

# Environmental Management Science Program

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## **Design and Development of a New Hybrid Spectroelectrochemical Sensor**

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## Design and Development of a New Hybrid Spectroelectrochemical Sensor

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### Research Objective

A new concept for a chemical sensor that demonstrates three modes of selectivity (electrochemistry, spectroscopy, and selective partitioning) is being developed. The spectroelectrochemical sensor consists of an optically transparent electrode (OTE) coated with a selective film. Sensing is based on the change in optical signal of light passing through the OTE that accompanies an electrochemical reaction of the analyte at the electrode surface. The purpose of this new sensor is to significantly broaden the applicability of sensors to real samples by improving selectivity. The concept is to be demonstrated with a sensor for ferrocyanide in waste from tanks at the Hanford site.

### Research Progress and Implications

This report summarizes work after 1 1/2 years of a 3-year project.

The novel sensor concept has been clearly demonstrated to work. The sensor prototype consisted of an OTE made of indium tin oxide coated on glass that was coated with a sol-gel derived charge-selective thin film. Attenuated total (internal) reflection (ATR) was the optical detection mode. The following goals have been achieved:

- (1) Sensors for four analytes that are representative of inorganic and organic contaminants have been demonstrated with quantitative calibration plots: ferrocyanide,  $\text{Fe}(\text{CN})_{64}^-$ ;  $\text{Ru}(\text{bipy})_{32}^+$  where bipy = bipyridyl;  $\text{Re}(\text{DMPE})_3^+$  where DMPE = 1,2-bis(dimethylphosphino)ethane, and methyl viologen. Our success with the sensor for ferrocyanide is especially important since this is the sensor that we plan to develop for demonstration with samples of waste from tanks at Hanford with our collaborators at PNNL.
- (2) The three modes of selectivity have been demonstrated using mixtures of the model analytes  $\text{Fe}(\text{CN})_{64}^-$ ,  $\text{Fe}(\text{CN})_{63}^-$ ,  $\text{Ru}(\text{bipy})_{32}^+$ , and  $\text{Ru}(\text{CN})_{64}^-$ . The level of selectivity imparted by each of the three sensor selectivity modes (selective coating material, electrolysis potential, and wavelength) was demonstrated.
- (3) We have explored a variety of materials to make selective optical thin films that are also rugged and adhere well to the OTE surface. We have clearly shown that the selectivity properties of polymers such as Nafion and PDMDAAC, where PDMDAAC = poly(dimethyldiallylammonium chloride), and PAA, where PAA = poly(acrylic acid), and PVTAC, where PVTAC = poly(vinylbenzyltrimethylammonium chloride) can be imparted to sol-gel processed silica glass or a polymer-based host material. For example, an anion-selective sol-gel processed PDMDAAC-SiO<sub>2</sub> composite film and a cation-selective sol-gel derived Nafion-SiO<sub>2</sub> composite film have been applied to sensors and their use as sensors demonstrated with the analytes listed above.
- (4) A comprehensive sensor instrumentation package has been developed to enable the use of signal averaging of repetitive optical response signals from the new sensor to achieve lower limits of detection. Improvements on the order of 100x have been demonstrated.
- (5) We have made both slab and channel waveguides and have established the masking and polishing procedures to make channels of a variety of widths and depths ranging from single to multimode devices. The procedures for making channel waveguides with electrodes placed

next to the waveguide channel are currently being refined. Measurements with multimode planar waveguides coated with selective sol-gel processed thin films have shown that we can achieve about 3 orders of magnitude reduction in the limit of detection compared to our prototype multiple reflection (ATR) sensor. We have increased the versatility and portability of the sensor by operating the waveguide with a small HeCd laser (442 nm). We are also evaluating slab waveguides made of germania-doped silica top-coated with indium tin oxide as spectroelectrochemical sensors.

- (6) Since the immediate application of the sensor concept will be for the detection of ferrocyanide in a highly radioactive environment, we have evaluated the effect of high doses of gamma radiation on various sensor components and found the sensor to be adequately rugged.

## Planned Activities

The following work is planned for the second 1 1/2 years of the project:

- (1) Evaluation of the sensor for ferrocyanide using simulant samples prepared by PNNL.
- (2) Continued development of waveguides to improve detection limits and for device miniaturization.
- (3) Construction of a portable sensor to test at PNNL for detection of ferrocyanide in actual samples from waste tanks at the Hanford site.
- (4) Further evaluation of selectivity properties, detection limits, and ruggedness of sensors.
- (5) Evaluation of extension of the sensor concept to other analytes of DOE interest.

## Other Access To Information

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