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1. AGENCY USE ONLY (Leave Blank)

2. REPORT DATE
4 March 2002

3. REPORT TYPE AND DATES COVERED
Final Progress Report 6/1/1998 - 12/31/2001

4. TITLE AND SUBTITLE
Nanocomposites As Designed Catalysts For Direct Methanol Fuel Cells

5. FUNDING NUMBERS
DAAG55-98-1-0362

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER

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
38717.26-CH

11. SUPPLEMENTARY NOTES
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12 a. DISTRIBUTION / AVAILABILITY STATEMENT
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12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The specific aim of this research project is the development of novel methods for preparing improved catalysts for direct methanol fuel cells (DMFCs). These catalysts consist of metal alloy nanoclusters dispersed onto a conductive carbon support. Synthetic control of the alloy nanocluster composition is achieved by preparing molecular precursors in which the precursor contains two or more metals of a desired stoichiometry. Adsorption of single-source molecular precursors onto Vulcan carbon powder followed by appropriate thermal treatment affords metal alloy or intermetallic/carbon nanocomposites. Tests performed in an operating DMFC indicate that the catalytic activity of PtRu/Vulcan carbon nanocomposites prepared by this method as anode catalysts is superior to that of a similar commercial PtRu/Vulcan carbon catalyst. A rapid synthesis of such binary alloy/Vulcan carbon nanocomposites using microwave heating also has been discovered and reported.

14. SUBJECT TERMS
DMFC Catalysts, Designed Anode Catalysts

15. NUMBER OF PAGES
10

16. PRICE CODE

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

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. 239-18
298-102

20030605 188

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(3) List of Appendixes, Illustrations and Tables

Not applicable

(4) Statement of the Problem Studied

One research objective of the Army Research Office is the development of improved catalysts for the oxidation of methanol in direct-methanol-fuel-cells (DMFCs). Practical DMFCs would be attractive compact power sources for electrical power production. Current wisdom dictates that crystalline metal alloy nanoclusters of particular compositions should be highly active catalysts for methanol oxidation. To minimize the unit cost of metal, these alloy particles should be supported on an electrically conducting carbon powder (such as Vulcan carbon) forming a nanocomposite catalyst.

The research hypothesis being investigated in this project is the following: Can molecules serve as single-source precursors to crystalline binary intermetallic or alloy nanoparticles supported on various types of carbon supports? More specifically, molecules containing a precise stoichiometry of two or more different metals might serve as precursors to crystalline nanoclusters of metal alloy having the same metal stoichiometry. Because metal alloy/carbon nanocomposites are known to be active as DMFC anode catalysts, better control of the metal alloy stoichiometry at the nanoparticle scale might afford DMFC anode catalysts having higher activity. The activity of DMFC anode catalysts might also be improved through better control of metal catalyst particle size, the use innovative thermal treatment conditions using microwave irradiation, and by support effects arising from the use of carbon supports having unique atomic structures. Selected investigation of these aspects relating to catalyst activity has also been undertaken during this project period.

(5) Summary of the Most Important Results

- Pt-Ru/tubular herringbone graphitic carbon nanofiber nanocomposites as anode catalysts in DMFCs exhibit a fuel cell performance reproducibly enhanced by 50-64% over that recorded for a standard Pt-Ru unsupported catalyst.
- Pt-Ru/herringbone graphitic carbon nanocomposite prepared using microwave heating as anode catalysts in DMFCs exhibit a fuel cell performance comparable to that of a standard Pt-Ru unsupported catalyst.
- Pt-Ru/Vulcan carbon nanocomposites prepared using microwave or conventional heating as anode catalysts in DMFCs exhibit a fuel cell performance comparable to that of a standard Pt-Ru unsupported catalyst.
- Pt, Pd, or Pt-Ru/carbon nanocomposites having crystalline metal nanoparticles can be prepared rapidly within one or two minutes of heating using microwave irradiation.
- Pt-Os, Os, Ru-Mo, Pt-Sn, Pt-Re and various Pt-Mo/carbon nanocomposites have been prepared using single-source molecular precursors as the source of metal. DMFC testing data reveal that the Os/carbon nanocomposites do not give high performance as DMFC anode catalysts, and that the other metal catalyst compositions give a DMFC performance less than that obtained when using Pt-Ru anode catalysts.
- A new synthesis method for preparing graphitic carbon nanofibers using water-soluble supports was discovered and reported.
- Graphitic carbon nanofiber/polyimide films having a fiber/polymer interface of high covalent character have been synthesized and reported.
- Hexagonal Bi-Te nanocrystals have been prepared in a ceramic matrix on the way to preparing nanoscale Bi materials relevant to thermoelectric applications.
- A U.S. Patent has been issued for our DMFC catalyst research supported by ARO funding.

(6) List of all Publications, Technical Reports, and Technical Presentations

(a) Publications published in peer-reviewed journals:

"Synthesis and Molecular Structure of the Mercury-Bridged Heteronuclear Complex $[Pt_3(dppm)_3\{\mu_3\text{-}Hg\text{-}RuCp(CO)_2\}_2][PF_6]_2$," William D. King and Charles M. Lukehart, **J. Cluster Sci., 1998**, *9*, 107 - 121.

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"Preparation of Graphitic Carbon Nanofibers (GCNFs) Using Water-Soluble Supports," Eve S. Steigerwalt and C. M. Lukehart, **J. Nanosci. Nanotech., 2002,** *2*, 1 - 4.

(b) Publications published in non-peer-reviewed journals or in conference proceedings:

"Preparation of Pt-Ru or Pt-Mo Supported Catalysts for PEM or Direct Methanol Fuel Cells from Single-Source Molecular Precursors," C. M. Lukehart, D. L. Boxall, J. D. Corn, M. Hariharasarma, W. D. King, K. C. Kwiatkowski, E. S. Steigerwalt, and E. A. Kenik, **Am. Chem. Soc., Fuel Chem. Div. Preprints, 1999**, *44*, No. 4, 982 - 986.

"On-Particle EDS Analysis of PtRu/C DMFC Catalysts Using High-Resolution TEM," D. L. Boxall, C. M. Lukehart, and E. A. Kenik, **Proc. ASME Advanced Energy Systems Div., 1999**, *39*, 327 - 336.

"Metal Alloy/Vulcan Carbon Nanocomposites of Controlled Alloy Stoichiometry Prepared from Single-Source Molecular Precursors as DMFC Anode Catalysts," Charles M. Lukehart, Chapter in "Small Fuel Cells and Battery Technologies," Knowledge Foundation, **1999**, Chapter 7, pp. 51 - 62.

"Nanocomposites Prepared by Sol-Gel Methods: Synthesis and Characterization," Krzysztof C. Kwiatkowski and C. M. Lukehart, "**Handbook of Nanostructured Materials and Nanotechnology**," H. S. Nalwa, Ed., Volume 1, Chapter 8, pp. 387 - 421: Academic Press (2000).

"On-Particle EDS Analysis of Bimetallic, Carbon-Supported Catalysts," Deborah L. Boxall, Edward A. Kenik, and Charles M. Lukehart, **Mater. Res. Soc. Sym. Proc., 2001**, *589*, 265 - 270.

"Polymer Material Property Enhancement Through Nanocomposite Technology," J. P. Paxton, E. D. Mowles, C. M. Lukehart and A. J. Witzig, **Proc. Am. Soc. Composites,** M. W. Hyer and A. C. Loos, Eds., pp. 215 - 221: CRC Press (2001).

"Nanocomposites Prepared by Sol-Gel Methods: Synthesis and Characterization," Krzysztof C. Kwiatkowski and C. M. Lukehart, "**Nanostructured Materials and Nanotechnology**," H. S. Nalwa, Ed., Chapter 2, pp. 57 - 91: Academic Press (2002).

(c) Papers published at meetings as abstracts, but not published in conference proceedings:

"Preparation of Carbon-Supported Bimetallic and Alloy Phase Nanocrystals Using Single-Source Molecular Precursors," Deborah L. Boxall, James D. Corn, and Charles M. Lukehart, American Chemical Society, 215th National Meeting, March. 1998, Dallas, TX.

"Preparation of Gold Nanoclusters on Water-Soluble Supports," Eve S. Steigerwalt, Charles M. Lukehart and Kevin M. Warren, American Chemical Society, 216th National Meeting, August. 1998, Boston, MA.

"Rapid Synthesis of Carbon-Supported Metal Nanocrystals," Deborah L. Boxall, William D. King and Charles M. Lukehart, American Chemical Society, 216th National Meeting, August. 1998, Boston, MA.

"Designed Syntheses of Binary Metal Alloy Nanocomposites Using Single-Source Molecular Precursors," Deborah L. Boxall, James D. Corn, William D. King and C. M. Lukehart, Seventh Annual Workshop of the Consortium for Nanostructured Materials, October 1998, Richmond, VA.

"Designed Syntheses of Intermetallic or Alloy Binary Metal Nanocomposites Using Single-Source Molecular Precursors," C. M. Lukehart, D. L. Boxall, J. P. Carpenter, J. D. Corn, F. E. Jones, III, W. D. King, S. B. Milne and S. R. Stock, American Chemical Society, Southeast Regional Meeting, November, 1998, Research Triangle Park, NC.

"Pt-Ru and Pt-Sn/Vulcan Carbon Nanocomposites of Controlled Stoichiometry Prepared from Single-Source Molecular Precursors as DMFC Anode Catalysts," D. L. Boxall, J. D. Corn, F. E. Jones, III, W. D. King and C. M. Lukehart, 1998 Fuel Cell Seminar, November 1998, Palm Springs, CA.

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"Preparation and Characterization of a Pt_1Ru_1/Graphitic Carbon Nanofiber Nanocomposite Using a Single-Source Molecular Precursor," C. M. Lukehart and E. S. Steigerwalt, American Chemical Society, 218th National Meeting, August 1999, New Orleans, LA.

"Synthesis of Compounds Containing Pt_xMo_y-core Stoichiometries and the Preparation of Carbon-Supported Metal Alloy Nanoparticles," C. M. Lukehart and K. C. Kwiatkowski, American Chemical Society, 218th National Meeting, August. 1999, New Orleans, LA.

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"Preparation of Binary Metal Alloy/Carbon Nanocomposites Using Single-Source Molecular Precursors," C. M. Lukehart, D. L. Boxall, J. D. Corn, M. Hariharasarma, W. D. King, K. C. Kwiatkowski, E. S. Steigerwalt, and E. A. Kenik, American Chemical Society, 51st Southeast Regional Meeting, October 1999, Knoxville, TN.

"Binary Alloy/Carbon Nanocomposites Using Single-Source Molecular Precursors," Charles. M. Lukehart, Second Annual Southern Illinois Materials Chemistry Conference, October 1999, Carbondale, IL.

"On-Particle EDS Analysis of PtRu/C DMFC Catalysts Using High-Resolution TEM," Deborah L. Boxall, Charles M. Lukehart, and Edward A. Kenik, 1999 ASME International Mechanical Engineering Congress and Exposition, November 1999, Nashville, TN.

"On-Particle EDS Analysis of Bimetallic, Carbon-Supported Catalysts," Deborah L. Boxall, Edward A. Kenik, and Charles M. Lukehart, Materials Research Society, 1999 Fall National Meeting, November 1999, Boston, MA.

"Metal/Carbon Nanocomposites: An Update," C. M. Lukehart, Ninth Annual Workshop of the Consortium for Nanostructured Materials, September 2000, Richmond, VA.

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"A Platinum-Ruthenium/graphitic Nanofiber Nanocomposite Exhibiting High Performance in Methanol Electrooxidation," E. S. Steigerwalt, G. A. Deluga, and C. M. Lukehart, American Chemical Society, 52nd Southeast/56th Southwest Joint Regional Meeting, December 2000, New Orleans, LA.

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"Preparation of Os/Carbon and Os_1Pt_1/Carbon Nanocomposites as Direct Methanol Fuel Cell Anode Catalysts," Joshua T. Moore, C. M. Lukehart, G. Deluga, and D. Chu, American Chemical Society, 222nd National Meeting, August 2001, Chicago, IL.

"Preparation of Bismuth and Bismuth Alloy Nanocomposites from Mixed-Metal Gel Precursors," Joshua T. Moore and C. M. Lukehart, American Chemical Society, 222nd National Meeting, August 2001, Chicago, IL.

(d) Manuscripts submitted, but not yet published

"Synthesis and Characterization of PtSn/Carbon and Pt_3Sn/Carbon Nanocomposites as Methanol Electrooxidation Catalysts," Frank E. Jones, III, Stephen B. Milne, Bogdan Gurau, Eugene S. Smotkin, Stuart R. Stock, and C. M. Lukehart, **J. Nanosci. Nanotech.**, in press.

"Synthesis of PtSn/Carbon Nanocomposite Using trans-$PtCl(PEt_3)_2(SnCl_3)$ as a Source of Metal," Deborah L. Boxall, Edward A. Kenik, and C. M. Lukehart, **Chem. Mater.**, in press.

"Synthesis and Characterization of a Pt-Os/Carbon Nanocomposite for Methanol Electrooxidation," Joshua T. Moore, Deryn Chu, Rongzhong Jiang, Gregg A. Deluga, and C. M. Lukehart, **J. Phys. Chem. B**, submitted for publication.

"Formation of Bi-Sb, Bi-Sn, and Bi-Sb-Sn Nanoclusters in Silica Xerogel Matrices from Mixed-Metal Oxide Precursors," Joshua T. Moore and Charles M. Lukehart, **J.Cluster Sci.,** submitted for publication.

"Synthesis and Characterization of Os/Carbon Nanocomposites and Reactivity in Methanol Electrooxidation," Joshua T. Moore, Deryn Chu, Rongzhong Jiang, Gregg A. Deluga, and C. M. Lukehart, **Chem. Mater.**, submitted for publication.

"Rapid Preparation of Pt-Ru/Graphitic Carbon Nanofiber Nanocomposites Using Microwave Irradiation: A DMFC Anode Catalyst of High Relative Performance," Eve S. Steigerwalt, Gregg A. Deluga, and C. M. Lukehart, **J. Catal.,** submitted for publication.

(e) Technical reports:

(a) "ARO Interim Progress Report," 1 June 1998 - 31 December 1998

(b) "ARO Interim Progress Report," 1 January 1999 - 31 December 1999

(c) "ARO Interim Progress Report," 1 January 2000 - 31 December 2000

(7) List of all Participating Scientific Personnel (employed or unemployed)

Angela D. Anderson (graduate student)
Deborah L. Boxall (graduate student)
Krzysztof C. Kwiatkowski (graduate student)
Eric D. Mowles (graduate student)
Eve S. Steigerwalt (graduate student)
Joshua T. Moore (graduate student)
Lisa M. Baker (graduate student)
Jiang Li (graduate student)

Degrees Awarded During Project Period:

2000	Boxall, Deborah L.	"Preparation of Carbon-Supported, Bimetallic Nanocomposites From Single-Source Molecular Precursors." (Ph.D.)
2000	Anderson, Angela D.	"Synthesis and Characterization of a PtRe Single-Source Molecular Precursor and Nano-composite." (M.S.)
2000	Kwiatkowski, Krzysztof C.	"New Bimetallic Catalysts for Direct Methanol (DMFC) and Proton Exchange Membrane (PEM) Fuel Cells." (Ph.D.)
2001	Eric D. Mowles	"Surface Functionalization of VGCNFs with Pendant Amino Groups" (M.S.)
2001	Eve S. Steigerwalt	"Preparation and Characterization of Novel Nanocomposite Materials" (Ph.D.)

(8) Report of Inventions

"Polymetallic Precursors and Compositions and Methods for Making Supported Polymetallic Nanocomposites," U.S. Patent 6,232,264, issued May 15, **2001** (40 pages).

(9) Bibliography

See publication citations above.

(10) Appendixes

Not applicable.

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