

*Project Title:* Design and Development of A New Hybrid Spectroelectrochemical Sensor  
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## *Progress report*

### RESEARCH OBJECTIVE

The general aim of this project is to design and implement a new sensor technology that offers the unprecedented levels of specificity needed for analysis of the complex chemical mixtures found at USDOE 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. We have had three major goals:

- Demonstration of the general sensor concept on seven model systems
- Development of a prototype sensor for ferrocyanide with associated instrumentation
- Testing prototype sensor for ferrocyanide on waste tank simulant (U-Plant-2 Simulant Solution) provided by PNNL and then on actual tank waste (Tank 241-C-112) at PNNL/Hanford

### RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work during the period 9/15/96 to 9/14/00. The project was funded for three years; the fourth year was a no cost extension. During this time we accomplished the following goals:

- Sensor concept demonstrated with an indium tin oxide coated glass guided wave device over-coated with the selective film
- Three charge-selective thin films evaluated and used in sensors: sol-gel derived PDMDAAC-SiO<sub>2</sub> composite [PDMDAAC = poly(dimethyl diallylammonium chloride)], sol-gel derived Nafion-SiO<sub>2</sub> composite [Nafion is a perfluorosulfonated ionomer], and poly(vinyl alcohol)-polyelectrolyte blend
- Sensor concept demonstrated on seven model analytes: Fe(CN)<sub>6</sub><sup>4-</sup>, Fe(CN)<sub>6</sub><sup>3-</sup>, Ru(CN)<sub>6</sub><sup>4-</sup>, Ru(bipy)<sub>3</sub><sup>2+</sup> [bipy = 2,2'-bipyridine], Re(DMPE)<sub>3</sub><sup>1+</sup> [DMPE = 1,2-bis(dimethylphosphino)ethane], MV<sup>2+</sup> (methyl viologen dication), and ascorbate
- Performance characteristics for some of the above analytes evaluated: selectivity, sensitivity, detection limit, response range, response time, and reversibility
- Detection limits improved by ensemble averaging a repetitive signal
- Effect of different waveforms for modulation on sensor performance investigated
- Smaller sensors based on optical waveguides fabricated
- Small portable sensor unit including virtual interface, control electronics and optics developed
- Sensor package (microcell and instrumentation) developed for demonstration of ferrocyanide detection in waste tank sample at PNNL/Hanford
- Prototype sensor for ferrocyanide tested for possible interference by known constituents in Hanford waste tank
- Analytical procedure for determination of ferrocyanide in Hanford waste tank simulant solution (U-Plant-2 simulant prepared at PNNL) developed
- Prototype ferrocyanide sensor successfully tested on waste tank simulant (U-Plant-2 Simulant Solution) and actual waste (Tank 241-C-112) at PNNL/Hanford, April 2000
- 30 presentations at scientific meetings
- 14 original research articles published in scientific journals

The implications of this research are as follows:

- Combining electrochemistry and spectroscopy in a single device to form a sensor with improved selectivity is feasible.
- The spectroelectrochemical sensor concept is applicable to the analysis of complex samples such as are found at DOE sites, as demonstrated by the determination of ferrocyanide in real sample from a Hanford waste tank.
- The sensor concept is broadly applicable; sensors for other compounds of interest to DOE could be developed.

A no-cost extension of one year was requested to enable us to demonstrate the novel sensor concept for the determination of ferrocyanide on a real sample of tank waste at the Hanford site. To this end, a portable sensor package including a sensor microcell and associated instrumentation was developed and successfully demonstrated on Hanford tank simulant solution at the University of Cincinnati (UC). Based on this success, a UC graduate student, Mke Stegemiller, traveled to Hanford during the period April 1 – 8, 2000, to test the sensor on simulant at the Radiochemical Processing Laboratory at PNNL. Working with our collaborator, Dr. Sam Bryan at PNNL, and a technician from PNNL, Mr. Richard Sell, Mr. Stegemiller was able to demonstrate that the sensor worked on their simulant solution. Based on that success, they analyzed a real sample from Tank 241-C-112 for ferrocyanide. The sensor gave a result of 1.0 mM ferrocyanide and the accepted FTIR method gave 0.67 mM. The relatively good agreement between the sensor and the laboratory method attests to the practical utility of this type of sensor for DOE needs.

#### PLANNED ACTIVITIES

Because this grant has ended and the proposed research has been completed, no further experimental work is planned. Submission of manuscripts describing research from this project to scientific journals will continue until all results relating to this project have been published.

This new concept for a sensor lends itself to the development of sensors for other species of interest to DOE. In another project, “Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone” (Project ID 70010) we are developing a technetium sensor that could monitor pertechnetate and other forms of technetium in the Vadose Zone and associated subsurface water at the Hanford site. That project relies heavily on results from this completed project.

#### INFORMATION ACCESS

Original research articles resulting from this project that are published, submitted or in preparation are listed below.

#### **Spectroelectrochemical sensor:**

- (1) Slaterbeck, AF; Shi, Y; Ridgway, TH; Seliskar, CJ; Heineman, WR. *Spectroelectrochemical 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; Seliskar, CJ; Heineman, WR. *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 4. Sensing with Poly(vinyl alcohol) – Polyelectrolyte Blend Modified Optically Transparent Electrodes*, Anal. Chem. **1999**, 71, 4061-4068.
- (9) Slaterbeck, AF; Stegemiller, ML; Seliskar, CJ; Ridgway, TH; Heineman, WR;. *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 5. Simulation of Sensor Response for Different Excitation Potential Waveforms*. Anal. Chem. **2000**, 72, 5567-5575.
- (10) DiVirgilio-Thomas, JM; Heineman, WR; Seliskar, CJ. *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 6. Sensing with a Mediator*. Anal. Chem. **2000**, 72, 3461-3467.
- (11) Maizels, M; Heineman, WR; Seliskar, CJ. *Graphite Electrodes Coated with Poly(dimethyldiallylammonium)chloride Network Films Cross-Linked by Gamma-Irradiation*. Electroanalysis **2000**, 12, 241-247.
- (12) Ross, SE; Seliskar, CJ; Heineman, WR. *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 9. Incorporation of Planar Waveguide Technology*. Anal. Chem. **2000**, 72, 5549-5555.
- (13) Maizels, M; Stegemiller, M; Ross, S; Slaterbeck, A; Shi, Y; Ridgway, TH; Heineman, WR; Seliskar, CJ; Bryan, SA. *Novel Spectroelectrochemical Sensor for Ferrocyanide in Hanford Waste Simulant*. In “Nuclear Site Remediation: First Accomplishments of the Environmental Management Science Program”, PG Eller and WR Heineman, eds., ACS Symposium Series, vol. 77, Washington, D.C., 2001, pp. 364-378.
- (14) Gao, L; Seliskar, CJ; Heineman, WR. *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 8. Selectivity at Poly(vinyl alcohol)-Polyelectrolyte Blend Modified Optically Transparent Electrodes*. Electroanalysis, in press.
- (15) Maizels, M; Seliskar, CJ; Heineman, WR. *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 7. Sensing of  $Fe(CN)_6^{4-}$* . Electroanalysis, in press.
- (16) Maizels, M; Seliskar, CJ; Heineman, WR; Bryan, SA. *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 10. Sensing of Ferrocyanide in Hanford Tank Simulant*. In preparation.

- (17) Stegemiller, ML; Heineman, WR; Seliskar, CJ; Ridgway, TH; Bryan, SA. *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 11. Design and Evaluation of a Portable Sensor for the Determination of Ferrocyanide in Hanford Tank Waste Samples.* In preparation.
- (18) Ross, SE; Seliskar, CJ; Heineman, WR; Aryol, S; Nevin, JH. *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 12. Characterization of a Channel Waveguide Sensor.* In preparation

#### **Materials development for selective coating on spectroelectrochemical sensor:**

- (19) Shi, Y; Seliskar, CJ. *Optically Transparent Polyelectrolyte-Silica Composite Materials: Preparation, Characterization and Applications in Optical Chemical Sensing.* Chem. Mater. **1997**, 9, 821-829.
- (20) 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.
- (21) Gao, L; Seliskar, CJ; Milstein, L. *Spectroscopic Sensing with Highly Transparent Ion-Exchangeable Polymer Blend.* Appl. Spectrosc. **1997**, 51, 1745-1752.
- (22) 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.
- (23) Gao, L; Seliskar, CJ. *Formulation, Characterization and Sensing Applications of Transparent Poly(vinyl alcohol)-Polyelectrolyte Blends.* Chem. Mater. **1998**, 10, 2481-2489.
- (24) 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.

#### **TECHNICAL REPORT**

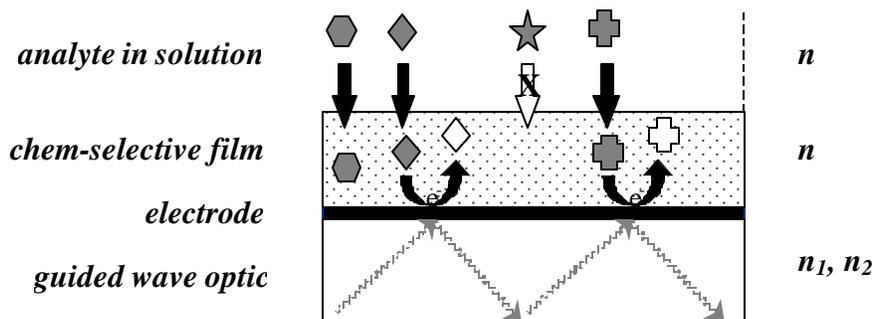
The research performed under the auspices of this grant is summarized below. The results have been reported in the published articles listed above. The reader is referred to these articles for details.

**1. Introduction.** The required remediation of over 300 underground nuclear waste storage tanks at USDOE sites together with the associated needs to characterize and monitor the chemical compositions of the tanks themselves presents a major scientific challenge (1-6). In addition to the previously identified chemical complexity of such storage materials, the added dimensions of limited tank access and harsh chemical and radiological environment preclude the straightforward application of well-established laboratory-based chemical analysis techniques to this national problem. Beyond any solution to this immediate problem also lies a present and long-term need to monitor low-level subsurface contaminations associated with such storage facilities. While an approach to removing high-level nuclear wastes has been identified (vitrification), the chemical analysis technology available in-hand to assist in this important task is inadequate.

The general aim of the work embodied in this project is to design and implement a new sensor technology that offers the unprecedented levels of specificity needed for analysis of the complex chemical mixtures found at USDOE 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. 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 (7).

A chemical sensor is a device that responds to varying concentrations of a single chemical (the analyte) or a specific class of chemicals. Interest in the development of new sensors for numerous chemical species in a wide range of applications has soared in the past few years (8). A significant problem in chemical sensor development is achieving adequate selectivity for determination of an analyte in a real sample where interferences often confuse the sensor measurement. Selectivity in presently available sensors is usually achieved in one of several ways. Electrochemical sensors based on electrolysis typically have two modes of selectivity. The first level of selectivity is based on the specificity that the applied potential provides. This alone is usually inadequate. The second mode of selectivity is typically provided by modification of the electrode surface with a selective coating or membrane. Likewise, fiber optic chemical sensors have two analogous modes of selectivity: the wavelength of light and a selective coating or membrane. These two modes of selectivity are insufficient for many applications.

**2. Concept of Spectroelectrochemical Sensor.** Recently, we have sought to increase the selectivity in chemical sensors by combining the capabilities of electrochemical and optical sensors into a single device. In general, such a strategy for chemical sensing would require three characteristics of an analyte: that it specifically interact with an applied sensor coating, that it be electrolyzed at the chosen potential, and that it have an optical change at the wavelength chosen for sensing. This sensor concept is illustrated in **Figure 1** where the diagram of the critical



**Figure 1.** Cross-sectional view of a prototypical spectroelectrochemical sensor consisting of three phases (guided wave optic, optically transparent electrode, chemically-selective film) and the sample solution. The vertical arrows denote transport (solid) or prevented transport (unfilled) of analytes into the chemically-selective film. The half-circle arrows denote electrode processes (oxidation, reduction) of analytes that have diffused to the electrode surface. The guided wave optic represents the optical medium in which light is transmitted through the sensor that is diminished by evanescent field interaction with analytes that absorb at the sensor wavelength.

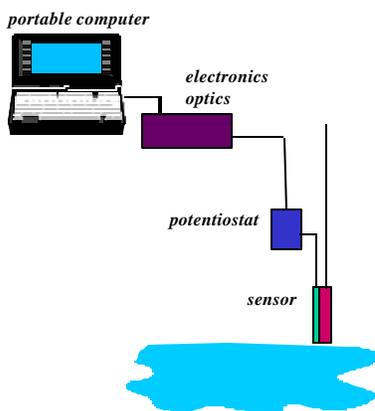
interfacial region of such a device is shown. One can think of the sensor structure as one based on an optically transparent electrode (OTE); in other words, a guided wave optic that exhibits multiple internal reflection (MIR) with a transparent electrode deposited on it. The OTE is coated by a thin chemically-selective film that serves to enhance detection limit by preconcentrating the analyte at the OTE surface. The evanescent field at the points of internal reflection within the

guided wave optic penetrates the film so that electrochemical events within the film can be monitored optically.

In its operation, a potential excitation signal is applied to the OTE to cause electrolysis of analyte that has partitioned into the film, and the change in the light propagated by attenuated total internal reflection due to disappearance of analyte by its electrolysis or appearance of an electrolysis product is monitored. (This is illustrated by the plus symbol in Figure 1.) Thus, sensor transmittance or absorbance changes measured in concert with an electrochemical modulation become the analytical signal. Quantitation of the analyte is based on the magnitude of the change in absorbance, which is proportional to concentration of analyte in the film which, in turn, is proportional to its concentration in the sample as defined by the partition coefficient. The remaining three symbols in Figure 1 represent classes of compounds (interferences) in the sample that do not pass these three tests. They either do not partition into the film (star symbol), do not undergo electrolysis (hexagon), or do not absorb light at the wavelength being used to detect the analyte (diamond). Selectivity for the analyte relative to these other solution components is obtained by choice of coating material, electrolysis potential, and wavelength for optical monitoring. This concept, therefore, adds an additional component of selectivity compared with many of the existing chemical sensors and is very important for its practical application.

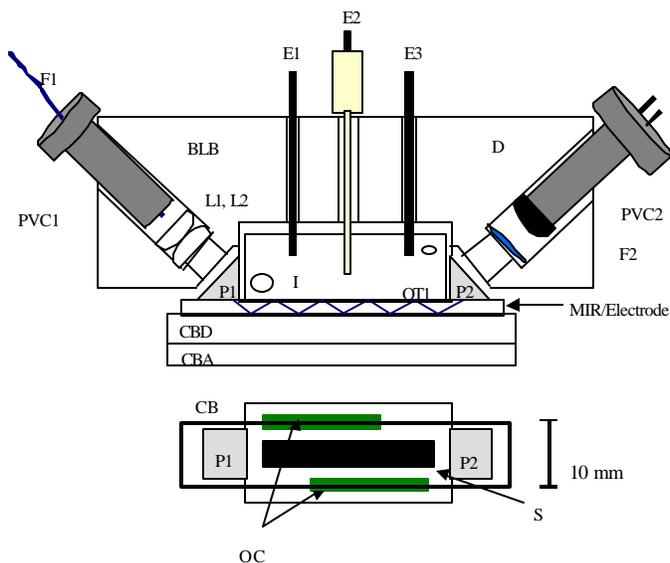
The new sensor concept has been demonstrated mainly with an indium tin oxide (ITO) coated glass guided wave device that has been over-coated with a charge-selective thin film. The ITO is the transparent electrode shown in Figure 1. The charge selective coating has been either a sol-gel processed polymer-SiO<sub>2</sub> composite film or a chemically attached polymer blend. Prototype analytes have been used to demonstrate that the change in the transmittance of the waveguide resulting from electrochemical oxidation/reduction can be used to quantify an analyte.

**3. Design and Fabrication of a Field Portable Spectroelectrochemical Sensor.** The sensor design and the associated instrumentation for electrochemistry and optical measurements evolved during the course of the project (9-11). Here, we describe only the final prototype sensor and associated instrumentation (11), which is the portable unit used to demonstrate the sensor on actual tank waste at PNNL/ Hanford (*vide infra*). The instrumentation developed for the portable unit consists of the following components: the sensor itself, control electronics for the electrochemistry (potentiostat), electronics for the optical components, and a virtual interface to a computer through which the experiments can be performed and the data acquired and analyzed (Figure 2).



**Figure 2.** Overview of portable spectroelectrochemical sensor.

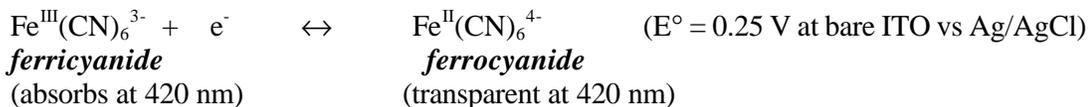
The sensor itself is shown in **Figure 3**. In this configuration, sample is added to the sensing chamber for its analysis. After a fixed period of time to allow the analyte to partition into the film, the analyte is modulated spectroelectrochemically and the absorbance change is used to quantify it.



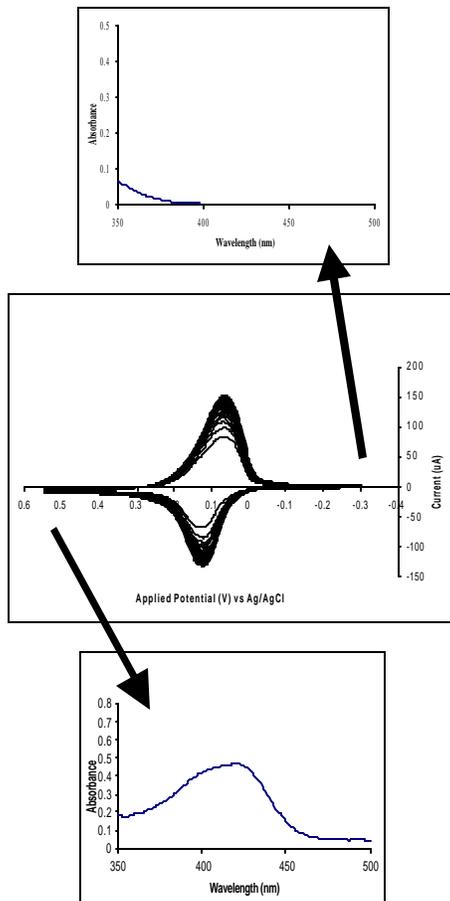
**Figure 3.** Schematic diagram of spectroelectrochemical sensor: Top, cross-section; Bottom, top-view of MIR optic with electrochemical contacts. BLB: Fixed Optics Case, F<sub>1</sub>: Superguide optical fiber, PVC<sub>1</sub>: Fiber Optic chuck, PVC<sub>2</sub>: Detector chuck, L<sub>1,2</sub>: BK7 lens pair, L<sub>3</sub>: filter, D: photodiode detector, MIR/Electrode : ITO coated slide, E<sub>1</sub> and E<sub>3</sub>: Pt. Auxiliary electrodes, E<sub>2</sub>: Ag/AgCl reference electrode, I: inlet for sample, OT<sub>1</sub>: sample outlet, P<sub>1</sub>: incoupling prism, P<sub>2</sub>: decoupling prism, CBD: cell base delrin, CBS: cell base aluminum, S: sample chamber, ZC: copper covered zebra strip

The electronics portion of this unit is similar to that described previously (10). The user interface for the control system developed was centered on a data acquisition card (DAQ) installed in a personal computer. The DAQ controls all of the signals to and from the electronics, and is itself controlled through software. A “virtual instrument” was assembled with the interface and signal generation being software-based. Instrument front-panels traditionally found have been replaced by software controls that respond to “point and click” commands similar to any Windows interface.

**4. Sensor for Ferrocyanide.** To demonstrate the basic functioning and selective sensing capability, we chose ferrocyanide, Fe(CN)<sub>6</sub><sup>4-</sup>, as an example of an important anion at Hanford. Ferrocyanide is part of a redox couple with well-defined, reversible electrochemistry that is accompanied by distinct spectral changes in the visible wavelength region (9).

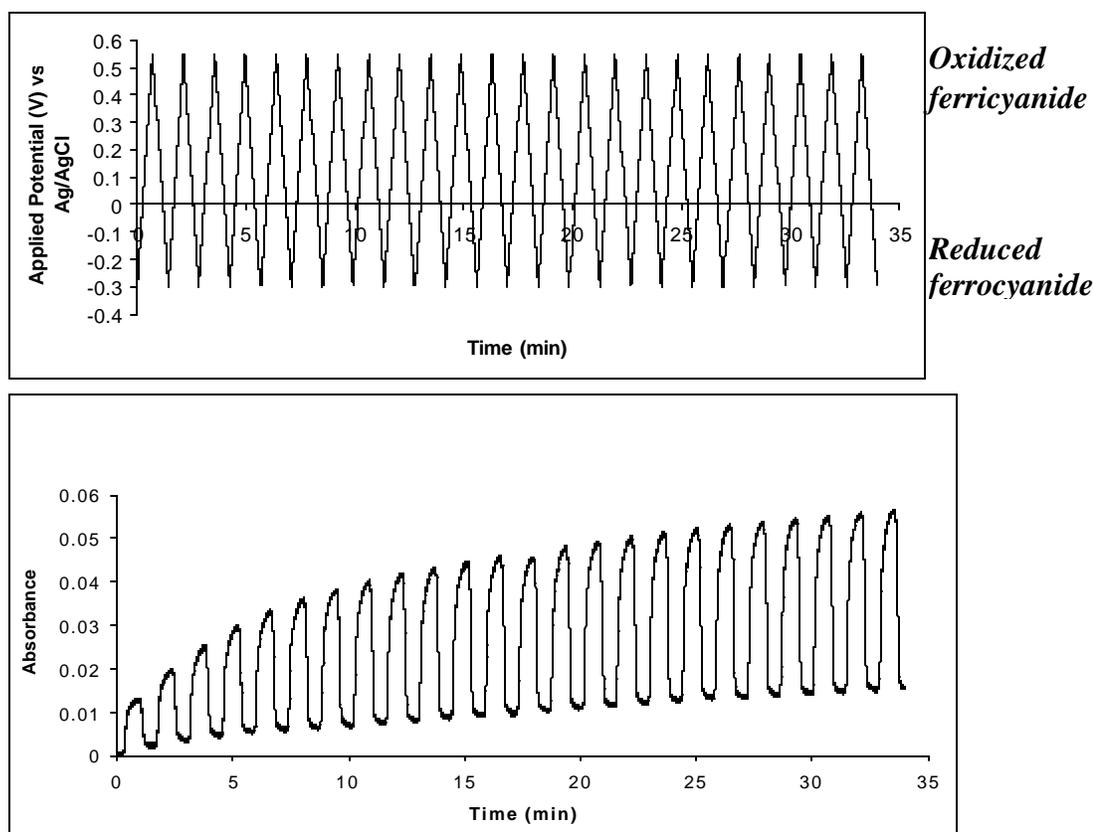


We have used a sol-gel processed PDMDAAC-SiO<sub>2</sub> film as an anion exchange selective film for partitioning of the Fe(CN)<sub>6</sub><sup>3-/4-</sup> couple. The electrochemical and spectroscopic characteristics of ferri/ferrocyanide at ITO coated with PDMDAAC-SiO<sub>2</sub> are shown by the cyclic voltammograms and spectra in **Figure 4**.



**Figure 4.** Cyclic voltammograms corresponding to the uptake of ferrocyanide from a solution of 0.40 mM ferrocyanide in 0.10 M KNO<sub>3</sub> (aq) into a PDMDAAC-SiO<sub>2</sub> film coated onto ITO-glass are shown in the central portion of the figure. The potential was scanned continuously at 20 mV/s between - 0.30 V to + 0.55 V. Above and below these cyclic voltammograms are the absorbance spectra of 0.4 mM ferrocyanide (top) and ferricyanide (bottom) that represent the optical spectra of the couple at the extremes of the potential scans.

In this case, spectroelectrochemical modulation is accomplished by either scanning or stepping the potential from -0.3 V, at which no light is absorbed by ferrocyanide in the film, to +0.55 V at which light is absorbed (420nm maximum) by the electrogenerated ferricyanide in the film. An illustration of the performance of the spectroelectrochemical sensor operating for the detection of Fe(CN)<sub>6</sub><sup>4-</sup> in pure sample solutions is shown in **Figure 5**.



**Figure 5.** The optical signal modulation at 450 nm (filtered Panasonic LED) for the ferri/ferrocyanide couple incorporated in PDMDAAC film on ITO-glass with continuous scanning of the potential (top portion of figure) as described in Figure 4. The multiple-internal reflection optic (10 mm x 40 mm) was aligned for 4 reflections.

The cyclic potential applied shown in the top figure caused periodic changes in absorbance that correspond to the periodic depletion of  $\text{Fe}(\text{CN})_6^{4-}$  as it is electrochemically oxidized to  $\text{Fe}(\text{CN})_6^{3-}$ , ferricyanide, and reformed. The change in absorbance caused by spectroelectrochemical modulation ( $\Delta A$ ) is proportional to the concentration of  $\text{Fe}(\text{CN})_6^{4-}$  in the film, which is in turn proportional to the concentration in solution. To use the sensor, a series of standards is used to establish a calibration curve of  $\Delta A$  vs. concentration of each standard, which is then used to quantify the unknown from its  $\Delta A$ . Calibration curves are typically linear in the low concentration range, with negative deviation occurring at the higher concentrations associated with saturation of the film. Alternatively, the technique of standard addition can be used (*vide infra*).

**5. Demonstration of the Sensor for Ferrocyanide in Hanford Waste Tank Sample.** A major objective of this project was demonstration of the spectroelectrochemical sensor concept on a real sample that was relevant to DOE interests. For this demonstration we chose the determination of ferrocyanide in an actual Hanford tank waste sample. We collaborated with Dr. Sam Bryan of PNNL for this phase of the project. Dr. Bryan was supported by a subcontract from our grant.

Simulants have been prepared at the Pacific Northwest National Laboratory for the purpose of providing non-radioactive media that can be used to mimic tank waste conditions at Hanford. In

the case of those wastes containing ferrocyanide, Bryan, *et al.* (12) have reported a procedure for dissolving simulant ferrocyanide sludges with an elixir composed of aqueous ethylenediamine (EN) and ethylenediaminetetraacetic acid (EDTA) to produce simulant solutions. The sludge and the derived solution that results from treatment of the sludge with elixir (the simulant solution) have been provided for these studies. The approximate composition of the simulant solution is given in **Table 1**.

**Table 1. Approximate Composition of the Simulant Solution**

<i>Species</i>	<i>wt%</i>	<i>Species</i>	<i>wt%</i>
Na <sup>+</sup>	0.78	Ni <sup>2+</sup>	0.04
NO <sub>3</sub> <sup>-</sup>	1.23	Fe <sup>2+</sup>	0.04
NO <sub>2</sub> <sup>-</sup>	0.30	Fe <sup>3+</sup>	0.12
SO <sub>4</sub> <sup>2-</sup>	0.42	CN <sup>-</sup>	0.106
SO <sub>3</sub> <sup>2-</sup>	0.02	EN	4.54
PO <sub>4</sub> <sup>3-</sup>	0.23	EDTA	4.54
NH <sub>4</sub> <sup>+</sup>	0.01	H <sub>2</sub> O	87
Ca <sup>2+</sup>	0.08		

Note: cyanide concentration is measured value

The simulant solution, like the actual waste solution resulting from dissolution by elixir, is a complex, high pH (pH = 10) mixture with high concentrations of such oxyions as NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, and PO<sub>4</sub><sup>2-</sup>.

The research involved three stages:

*a. Systematic evaluation of possible interferences.* With the information provided by Dr. Bryan about the known constituents of the tank waste, we systematically evaluated species for interference with the sensor. The species were divided into five categories based on the type of interference to be expected.

1. Cations that should be rejected by the film and therefore should not interfere.
2. Anions that would be attracted into the film but are not electroactive or optically absorbing. Even though these species but would not interfere with the modulation process, they would be expected to compete in the ion-exchange process and therefore depress the signal for ferrocyanide, if their concentrations were sufficiently high.
3. Anions that that would be attracted into the film, are optically absorbing, but are not electroactive. These species would not be expected to interfere because they would not participate in the electromodulation process.
4. Anions that that would be attracted into the film, are electroactive, but are not optically absorbing. These species would not be expected to interfere because they would not interfere with electromodulation of the optical signal.
5. Anions that that would be attracted into the film and are both electroactive and optically absorbing. These species would be expected to interfere because they would interfere with electromodulation of the optical signal.

Systematic evaluation of chemical species known to be in tank waste showed only one interference of concern (13,14). The very high ionic strength of the waste tanks gives anion

concentrations that are high enough to substantially depress the signal for ferrocyanide by competition with the ion exchange process into the film. This general anion interference must be taken into account in the calibration process. The only other species that was found to possibly interfere was the EDTA complex of iron,  $\text{Fe}(\text{EDTA})^{2-}$ . The reduction potential of this species is sufficiently close to that of ferrocyanide that it undergoes partial modulation in the potential range used to fully electromodulate ferrocyanide. It also absorbs light modestly at the wavelength used to detect ferrocyanide. However, its electromodulation signal was found to be less than 1% of that of ferrocyanide at relevant concentrations of each.

*b. Evaluation of sensor on simulant solution.* Given the conclusion that the only interference of concern is the high concentration of anions, the sensor was then tested on simulated tank waste (Hanford U-Plant-2 Simulant Solution) provided by Dr. Bryan. The modulated signal for simulant gave absorbance values about three times smaller when compared to those obtained for the same ferrocyanide concentration in pure samples with dilute supporting electrolyte in an identical instrument alignment after a similar sensor exposure. However, a procedure of standard additions was developed whereby the sensor gave results for the determination of ferrocyanide that agreed with the known concentration of ferrocyanide in the simulant.

*c. Testing of portable sensor on actual tank waste.* The sensor was then tested at Hanford during the period April 1 – 8, 2000 by a team consisting of one of our graduate students Michael Stegemiller, our collaborator from PNNL Dr. Bryan, and a PNNL technician Mr. Richard Sell (11). A simulant solution (U-Plant-2) containing 9.38 mM ferrocyanide was prepared according to Hanford process flow sheets. The spectroelectrochemical sensor found a concentration of 9.2 mM ferrocyanide. Given the close agreement between the sensor and the known concentration, it was decided to analyze a sample of actual tank waste. The concentration of ferrocyanide in a radioactive tank waste sample from Hanford Tank 241-C-112 was determined to be 1.0 mM using the portable spectroelectrochemical sensor. The accepted value for ferrocyanide concentration in the sample is 0.67 mM as determined by FTIR. Thus, the sensor was in reasonable agreement with the accepted method.

**6. Sensors for  $\text{Ru}(\text{bipy})_3^{2+}$ ,  $\text{Ru}(\text{CN})_6^{4-}$ ,  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\text{Re}(\text{DMPE})_3^+$ , Methyl Viologen and Ascorbate.** In order to demonstrate the general applicability of the sensor to positively and negatively charged inorganic coordination compounds and organic compounds, we have shown the sensor concept to work for the following compounds in addition to ferrocyanide described in the previous section:  $\text{Ru}(\text{bipy})_3^{2+}$  (15-17),  $\text{Ru}(\text{CN})_6^{4-}$  (16, 17),  $\text{Fe}(\text{CN})_6^{3-}$  (16, 17),  $[\text{Re}^{\text{I}}(\text{DMPE})_3]^+$  (18), and methyl viologen. In general, the performance of the sensor for these other analytes is similar to that described above for ferrocyanide. Because rhenium is being used as a surrogate for technetium in another DOE funded project proposal, results for  $\text{Re}(\text{DMPE})_3^+$  are briefly discussed as illustrative of these three compounds.

$[\text{Re}^{\text{I}}(\text{DMPE})_3]^+$ , where DMPE = 1,2-bis(dimethylphosphino)ethane, is a non-radioactive analog of the radioactive cation,  $[\text{}^{99\text{m}}\text{Tc}^{\text{I}}(\text{DMPE})_3]^+$ , which represents a step in the development of technetium myocardial perfusion imaging agents as well as a model analyte that represents Tc complexes that are thought to exist in the Tc wastes at Hanford.  $[\text{Re}^{\text{I}}(\text{DMPE})_3]^+$  is electroactive. It undergoes reversible one-electron electrochemical oxidation to  $[\text{Re}^{\text{II}}(\text{DMPE})_3]^{2+}$  with a formal potential around 0.0 V versus Ag/AgCl, depending on the nature of the electrode and the electrolyte solution. The oxidized form,  $[\text{Re}^{\text{II}}(\text{DMPE})_3]^{2+}$ , absorbs light in the visible region, whereas  $[\text{Re}^{\text{I}}(\text{DMPE})_3]^+$  is colorless. With a suitable coating that allows the partitioning of  $[\text{Re}^{\text{I}}(\text{DMPE})_3]^+$  and limits the access of some potential interferences to the electrode surface,  $[\text{Re}^{\text{I}}(\text{DMPE})_3]^+$  can be selectively preconcentrated in the film. With an applied electrolysis

potential, at which  $[\text{Re}^{\text{I}}(\text{DMPE})_3]^+$  is oxidized to  $[\text{Re}^{\text{II}}(\text{DMPE})_3]^{2+}$ , and with light of selected wavelength at which  $[\text{Re}^{\text{II}}(\text{DMPE})_3]^{2+}$  absorbs (528nm),  $[\text{Re}^{\text{I}}(\text{DMPE})_3]^+$  passes all of the three levels of sensor interrogation. The capability of simultaneously monitoring the electrochemical and optical events of the rhenium complex, and by extension the analogous technetium complex, was demonstrated (18).

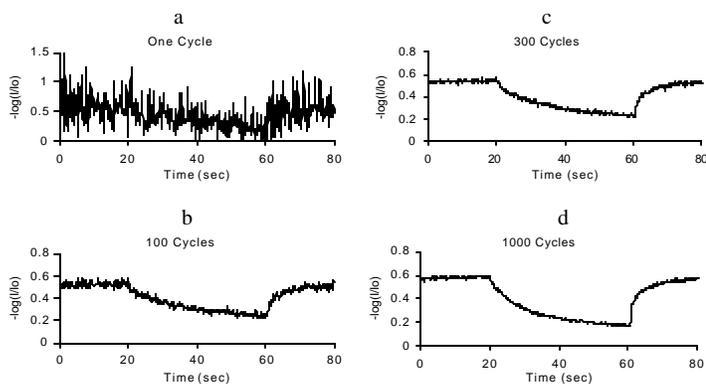
In all of the above examples, the analyte is detected directly as it undergoes spectroelectrochemical modulation. However, this approach would not work if neither the analyte nor its electrolysis product absorbs light. Consequently, we developed a strategy whereby a redox mediator can be used to indirectly reduce/oxidize the analyte. In this case the effect of the analyte on the spectroelectrochemical modulation of the redox mediator is used to quantify the analyte. This concept was demonstrated using ascorbate as the analyte and  $\text{Ru}(\text{bipy})_3^{2+}$  trapped in Nafion-SiO<sub>2</sub> as the mediator (19).

**8. Demonstration of Sensing in the Presence of Direct Interferences.** Operation and performance of the three modes of selectivity for detection of analytes in the presence of direct interferences were investigated using binary mixture systems (17). These binary mixtures consisted of  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{Ru}(\text{bpy})_3^{2+}$ , and of  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Ru}(\text{CN})_6^{4-}$  in aqueous solutions. Results on the  $\text{Fe}(\text{CN})_6^{3-}/\text{Ru}(\text{bpy})_3^{2+}$  binary mixture showed that an anion-exchange coating consisting of PDMDAAC-SiO<sub>2</sub> [where PDMDAAC = poly(dimethyldiallylammonium chloride)] and a cation-exchange coating consisting of Nafion-SiO<sub>2</sub> can trap and preconcentrate analytes with charge selection. At the same time such coatings exclude interferences carrying the same type of charge as that of the exchange sites in the sensor coating. Using the  $\text{Fe}(\text{CN})_6^{4-}/\text{Ru}(\text{CN})_6^{4-}$  binary mixture, the  $\text{Fe}(\text{CN})_6^{4-}$  component can be selectively detected by restricting the modulation potential cycled to a range specific to the redox-active  $\text{Fe}(\text{CN})_6^{4-}$  component and simultaneously monitoring the optical response at the overlapping wavelength of 420 nm. It was also shown that when the wavelength for optical monitoring was chosen as 500 nm, which is specific to the  $\text{Ru}(\text{CN})_6^{4-}$  component, interference from the  $\text{Fe}(\text{CN})_6^{4-}$  component for spectroelectrochemical detection of  $\text{Ru}(\text{CN})_6^{4-}$  was significantly suppressed even though the cyclic modulation potential encompassed the redox range for the  $\text{Fe}(\text{CN})_6^{4-}$  component. Similar experiments were performed using poly(vinyl alcohol)-polyelectrolyte films (20)

**9. Materials for Selective Films.** Coincident with our work on sensor design, we have developed two new series of chemically-selective optical materials (21-25). These new materials are essential to the functioning of our new spectroelectrochemical sensors. One new series consists of polyelectrolyte-containing silica composites prepared by sol-gel processing. Sol-gel processed polymer-SiO<sub>2</sub> composite films have been shown to possess a series of properties suited to construction of both electrochemical and optochemical sensors, such as ion-exchangeability, nano-scale porosity, high optical transparency, variable thickness (0.1 - 3.0  $\mu\text{m}$ ), and physicochemical stability. Most importantly, it was found that this silica-based, polyelectrolyte-containing composite material can also form uniform and well-adhered thin films on ITO glass by the spin-coating method, thereby making it more useful in ITO-based spectroelectrochemical sensing applications compared with, for example, SiO<sub>2</sub> on gold surfaces.

Another new series of materials was based on polymer blending in a host of glutaraldehyde cross-linked poly(vinyl alcohol). Chemically-selective dopants in this host demonstrate property-selective separations of chemicals from mixtures. We have optimized the composition, optical properties and the coating procedures for several specific blends for optical sensing. These blends have clear UV and visible spectral regions for direct spectroscopic sensing and they are excellent absorbers of many inorganic and organic charged species from aqueous environments.

**9. Ensemble Averaging.** Because the spectroelectrochemical modulation signal can be easily repeated by using a repetitive potential excitation signal, ensemble averaging of the optical response can be used to improve the signal to noise ratio, which leads to lower detection limits. We have demonstrated this with a sensor comprised of indium tin oxide coated glass over-coated with a sol-gel processed Nafion-SiO<sub>2</sub> and *tris*-(2,2'-bipyridyl)ruthenium(II) chloride as a model analyte (26). The optical responses after increasing degrees of ensemble averaging for a square wave excitation potential are shown in **Figure 6**. After 1000 cycles, the signal-to-noise ratio increased to 60:1, Fig 9d. As expected, signal averaging lowers the limit of detection, as shown in a plot of the amplitude of optical modulation ( $\Delta A$ ) vs. concentration.



**Figure 6.** Effect of ensemble averaging on optical response: Square wave excitation,  $J = 40$  s, LED source, PMT detector. Optical response to (a) one cycle ( $S:N = 2:1$ ). Averaged optical response after 100 cycles ( $S:N = 21:1$ ); c) 300 cycles ( $S:N = 36:1$ ); d) 1000 cycles ( $S:N = 60:1$ ).

**10. Evaluation of Different Excitation Potential Waveforms.** The electrochemical reaction of analyte that is partitioned into the selective film of the sensor is controlled by the excitation potential waveform. Mostly, we have used either a triangular waveform (i.e., cyclic voltammetry) or a potential step waveform (i.e., chronoamperometry) in our research. However, other waveforms are possible, and may be advantageous compared to these two. A fundamental question arises regarding the excitation potential waveforms employed to initiate the electrochemical changes observed. Historically in spectroelectrochemistry, selection has been based solely upon the effectiveness of the waveform to quickly electrolyze any analyte observable by the optical detection method employed. There are additional requirements, such as power consumption, by which the waveform should be selected for use in a remote sensing configuration. The effectiveness of explicit finite difference simulation as a tool for investigating the applicability of three different excitation potential waveforms (square, triangle, and sinusoid) was demonstrated (27). The simulated response was compared to experimental results obtained from a prototype sensing platform consisting of an indium tin oxide OTE coated with a cation selective, sol-gel derived Nafion composite film designed for the detection of a model analyte, *tris*(2,2'-bipyridyl) ruthenium(II) chloride. Using a diffusion coefficient determined from experimental data ( $5.8 \times 10^{-11}$  cm/s for  $5 \times 10^{-6}$  M Ru(bipy)<sub>3</sub><sup>2+</sup>) the simulator program was able to accurately predict the magnitude of the absorbance change for each potential waveform (0.497 for square, 0.403 for triangular, and 0.421 for sinusoid), but underestimated the number of cycles required to approach steady-state. The simulator program predicted 2 cycles (square), 3 cycles

(triangular), and 5 cycles (sinusoid), while 5 (square), 15 (triangular), and 10 (sinusoid) were observed experimentally.

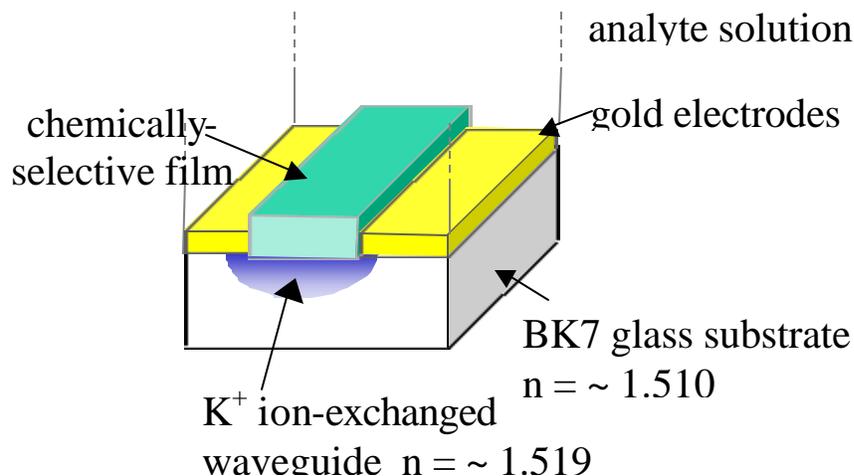
**11. Waveguide Sensors.** Three improvements in our spectroelectrochemical sensor prototype can be realized by replacing the multiple internal reflection optic with a multimode planar waveguide: 1. increased sensitivity and better detection limits due to higher density of reflections; 2. greater versatility in choice of optical designs, including more sophisticated configurations, like Mach Zehnder interferometers; and 3. the ability to micromachine sensors in complex platforms. Consequently, incorporation of planar waveguide technology into a spectroelectrochemical sensor was explored.

*a. Multimode thin-film planar waveguide.* In this sensor design, a potassium ion-exchanged BK7 glass waveguide was over-coated with a thin film of ITO that served as an optically-transparent electrode (28). A chemically-selective film was spin-coated on top of the ITO film. The sensor supported five optical modes at 442 nm and three at 633 nm. The impact of the ITO film on the optical properties of the waveguide and on the spectroelectrochemical performance of the sensor was investigated. By applying either a triangular or square wave excitation potential waveform, electromodulation of the optical signal has been demonstrated with  $\text{Fe}(\text{CN})_6^{-3/-4}$  as a model electroactive couple that partitions into a PDMDAAC-SiO<sub>2</sub> film.

A simple approximate analysis of the IEBK7 graded-index waveguide using a combination of literature and experimental estimates of the appropriate physical constants and a relationship for the penetration depth resulted in an acceptable description of the waveguide mode structures observed by the M-line technique. Overall attenuation losses within the sensor were large due to the layering of ITO directly onto the waveguide and to inefficient (prism) coupling. The losses due to ITO may be attributed to a significant free carrier absorption within the semiconductor. The high electrical resistance of the ITO layer was accompanied by significant changes in its optical properties during electromodulation over the potential range of the analyte, the ferri/ferrocyanide couple. Nonetheless, the contribution of ITO is linear with applied potential and can be quantitatively subtracted from the overall optical modulation signal yielding an adequate calibration curve for the analyte. Despite the associated relatively high detection limit, this prototype waveguide spectroelectrochemical sensor yielded a moderate improvement in sensitivity over the corresponding MIR device.

In order to obtain better sensitivity and detection limits, improvements in the prototype waveguide need to be made. These might include: direct fiber coupling to the waveguide or grating coupling as a replacement for prism coupling; optimization of the ITO layer (thickness and resistance) and possibly its isolation from the waveguide layer by insertion of a silica buffer layer; and, optimization of the chemically-selective film (thickness and polyelectrolyte concentration) to maximize analyte uptake and preconcentration.

*b. Multimode embedded channel planar waveguides.* In a second sensor design a potassium ion-exchanged BK7 glass channel waveguide was made by established photolithographic and molten salt techniques (29). A pair of gold electrodes were then deposited alongside the waveguide channel in a buss-bar configuration, as shown in **Figure 7**. The chemically-selective film was



**Figure 7.** Channel waveguide.

then spin-coated into the channel between the two electrode strips. This approach has the two advantages of light not passing through the electrode and minimum resistance in the electrode compared to an OTE. Electromodulation with this sensor was demonstrated with the same system described in the previous section. However, sensitivity was low because of poor bonding of the selective film to the waveguide channel surface. In order to obtain better sensitivity and detection limits, improvements in the prototype waveguide need to be made.

**12. Conclusions.** The basic concept of the spectroelectrochemical sensor has been demonstrated on a variety of chemical systems. The sensor has sufficient selectivity for its application to complex samples such as Hanford tank waste. The sensor is most directly applicable for the detection of ionic species that are electroactive and that exhibit an optical change upon electrolysis. However, some species not meeting this requirement can be sensed indirectly by their interaction with a redox mediator. This new sensor is infant in its development. Future research will result in significant improvements in detection limit, response time, size, and ruggedness and in greater breadth of application.

### 13. References

1. G. Zorpette, *G. Sci. Am.* May 1996, pp. 88-97.
2. D. J. Bradley, D. J.; Frank, C. W.; Mikerin, Y. *Physics Today*, April 1996, pp. 40-45.
3. Campbell, J. A.; Stromatt, R. W.; Smith, M. R.; Koppenaal, D. W.; Bean, R. M.; Jones, T. E.; Strachan, D. M.; Babad, H. *Anal. Chem.* 1994, *66*, 1208A-1215A.
4. Choppin, G. R. *J. Chem. Ed.*, 1994, *71*, 826-829.
5. U.S. Department of Energy, Office of Environmental Management, *Closing the Circle on the Splitting of the Atom*, second printing, 1996.
6. Gephart, R. E.; Lundgren, R. E. *Report PNL-10773*, Pacific Northwest National Laboratory, Richland, WA, 1995.
7. Burger, L. L.; Reynolds, D. A.; Schulz, W. W.; Strachan, D. M. *Report PNL-7822*, Pacific Northwest Laboratory, Richland, WA, 1991
8. Janata, A.; Josowicz, M.; Vanysek, P.; DeVaney, D. M. *Anal. Chem.* 1998, *70*, 179R-208R.
9. Shi, Y.; Slaterbeck, A. F.; Seliskar, C. J.; Heineman, W. R. *Anal. Chem.* 1997, *69*, 3679-3686.

10. Slaterbeck, A. F; Ridgway, T. H; Seliskar, C. J; Heineman, W. R. *Anal. Chem.* 1999, *71*, 1196-1203.
11. Stegemiller, ML; Heineman, WR; Seliskar, CJ; Ridgway, TH; Bryan, SA. In preparation.
12. Bryan, S. A.; Pool, K. H.; Bryan, S. L.; Forbes, S. V.; Hoopes, F. V.; Lerner, B. D.; Mong, G. M.; Nguyen, P. T.; Schiefelbein, G. F.; Sell, R. L.; Thomas, L. M. P. *Report PNL-10696*, Pacific Northwest National Laboratory, Richland, WA, 1995.
13. Maizels, M; Seliskar, CJ; Heineman, WR. *Electroanalysis* 2000, *12*, in press.
14. Maizels, M; Seliskar, CJ; Heineman, WR; Bryan, SA. In preparation.
15. Slaterbeck, AF; Shi, Y; Ridgway, TH; Seliskar, CJ; Heineman, WR. Proceedings for the Symposium on Chemical and Biological Sensors and Analytical Electrochemical Methods, Proceedings Vol. 97-19, Ricco, AJ; Butler, MA; Vanysek, P; Horval, G; Silva, AF, eds., 1997; pp 50-60.
16. Shi, Y; Seliskar, C. J; Heineman, W. R. *Anal. Chem.* 1997, *69*, 4819-4827.
17. Gao, L; Seliskar, C. J.; Heineman, W. R. *Anal. Chem.* 1999, *71*, 4061-4068.
18. Hu, Z; Slaterbeck, A. F.; Seliskar, C. J.; Ridgway, T. H.; Heineman, W. R. *Langmuir* 1999, *15*, 767-773.
19. DiVirgilio-Thomas, JM; Heineman, WR; Seliskar, CJ. *Anal. Chem.* 2000, *72*, 3461-3467.
20. Gao, L; Seliskar, CJ; Heineman, WR. *Electroanalysis* 2000, *12*, in press.
21. Shi, Y; Seliskar, C. J. *Chem. Mater.* 1997, *9*, 821-829.
22. Gao, L; Shi, Y; Slaterbeck, A. F.; Seliskar, C. J.; Heineman, W. R.. *Proc. SPIE* 1998, *Series 3258*, 66-74.
23. Gao, L; Seliskar, C. J.; Milstein, L. *Appl. Spectrosc.* 1997, *51*, 1745-1752.
24. Dasenbrock, C. O.; Ridgway, T. H.; Seliskar, C. J., Heineman, W. R.. *Electrochim. Acta* 1998, *43*, 3497-3502.
25. Gao, L; Seliskar, C. J. *Chem. Mater.* 1998, *10*, 2481-2489.
26. Slaterbeck, AF; Ridgway, TH; Seliskar, CJ; Heineman, WR. *Anal. Chem.* 1999, *71*, 1196-1203.
27. Slaterbeck, AF; Stegemiller, ML; Seliskar, CJ; Ridgway, TH; Heineman, WR;.. *Anal. Chem.* 2000, *72*, 5567-5575.
28. Ross, SE; Seliskar, CJ; Heineman, WR. *Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 9. Incorporation of Planar Waveguide Technology.* *Anal. Chem.* 2000, *72*, 5549-5555.
29. Ross, SE; Seliskar, CJ; Heineman, WR; Aryol, S; Nevin, JH. In preparation.