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Project Titles: Design and Development of a New Hybrid Spectroelectrochemical Sensor; Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone
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Number of Graduate Students Actively Involved in the Project: 9 Ph.D. students are currently working on the project.
Research Objective: The general objective is 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 specific objectives are threefold: demonstration of the general sensor concept on a variety of model systems; development of a sensor for ferrocyanide with testing on waste tank simulant; and development of a sensor for pertechnetate applicable to the Vadose Zone.
Research Progress and Implications: This report summarizes work after 3 ½ years on the general development of the sensor concept with model systems and of the sensor for ferrocyanide and work after ½ year on the pertechnetate sensor.

The spectroelectrochemical sensor embodies two modes of instrumental selectivity (electrochemical and spectroscopic) in addition to selective partitioning into a chemically-selective film. The sensor consists of a planar optical substrate/electrode coated with the selective film. Sensing of analyte that partitions into the film is based on the change in the attenuation of light passing through the guided wave substrate that accompanies an electrochemical reaction of the analyte induced by electromodulation. Threefold selectivity for a chosen analyte relative to other environmental components is obtained by the choice of coating material, the electromodulation potentials, and the wavelength for optical monitoring.

The sensor concept has been demonstrated with an indium tin oxide coated glass guided wave device that has been over-coated with the the selective film. The following charge-selective thin films have been evaluated: sol-gel derived PDMDAAC-SiO_2 composite (where PDMDAAC = poly(dimethyl diallylammonium chloride)), sol-gel derived Nafion-SiO_2 composite (where Nafion is a perfluorosulfonated ionomer), and poly(vinyl alcohol)-polyelectrolyte blend. Model analytes that have been used are $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, $Ru(bipy)_3^{2+}$ (where bipy = 2,2'–bipyridine), $Re(DMPE)_3^{1+}$ (where DMPE = 1,2-bis(dimethylphosphino)ethane), and MV^{2+} (methyl viologen dication). Performance characteristics such as selectivity, sensitivity, detection limit, response range, response time, and reversibility have been measured for these sensors. Improvement in detection limit by ensemble averaging a repetitive signal modulated by a potential step or potential scan excitation signal has been demonstrated. The effect of different waveforms for modulation on sensor performance has been investigated. Smaller sensors based on optical waveguides have been fabricated and their enhanced sensitivity demonstrated. A small portable sensor unit including a virtual interface, control electronics and optics has been developed. A procedure for the determination of ferrocyanide in Hanford waste tank simulant solution (U-Plant-2, prepared at PNNL) has been developed.

The development of a sensor for technetium in the TcO_4^- form that is applicable to characterizing and monitoring the Vadose Zone and associated subsurface water at the Hanford site began 6 months ago. The key to adapting the generic sensor concept to detect TcO_4^- lies in the development of unique chemistry within the chemically selective film to provide a modulated optical response. This film is being developed so that TcO_4^- in the sample will partition into it by electrostatic attraction. Once TcO_4^- is loaded into the film, it is electrochemically converted into a Tc coordination compound that gives a strong optical signal associated with an electrochemical reduction/oxidation process. The magnitude of the absorbance change accompanying the electrochemical modulation of this coordination compound will quantitate the concentration of Tc within the film, which is proportional to the concentration of TcO_4^- in the sample. Research during the first 6 months has focused on studying the electrochemistry of perrhenate, ReO_4^-, which is being used as a surrogate for TcO_4^-, and evaluating suitable ligands to form the coordination compound in the sensing film. A variety of diphosphonate- and thiol-based ligands with previously demonstrated capability for coordinating with Tc have been evaluated.

30 presentations at scientific meetings have been made since the inception of the project. 14 original research articles have been published in scientific journals.

Planned Activities:: The general development of the sensor concept and testing for ferrocyanide will be finished in the next 6 months. The ferrocyanide sensor is scheduled for testing on waste tank simulant at PNNL in April 2000. Results will be compared with a standard spectroscopic method developed by Bryan. The search for a good ligand and a good charged polymer for the sensing film for the pertechnetate sensor will continue for the next 6 months with the surrogate perrhenate. The best candidates will then be tested with pertechnetate at PNNL. Presentations at the following meetings will be made: Pittcon 2000 (5 by graduate students), spring ACS (1), ESEAC 2000 (1).

Information Access: Original research articles resulting from this project (11 of 14 are listed):

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 1. Demonstration of Concept with Ferricyanide, Y. Shi, A. F. Slaterbeck, C. J. Seliskar, W. R. Heineman, *Anal. Chem.,* 69, 3679-3686 (1997).

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 2. Demonstration of Selectivity in the Presence of Direct Interferents, Y. Shi, C. J. Seliskar, W. R. Heineman, *Anal. Chem.,* 69(23), 4819-4827 (1997).

New Spectroelectrochemical Sensor, Y. Shi, A. F. Slaterbeck, S. Aryal, C. J. Seliskar, W. R. Heineman, T. H. Ridgway, J. H. Nevin, *SPIE,* 3258, 56-65 (1998).

New Chemically-Selective Optical Materials for Waveguide Sensors, L. Gao, Y. Shi, A. F. Slaterbeck, C. J. Seliskar, W. R. Heineman, *SPIE,* 3258, 66-74 (1998).

Evaluation of the Electrochemical Characteristics of a Poly(vinyl alcohol)/poly(acrylic acid) Polymer Blend, C. O. Dasenbrock, T. H. Ridgway, C. J. Seliskar, W. R. Heineman, *Electrochim. Acta*, 43(23), 3497-3502 (1998).

Electrochemical Behavior of Methyl Viologen at Graphite Electrodes Modified with Nafion Sol-Gel Composite, B. Barroso-Fernandez, M. T. Lee-Alvarez, C. J. Seliskar, W. R. Heineman, *Anal. Chim. Acta*, 370, 221-230 (1998).

Dual Analyte Spectroscopic Sensing in Sol-Gel Derived Polyelectrolyte-Silica Composite Thin Films, Y. Shi, C. J. Seliskar, W. R. Heineman, *Talanta,* 47, 1071-1076 (1998).

Voltammetry of $[Re(DMPE)_3]^+$ at Ionomer-Entrapped Composite-Modified Electrodes, Z. Hu, C. J. Seliskar, W. R. Heineman, *Anal. Chem.,* 70, 5230-5236 (1998).

Tailoring Perfluorosulfonated Ionomer-Entrapped Sol-Gel-Derived Silica Nanocomposite for Spectroelectrochemical Sensing of $Re(DMPE)_3^+$, Z. Hu, A. Slaterbeck, C. J. Seliskar, T. H. Ridgway, W. R. Heineman, *Langmuir*, 15, 767-773 (1999).

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 3. Effect of Signal Averaging on Limit of Detection, A.F. Slaterbeck, T.H. Ridgway, C. J. Seliskar, W. R. Heineman, *Anal. Chem.,* 71, 1196-1203 (1999).

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 4. Sensing with Poly(vinyl alcohol)-Polyelectrolyte Blend Modified Optically Transparent Electrodes, L.Gao, C. J. Seliskar, W. R. Heineman, *Anal. Chem.,* 71, 4061-4068 (1999).