon)imide (HTFSI) as Brϕnsted acid and base, respectively, and studied the physicochemical properties and the proton conduction behavior in detail. We finally aim at constructing solid-state anhydrous proton conductors in the form of ion gels by incorporation of ionic liquids in polymeric phase.

Appropriate amounts of BIm and HTFSI were combined in an Ar atmosphere glove box. The thermal behavior was studied by the measurements of differential scanning calorimetry (DSC) and thermo-gravimetry. Base rich compositions of this system show the behavior of a binary mixture and have the thermal stability over 300°C. The eutectic point is about 100°C. Ionic conductivity of BIm-HTFSI composition were determined by complex impedance method. Proton conductivity was evidenced by the combination of ionic conductivity and self-diffusion the coefficient from pulse gradient spin echo NMR (PGSE-NMR) measurements. Proton conduction in BIm-HTFSI system follows a combination of Grotthuss and vehicle mechanisms. Proton exchange reaction between BIm and $HBIm^+$ could be inferred for the system. The protic ionic liquids exhibited electroactivity at a Pt electrode for H_2 oxidation and O_2 reduction and serve as fuel cell electrolytes at elevated temperature (>130°C) under non-humidifying conditions.

We finally incorporate the ionic liquids in polymeric phase to prepare ion gels. The methodology involves dissolving ionic liquids in a polymer solution, followed by the evaporation of the solvent under vacuum. The thermal behavior and ionic conductivity behavior of the ion gels will be investigated in detail.

Acknowledgement
This research was supported in part by Grant-in-Aid or Scientific Research (#404/11167234 and #14350452) from the Japanese Ministry of Education, Science, Sports, and Culture and by NEDO Technology Research Grant.

References

[1] K. D. Kreuer, A. Fuchs, M. Ise, M. Spaeth, and J. Maier, *Electrochim. Acta*, **43**(1998), p.1281
[2](a) A. Noda, M.A.B.H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu, and M. Watanabe, *J. Phys. Chem. B.*,**107**(2003), p.4024 (b) M.A.B.H. Susan, M. Yoo, H. Nakamoto, and M. Watanabe, *Chem. Lett.*, **32**(2003), p.836 (c) M.A.B.H. Susan, H. Nakamoto, M. Yoo, and M. Watanabe, *Trans Mat. Res. Soc.*, in press

Proton-conducting ionomers by chemical grafting reactions on arylene main chain polymers

Benoît Lafitte, Lina E. Karlsson, **Mario Puchner**, and Patric Jannasch
Polymer Science and Engineering, Lund University, P.O. BOX 124,
SE 22100 Lund, Sweden, www.polymer.lth.se
e-mail: mario.puchner@polymer.lth.se, tel (+) 46 46 222 7308 fax (+) 46 46 222 4115

Introduction

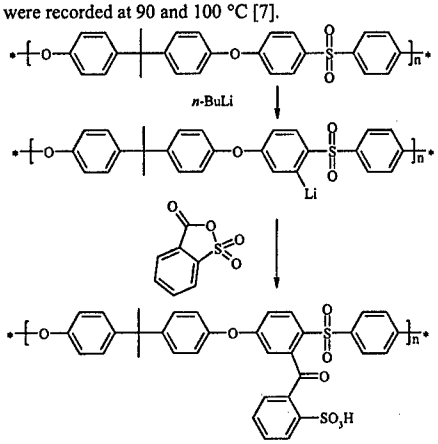
The need of high performance proton conducting membranes of low cost for fuel cell application has triggered intensive research activities [1, 2]. The use of sulfonated arylene main-chain polymers seems to be very promising and therefore directly sulfonated polysulfones have been brought into focus. However, polysulfones bearing sulfonic groups directly attached to the polymer backbone typically show extensive swelling at temperatures above 100 °C, or when the degree of sulfonation exceeds 80% [3]. In order to keep the ionomer membrane mechanical intact while operating under aqueous condition at elevated temperature, nanophase separation of hydrophobic and hydrophilic domains is required. This can be achieved by separating the sulfonic acid groups from the main chain of the polymer. By chemical grafting we have recently prepared a series of new proton-conducting polymers carrying acid moieties attached to the polymer backbone via rigid spacers. Sulfophenylation is just one example for the modification of polysulfones that has been investigated [4-6].

Experimental

The neat polysulfones were dissolved in anhydrous THF, and then degassed and cooled to -40 °C. Next, n-butyllithium was introduced to the solution followed by the addition of 2-sulfobenzoic acid cyclic anhydride. The modified polymers were precipitated in isopropanol, filtered off and dried in vacuum. Characterisation was carried out using standard spectroscopic techniques.

Results and discussion

The sulfophenylation of commercially available polysulfones was conveniently performed via a one-pot synthesis with BuLi as metalating agent (Scheme 1). Subsequent reaction with an electrophilic compound yielded the desired polysulfones. Membranes cast from *N,N*-dimethylacetamide solutions showed promising properties concerning water uptake, thermal stability and proton conductivity. Analysis of the thermal stability revealed an onset of degradation at temperatures between 300 °C and 350 °C under inert gas atmosphere. The water uptake under immersed conditions corresponded to 15 H_2O/SO_3H, and was approximately constant up to 140 °C. A Sulfophenylated polysulfone with a degree of substitution of 0.9 showed a proton conductivity of 34 mS/cm at 60 °C. To evaluate the membrane behavior under realistic conditions, in-situ fuel cell tests are currently under way Preliminary results demonstrate good durability up to 300 h and the best performances were recorded at 90 and 100 °C [7].



Scheme 1: Sulfophenylation of polysulfone

Conclusions

Membranes based on sulfophenylated polysulfone show both excellent swelling behavior and proton-conductivity sufficient for use in proton-exchange membrane fuel cells. The initial results with these materials have stimulated further investigations of new synthetic methods and of the influence of different aromatic side chains on the membrane properties.

References

[1] J. Roziere, D. J. Jones, *Annual Reviews in Material Research* **33** (2003), p. 503.
[2] P. Jannasch, *Current opinions in Colloid and Interface Science* **8** (2003), p. 96
[3] J. Kerres, W. Cui, S. Reichle, *Journal of Polymer Science, Part A: Polymer Chemistry* **34** (1996), p. 2421.
[4] B. Lafitte, L. E. Karlsson, P. Jannasch, *Macromolecular Rapid Communications* **23** (2002), p. 896.
[5] L.E. Karlsson, P. Jannasch, *Journal of Membrane Science* **230** (2004), p.61
[6] L.E. Karlsson, P. Jannasch, Submitted to *Electrochimica Acta*
[7] H. Ekström, P. Jannasch, B. Lafitte, G. Lindbergh, A. Lundblad, 204th meeting of the Electrochemical Society, Orlando (2003), abstract #992.

Protonic Conductors on the basis of polybenzimidazole (PBI) - H_3PO_4, Crosslinked membranes

R.Kalim, U.Maehr, **A.Reiche**
*Sartorius AG, Weender Landstraße 94-108, D-37075 Göttingen, Germany
e-mail: **Ratna.Kalim@Sartorius.com**, tel (+)49 551 308 1282, fax (+)49 551 308 2062

Introduction

Proton conducting polymer electrolyte membranes on the basis of complexes between poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (PBI) and H_3PO_4 are one alternative to state of the art Nafion type membranes for use in polymer-electrolyte fuel cells. The materials were introduced by Savinell et al. [1]. An overview about the current level of knowledge concerning the protonic transport and structure property relationships are given in Ref. [2]. The protonic transport is not related to the presence of water in these electrolyte systems. Therefore, the use of PBI-membranes allows the operation of the fuel cell at temperatures >> 100°C and leads to a technical simplification of the entire fuel cell system. Technical limitations arise from the low mechanical stability of highly H_3PO_4 doped PBI membranes and the danger of phosphoric acid loss during fuel cell operation at temperatures below 100°C.

The mechanical stability of the polymer membranes can be improved by chemical crosslinking with diepoxide or diisocyanate compounds [3].

Results and discussion

This study investigates the kinetics of the crosslinking reaction of PBI with diepoxides as 1,4- butanediol digylcidyl ether and N,N-Bis-(2,3-epoxypropyl)-anilin to find the optimal parameters for a technical process of membrane production by a casting technology. Reaction enthalpy, conversion and viscosity development of the gelation were studied in dependence on the epoxide content and the temperature.

Conclusions

The results show that N,N-Bis-(2,3-epoxypropyl)-anilin is not suitable because of thermal degradation at temperatures around 200°C. However the measured reaction enthalpy was comparable, ca. 110 kJ/mol for both systems. The increase of the content of the crosslinker leads to a slowing down of the gelation due to the enhancement of non crosslinking side reaction. A kinetical model of the crosslinking reaction of PBI with 1,4- butanediol digylcidyl ether was developed.

Additionally, mechanical data and electrochemical performance of crosslinked membranes in single fuel cells with 50 cm^2 active area will be presented.

References

[1] US patent 5,525,436
[2] Y.-L.Ma, J.S.Wainright, M.H.Litt, R.F.Savinell, J. Electrochem. Soc. 151 (2004) A8
[3] US patent 5,429,759

P O S T E R

P44

Protonic Conductors on the basis of polybenzimidazole (PBI)-H_3PO_4 membranes - Solid State NMR and Conductivity Study

C.Hughes#, R.Kalim*, S.Haufe*, U.Maehr*, B.Angerstein#, M.Baldus#, **A.Reiche***
*Sartorius AG, Weender Landstraße 94-108, D-37075 Göttingen, Germany
#Department of NMR based Structural Biology, Max Planck Institute for Biophysical Chemistry, Am Faßberg 11, D-37077 Göttingen, Germany
e-mail: **Annette.Reiche@Sartorius.com**, tel (+)49 551 308 1259, fax (+)49 551 308 2062

Introduction
Proton conducting polymer electrolyte membranes on the basis of complexes between poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (PBI) and H_3PO_4 are one alternative to state of the art Nafion type membranes for use in polymer-electrolyte fuel cells. The protonic transport is not related to the presence of water in these electrolyte systems. Therefore, the use of PBI- membranes allows the operation of the fuel cell at temperatures >> 100°C and leads to a technical simplification of the entire fuel cell system.

The materials were introduced by Savinell et al. [1]. An overview about the current level of knowledge concerning the protonic transport and structure property relationships are given in Ref. [2]. However, the nature of the charge carrier transport is not fully understood

Results and discussion
This study combines an investigation of the interaction between polymer and acid by solid state NMR, a comparison of NMR-relaxation data of ^1H and ^{31}P resonances of the acid with the conductivity of the electrolytes and the results of DSC measurements of the glass transition and crystallization behavior.
The structure data were measured for complexes of PBI with different concentration of deuterated phosphoric acid (D_3PO_4) to reduce the ^1H signals of the acid. The conductivity was calculated from impedance measurement of fuel cells at different temperatures. The same membranes were used for conductivity and NMR-relaxation time measurement

Conclusions
The results allow the assignment of NMR signals to the presence of free and bound phosphoric acid and free and bound $H_2PO_4^-$. DSC measurements indicate amorphous samples with glass transition in the range of 160°C for samples containing 85 wt% H_3PO_4. We have observed a reduction in local motion at higher temperature. This reduction is not accompanied by a reduction in the conductivity but by a decline in the activation energy of conductivity. For the highly doped samples at high temperatures, conductivity activation energies were observed which are similar to those for water, suggesting that a similar conductivity mechanism may be occurring.

This work was funded in part by an Alexander–von Humboldt post–doctoral fellowship for C.E.H and the MPG.

References
[1] US patent 5,525,436
[2] Y.-L.Ma, J.S.Wainright, M.H.Litt, R.F.Savinell, J. Electrochem. Soc. 151 (2004) A8

Solid polymer electrolytes based on blends of poly(trimethylene carbonate) and poly(ethylene oxide)

M. M. Silva#, S. C. Barros#, D. N. Januário#, A. Evans#, M. J. Smith# and J. R. MacCallum*
#CQ-FCT, University of Minho, Braga, Portugal
*School of Chemistry, University of St. Andrews, Scotland
e-mail: nini@quimica.uminho.pt, tel (+351) 253 604386, fax (+351) 253 604051

Introduction

Since the earliest studies of solid polymer electrolytes in 1973, an impressive variety of strategies has been applied to attain the combination of properties necessary for successful application in commercial devices. Extensive research in this domain has resulted in the development of many electrolytes based on poly(ethylene oxide) or PEO-derived hosts, novel polymer systems, improved guest salts and conductivity-enhancing additives. The exploration of inter-penetrating or inter-connecting polymer blends has also been reported. In this presentation a recently introduced host polymer, poly(trimethylene carbonate), p(TMC), was combined with PEO to produce a material with encouraging physical characteristics.

Experimental

Electrolyte samples were produced by dissolving controlled quantities of polymer and guest salt in a common solvent. The resulting mixture was stirred to produce a homogeneous solution which was cast into supporting rings on a glass plate. The excess liquid was evaporated and residual solvent was removed by heating in a vacuum oven. The thin, flexible films produced were subjected to conductivity measurements, thermal analysis and cyclic voltammetry. All electrolyte preparation, manipulation and characterization was carried out under an inert argon atmosphere.

Results and discussion

While moderate conductivities have been reported with solvent-free SPEs based on p(TMC) with a variety of guest salts[1, 2], the levels of performance observed are insufficient for this host to compete directly with PEO-based materials. The principal advantages of the former systems are that they provide thin films which are completely amorphous and mechanically robust. SPE compositions based on semi-crystalline PEO have poor mechanical properties at near-ambient temperatures and amorphous PEO has a marked tendency to creep under load. A range of PEO/p(TMC) component and salt compositions was studied with the objective of identifying a formulation with optimal mechanical and electrochemical performance.

Conclusions

The results of this research confirm that the addition of small amounts of a compatible polymer can produce an improvement in the behaviour of solvent-free SPE compositions [3]. In this respect p(TMC) may be more useful as as a performance-enhancing additive than as a host polymer.

References

[1] M. J. Smith, M. M. Silva, S. Cerqueira and J. R. MacCallum, Solid State Ionics **140** (2001) p. 345.
[2] M. M. Silva, S. C. Barros, M. J. Smith and J. R. MacCallum, Electrochimica Acta **49** (2004) p. 1887.
[3] R. Tanaka, M. Sakurai, H. Sekiguchi and M. Inoue, Electrochimica Acta **48** (2003) 2311.

Specific Charge Transport of an I^- / I_3^- Redox Couple in an Ionic Liquid and Ion gels

Ryuji KAWANO and Masayoshi WATANABE

Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan ***e-mail:*** *d02sa101@ynu.ac.jp,* ***Tel &Fax (+81)-45-339-3955***

Introduction

Dye-sensitized solar cells present an important alternative to current solar technology. Photo-electrochemical cells based on sensitization of nano-crystalline TiO_2 by molecular dyes have attracted great attention since their recognition as efficient photovoltaic devices. Usually an iodide/tri-iodide redox (I^-/I_3^-) active couple dissolved in organic solvents is used for the electrolyte, which has restricted use for the evaporation of solvent. Ionic liquids, due to their unique properties such as non-volatility, non-flammability, relatively high conductivity and gel-forming property with polymers have also been applied to the solar cells. However, fundamental properties of an (I^-/I_3^-) redox couple in ionic liquids, including the equilibrium potentials and the charge transport mechanism, have not been revealed yet. In this study, we elucidate the fundamental properties of an ionic liquid and ion gels using ultra-microelectrode technique and discuss the prospect of the redox active ionic liquids as the charge transport layer of the solar cells.

Experimental

1-Ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (EMImTFSI) was used as the ionic liquid, and EMImI and I_2 were dissolved in it as a redox couple. Steady-state microelectrode voltammograms of EMImI/I_2 mixtures were obtained. Since the redox responses are dependent on the [EMImI]/[I_2] ratios, the reactions occurring in the ionic liquid can be assigned.

The ion gels that could be prepared by in-situ urethane cross-linking of two kinds of macro-monomers (methacrylate and PEG systems) in ionic liquids, were adopted as an electrolyte in order to render the electrolyte non-volatile and thermally stable. Solar cells performances using an ionic liquid and ion gels have also been studied.

Results and discussion

Limiting currents (I_{lim}) in these measurements, corresponding to the reaction ($I_3^- + 2e^- \rightleftarrows 3I^-$), which is believed to occur in the solar cells, are given by $I_{lim} = 4nFDcr$. D is the average diffusion coefficient of I^- and I_3^- and seems to include both physical diffusion and exchange-reaction-based-diffusion in such viscous media. When diffusion coefficient includes physical diffusion and exchange-reaction-based-diffusion, D is expressed by $D = D_{phys} + 1/6k_{ex}\delta^2 c$, where k_{ex} is the self-exchange rate constant, δ is the center-to-center interstice distance at transfer reaction. The limiting currents were measured by changing both EMImI concentration and the [EMImI]/[I_2] ratios. Non-linearity of the limiting currents allows us to separate the physical diffusion and the exchange-reaction-based-diffusion between I^- and I_3^-. The contribution of the exchange reaction becomes predominant when the concentration is high, and [I^-] and [I_3^-] are comparable[1]. Performances of solar cells with ionic liquids as their electrolytes have been investigated in detail. In spite of their high viscosities, the solar cells with ionic liquid electrolytes exhibit relatively high performances. Especially, the photocurrent density reaches higher than 80% of the cell with organic solvents[2], although the viscosity of the ionic liquid electrolytes is more than 10 times higher than that of the organic solvents. The main reason for this phenomenon seems to be caused by the contribution of the exchange-reaction-based diffusion process between I^- and I_3^- dissolved in the ionic liquids as a redox couple. Similar results could also be obtained for ion gels as electrolytes.

References

1) R. Kawano *et al., Chem. Commun.*, **2003**, 330.
2) R. Kawano *et al., J. Photochem. Photobiol. A: Chem.*, in press.

Study on Acidity and Condictivities of Systems Consisting of [bmim][Cl] and an Alcohol

Ewa Bogel-Łukasik*, **Rafał Bogel-Łukasik**+, Urszula Domańska-Żelazna
Laboratory of Applied Thermodynamics, Physical chemistry Division, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
*bogelukasik@go2.pl,+lukasikr@o2.pl

Ionic liquids (ILs) are one of the goals of Green Chemistry because they create a cleaner and more sustainable chemistry. It is an umbrella concept that describes the search for reducing or even eliminating the use of substances in chemical products and reactions which are hazardous to human health and environment. Especially ionic liquids based on imidazolium cation are well known at present. There are a lot of new kinds of ILs basing on modern cations such as phosphonium, ammonium, etc. The world of ILs is developing from day to day. It is very important to could apply the results of investigations into chemical industries to use the best as it is possible their unique physico-chemical properties. The creation of ILs systems with organic and inorganic solvents advantageous for environmental, human cell and being the ideal replacements for volatile organic solvents, traditionally used as industrial solvents. That is the reason why our investigation goes into researching the properties of one of typical representatives of the promising greener ILs (1-butyl-3-methylimidazolium chloride) and the general solvents such as alcohols. We decided to check the conductivities and pH values in binary system based on [bmim][Cl] and an alcohol (from C_2 to C_{10} as exemplary). The alcohols investigated in this work were: ethanol, 1-butanol, 1-hexanol, 1-octanol, 1-decanol, 2-butanol, 2-methyl-2-propanol (tert-butanol). The measurements were carried out in the range of ionic liquid's concentrations (c_1) from 0.7×10^{-2} mol·dm^{-3} to 3.51×10^{-2} mol·dm^{-3} at the temperatures from 290 to 348.15 K. The pH measurements were made at the same conditions. The conductivities and pH of pure alcohols in the same range of temperatures like for binary mixtures were determined.

In this investigation, the values of limiting conductance of solutions of [bmim][Cl] in alcohols were found. The limiting conductances of solutions of [bmim][Cl] were determined by the Onsager limiting law. The molar conductivity of these systems was calculated. The description of conductivities data by Arrhenius and Vogel-Tammen-Fulcher equations was made. Obtained results show smaller standard mean deviation for VTF equation contrary to the Arrhenius equation.

It was found both conductivities and pH values dependence on temperature, concentration of [bmim][Cl] and the length of an alcohol.
We have proved in this work that as it was expected, the addition of [bmim][Cl] to the alcohol permits to find the required range of the pH values from 3.0 to 8.5. Thank of that it is possible to easy modify the range of the pH values of the reaction carried out in the mixtures of 1-butyl-3-metylimidazolium chloride and an alcohol.

Supramolecular additives as a method to improve ionic transport properties in composite electrolytes based on lithium salts and PEO matrix.

M. Ciosek, M. Kalita, M. Bukat, M. Siekierski, A. Plewa, G. Rokicki, W. Wieczorek
Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3 r. 348,
00-664 Warsaw, POLAND
tel (+) 48 602 611 970, fax (+) 48 22 628 27 41, e-mail: **admin@soliton.ch.pw.edu.pl**

In the present work the impact of addition selective, neutral supramolecular anion receptor like: 1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethylcalix[6]pyrrole on transport properties such as conductivity, diffusion coefficient and cation transference number in electrolyte based on the low molecular weight poly(ethylene oxide) dimethyl ether (PEO-DME Mw=500) capped with different lithium salts are determined. Salt concentration varies from $5e^{-3}$ to 1.5 $mol*kg^{-1}$ and receptor addition is proportional to its quantity in 3:1 or 2:1 molar ratio.

Cation transference number (t_+) strongly depends on salt concentration and addition of supramolecular compound. In system without anion receptor the t_+ value trend decreases with increasing salt concentration without distinct maximum while for system with calix[6]pyrrole addition has convergent t_+ trend to conductivity changes in the system.

Supramolecular additives are characterized by high selectivity on size and charge of an ion. Polymer with calyx[6]pyrrole is homogeneous, viscous and non-transparent.

The system conductivity decreases with the calyx[6]pyrrole addition but the change is not significant. It may come from salt dilution. Temperature conductivity dependency shows increase of the conductivity energy activation which may be a proof of anion immobilization.

Investigated lithium transference number with polarization method and Newman's method shows strong value increase.

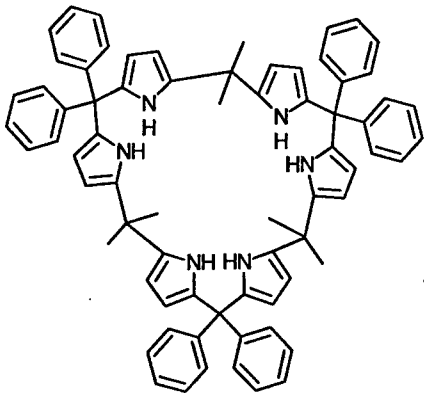


Figure 1.
1,1,3,3,5,5-*meso*-hexaphenyl-2,2,4,4,6,6-*meso*-hexamethylcalix[6]pyrrole

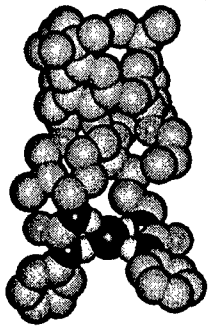


Figure 2.
Calix[6]pyrrole anion complexation scheme.
Molecule in the centre symbolize coordinated anion.

Synthesis of novel lithium salt monomers based on sulfonamide and single-ion conductivity of their polymer electrolytes

Sun-Jung HWANG, Md. Khalilur RAHMAN, Sei-ichiro TABATA and Masayoshi WATANABE
Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
E-mail:**d03ga192@ynu.ac.jp**,Tel:+81-45-339-3955, Fax:+81-45-339-3955

Introduction

The demand to obtain solid-state Li^+-conductors has resulted in the focus of intense research on the development of Li^+-conducting polymer electrolytes for the use in rechargeable polymer batteries. The polymer electrolytes that permit only cation transport, the so-called single ion conductor, can be realized by fixing anionic structure in a polymer backbone. In this study, highly dissociable, thermally and electrochemically stable novel lithium salt monomers based on sulfonamide were synthesized. The copolymerization was carried out with the novel lithium salt monomers and a macro-monomer with oxyethylene repeating units. The lithium ion conductivity of the polymer electrolytes has been studied in detail by means of electrochemical and NMR methods

Experimental

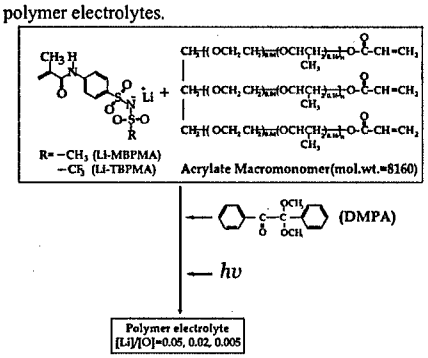
In order to enhance the degree of dissociation, a strongly electron-withdrawing group was introduced into a sulfonamide. Furthermore, in order to make the polymerization possible, the new lithium sulfonamide type monomers, Li-*N*-[4-methyl-bis(sulfonyl)imide] phenyl-2-methylacrylamide (Li-MBPMA) and Li-*N*-[4-trifluoromethyl-bis(sulfonyl)imide]phenyl-2-methylacrylamide (Li-TBPMA), were allowed to have methacrylamide groups.

Results and discussion

It was identified that p*K*a of these monomers is zero or less and that they are strong acids.

The chemical structure was identified by ^{1}H-NMR, ^{7}Li-NMR, etc.

Scheme 1 shows the procedure for the preparation of polymer electrolytes.



Scheme 1. Preparation of polymer electrolytes.

Copolymerization of the novel lithium salt monomers was carried out with poly(ethylene oxide-co-propylene oxide)triacrylate (TA, M_n=8160). The membranes were flexible, and transparent. The complex impedance of the polymer electroytes was measured with changing temperatures. The ionic conductivity, ransference number, electrochemical stability, and Li^+-diffusivity were explored with focusing on the structure of the novel lithium salt monomers.

References

[1] M. K. Rahman, G. Aiba, M. A. B. H. Susan, and M. Watanabe, *Electrochim. Acta,* in press.

The Synthesis of a New Family of Aluminum-Based Anion Receptors and the Study of Their Effects on Ion Conductivity in Liquid Electrolytes

Yong Min Lee, Jeong-Eun Seo, Nam-Soon Choi, Wan-Ho Seol, Je An Lee, and Jung-Ki Park*
Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, Republic of Korea
e-mail: **yongmin_lee@kaist.ac.kr**, **pjk@mail.kaist.ac.kr**, tel (+) 82-42-869-3925 fax (+) 82-42-869-3910

Introduction

Rechargeable lithium batteries have become the most powerful energy storage system mainly due to their high energy density and operating voltage. However, the growth rate of their energy density could not keep pace with that of demand of electronic devices. It is basically because it's hard to find out new electrode active materials showing higher energy density. So, intensive efforts have been to the search of various additives for advanced electrolytes to enhance cycle characteristics nowadays.

Various additive materials have been added to the liquid electrolytes consisting of organic solvent and lithium salts to enhance the electrochemical performance and safety. Those additives with small amount less than 5wt% have known to be very effective to form stable SEI (Solid Electrolyte Interphase) layer or to enhance safety by preventing overcharge or flame generation. Among various additives, anion receptors have been newly under research for $LiPF_6$-based electrolyte system.

Experimental

Synthesis and characterization: Various fluorinated Al-based compounds were synthesized through various methods. The starting compounds were purchased from Aldrich. All the reactions and process were performed under Ar or N_2 atmosphere. NMR, FT-IR, and mass spectroscopy were used to identify the each chemical structure.

Electrochemical Measurement: The separator dipped in liquid electrolyte was sandwiched between the two stainless steel (SS) electrodes to measure the ionic conductivity. The ionic conductivity was obtained from bulk resistance measured by a.c. complex impedance analysis. A linear sweep voltammetry experiment was carried out on a SS working electrode with lithium electrode as the counter and reference electrode at a scanning rate of 1.0 mV/s.

Results and discussion

A family of anion receptors based on fluorinated Al-based compounds was newly used as anion receptors in lithium battery electrolytes. The ionic conductivity showed maximum value at a certain conc. of anion receptor. Because the increase of the number of Li^+ was more dominant than mobility decease of Li^+ due to the viscosity increase in low concentration of anion receptor and reverse in high concentration. In addition, transference number was enhanced highly. High transference number can cause stable current density and decrease anion decomposition. Linear sweep voltammetry data showed that anion receptor made the decomposition voltage of anion to be higher.

Conclusions

A family of anion receptors was newly synthesized and their electrochemical properties were characterized. Fluorinated Al-based compounds showed high possibility as an anion receptor usage.

References

[1] H.S. Lee, X.Q. Yang, C.L. Xiang, J. McBreen, J. Electrochem. Soc., 145(8) (1998) 2813

Acknowledgement

This work was supported by the Human Resources Development in Industrial Technology Program of KOTEF in Republic of Korea.

Transparent Chitosan Based Polymer Electrolites

Sandra Fuentes, Jaime Retuert, **Guillermo González***
Faulty of Sciences, Universidad de Chile, Las Palmeras 3425, Santiago, Chile
e-mail: **ggonzale@uchile.cl**, tel (+562) 678 7255, fax (+) 271 3888

Introduction

Although electrical conductivity as well as mechanical and chemical stability are in general the most important properties of materials to be used as electrolytes in solid state devices, often there are other properties like flexibility of the materials or the transparency in a given light frequency range which may be much appreciated for determined applications. During the past two decades much attention have been paid to polymer electrolytes, specially to those based in polyethers like poly(ethylene oxide) (PEO) or poly(propylene oxide). Thus for instance, composites containing the polymers and a lithium salt as main component have been found to constitute enough robust materials with conductivities of the order of 10^{-6} - 10^{-7} Scm^{-1}. However, factors like high crystallinity at room temperature often affects not only the conductivity but, also the transparency and flexibility of the films formed by these polyelectrolytes. Some funtionalized polysacharide like chitosan have been also considered as a potential polyelectrolyte component which could be specially interesting because the exceptional film-forming aptitude of chitosan. The transparency of chitosan films is in general poor because of its relatively high crystallinity. However recently we have found that nanocomposites arising from the reaction of chitosan with aminopropyltriethoxysilane (APS) forms a polymer complex leading to transparent films. Furthermore, the addition of a lithium salt to these composites leads to transparent ionic conductor films. Considering the relevance of PEO in the preparation of solid ionic conductors we have investigated the influence of the addition of these polyether to the Chitosane/APS molecular complexes.

Experimental

1% Solutions of purified Chitosan (QO) (Bioquímica Austral Ltd., av. Mw $3.5*10^5$, deacetylation degree 87.5%) in 5% formic acid were stirred for 24 h at r.t. with a solution of 3-Aminopropyltriethoxysilane oligomer (pAPS), Mw ≅ 800, prepared by partial hydrolysis of APS (Aldrich) in 0.5M formic acid, 3 days at 45 °C, an 0.1 M aqueous solution of PEO (Aldrich, Mw ≅ $4.0*10^6$), and a 1M solution of anhydrous lithium perchlorate (Merck) in absolute ethanol, using differents ratios. Films 0.07-1.5 mm-thick, prepared by solution casting on polyethylene and dried by evaporation at r.t., were characterized by simultaneous thermal analysis, DSC/TGA, X-ray diffraction analysis, and Scanning Electron Microscopy. Electrochemical Impedance Spectroscopy (EIS analyzer, PAR Model 6310)in range 100 mHz-100 KHz was performed using gold ion-blocking electrodes at 40 ±0.2 °C under argon atmosphere.

Results and discussion

The ternary diagram illustrated in Figure 1 indicates the concentration ranges of the components for which mechanically stable, self supported films are obtained. The amount of chitosan appears to be determinant for the mechanic stability of the films. The lower part of the diagram, dominated by the influence of pAPS, groups mixtures leading to viscous liquids or soft solids which do not permit the formation of films. No appropriate binary PEO-pAPS materials were indeed obtained. Although binary mixtures of POE and chitosan always lead to robust films, PEO-rich mixtures originate brittle materials. In the chitosan-pAPS binary mixtures, the maximal amount of pAPS for obtaining workable films is about 50%.

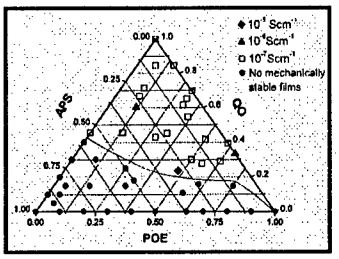


Figure 1. Ternary phase diagram Chitosan, QO, pAPS and PEO illustrating the composition window for transparent self-supporting films as well as the order of magnitude of corresponding electrical conductivity.

There are only two relatively narrow zones where that occurs. Binary chitosan-pAPS mixtures containing a maximum of 50% pAPS are transparent while the chitosan-PEO ones meet that condition until 70% PEO. Ternary mixtures form transparent films in the composition window defined in approximately the ranges 25 values of 10^{-6} Scm^{-1} are observed, namely the points $6.6*10^{-6}$ and $1.2*10^{-6}$ Scm^{-1} and a very singular point with the composition PEO/QO/pAPS/Li^+ 1:0.5:0.6:0.2 located in the window of the molecularly compatible mixtures where a maximal value of $1.7*10^{-5}$ Scm^{-1} is reached.

Acknowledgements

Research partially financed by FONDECYT (grant 1010924) and the Universidad de Chile.

References

[1] S.Fuentes, P.Retuert, A. Ubilla, J.Fernández G.González, Biomacromolecules **1** (2000) 239.
[2] S.Fuentes, P.Retuert, G.González, Electrochim Acta, **48** (2003) 2015.

Zwitterion effect in polyelectrolyte gels based on lithium methacrylate-N,N-dimethyl acrylamide copolymer

J. Sun*[1], D.R. MacFarlane[2] and **M. Forsyth**[1]

[1]School of Physics and Materials Engineering, Monash University, Clayton, VIC 3800, Australia [2]School of Chemistry, Monash University, Clayton, VIC 3800, Australia

*email: **Jiazeng.sun@sci.monash.edu.au**, tel.: +61+3-99051679; fax: +61+3-99054940

Lithium polyelectrolytes, such as poly(lithium 2-acrylamido-2-methyl propanesulfonate) (PAMPSLi), have been used as main component in gel polymer electrolyte materials[1-3]. This type of polyelectrolytes was designed with specific negative groups bounded to the polymer chains, for example, sulfonate groups in PAMPSLi. With this polymer structure, lithium cations in the polymer will be the dominant charge carrier in an appropriate environment, and transference number of lithium will therefore be close to unity, as required in application of these materials as electrolytes in the electrochemical devices, such as lithium batteries. It was found in our previous work[3] that zwitterion compounds could be used in polyelectrolyte gel systems as lithium dissociation enhancers. In this work, we used 1-butylimidazolium-3-(n-butanesulfonate) as a zwittrion additive to investigate the zwitterion effect in polyelectrolyte gels based on poly(lithium methacrylate-co-N,N-dimethyl acrylamide). Results of conductivity, thermal properties, and lithium diffusion coefficient of these systems will be presented, and discussed with respect to the effect of the zwitterion additive in these materials. This work has shown that the zwitterion compound has a positive effect on conductivity and lithium diffusion in some gel systems, and mechanism of this effect will also be discussed.

References

[1] J. Sun, D. R. MacFarlane, M. Forsyth, Solid State Ionics, 147 (2002) 33.

[2] M. Forsyth, J. Sun, F. Zhou, D. R. MacFarlane, Electrochimica Acta, 48(14-16) (2003) 2129.

[3] C. Tiyapiboonchaiya, J. M. Pringle, J. Sun, N. Byrne, P. C. Howlett, D. R. MacFarlane, M. Forsyth, Nature Materials, 3 (2004) 29.

AUTHORS INDEX

Aabloo, A. 23, 185
Adebahr, J. 45
Affek, A. 89, 133, 151, 169, 193
Agrawal, S.L. 143
Albinson, I. 149, 153, 199
Alessandrini, F. 117
Alloin, F. 69, 141, 188
Andreev, Y.G. 15, 181
Angerstein, B. 211
Appetecchi, G.B. 117
Asai, S. 175, 179
Azizi Samir, M.A.S. 69
Balbuena, P.B. 17, 25
Baldus, M. 211
Barros, S.C. 137, 213
Basch, A. 121
Benavente, E. 59, 171
Benicewicz, B. 95
Bertucco , A. 71
Besenhard, J.O. 121
Bogel-Łukasik, E. 217
Bogel-Łukasik, R. 217
Börjesson, L. 105
Bouchet, R. 113
Brandell, D. 23
Bruce, P.G. 15, 181
Bukat, M. 219
Byrne, N. 31, 73
Carlos, L.D. 137
Carlsson, J. 149
Carollo, A. 187
Carrado, K.A. 65
Castagnola, N. 65
Chami, M. 113
Chauvin, C. 141, 188
Chelmecki, M. 123
Choi, N.S. 223
Chojak, M. 125
Christie, A.M. 181
Chung, S.H. 37, 95
Ciosek, M. 75, 219
Ciszewska, M. 161
Cronauer, C. 77
Crowther, R.O. 103
de Zea Bermudez, V. 137
Di Noto, V. 71, 109
Diard, J.P. 167
Dissanayake, M.A.K.L. 199
Domańska-Żelazna, U. 217
Donoso, J.P. 197
Dufresne, A. 69
Dunn, B. 185
Durantino, L. 95
Duvdevani, T. 195
Dygas, J.R. 89, 169, 193
Edman, L. 53
Egashira, S. 63, 145
Eisenblätter, J. 39
Endo, N. 145
Evans, A. 213
Feiglin, T. 195
Feld, W.A. 17
Fellner, J.P. 103
Ferreira, H.C.A. 61
Florjańczyk, Z. 35, 89, 133, 151, 169, 193
Forsyth, M. 29, 31, 45, 73, 155, 227
Frech, R. 39, 85, 131
Fredriksson, M. 149
Fuentes, S. 225
Fujino, Y. 63
Funke, K. 91
Furlani, M. 149, 153, 165
Furneaux, J.E. 85
Gautier-Luneau, I. 141
Genova-Dimitrova, P. 139
Giffin, G.A. 39
Glatzhofer, D.T. 39
Gollas, B. 121
Golodnitsky, D. 37, 121
González, G. 59, 171, 225
Gorecki, W. 69
Grandi, S. 187
Greenbaum, S.G. 37, 83, 95
Grugeon, S. 113
Guindet, J. 107, 167
Han, J.-H. 121
Hatemura, K. 145
Haufe, S. 211
Hayamizu, K. 51, 203
Henderson, W.H. 117
Higa, M. 63, 145
Hill, A.J. 29, 91, 163
Hirahara, S. 179
Hirai, K. 41
Howlett, P. 31
Hughes, C. 211
Hwang, S.J. 221
Igawa, S. 175

Ingram, M.D. 91
Iojoiu, C. 139, 141
Ishibashi, N. 177
Iwahori, T. 119
Jacob, S. 101
Jacobsson, P. 27, 105
Jannasch, P. 129, 157, 207
Januário, D.N. 213
Jayakody, J.R.P. 95
Jayathilaka, P.A.R.D. 199
Jeffrey, K.R. 111
Johansson, P. 27
Kalim, R. 209, 211
Kalita, M. 219
Karlsson, L.E. 207
Kasemägi, H. 23, 185
Kawano, R. 201, 215
Kii, K. 41
Kitani, R. 63
Kizilel, R. 65
Kobayashi, N. 57, 119
Koumoto, T. 63
Kovarsky, R. 19, 37
Kreuer, K.D. 97
Krok, F. 89, 169, 193
Krztoń-Maziopa, A. 159
Kulesza, P.J. 125
Kumar, S. 21
Lafitte, B. 207
Lamas, E. J. 25
Langwald, N. 35
Lavina, S. 71, 109
Le Nest, J.F. 188
Lee, J.A. 223
Lee, Y.M. 223
Leitner, K. 121
Lewera, A. 125
Liao, Y.P. 33, 183
Liivat, A. 23
Liu, J. 33, 183
Livshits, E. 19, 37
Lopes, L.V.S. 197
Lucente, L.R. 17
Łasińska, A. 89, 169, 193
MacCallum, J.R. 213
MacFarlane , D.R. 29, 31, 45, 73, 155, 227
Machado, GO . 61, 197
Maehr, U. 209, 211
Magistris, A. 187
Maier, J. 97
Malinowska, M. 191
Marcinek, M. 81
Marchal, M. 107, 139, 167
Martinelli, A. 105
Marzantowicz, M. 89, 169, 193
Matic, A. 105
Matsumi, N. 79
Matsuoka, H. 135
Matsusaki, K. 145
Matsuyama, C. 201
Mayes, A.M. 21
McCoy, A.M. 85
Mellander, B.E. 149, 153, 199,
Meyer, W.H. 123
Miecznikowski , K. 125
Mita, Y. 119
Miyashiro, H. 119
Mizumo, T. 79
Möller, K.-C. 121
Morita , M. 47
Murata, S. 41
Mustarelli, P. 187
Nadara, K. 67, 111
Nakagawa, H. 51
Nakamoto, H. 135, 177, 205,
Nanjo, S. 115
Navarra, M.A. 105
Niklasson, G. 165
Nishimura, M. 57
Nishimura, N. 147
Noda, A. 97, 99
Nomura, Y. 147
Nunes, S.C. 137
Obeidi, S. 87
Ohno, H. 79, 147
Ohtomo, H. 57
Ollivrin, X. 188
Olsowski, B. 77
Palacios, I. 173
Pandey, S. 143
Panero, S. 105
Papaefthimiou, S. 157
Park, J.K. 223
Pas, S.J. 29, 91, 163,
Passerini, S. 117
Pawlicka, A. 61, 197
Peled, E. 19, 37, 195,
Pennarun, P.Y. 157
Perez del Valle, C. 141
Persson, C. 129
Philosoph, M. 195
Piekarska, J. 191
Plewa, A. 219
Płocharski , J. 159, 161
Poinsignon, C. 101, 139

Popall, M. 77, 101
Pringle, J.M. 73, 155
Puchner, M. 207
Quartarone, E. 187
Rager, T. 97
Rahman, Md.K. 221
Rakhman, M. 195
Reiche, A. 209, 211
Retuert, J. 225
Rocha, J. 137
Rocher, N.M. 131
Rokicki, G. 219
Ryu, S.W. 21
Sá Ferreira, R.A. 137
Saei, N. 153
Saito, Y. 41
Sakai, T. 41
Sakamoto, K. 79
Sanchez, J.-Y. 69, 107, 139, 141, 167, 188
Sanders, R. 39
Sandhu, S.S. 103
Sandí, G. 17, 65
Sannier, L. 113
Santa Ana, M.A. 59, 171
Sato, A. 201
Scanlon, L.G. 17
Schulz, J. 77
Schuster, M. 97
Scrosati , B. 105
Seki, S. 119, 163
Seneviratne, V. 85
Seo, J.E. 223
Seol, W.H. 223
Shao-Horn, Y. 21
Shin, J.H. 117
Shirai, T. 47
Shobukawa, H. 49
Siekierski , M. 67, 75, 191, 219
Siewert, P. 153
Silva, M.M. 137, 213
Smith , M.J. 137, 213
Stappen, C. 165
Staunton, E. 181
Stevens, J. R. 55, 111
Stolwijk, N.A. 87
Suarez, S. 37
Sumita, M. 175, 179
Sun, J. 227
Susan, Md.A.B.H. 99, 177, 203,
Tabata, S. 221
Tarascon, J-M. 113
Thernström, S. 153
Thomas, J. 23, 185
Tiyapiboonchaiya, C. 31, 73
Tokuda, H. 49, 203
Tomasi, C. 187
Tomaszewska, A. 35, 133, 151, 193
Tominaga, Y. 175, 179
Turner, A. 17
Ungar, G. 33, 183
Vargas, R.A. 173
Vezzu, K. 71
Vittadello, M. 71, 109
Wallace, G.G. 155
Wang, Y. 25
Watanabe, M. 43, 49, 99, 115, 135, 163, 177, 201, 203, 205, 215, 221
Wegner, G. 123
Wieczorek, W. 35, 81, 125, 219
Winter, M. 121
Wright, P.V. 33, 183
Xiao, L. 95
Yamanaka, A. 119
Yianoulis, P. 157
Yoshimoto, N. 47
Zapata, V.H. 173
Zazoum, B. 87
Zelenay , P. 93
Zhang, H. 95
Zheng, Y. 33, 183
Zygadło-Monikowska, E. 35, 89, 133, 151, 193
Żukowska, G.Z. 81, 111, 125, 191