

Project Title: Electroactive Materials for Anion Separation – Technetium from Nitrate

Project ID Number: 81912

Publication Date: June 23, 2003

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Progress Report

RESEARCH OBJECTIVE

The aim of the proposed research is to use electroactive ion exchange materials to remove anionic contaminants from HLW wastes and process streams. An ion exchange process using electroactive materials sorbs contaminants selectively and then expels (elutes) them electrochemically by changing the charge balance through redox reactions in the sorbent as opposed to requiring the addition of a chemical eluant. Such processes can theoretically remove anions (e.g., pertechnetate, chromate, and perchlorate) and concentrate them in a separate product stream while adding no process chemicals. A practical implementation in HLW process facilities would be a breakthrough in the ability of DOE to economically minimize waste and prevent pollution throughout the complex. To enable this, our work focuses on manipulating specific properties of redox polymers to control the hydrophobicity and ion-pair properties pertinent to the reversibility, selectivity, stability, intercalation/de-intercalation rates, and capacity of the polymers. Of primary focus in the immediate future is to prepare materials with greater pH stability and selectivity as our previous studies with polyvinylferrocene (PVF) polymers don't meet the material requirements for the intended application.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work during 6/01/02 - 6/01/03 of a six-year project that began on 10/01/97. During this period our efforts have focused on four areas that are discussed in the following sections.

- X-ray absorption spectroscopy (XAS) analysis of Polyvinylferrocene (PVF) samples loaded with pertechnetate ion, TcO_4^- , at the National Synchrotron Light Source (NSLS)
- Preparation of new complexes and polymers to improve pH stability and selectivity

1. X-ray absorption spectroscopy (XAS) analysis of Polyvinylferrocene (PVF) samples loaded with pertechnetate ion, TcO_4^- , at the National Synchrotron Light Source (NSLS)

Most of the work for this project has centered on use of the redox polymer polyvinylferrocene (PVF). Our initial work indicated that this electroactive material was selective for perrhenate ion, ReO_4^- , (a non-radioactive surrogate for the pertechnetate ion, TcO_4^-) in the presence of nitrate ion. Our plan was to examine the PVF polymer and the interactions it may have with TcO_4^- using x-ray absorption spectroscopy (XAS) since previous studies indicated there may be some interaction between the iron (III) centers in the PVF polymer with ReO_4^- as evidenced by some distortion of the tetrahedral structure of the anion. Samples of PVF polymer were carefully coated onto carbon cloth and the samples were weighed to determine the amount of polymer on the carbon cloth. These samples were then loaded electrochemically with TcO_4^- . The maximum permissible activity allowed in the samples sent to the NSLS was 100 μCi , hence the solutions used in the experiments were prepared such that the activity could not be above this level (the supporting electrolyte used was 0.1 M NaNO_3 , with 3.0×10^{-3} M TcO_4^-). Upon completion of the polymer loadings (potential step to 600 mV for 30 minutes), all materials were triple-rinsed and all solutions were analyzed for TcO_4^- . The samples were shipped to our collaborators at Brookhaven National Laboratory for analysis. XAS studies suggested that at least 80% of the ferrocene sites were oxidized to ferrocenium, and the K_d was calculated to be about 4.5 mL/g (for ReO_4^- , the K_d was calculated to be

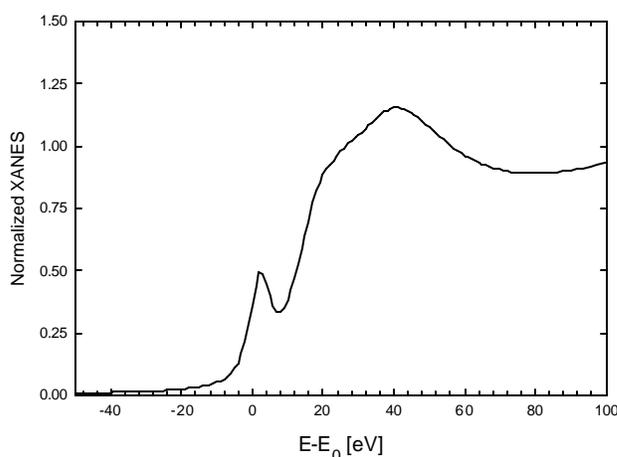


Figure 1. Tc K-edge XANES for PVF polymer loaded with TcO_4^- .

about 6 mL/g). The ion-ion interactions between the ferrocenium and TcO_4^- were probed using XAS. The Tc K-edge X-ray Absorption Near Edge Structure (XANES, Figure 1) showed a strong pre-edge peak which arises from a $1s \rightarrow 4d$ transition (This feature is a fingerprint of the TcO_4^- anion), while oxidation of ferrocene to ferrocenium yields the expected edge shift in the Fe K edge XANES spectrum. The EXAFS results (Figure 2) clearly indicated that Tc is present as a TcO_4^- moiety in the sample. However, no strong correlations from Tc or Fe further neighbors were visible in the Extended X-ray Absorption Fine

Structure (EXAFS) data leading to the conclusion that there is no direct interaction of the TcO_4^- with the oxidized polymer.

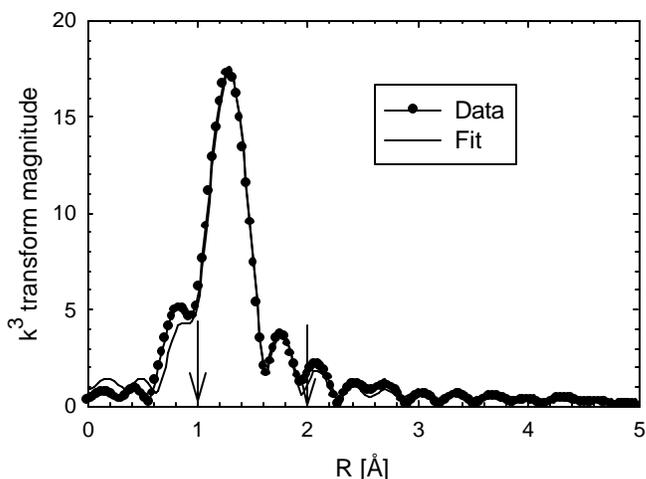


Figure 2. Tc K-edge EXAFS for PVF polymer loaded with TcO_4^- .

2. Preparation of new complexes and polymers to improve pH stability and selectivity

The PVF class of polymers have two primary issues affecting their potential use as materials for removal of TcO_4^- from high level waste (HLW): 1) the oxidized polymers (i.e., ferrocenium form) are not stable under the high pH conditions (highly alkaline) that is encountered for the wastes; 2) the slight selectivities observed are most likely due to hydration energy effects of the anions (TcO_4^- has a smaller hydration energy than NO_3^- , and therefore it will occupy hydrophobic polymers more readily than NO_3^-). In previous studies, we have examined the effects of alkylating the cyclopentadienyl rings of the ferrocene moiety in the polymers to enhance the alkaline stability of the polymers, and have seen evidence that this does provide some improvement (we can cycle the polymer through redox in 1 M NaOH solution before the ferrocenium centers all decompose). Alkylation also provides a more hydrophobic environment which improves the selectivity of the polymer for TcO_4^- . However, preparation of alkylated PVF materials have many inherent difficulties; alkylation brings back the issue of low MW polymer since the alkyl chains tend to interfere with rapid growth of the polymer chain, hence the zwitterionic intermediates formed from vinylferrocene derivatives quench the polymerization process.

We are now turning our attention to iron complexes of the dipyriddy, terpyridyl, and phenanthroline types. In conjunction with another EMSP project (Project # 70010), we have developed some synthetic strategies that can be used to prepare polymerizable ligands with a selective structure component. For example, in the case of dipyriddy ligands, we are functionalizing two pyridine rings, one with the polymerizable vinyl group, another with a group to enhance selectivity (e.g., guanidinium group). The two rings are then coupled and the dipyriddy ligand is then complexed to an iron center.

Some of the advantages of these materials over the PVF polymers include a richer chemistry for functionalization of the ligands, the potential to more easily create hydrophobic pockets about the metal centers to prevent alkaline decomposition during oxidation, and the ability to take advantage of the styrenic moieties to copolymerize the complexes successfully with materials such as styrene, vinylpyridine, etc. (vinylferrocene does not readily copolymerize with other materials due to the high chain transfer constant of the material). An example of one of the neutral complexes that we're currently studying is given in Figure 3.

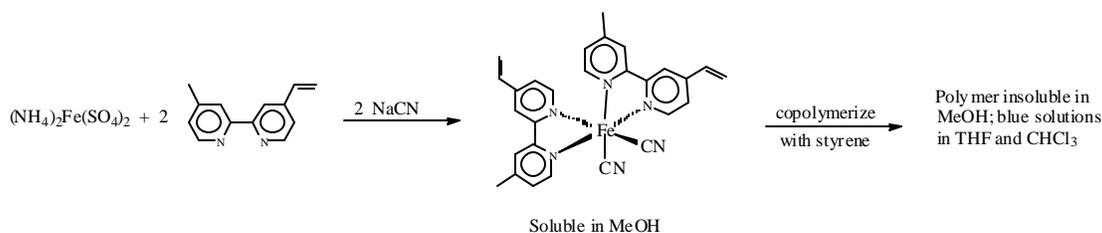


Figure 3. Synthesis of a neutral bis-dipyridyl iron complex with polymerizable groups.

PLANNED ACTIVITIES

During the next year, we plan to continue development of complexes by functionalization of ligands with groups that potentially enhance the selectivity of tetrahedral anions and with with polymerizable moieties (vinyl is the most common group here). Some specific aims are:

- Complete preparation of new ligands and complexes
- Complete preparation/characterization of new polymers
- Perform electrochemical experiments on the new materials with ReO_4^- , TcO_4^-
- Demonstrate and characterize new nanomaterials based on the PNNL prepared polymers working with U. Minnesota project collaborator for ReO_4^- , TcO_4^-
- Explore the use of PVF and the new materials for other contaminants such as ClO_4^- where pH is not a limitation for use of the materials.

INFORMATION ACCESS

Presentation

M. Balasubramanian, M.T. Giacomini, H. Lee and J. McBreen*, T.L. Hubler, S.D. Rassat, and D.J. Monk, "X-Ray Absorption Studies of Electroactive Polymer Electrodes for Anion Separation: Technetium from Nitrate," 203rd Meeting of the Electrochemical Society, Paris, France, May 2003.