Project ID: **54674**

Design and Development of a New Hybrid Spectroelectrochemical Sensor

Lead Principal Investigator:

Dr. William R. Heineman
Distinguished Research Professor
Department of Chemistry
University of Cincinnati
P.O. Box 210172
Cincinnati, Ohio 45221--0172
Telephone: 513-556-9210
e-mail: William.Heineman@UC.Edu

Co Principal Investigators:

Carl J. Seliskar
Professor
Department of Chemistry
University of Cincinnati
P.O. Box 210172
Cincinnati Ohio 45221 -0172
USA
Telephone: 513-556-9213
e-mail: carl.seliskar@uc.edu

Thomas H. Ridgway
Professor
Department of Chemistry
University of Cincinnati
P.O. Box 210172
Cincinnati Ohio 45221 -0172
USA
Telephone: 513-556-9251
e-mail:thomas.ridgway@uc.edu

Graduate Students:

Graduate students in Ph.D. program:
Cathy Dasenbrock, Ph.D. 1996,
Hong Shen, Ph.D. 1997
Andrew Slaterbeck, Ph.D. 1998
Yining Shi, Ph.D. 1998
Letian Gao, Ph.D. 1998
Zhongmin Hu, , Ph.D. 1998
Mila Maizels, 4th year
Susan Ross, 4th year
Michael Clager, 4th year
Michael Stegemiller, 2nd year
Jennifer DiVirgilio-Thomas, 2nd year
Mark Wanamaker, 2nd year
Imants Zudans, 1st year
Tonya Rarog, 1st year

Masters Student:
Saroj Aryal, 2nd year

Visiting Graduate student in Ph.D. Program at Bonn University, Germany:
Karin Renner, 4th year

Progress report

RESEARCH OBJECTIVE

The general aim of this project is to design and implement a new sensor technology which offers the unprecedented levels of specificity needed for analysis of the complex chemical mixtures found at USDOE sites nationwide. The new sensor concept proposed combines the elements of electrochemistry, spectroscopy and selective partitioning into a single device that provides three levels of selectivity. This type of sensor has many potential applications at DOE sites. As an example, the enhanced specificity embodied in this new sensor design is well-suited to the analytical problem posed by the addition of ferrocyanide to radioactive tank wastes at the USDOE Hanford Site.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work after 2 ¾ years of a 3-year project. During this time we have accomplished the following goals:

1. Sensor concept demonstrated for detection of ferrocyanide, $Re(DMPE)_3^+$, $Ru(bipy)_3^{2+}$, and methyl viologen dication
2. Demonstration of selectivity against direct interferences
3. Development of prototype instrumentation package to control electrochemical modulation and optical readout

4. Demonstration of signal averaging to improve detection limit
5. Development of robust materials with required properties for sensing layer for detection of both cationic and anionic analytes
6. Demonstration of sensor for detection of ferrocyanide in Hanford U-Plant 2 simulant solution
7. Development of sensor package (microcell and instrumentation) for demonstration of ferrocyanide detection in waste tank sample at Hanford

The successful demonstration of the novel sensor concept on several chemical systems and for the detection of ferrocyanide in Hanford U-Plant 2 simulant attests to the practical utility of this type of sensor for DOE needs.

PLANNED ACTIVITIES

1. Demonstration of sensor package (microcell and instrumentation) for ferrocyanide detection in waste tank sample at Hanford during summer 1999. This system will serve as a mock-up for training and sensor testing using simulated waste material at the Radiochemical Processing Laboratory at PNNL. It is anticipated that this chemical sensor system or an additional system will be deployed into a radiologically controlled ("hot") laboratory for measurement of actual ferrocyanide waste material in future years.

2. The sensor concept also lends itself to the development of sensors for other species of interest to DOE. We are beginning to develop a sensor for technetium that could monitor pertechnetate in the Vadose Zone and associated subsurface water at the Hanford site.

INFORMATION ACCESS

Original research articles resulting from this project are listed below.

Spectroelectrochemical sensor:

(1) Slaterbeck, AF; Shi, Y; Ridgway, TH; Seliskar, CJ; Heineman, WR. *Spectroelectochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device, in Chemical and Biological Sensors and Analytical Electrochemical Methods.* Ricco, AJ; Butler, MA; Vanysek, P; Horval, G; Silva, AF, eds. Proceedings for the Symposium on Chemical and Biological Sensors and Analytical Electrochemical Methods, Proceedings Vol. 97-19, **1997**; pp 50-60.
(2) Shi, Y; Slaterbeck, AF; Seliskar, CJ; Heineman, WR. *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 1. Demonstration of Concept with Ferricyanide*. Anal. Chem. **1997**, *69*, 3679-3686.
(3) Shi, Y; Seliskar, CJ; Heineman, WR. *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 2. Demonstration of Selectivity in the Presence of Direct Interferents.* Anal. Chem. **1997**, *69*, 4819-4827.
(4) Shi, Y; Slaterbeck, AF; Aryal, S; Seliskar, CJ; Heineman, WR; Ridgway, TH; Nevin, JH. *New Spectroelectrochemical Sensor*, Proc. SPIE, **1998**, *Series 3258*, pp 56-65.
(5) Ross, SE; Slaterbeck, AF; Shi, Y; Aryal, S; Maizels, M; Seliskar, CJ; Heineman, WR; Ridgway, TH; Nevin, JH. *Spectroelectrochemical Sensors – Materials, Incorporation of Planar Waveguide Technologies and Instrumentation*, Proc. SPIE, **1999,** *Series 3537*, 268-279.
(6) Slaterbeck, AF; Ridgway, TH; Seliskar, CJ; Heineman, WR. *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 3. Effect of Signal Averaging on Limit of Detection*. Anal. Chem. **1999**, *71*, 1196-1203.

(7) Hu, Z; Slaterbeck, AF; Seliskar, CJ; Ridgway, TH; Heineman, WR. *Tailoring Perfluorosulfonated Ionomer-Entrapped Sol-Gel Derived Silica Nanocomposite for Spectroelectrochemical Sensing of $Re(DMPE)_3^+$*. Langmuir **1999**, *15*, 767-773.
(8) Gao, L; CJ Seliskar; WR Heineman, *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 4. Sensing with Poly(vinyl alcohol) – Polyelectrolyte Blend Modified Optically Transparent Electrodes*, submitted to Anal. Chem., (1999).

Materials development for selective coating on spectroelectrochemical sensor:

(9) Shi, Y; Seliskar, CJ. *Optically Transparent Polyelectrolyte-Silica Composite Materials: Preparation, Characterization and Applications in Optical Chemical Sensing.* Chem. Mater. **1997**, *9*, 821-829.
(10) Gao, L; Shi, Y; Slaterbeck, AF; Seliskar, CJ; Heineman, WR. *New Chemically-Selective Optical Materials for Waveguide Sensors*, Proc. SPIE, **1998**, *Series 3258*, 66-74.
(11) Gao, L; Seliskar, CJ; Milstein, L. *Spectroscopic Sensing with Highly Transparent Ion-Exchangeable Polymer Blend*. Appl. Spectrosc. **1997**, *51*, 1745-1752.
(12) Dasenbrock, CO; Ridgway, TH; Seliskar, CJ, Heineman, WR. *Evaluation of the Electrochemical Characteristics of a Poly(vinyl alcohol)/poly(acrylic acid) Polymer Blend*. Electrochim. Acta **1998**, *43*, 3497-3502.
(13) Gao, L; Seliskar, CJ. *Formulation, Characterization and Sensing Applications of Transparent Poly(vinyl alcohol)-Polyelectrolyte Blends*. Chem. Mater. **1998**, *10*, 2481-2489.
(14) Hu, Z; Seliskar, CJ; Heineman, WR. *Voltammetry of $[Re(DMPE)_3]^+$, where DMPE = 1,2-bis(dimethylphosphino)ethane, at Ionomer-Entrapped Composite Modified Electrodes*. Anal. Chem. **1998**, ***70***, 5230-5236.