Project ID: **65409**

Project Title: **Electroactive Materials for Anion Separation - Technetium from Nitrate**

Lead Principal Investigator:

Dr. Johanes H. Sukamto
Senior Research Engineer
Pacific Northwest National Laboratory
MSIN K8-93
P. O. Box 999
Richland, Washington 99352
Telephone: 509-373-1473
e-mail: johanes.sukamto@pnl.gov

Co Principal Investigators:

Dr. James McBreen
Brookhaven National Laboratory
P.O. Box 5000
Upton New York 11973
Telephone: 516-344-4513
e-mail: jmcbreen@bnl.gov

Dr. William H. Smyrl
Professor
Corrosion Research Center
University of Minnesota
112 Amundson Hall
221 Church Street, S.E.
Minneapolis Minnesota 55455
Telephone: 612-625-0717
e-mail: smyrl001@maroon.tc.umn.edu

Electroactive Materials for Anion Separation – Technetium from Nitrate

(First Year of Funding: 1998)

Principal Investigators (Pacific Northwest National Laboratory)

Johanes H. Sukamto
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K8-93
Richland, WA 99352
(509) 373-1473 (phone)
johanes.sukamto@pnl.gov

Scot D. Rassat
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K6-28
Richland, WA 99352
(509) 376-1410 (phone)
sd.rassat@pnl.gov

Timothy L. Hubler
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K8-93
Richland, WA 99352
(509) 373-0249 (phone)
tim.hubler@pnl.gov

Gregory M. Anderson
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K8-93
Richland, WA 99352
(509) 376-1410 (phone)
Gregory.Anderson@pnl.gov

Michael A. Lilga
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K2-12
Richland, WA 99352
(509) 375-4354 (phone)
mike.lilga@pnl.gov

Principal Investigator (University of Minnesota)

William H. Smyrl
Corrosion Research Center
Department of Chemical Engineering and Materials Science
University of Minnesota, Minneapolis
221 Church Street SE
Minneapolis, MN 55455
(612) 625-0717 (phone)
smyrl001@maroon.tc.umn.edu

Principal Investigators (Brookhaven National Laboratory)

James McBreen
Brookhaven National Laboratory
DAS, Bldg. 480
Upton, NY 11973
(516) 344-4513 (phone)
jmcbreen@bnl.gov

Research Objectives

The focus of the project is to develop a fundamental understanding of how the physical and chemical properties of electroactive ion exchange (EaIX) materials control their efficiency when used as mass separation agents. Specifically, the desirable characteristics of EaIX materials for separation applications are 1) high reversibility, 2) high selectivity, 3) acceptable physical and chemical stability, 4) rapid intercalation and de-intercalation rates, and 5) high capacity. Because of these requirements, EaIX materials share many properties in common with conventional ion exchangers and electroactive polymers. For example, EaIX materials require the selectivity typically found in ion exchangers; they also require the redox reversibility of electroactive polymers. The results of this work will allow the rational design of new materials and processes tailored for the separation of specific anions.

The specific objectives and their relevance are discussed. The first three objectives address specific material properties, and the last objective explores the scientific issues related to the preparation of high-capacity EaIX material.

1. Determine the effects of the distribution/concentration and mobility of electroactive sites. A high concentration of electroactive sites is favorable for high capacity and fast electronic propagation through the material. However, increased site-to-site interactions can also be expected, which may reduce the intercalation rate and the utilization efficiency. Increasing the mobility of the electroactive sites will enhance charge propagation rates without increasing the site concentration.

2. Determine the effects of branching/cross-linking. Cross-linking makes the polymer less prone to swell. This can increase the selectivity for anions with lower hydration energy. Less swelling may also enhance the stability to delamination. But increased cross-linking can also reduce the penetrability of the polymer to all anions in addition to restricting segmental motion, which will, in turn, reduce the capacity and transport rates.

3. Determine the effects of polymeric chain length or molecular weight. A higher molecular weight polymer has an overall lower free energy of sticking to the electrode surface (provided that each segment is hydrophobic), and therefore, it is more stable. On the other hand, long polymeric chain length may result in entanglements. Entanglements may lead to restricted segmental motion and reduced free volume required for counter-ion diffusion. Ultimately, the intercalation/de-intercalation rates are reduced. Restricted segmental motion can also result in increased site-to-site interactions, which, as before, may reduce the intercalation rate and utilization efficiency.

4. Prepare and characterize high-surface-area EaIX materials using aerogel and phase-inversion techniques. If high-surface-area (based on the geometric or projected surface area) materials can be prepared, increased efficiency can be realized.

Problem Statement

Many contaminants of interest to the U.S. Department of Energy (DOE) exist as anions. These include the high-priority pollutants chromate, pertechnetate, and nitrate ions. In addition, there are also industrial and urban applications where the separation of anionic species from aqueous streams is critical.

Examples include industrial water recycle and waste water treatment (e.g., chloride ion removal for the pulp and paper industry, borate ion in the chemical and nuclear industries) and drinking water and agricultural waste treatment (e.g., nitrate removal).

In the proposed research, technetium is chosen as the target pollutant. Because of its half-life of 213,000 years, technetium (^{99}Tc) presents a long-term hazard for waste disposal. Much of the ^{99}Tc in the tank wastes is present as pertechnetate (TcO_4^-), accounting for its high solubility and mobility in aqueous systems. Several sorbents are available for removing TcO_4^- from alkaline waste brines, but each has important drawbacks. The use of commercial ion exchange (IX) resins to extract TcO_4^-, e.g., Reillex™-HPQ (Reilly Industries) and ABEC 5000 (Eichrom Industries), generates significant secondary waste. The elution of TcO_4^- from Reillex™-HPQ resins requires either concentrated nitric acid or a concentrated caustic solution of ethylene-diamine containing a small amount of tin chloride. This eluant has a short shelf life requiring frequent preparation, and the ^{99}Tc is delivered in a complexed, reduced form. While TcO_4^- can be eluted from ABEC 5000 resins using de-ionized water, the much-reduced capacity of ABEC 5000 resins in comparison to the Reillex™-HPQ resins leads to a low column capacity. In general, unwanted secondary wastes are generated because 1) the only effective eluant happens to be hazardous and/or 2) the IX material has a low capacity or selectivity for the target ion, resulting in more frequent elution and column replacements.

Alternative IX materials that have high capacities, can be regenerated easily, and are highly selective for TcO_4^- would avoid these problems. EaIX media meet these criteria. Such an IX system uses electrically induced changes in the media to expel sorbed ions through a charge imbalance rather than requiring chemical eluants to “strip” them. Therefore, this medium eliminates the need to prepare, store, and dispose of many of the process chemicals normally required for IX operations.

Research Progress and Implications

The two main activities of the project are 1) synthesis and characterization of EaIX polymers and 2) determination of the resulting EaIX characteristics. Briefly, effects of electroactive site density and mobility, polymer chain length, and degree of cross-linking will be systematically explored by synthesizing 1) polymers of polyvinylferrocene (PVF) and 2) polymers obtained through the polymerization of vinyl ether monomers. PVF is chosen because it has been widely studied, it is widely accepted as one of the model redox polymers, and it promises to extract TcO_4^-. Both the molecular weight and cross-linking of PVF can be synthetically controlled. Copolymerization of PVF, e.g., with acrylonitrile and styrene, has also been reported, and this technique will be used to control the electroactive site density. The (vinyl ether)-based polymers are chosen because of the synthetic flexibility they afford to control the structural features listed above. High-surface-area electrodes will be prepared from both types of polymers using aerogel and phase-inversion techniques.

The EaIX characteristics of interest are reversibility, selectivity, stability, intercalation/ de-intercalation rates, and capacity. Conventional electrochemical methods (e.g., cyclic voltammetry and impedance) will be used to provide macroscopic characterization. Selectivity will be further characterized by in situ Raman and x-ray absorption spectroscopy. Correlation with morphology will be determined by means of Scanning ElectroChemical Microscopy-Topography (SECM-Topography) and Atomic Force Microscopy (AFM).

Synthesis and Characterization of EaIX Polymers

Progress has been made in both the synthesis and characterization of EaIX polymers. To date, we have initiated work in synthesizing cross-linking agents, preparing EaIX materials containing electro-active sites with varying mobility, post-polymerization cross-linking using a nitrogen plasma, and making large-surface-area, porous EaIX assemblies. For characterization of the polymers, we are developing the proper analytical techniques. Primarily we are examining the use of gel permeation chromatography (GPC), which uses a triple angle light-scattering detector in series with a concentration detector (in this case UV/Vis). We are analyzing data to determine if we can obtain reproducible molecular weight data for PVF polymers. Additionally, we are incorporating an Fourier transform infrared (FTIR) probe as we analyze the crude polymer mixtures. Hence, the entire system consists of a liquid chromatographic separation using a GPC column, with subsequent FTIR, UV/Vis, and triple-angle light-scattering detection of the separated polymer fractions. The FTIR analysis is used to characterize the chemical functionality of the polymers (e.g., the number of unpolymerized vinyl groups in the polymer can be detected).

Synthetic routes leading to enhanced cross-linking in PVF polymers are in progress. One method involves the use of 1,1'-divinylferrocene as a cross-linking agent. Because the preparation of this material is plagued by poor yields, a similar cross-linking material is also being considered whereby 1,1'-diacetylferrocene undergoes a Wittig reaction producing the propenyl analogue of 1,1'-divinylferrocene. The methyl groups should not cause undue steric hindrance of polymerization and cross-linking of the vinylferrocene polymers and yet may be easier to produce in high yield than the 1,1'-divinylferrocene itself. We anticipate that we will produce polymers incorporating these cross-linking agents during the fourth quarter of this fiscal year. In addition to these chemical routes for preparing cross-linked PVF, the use of plasma for post cross-linking PVF is also pursued. Here, PVF is prepared using conventional means; after depositing the PVF on an electrode surface (e.g., by means of spin coating), the PVF/electrode assembly is exposed to a plasma that is known to induce cross-linking. Preliminary results using a nitrogen plasma will be discussed below; additional gases of interest include argon.

Work to synthesize EaIX materials based on (vinyl ether)-based polymers has been initiated. The initial target is to synthesize materials with varying electroactive site mobility. Monomers containing ferrocene tethered to reactive vinyl groups by carbon chains of varying length are being prepared. These monomers are designed to produce polymers with varying mobility of the electroactive group by altering their distance from the rigid backbone. Progress has been made in preparing the desired monomers, but yields have been low. The reason for the low yield is known, and modified synthetic strategies are now being evaluated.

Electrodeposition of PVF onto conductive porous nickel substrates produced stable films, which demonstrated the same current densities as films deposited on flat electrodes. The current scaled with the amount of available surface area. Phase inversion, a solvent/non-solvent exchange process commonly used in membrane manufacture, yielded a powdery film with poor physical stability. Spray coating of PVF and carbon particles and evaporative coating of PVF on conductive porous substrates also yielded less stable products than PVF spin-coated onto flat electrodes. Difficulties encountered with the solvent/non-solvent exchange process are caused by the insufficiently low viscosity of the starting polymer solution. Attempts to increase the initial solution viscosity by increasing the polymer concentration and using thickening agents were not successful. Another alternative is to increase the MW of the polymer. To date, only commercial PVF has been used; according to the vendor (Polysciences, Inc.), it has an average MW of 50,000. The MW can be increased by 1) increasing the chain length, 2) cross-linking

shorter chains, or 3) a combination of the two. Possible use of both post-polymerization plasma cross-linked PVF and cross-linked PVF obtained from using cross-linking agents during the actual polymerization to prepare porous EaIX materials will be considered.

Determination of EaIX Characteristics

To date, we have made progress in developing standard experimental and data analysis procedures that will allow appropriate comparison of different EaIX materials. In addition, this will also aid in furthering fundamental understanding of the structure/property relationships of EaIX materials. As noted earlier, the EaIX characteristics of interest are reversibility, selectivity, stability, intercalation/ de-intercalation rates, and capacity.

Selectivity of PVF for ReO_4^- over NO_3^- has been verified. Electrochemical and gravimetric results of a PVF film potential cycled in solutions of 1) only NO_3^-, 2) only ReO_4^-, and 3) a mixture of NO_3^- and ReO_4^- are shown in Figures 1 and 2. The potential dependence of the current (CV), shown in Figure 1, shows that the oxidation and reduction of PVF is more facile in a solution of only ReO_4^- than in a solution of only NO_3^-. These results imply that ReO_4^- stabilizes the ferrocenium (Fc^+) cation to a higher degree than NO_3^-. Equivalently, the complex formation constant of the (Fc^+)(ReO_4^-) salt is larger than that of the (Fc^+)(NO_3^-) salt (see also Inzelt and Horányi 1986). Gravimetric measurement results shown in Figure 2 were obtained simultaneously with the electrochemical results shown in Figure 1. Comparison of the data shown in Figures 1 and 2 shows that oxidation of the PVF film is accompanied with an increase in mass loading (represented as a decrease in the fundamental frequency of the quartz crystal). Furthermore, more mass loading accompanies the oxidation of the PVF film in a solution of only ReO_4^-, which is consistent with the higher molecular weight of ReO_4^- as compared to NO_3^-. As detailed in Rassat et al. (1999), the data shown in Figures 1 and 2 can be used to calculate the separation factor, $\alpha_B^A = \dfrac{\overline{C}_A/\overline{C}_B}{C_A/C_B}$ with A = ReO_4^-, B = NO_3^-, C_i is the concentration in the bulk solution, and $\overline{C}_i$ is the concentration within the EaIX material. The average separation factor was determined to be 30 ± 20%. The use of x-ray photoelectron spectroscopy (XPS) (Zeng et al. 1988) to measure the amount of ions intercalated into PVF will be pursued; this will provide additional verification of the electrochemical and gravimetric measurements presented here.

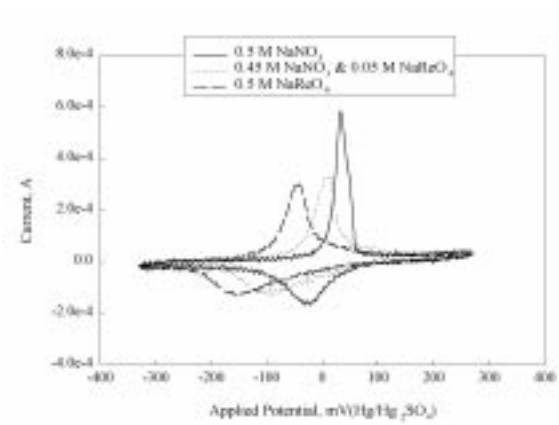

Figure 1. CVs of PVF in Different Solutions

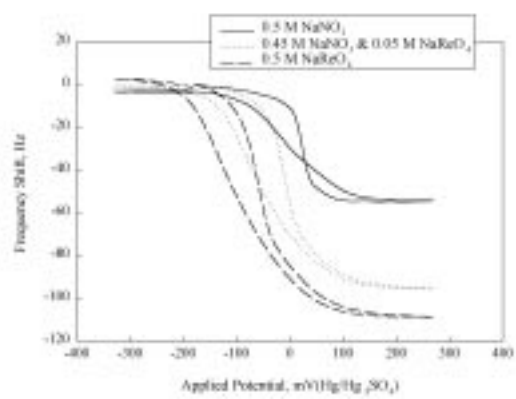

Figure 2. Measured Frequency Shifts Corresponding CVs in to Figure 1

To be of practical use, EaIX materials need to be both physically and chemically stable. Chemical instability of ferrocenes and possible means to overcome it under alkaline conditions have been reported (Chambliss et al. 1998, Clark et al. 1996), and we are currently investigating these issues as they pertain to PVF. Physical instabilities (e.g., caused by swelling/de-swelling of the PVF) during potential cycling are also issues that need to be addressed. The current-potential characteristics of a spin coated PVF film in 0.5 M $NaNO_3$ are shown in Figure 3 for the 3rd and 50th cycle. The integrated charge passed of the 50th cycle is 34% of that measured for the 3rd cycle. In contrast, a spin-coated PVF film that was exposed to a nitrogen plasma showed enhanced stability (see Figure 4); the charge measured in the 50th cycle is 62% of that measured for the 3rd cycle. The most likely explanation for the observed decrease in capacity with potential cycling (for both films) is the uncoiling and dissolution of individual PVF chains. PVF films typically swell during oxidation, and oxidation in the presence of highly hydrated anions, e.g., NO_3^-, will likely increase the degree of swelling. The degree of uncoiling and dissolution of individual PVF chains are likely to correlate directly with the degree of swelling. Exposure of a PVF film to a nitrogen plasma is expected to cross-link some of the chains, which, in turn, should reduce film swelling.

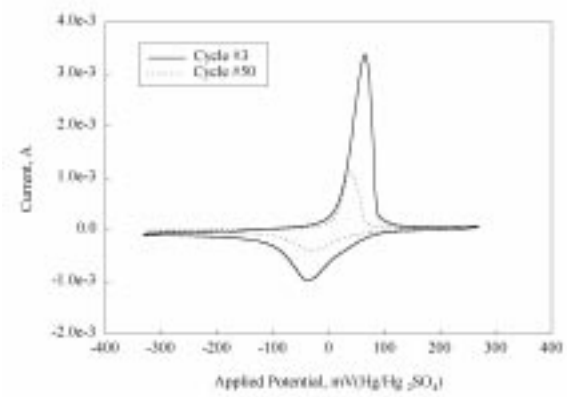

Figure 3. CVs of Spin-Coated PVF

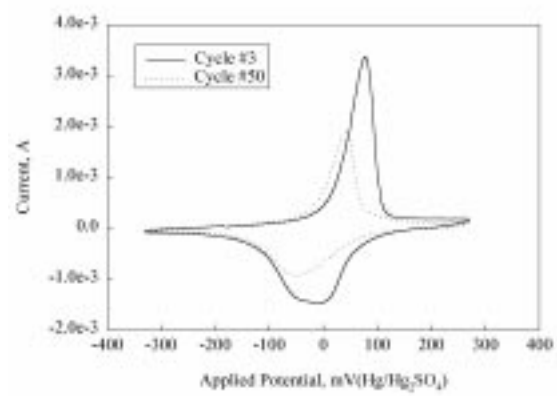

Figure 4. CVs of Plasma-Treated Spin-Coated PVF

Work has been initiated in developing techniques for obtaining good x-ray absorption (XAS) spectra for PVF under in situ conditions in an electrochemical cell. Early work was done on spin-coated films of PVF on sputtered platinum on glass slides. However, preliminary ex situ XAS studies on these films indicated that more concentrated samples were needed to obtain good XAS spectra. Electrochemical methods were developed to prepare samples with higher loadings per unit area. The most satisfactory method so far has been the electrodeposition of films on carbon cloth from solutions of 2 mM PVF in CH_2Cl_2 containing either 0.1 M tetrabutylammonium perchlorate or 0.1 M tetrabutylammonium perrhenate.

A special cell for in situ XAS was designed and built for XAS studies at both the Fe K edge and the Re L_3 edge. The cell materials were compatible with CH_2Cl_2, so electrode preparation could be done in the same cell. Both in ex situ and in situ XAS studies were done on PVF films that were electrodeposited on carbon cloth. Deposition was done, as noted earlier. Subsequent electrochemistry and in situ XAS were done in the same cell with 0.1 M NH_4ReO_4 or $LiCLO_4$ in water, or 0.1 M $TBAClO_4$ or $TBAReO_4$ in acetonitrile. Ex situ measurements were also done on films that were washed and dried after preparation.

Excellent in ex situ and in situ XAS spectra were obtained at the Fe K edge. Good ex situ XAS were obtained at the Re L_3 edge. However, soluble ReO_4^-, entrained in the electrolyte in the pores of the carbon cloth, interfered with the spectra. This problem requires a new design for the electrochemical cell that will permit electrolyte exchange while maintaining the electrode under potential control. XAS spectra were also obtained on several standard compounds such as various iron oxides, ferrocene, ferrocenium hexafluorophosphate, and ferrocenium tetrafluoroborate.

Figure 5 shows x-ray absorption near-edge spectrometry (XANES) spectra at the Fe K edge for ferrocene and ferrocenium hexafluorophosphate. The data show a shift in the absorption edge to higher energies for the ferrocenium hexafluorophosphate. The shift is due to an increase in the Fe oxidation state. The peak at about a step height of 0.7 was observed for both ferrocenium compounds. It is due to some electronic effect such as mixing of empty p and d states above the Fermi level.

Figure 6 shows in situ Fe XANES spectra for a PVF electrode in a 0.1 M solution of $TBAReO_4$ in acetonitrile at 0.0 V and 0.8 V vs. Ag/AgCl reference electrode. There is an edge shift at 0.8 V, indicating oxidation of the ferrocene moieties. However, the edge peak at a step height of 0.6 is less pronounced than that seen for the ferrocenium compounds. Figure 7 shows the FTIR of the Fe EXAFS at 0.0 and 0.8 V. The data have not yet been analyzed.

At present, we are trying to synthesize and purify ferrocenium perrhenate, which will be used as a model compound for analysis of the EXAFS.

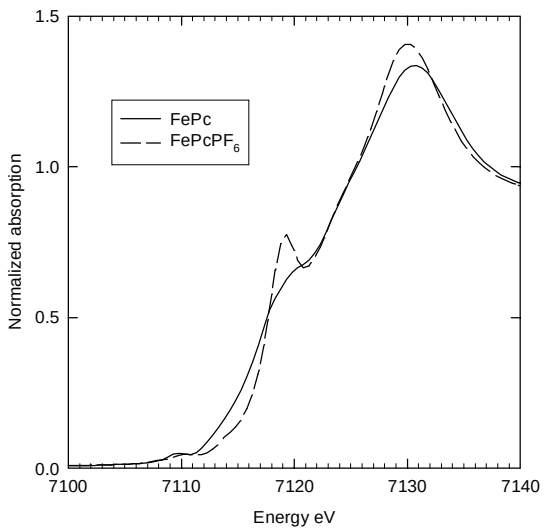

Figure 5. Fe XANES Spectra for Ferrocene and Ferrocenium Hexafluorophosphate

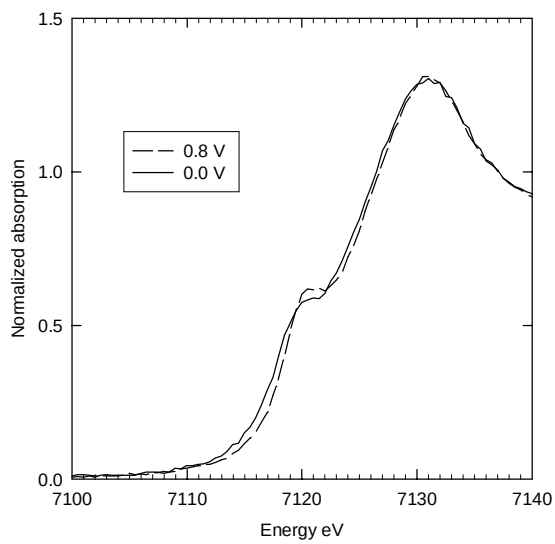

Figure 6. In situ Fe XANES Spectra for a PVFc Electrode in a 0.1 M Solution of $TBAReO_4$ in Acetonitrile at 0.0 V and 0.8 V Versus Ag/AgCl Reference Electrode

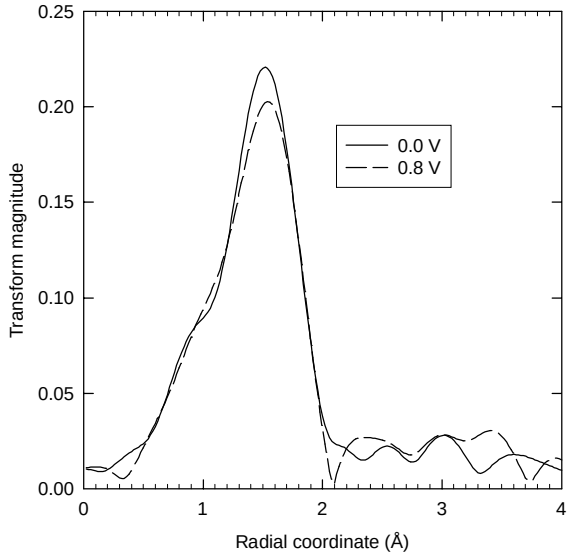

Figure 7. FTIR of In Situ Fe XANES Spectra for PVFc in 0.1 M Solution of $TBAReO_4$ in Acetonitrile at 0.0 V and 0.8 V Versus Ag/AgCl Reference Electrode

Planned Activities

As noted above, plasma and chemically cross-linked PVF will be prepared and characterized. Preparation of EaIX with varying electroactive site mobility will also continue. To understand better how the swelling/ de-swelling processes (that accompany the oxidation/reduction processes) of the PVF films lead to uncoiling/delamination of the films, experimental methods that are more sensitive to morphological changes will be used (e.g., ellipsometry or AFM). Chemical stability studies of PVF in alkaline solutions will be undertaken. More specifically, the degradation mechanism/products of PVF caused by potential cycling in alkaline solutions need to be determined. If PVF degrades in the same manner as ferrocenes, then stabilization strategies (e.g., alkylation) that have been successful for ferrocenes can be expected to work for PVF as well. XANES analysis will also be pursued, as outlined.

Publications and Presentations

Hubler TL, GM Anderson, JH Sukamto, MA Lilga, and SD Rassat. "Polyvinylferrocene (PVF) polymers as electroactive ion-exchange materials for separation of pertechnetate ion from high nitrate ion containing wastes: Issues and synthetic strategies." Abstract submitted to the 218th ACS National Meeting, August 22-26, 1999, New Orleans.

Gronda AM and WH Smyrl. "High capacity electroactive polymers for radioactive waste removal." Abstract submitted to the 196th Electrochemical Society Meeting, October 17-22, 1999, Honolulu.

References

Chambliss CK, MA Odom, CML Morales, CR Martin, and SH Strauss. 1998. "A strategy for separating and recovering aqueous ions: Redox-recyclable ion-exchange materials containing a physisorbed, redox-active, organometallic complex." *Analytical Chemistry* 70:757.

Clark JF, DL Clark, GD Whitener, NC Schroeder, and SH Strauss. 1996. "Isolation of soluble ^{99}Tc as a compact solid using a recyclable, redox-active, metal-complex extractant." *Environmental Science & Technology* 30:3124.

Inzelt G, and G. Horányi. 1986. "Combined cyclic voltammetric and radiometric study of polymer film electrodes." *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 200:405.

Rassat SD, JH Sukamto, RJ Orth, MA Lilga, and RT Hallen. 1999. "Development of an electrically switched ion exchange process for selective ion separation." *Separation and Purification Technology* 15:207.

Zeng X, S Moon, S Bruckenstein, and AR Hillman. 1998. "XPS study of counterion incorporation into poly(vinylferrocene)." *Analytical Chemistry* 70:2613.