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As noted in the previous technical report, we are interested in using interfacial polymerization to synthesize ultrathin film composite membranes based on electronically conductive polymers. During the previous year of AASERT fundir' we have expanded on this idea in a number of ways. We have done such interfacial polymerizations to make new composites for membrane-based separations, and to make novel coated-hollow-fiber membranes.

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Contract AFOSR-AASERT-92

ANNUAL TECHNICAL REPORT

for Period 1 June 1993 to 31 May 1994

"Anionically-Conductive Ultrathin Film Composite Membranes"

by

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Ft. Collins, CO 80523

ANNUAL TECHNICAL REPORT

This is the annual report for the AFOSR-AASERT-92 sponsored research project - "Anionically-Conductive Ultrathin Film Composite Membranes." This report summarizes progress made during the period June 1, 1993 to May 31, 1994.

I. Summary. As noted in the previous technical report, we are interested in using interfacial polymerization to synthesize ultrathin film composite membranes based on electronically conductive polymers. During the previous year of AASERT funding we have expanded on this idea in a number of ways. We have done such interfacial polymerizations to make conductive composite membranes, to make new composites for membrane-based separations, and to make novel coated-hollow-fiber membranes. These various advances on the central theme of the AASERT report are described in the 15 articles published under the AASERT grant. In addition this work is reviewed here.

II. Body. The ultrathin film composite membrane concept we have been exploring is extremely powerful. In the AASERT funded research we are taking it into many new dimensions. Some of these new dimensions will be reviewed here. Details can, of course, be found in the 15 papers published as part of this work.

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. The work on interfacial polymerization of ultrathin electronically conductive polymer films has opened many doors. We have reviewed some here and in our various research papers. We are now following up on these exciting research opportunities. Areas of particular emphasis are in novel biosensors and novel membranes for pervaporation separations.

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. We have discovered new ways to prepare new conductive composite membranes and new coated hollow fibers for sensors and membrane-based chemical separations.

VIII. Statement for Program Manager. The general concept of developing interfacial polymerizations for forming conductive polymer composites is proving to be quite fruitful. This new concept has opened a number of doors in membrane research and technology.