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.
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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:


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


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


(d) Manuscripts submitted, but not yet published


(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    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


(9) Bibliography

See publication citations above.

(10) Appendixes

Not applicable.
MEMORANDUM OF TRANSMITTAL

March 4, 2002
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Sincerely,

Charles M. Lukehart