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 comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	01/10/02	Final Progress/04/01/98-3/31/01

4. TITLE AND SUBTITLE

COMPOSITE, POLYMER-BASED ELECTROLYTES FOR ADVANCED BATTERIES

5. FUNDING NUMBERS

DAAG55-98-1-0233

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37411.6-CH

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park,, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

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12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The series of investigations based on synthesis, physical characterization, charge transport measurements, and appropriate modeling studies has been completed, in the general area of polymer based electrolyte systems. Several substantive advances towards new, improved performance electrolyte materials both for low temperature fuel cell applications and for advanced secondary lithium battery materials have been reported. Particular advances in discovery areas include rigid polymer based electrolyte systems using carbonates, Lewis acid enhancement mechanisms for ionic conductivity in salts, optimization of local basicity and polyelectrolytes, and understanding of a phase diagram in mixed polymer complex/polyelectrolyte structures.

20021107 011

14. SUBJECT TERMS

Ion containing polymers, polymer electrolytes, polyelectrolytes
Ion conduction in polymers, Battery materials, Fuel cell materials

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

COMPOSITE, POLYMER-BASED ELECTROLYTES FOR ADVANCED BATTERIES

FINAL PROGRESS REPORT

FOR PERIOD COVERING

APRIL 1, 1998 - MARCH 31, 2001

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SPONSOR AWARD NUMBER: DAAG55-98-1-0233

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STATEMENT OF THE PROBLEM STUDIED:

For both low temperature fuel cells and high performance secondary lithium batteries, it is critical that transport of lithium ions in the electrolyte phase be optimized. Optimization in this case means the highest possible ionic conductivity (increased power density), concomitant with maximization of cation transference number and operating within an extensive electrochemical stability window. The principal aim of the current research has been the preparation, structure analysis, transport measurements and theoretical modeling of a series of novel electrolytes based both on traditional polymer/salt complexes and on modified polymeric materials to optimize the lithium transport properties.

SUMMARY OF THE MOST IMPORTANT RESULTS:

Over the three year period, major progress was made in a series of subareas of polymer based electrolytic systems. These included:

1. Development of entirely new electrolyte species, including high conductivity systems based on rigid polycarbonates and on the Lewis acid enhancement of ionic conductivity in simple salts. The latter materials have been completely characterized, from the initial suggestion and measurement of high ionic conductivity through physical analysis (vibrational spectra, scanning calorimetry, neutron scattering structure analysis) to computational analysis based on ab-initio electronic structure methods.

2. Vibrational spectroscopy and simple ab-initio calculational methods have been used to analyze how nanoscale inert oxide fillers effect the transport in amorphous polymer electrolytes. For partially crystalline materials, the inert oxides have been shown to increase the conductivity by decreasing the crystallinity, and therefore increasing the effective transport by facilitation of the relaxation that modulates local ion mobility. In these fully amorphous polymer electrolyte systems, that enhancement mechanism is not operative. We find, by correlation of the vibrational spectra with the stoichiometry and electronic structure studies, that weak interactions between the oxide surfaces and both the mobile ions (lithium) and the oxide polymer changes the local structure, and can (in favorable instances) substantially reduce the ion paring that limits mobility in simple polymer/salt complexes.

3. A series of electronic structure calculations has shown general schemes for reduction of local Lewis basicity, and therefore for partial decoupling between motion of the ions and structural relaxation of the polymer host. It is this coupling which <u>fundamentally</u> limits ionic conductivity in polymer/salt complexes. The coupling itself has been known for ten years, and various schemes around it have been proposed (including the oxide fillers discussed in the last paragraph). These computational studies have suggested that one can control basicity in polyelectrolytes (polyelectrolyte systems have inherent advantages due to the unit transference number for the lithium cation). The local aluminate structure lends itself to control of basicity, by changing from

an aluminate to an aluminosilicate local geometry. The significant electron delocalization afforded by reduced binding polarity results in reduction of the basicity, weaker ion paring, and faster ion transport.

4. Both the experimental and computational work have permitted us to construct the complete phase diagram for conductivity of polymer electrolytes and polyelectrolytes as a function of mole fraction of bound anion, and of temperature. This is, to our knowledge, the first work of this kind: in this particular case, the theoretical model used is based on dynamic percolation theory, and included interionic interactions and full molecular dynamics simulation.

Taken as a totality, we believe that the publications that have ensued from this work, and the insights that have been gained, lead us to important new directions in polymer electrolyte structures. They also suggest substantial limitations of the current materials, and schemes for getting around them based on increased decoupling. Similarly highly publicized work from Bruce's laboratory on transport in crystalline polymer salt complexes goes in very much the same direction.

We are most excited about the work on the rigid carbonate-based polymer electrolyte systems, on the Lewis acid enhancement mechanism for ionic conductivity of simple salts, the phase diagram work on the polymer electrolytes and polyelectrolytes, and the understanding of the effect of the oxide fillers on

amorphous polymer electrolytes. Taken together, these indeed suggest important directions for polymer electrolytes, that can result in substantial increases in ionic conductivity. This will result in increased power density while maintaining the high energy density, the low cost, the flexibility and dimensional stability of polymer based materials for advanced batteries and fuel cell structures.

A. LISTING OF PAPERS AND BOOKS PUBLISHED:

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M. A. Ratner, "Ionic Charge Transport in Molecular Materials: Polymer Electrolytes," in Computational Studies of New Materials, D. A. Jelski and T. F. George, eds. pp.174-209 (1999).

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B. CONFERENCE PROCEEDINGS:

"Enhanced Ion Mobility in Aluminosilicate/Polysiloxane Network Polyelectrolytes," D. P. Siska and D. F. Shriver, in New Materials for Batteries and Fuel Cells, D. H. Doughty, L.F. Nazar, M. Arakawa, H. Brack, N. Naoi, eds; *Mat. Res. Soc. Symp. Proc.*, Vol. 575, 131-136 (2000).

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"Optimizing the Design of Polyelectrolytes Using Monte Carlo Simulations," J. F. Snyder, M. A. Ratner and D. F. Shriver, *J. Electrochem. Soc.*, December 2000.

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D. REPORT OF INVENTIONS: None