X-RAY ABSORPTION STUDIES OF ELECTROACTIVE POLYMER ELECTRODES FOR SEPARATION OF PERTECHNETATE FROM NITRATE

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Introduction

The objective of this project is to use an electrically conducting polymer (e.g. poly(vinyl ferrocene)) (PVFc) to electrochemically separate pertechnetate from nitrate in high level liquid nuclear waste (1). The work at Brookhaven National Laboratory involves the use of *in situ* x-ray absorption spectroscopy (XAS) to study the interaction of TcO_4^-. anions with the conductive polymer electrodes. Work was done on electrodes with pertechnetate anions and also on electrodes with perrhenate anions that were used as a non-radioactive surrogate for pertechnetate.

Experimental

A special spectroelectrochemical cell for *in situ* XAS was designed and built for XAS studies at both the Fe K edge and the Re L_3 edge. Both *ex situ* and *in situ* XAS studies were done on PVFc films that were prepared by dipping carbon cloth in solutions of PVFc in a CH_2Cl_2 solvent. In the case of the perrhenate subsequent electrochemistry and *in situ* XAS were done in a 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 perrhenate, entrained in the electrolyte in the pores of the carbon cloth, interfered with the spectra. It was necessary to wash the electrodes in either water or acetonitrile before taking measurements at the Re L_3 edge. Pertechnetate was electrochemically incorporated into PVFc films on carbon cloth at PNNL. The pertechnetate solution was prepared from a standard stock solution from waste tanks that also contained nitrate ions. The electrodes were washed and dried and six layers of the carbon cloth were incorporated into a sealed holder similar in design to the spectroelectrochemical cell. XAS data were obtained at the K edges of both Fe and Tc. XAS spectra were also obtained on several standard compounds such as various iron oxides, ferrocene, ferrocenium hexafluorophosphate, ferroceniun tetrafluoroborate, ferroceniun perrhenate and dimethyl ferroceniun perrhenate.

Near edge spectra (XANES) at the Fe K edge for both ferroceniun tetrafluoroborate and ferrocenium hexafluorophosphate showed a shift in the absorption edge to higher energies compared to ferrocene. In addition to the edge shift, a peak at about a step height of 0.7 was observed for both ferrocenium compounds. This is due to some electronic effect such as mixing of empty p and d states above the Fermi level.

Similar edge shifts were observed in the *in situ* Fe XANES spectra for a PVFc electrode in a 0.1 M solution of $TBAReO_4$ in acetonitrile at 0.8 V vs. a Ag/AgCl reference electrode. The edge shift at 0.8 V indicates oxidation of the ferrocene moieties. However, the edge peak at a step height of 0.7 is less pronounced than that seen for the ferrocenium compounds. We have synthesize and purified ferrocenium perrhenate and dimethylferrocenium perrhenate . The XAS spectra for ferrocenium perrhenate and dimethylferrocenium perrhenate were similar to those found for the oxidized PVFc electrode in perrhenate containing electrolytes. This strongly indicates that the interaction of both the tetrafluoroborate and the hexafluorophosphate anions with the PVFc is different than that found for the perrhenate anions. There was no evidence from either the Re L_3 XANES or EXAFS that that any of the anions interacted directly with the Fe in the oxidized polymer. It is highly likely that the anions interact with the ferrocenium cyclopentadiene rings. Abstraction of electrons from the ring by the flouorinated anions could generate empty electronic states for bound state transitions that could account for the edge peak at a step height of 0.7.

Figure 1 shows Tc K edge XANES for TcO_4^- in PVFc. There is a sharp edge peak that is indicative of the tetrahedral coordination in TcO_4^-. The quality of the Tc K edge EXAFS was excellent. Neither the Tc XANES nor the EXAFS gave any indication of direct interaction between the Fe and the Tc in the oxidized polymer.

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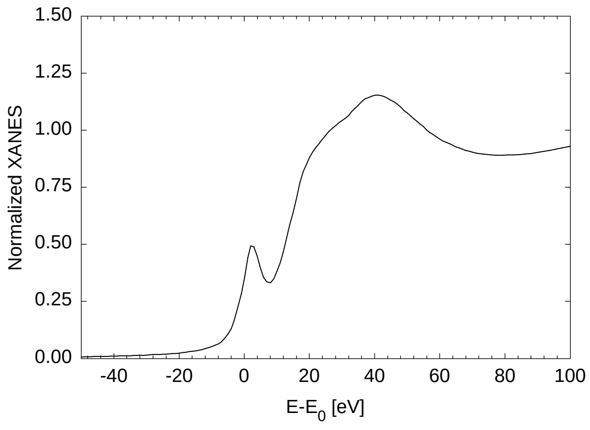

Figure 1 Tc K-edge XANES for TcO_4^- in the oxidized PVFc electrode.

Reference

1. M. Balasubramanian, M. T. Giacomini, H. S. Lee, J. McBreen, and J. H. Sukamto**,** *J. Electrochem. Soc.* **149**, D137 (2002).