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During the duration of this contract we have explored a variety of aspects of a general theme. The general theme is that of "ultrathin film composite membranes." Such membranes resulted from the need to make membranes-based separations that show high chemical selectivity yet also show high permeant flux. We have shown in the AFOSR work that these two goals (usually mutually exclusive) can be achieved and are quite useful in a variety of areas including chemical sensors and electrochemistry

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FINAL TECHNICAL REPORT

for Period 1 April 1993 to 31 March 1994

"ELECTROCHEMICAL SYNTHESIS OF ULTRATHIN FILM COMPOSITE MEMBRANES"

by

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Colorado State University
Ft. Collins, CO 80523

19 August 1994

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FINAL TECHNICAL REPORT

This is the final report for the AFOSR sponsored research project, "Electrochemical Synthesis of Ultrathin Film Composite Membranes," AFOSR-90-0282. This report summarizes progress made during the period April 1, 1993, to March 31, 1994.

I. Summary. During the duration of this contract we have explored a variety of aspects of a general theme. The general theme is that of "ultrathin film composite membranes." Such membranes resulted from the need to make membranes-based separations that show high chemical selectivity yet also show high permeant flux. We have shown in the AFOSR work that these two goals (usually mutually exclusive) can be achieved and are quite useful in a variety of areas including chemical sensors and electrochemistry.

II. Body. We have shown that the ultrathin film composite membrane concept is useful in a variety of new areas. These include:

1. A new way to make chemical sensors.
2. A new way to make electronically conductive composite membranes.
3. A new method for making coated hollow fibers for chemical separations.
4. A new way to couple electron and ion-transport across membranes.

These various new applications of this concept are described in the 15 papers published as a part of this work. This high level of scientific productivity points to the general importance of this idea. What we have, in essence, done is taken an idea that was generally thought of being in the purview of only one area and expanding it to a number of new and, heretofore, unimagined areas. Hence, we have cross-fertilized several different research areas. Some of this work is reviewed below:

A. New Conductive Composites. Fluropolymers have many highly-beneficial properties such as tremendous chemical and thermal stability, good mechanical properties, and good chemical processibility. These polymers are, however, electronic insulators with extremely high resistivity. We have been exploring the possibility of preparing composite membranes consisting of a fluoropolymer support and an electronically conductive polymer coating. If such composites could be prepared, they would combine the good attributes of the fluoropolymers (see above) with the electronic conductivity of the conductive polymers.

The potential pitfall in preparing composites based on fluoropolymers and conductive polymers is that the surface energy of the fluoropolymer is so low that the conductive polymer film will not stick to it. We have developed a novel approach for solving this problem. We first coat the fluoropolymer surface with a thin film of the perfluorosulfonate polymer Nafion.® Because both polymers are fluoropolymers, adhesion is good. We then use our interfacial polymerization method to coat the Nafion® film with the conductive polymer polypyrrole.

Because Nafion® is polyanionic and polypyrrole is polycationic, adhesion between the two is extremely good. In this way we have succeeded in preparing novel, highly-conductive fluoropolymer/conductive polymer composite membranes.

B. Membrane-Based Separations and Coated Hollow Fibers. We have been exploring the idea of using electronically conductive polymers as chemically-selective layers in membrane-based chemical separations. We are exploring the gas-transport properties of these polymers, and we are investigating the possibility of using these polymers in pervaporation separations. The interfacial polymerizations we have developed are used to prepare ultrathin films of conductive polymers for these investigations.

One of the most important breakthroughs was in developing interfacial polymerizations to coat hollow fiber membranes with ultrathin films of conductive polymers. Such coated hollow fibers have myriad potential applications in sensors, gas-separations, electrodialysis, pervaporation-separations, etc. We are continuing this research effort by exploring in particular sensor and pervaporation applications of these coated hollow fibers.

III. Status of Research. We are continuing this general line of research through research grants from private industry (e.g. Dow Chemical). Hence, this is a good example of DOD-sponsored research being incorporated into the industrial private sector.

IV. Research Articles.

1. Lei, J.; Menon, V. P.; Martin, C. R. "Chemical Preparation of Conductive Polypyrrole-Polytetrafluorothene Composites," Polymers for Advanced Technologies, **1993**, 4, 124-132.

2. Van Dyke, L. S.; Kuwabata, S.; Martin, C. R. "A Simple Chemical Procedure for Extending the Conductive State of Polypyrrole to More Negative Potentials," submitted, J. Electrochem. Soc., **1993**, 140, 2754-2759.

3. Martin, C. R.; Liang, W.; Menon, V.; Parthasarathy, R.; Parthasarathy A. "Electronically Conductive Polymers as Chemically-Selective Layers for Membrane-Based Separations," Synth. Met., **1993**, 55-57, 3766-3773.

4. Lawson, D. R.; Liang, W.; Martin, C. R. "Inorganic and Biological Electron Transfer Across an Electronically Conductive Composite Polymer Membrane," Chem. Mater., **1993**, 5, 400-402.

5. Martin, C. R.; Parthasarathy, R.; Menon, V. "Template Synthesis of Electronically Conductive Polymers - A New Route for Achieving Higher Electronic Conductivities," Synth. Met., **1993**, 55-57, 1165-1170.

6. Feldheim, D. L.; Lawson, D. R.; Martin, C. R. "Influence of the Sulfonate Countercation on the Thermal Stability of Nafion® Perfluorosulfonate Membranes," J. of Polymer Science, Part B: Polymer Physics, **1993**, 31, 953-957.

7. Colón, J. L.; Martin, C. R. "Luminescence Probe Studies of Ionomers. 3. Distribution of Decay Rate Constants for Tris Bipyridyl Ruthenium(II) in Nafion Membranes," Langmuir, **1993**, 9, 1066-1070.

8. Martin, C. R.; Lawson, D. R.; Liang, W. "Concerted Ion and Electron Transfer Across Electronically Conductive Polymer Membranes," Proceedings of the Materials Research Society Symposium on Polymer Electrolytes and Electrodes, Boston, Massachusetts, **1993**, 293, 153-157.

9. Martin, C. R.; Ballarin, B.; Brumlik, C. J.; Lawson, D. R. "Biosensors Based on Ultrathin Film Composite Membranes," Diagnostic Biosensor Polymers (Arthur Usmani and Naim Akmal, editors) ACS Books, Washington, DC, **1994**, 158-168. (Ch 13).

10. Van Dyke, L. S.; Brumlik, C. J.; Liang, W.; Lei, J.; Martin, C. R.; Yu, Z.; Li, L.; Collins, G. J. "Modification of Fluoropolymer Surfaces with Electronically Conductive Polymers," Synth. Met., **1994**, 62, 75-81.

11. Martin, C. R.; Foss, C. A., Jr. "Chemically Modified Electrodes" in "Laboratory Techniques in Electroanalytical Chemistry," P. T. Kissinger and W. R. Heineman, Editors, **1994**, in press.

12. Brumlik, C. J.; Parthasarathy, A.; Chen, W.-J.; Martin, C. R. "Plasma Polymerization of Sulfonated Fluorochlorocarbon Ionomer Films," J. Electrochem. Soc., **1994** accepted.

13. Parthasarathy, A.; Brumlik, C. J.; Martin, C. R.; Collins, G. E., "Interfacial Polymerization of Thin Polymer Films onto the Surface of a Microporous Hollow-Fiber Membrane," J. of Membr. Sci., **1994**, in press.

14. Chen, W.-J.; Martin, C. R., "Gas-Transport Properties of Sulfonated Polystyrenes," J. Membr. Sci., **1994**, accepted.

15. Aranda, P.; Chen, W.-J.; Martin, C. R. "Water Transport Across Polystyrenesulfonate/Alumina Composite Membranes," J. Membr. Sci., **1994**, submitted.

V. Participating Professionals.

A. Post docs, graduate students and other collaborators:

1. Leon Van Dyke
2. Del R. Lawson
3. Charles J. Brumlik
4. Wen-Janq Chen
5. Arvind Parthasarathy
6. Wenbin Liang

7. Barbara Ballarin

8. Venod Menon

9. Ranjani Parthasarathy

10. Daniel L. Feldheim

11. Jorge Colón

12. Junting Lei

13. George J. Collins

14. Z. Yu

15. Susumu Kuwabata

16. J. D. Klein

17. Michael J. Sailor

B. Degrees Granted:

1. Arvind Parathasarathy, "Oxygen Reduction at the Platinum/Nafion® Interface," Ph. D.

V. Interactions. Lectures presented:

1. "Electrochemistry and Electro-organic-chemistry," Schering-Plough Research Institute, Union, New Jersey, May 13, 1994.

2. "Conductive Polymer Microstructures--Synthesis and Applications," National ACS meeting, San Diego, California, March 14, 1994.

3. "Nanomaterials--A Membrane Based Approach," University of Utah, Salt Lake City, Utah, March 3, 1994.

4. "Nanomaterials--A Membrane Based Approach," Utah State University, Logan, Utah, March 2, 1994.

5. "Nanomaterials--A Membrane Based Approach," University of Puerto Rico, Rio Piedras, Puerto Rico, February 14, 1994.

6. "Nanochemistry and Nanomaterials," Southwest Analytical Professors' meeting, Fresno, California, January 22, 1994.

7. "Fabrication and Electrochemical Characterization of Ensembles of Nano-Disk Electrodes with Disk Diameters as Small as 100 Å," Gordon Conference on Electrochemistry, Ventura, California, January 19, 1994.

8. "Gas Transport Properties of Electronically Conductive Polymers and Related Materials," Dow Chemical, Michigan, November 12, 1993.

9. "Template Synthesis of Electronically Conductive Polymers," International Society of Electrochemistry, Berlin, GERMANY, September 5-10, 1993.

10. "Nanomaterials," National Renewable Energy Laboratory, Golden, Colorado, August 18, 1993.

11. "Membrane-based Separations with Electronically Conductive Polymers," Gordon Conference on Membranes: Materials and Processes, Plymouth State College, New Hampshire, August 1-6, 1993.

12. "Nanochemistry--A Membrane-Based Approach," University of Cincinnati, Cincinnati, Ohio, July 29, 1993.

VII. New Discoveries. During the course of this grant we have made many new discoveries. These include new ways to make sensors, conductive composites, coated hollow fibers and composite membranes.

VIII. Statement for Program Manager. While the AFOSR contract has terminated, aspects of this research has been funded and will continue with support from private industry.