

Project Title: Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone
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Progress Report

RESEARCH OBJECTIVE

The general aim of this project is to continue the design and implementation of a new sensor technology that offers the unprecedented levels of specificity needed for analysis of the complex chemical mixtures found at DOE sites nationwide. The new sensor concept combines the elements of electrochemistry, spectroscopy and selective partitioning into a single device that provides three levels of selectivity. The specific goal of this project is the development of a sensor for technetium (Tc) that is applicable to characterizing and monitoring the Vadose Zone and associated subsurface water at the Hanford site. The first goal is a sensor that determines technetium in the chemical form pertechnetate (TcO_4^-).

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work during 9/15/00 - 6/15/01 of a three-year project that began on 9/15/99. During this period effort was focused on Specific Tasks 1 and 2 of the proposed research. Until recently, all of our experiments used ReO_4^- and MnO_4^- as nonradioactive surrogates for TcO_4^- . Several months ago, two students spent one week at PNNL performing key experiments with TcO_4^- . These experiments confirmed that we have developed films that preconcentrate TcO_4^- at the sensor and that the preconcentrated TcO_4^- undergoes electrochemical reduction. Thus, we have succeeded in the first step in developing a sensor for TcO_4^- .

1) Choice of materials and fabrication of the chemically selective layer that initially traps TcO_4^- .

The optically transparent electrode (OTE) on which the spectroelectrochemical sensor is based is indium tin oxide (ITO) deposited on glass. As described in our previous report, we investigated the electrochemistry of ReO_4^- and MnO_4^- as nonradioactive surrogates for TcO_4^- on this material by cyclic voltammetry. The electrochemistry of TcO_4^- reduction has now been examined on bare ITO by cyclic voltammetry. Reduction of TcO_4^- commences at ca. -0.7 V vs. Ag/AgCl. The reduction wave blends with reduction of solvent and a clear peak is not observed. Other waves in the voltammogram suggest that a film is forming on the ITO surface that lowers the overpotential for solvent reduction.

As reported earlier, three polymers have been evaluated as candidates for the preconcentrating film that is coated on the ITO transparent electrode: PDMDAAC (polydimethyldiallylammonium chloride), PVTAC (polyvinylbenzyltrimethylammonium chloride), and QPVP (quarternary polyvinylpyridine). PDMDAAC, QPVP, and PVTAC have been immobilized in a porous silica film on ITO by the sol gel process. PVTAC has also been prepared as a polymer blend trapped in a network of PVA (polyvinyl alcohol) that is covalently bonded to the ITO. These films have all undergone the following development: measurement of film thickness by ellipsometry,

observation of film quality by scanning electron microscopy, and optimization of procedures for preparation of reproducible films. All films have demonstrated good uptake of anions such as ferrocyanide and the surrogates ReO_4^- and MnO_4^- .

Three of these four films have now been examined with TcO_4^- : QPVP in porous silica, PDMDAAC in porous silica, and PVTAC-PVA. These films show uptake of TcO_4^- and improvement of the electrochemical properties of TcO_4^- as studied by cyclic voltammetry. Immersion of an ITO electrode coated with a film in a solution of TcO_4^- shows the development of a reduction wave for TcO_4^- that has partitioned into the film. Compared to a bare ITO, this reduction shows three differences. First the reduction wave occurs as a well-defined wave with a distinct peak potential that is clearly separated from the solvent reduction wave. Second, the reduction wave has an oxidation wave counterpart. This behavior is suggestive of a change in the basic mechanism of reduction caused by the presence of the film. Third, the current is significantly enhanced compared to a bare electrode, indicating uptake of TcO_4^- by the polymer composite films. Composite films exhibited uptake increasing in the order $\text{QPVP} > \text{PDMDAAC} > \text{PVTAC} > \text{PVTAC-PVA}$.

The acquisition of an ellipsometer and an ESEM have enabled us to pursue more fundamental studies of the above films. The ellipsometer has been used to accurately measure film thickness and optical constants such as refractive index, which are important parameters in sensor performance. The ESEM has given us the ability to non-destructively examine sensor surfaces before and after use.

2) Choice of ligand that binds reduced Tc species within the chemically selective layer.

As described in the previous report, a variety of ligands for binding the reduced Tc species to form a coordination compound within the sensing layer have been evaluated for the requisite electrochemical and spectral properties by performing experiments with the surrogates ReO_4^- and MnO_4^- . Two ligands have now been evaluated with TcO_4^- : an N-donor ligand ethylenediamine (en) and an S-donor ligand meso-dimercaptosuccinic acid (DMSA). Cyclic voltammetry was performed on mixtures of ligand and TcO_4^- in an attempt to form a complex with an electrochemically formed lower oxidation state of Tc. In neither case was a complex formed that exhibited the desired reversible electrochemistry.

Another strategy that was tested involves ligand exchange between a preformed Re complex with ethylenediamine ($\text{Re(en)}_2\text{O}_2$) and an electrochemically formed lower oxidation state of Tc. Preliminary results are consistent with the electrogenerated Tc having displaced Re to form a Tc complex with the ligand.

Conclusions:

- ITO is an acceptable OTE for the sensor when tested with TcO_4^- .
- All three polymers (PDMDAAC, PVTAC, and QPVP) incorporated as composites are satisfactory for preconcentrating TcO_4^- on ITO. They also improve the electrochemical characteristics of TcO_4^- .
- The first step to building a successful sensor has been accomplished.
- Preliminary results suggest that an EN complex with Tc has been electrogenerated that might form the basis for the TcO_4^- sensor.

Instrument laboratory.

Through a large grant from the Ohio Board of Regents Hayes Fund, a consortium of three Ohio universities (OSU, M. Madou, PI; UC, C.J. Seliskar, UC-PI; and CWRU, C.C. Liu-CWRU-PI) devoted to MEMS and fabrication of chemical sensors resulted in purchase of new major equipment. The UC share of this grant allowed us to establish a chemical sensors instrumentation laboratory in our research area containing a Philips ESEM, a Woolham spectroscopic ellipsometer, a BiaCore SPR, a Metricon prism coupler, and several items of Buehler sawing, grinding and polishing equipment for sensor fabrication. This new facility is available to us free of charge to further reinforce our effort on our EMSP grant activities.

PLANNED ACTIVITIES

Given the encouraging results that were obtained for TcO_4^- at PNNL, a graduate student from UC will spend the summer at PNNL doing more experiments with TcO_4^- . TcO_4^- uptake into the polymer films will be quantified. The strategy of ligand exchange between a preformed Re complex such as ReEN_2O_2 and an electrochemically formed lower oxidation state of Tc will be further explored. Other ligands for complex formation with electrochemically reduced TcO_4^- will be evaluated.

We have observed that parameters such as film thickness and presoaking affect the rate of uptake of anions into the film. We are beginning a more systematic study of these parameters and their influence on sensor performance.

INFORMATION ACCESS

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