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13. ABSTRACT (Maximum 200 words)

This report summarizes the results obtained during four years (1987-1991) of research directed at the development of novel, polymeric coatings for electrode surfaces. The coating materials consisted of various polyelectrolytes based on functionalized polysiloxanes, newly synthesized block and random copolymers and commercially available Nafion. Coatings prepared from these materials were examined experimentally to assess their abilities to retain electroactive counterions incorporated within their structures and to provide efficient ionic and electronic conduction pathways across the coatings. The permselectivities of some coatings were tested under both static (no current found) and dynamic (with current flow) conditions. A new model to account for the unusual diffusive behavior of countercations in Nafion coatings was proposed and tested experimentally. The mobilities and counter-ion binding equilibria for a set of soluble polyelectrolytes was examined and new methods developed for evaluation of their diffusion coefficients. The coatings were tested for possible applications in electrocatalysis, electrosynthesis and electroanalysis.

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FINAL REPORT

FUNDAMENTAL PROCESSES OCCURRING AT ELECTRODES

The research being summarized was conducted during the period between July 1987 and July 1991. The primary focus of the research was on the synthesis and testing of various polyelectrolytic materials as coatings for electrode surfaces. A major objective was the development of improved types of electrode coatings for electrocatalytic, electrosynthetic and electroanalytical applications. The most notable results, all of which have been presented in the list of publications included later in this Report, included:

1. A comparison of ionic and electronic charge propagation rates in block and random copolymer coatings.
2. A description of the role of Donnan equilibrium in controlling the behavior of Nafion coatings on electrodes.
3. The synthesis and testing of new types of polyelectrolytic coatings based on functionalized polysiloxanes.
4. The preparation of a polysiloxane functionalized with a half-quaternized 4,4'-bipyridine group to examine metal ion binding by both electrostatic and coordinative interactions in a single coating.
5. Measurements of differences in mass transport rates of ionic complexes incorporated in polyelectrolyte coatings.
6. Demonstration of the dynamic consequences of ionic permselectivity in polyelectrolyte coatings on electrodes.
7. The development of a new theoretical model for the behavior of strongly bound counterions in Nafion coatings on electrodes and a comparison of the predictions of the model with experimental results.
8. A series of related studies of the association of soluble polyelectrolytes with electroactive counterions in solution as a means for measuring both equilibrium association constants and diffusion coefficients of the polyelectrolytes.

PUBLICATIONS RESULTING FROM THE RESEARCH

Structural Efects on the Elecrochemical Behavior of Redox Couples Incorporated in Electrode Coatings Prepared from Copolymers and Composites
Takeshi Inoue and Fred C. Anson
J. Phys. Chem., 91, 1519 (1987)

Electropolymerization of Ruthenium Bis(1,10-phenanthroline)(4-methyl-4'-vinyl-2,2'-bipyridine) Complexes through Direct Attack on the Ligand Ring System
Thomas F. Guarr and Fred C. Anson
J. Phys. Chem., 91, 4037 (1987)

Permselectivities of Polyelectrolyte Electrode Coatings as Inferred from Measurements v th Incorporated Redox Probes or Concentration Cells
Jody Redepenning and Fred C. Anson
J. Phys. Chem., 91, 4549 (1987)

Poly(2-vinylpyrazine) as a Soluble Polymeric Ligand and as an Electrode Coating. Reactions with Pentacyanoferrate(II)
Paolo Ugo and Fred C. Anson
Anal. Chem., 61, 1799 (1989)

Electrodeposition of Polyelectrolyte-Metal Complexes
Manshi Ohyanagi and Fred C. Anson
J. Electroanal. Chem., 258, 469 (1989)

Electrochemical Behavior of Electroactive Counter-Ions in Solutions of Polyelectrolytes
Manshi Ohyanagi and Fred C. Anson
J. Phys. Chem., 93, 8377 (1989)

Dynamic Consequences of Ionic Permselectivity. Rapid Ejection from Nafion Coatings of Anions Generated Electrochemically from Cationic Precursors
Ching-Fong Shu and Fred C. Anson
J. Am. Chem. Soc., 112, 9227 (1990)

Asscciation of Electroactive Counterions with Polyelectrolytes. 2. Comparison of Electrostatic and Coordinative Bonding to a Mixed Polycation-Polypyridine
Junya Kobayashi and Fred C. Anson
J. Phys. Chem., 95, 2595 (1991)

Ion Association and Electric Field Effects on Electron Hopping in Redox Polymers. Application to the $Os(bpy)_3^{3+/2+}$ Couple in Nafion
F. C. Anson, D. N. Blauch, J.-M. Saveant and C.-F. Shu
J. Am. Chem. Soc., 113, 1922 (1991)

Association of Electroactive Counterions with Polyelectrolytes. 3. Electrochemistry of Cationic Counterions Associated with Polystyrene-sulfonate
R. Jiang and F. C. Anson
J. Phys. Chem., 95, 5701(1991)

Effects of Interconversion and Electron Transfer on Voltammetric Responses for Two-component Systems with Differing Diffusion Coefficients
D. N. Blauch and F. C. Anson
J. Electroanal. Chem., 309, 313 (1991)

Time Resolved Measurement of Equilibrium Surface Tensions at the Electrified Mercury-Aqueous NaF Interphase by the Method of Wilhelmy
Donald D. Montgomery and Fred C. Anson
Langmuir, 7, 1000 (1991)

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Jody Redepenning (Postdoctoral Research Fellow)
Ching-Fong Shu (Postdoctoral Research Fellow)
Paolo Ugo (Visiting Associate)

The research did not lead to any inventions.

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