DESIGN AND DEVELOPMENT OF A NEW HYBRID SPECTROELECTROCHEMICAL SENSOR

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Project Description

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. Thus, for an analyte to be detected, it must partition into the selective coating, be electrolyzed at the potential applied to the electrode, and either the analyte or its electrolysis product must absorb light at the wavelength chosen. Selectivity for the analyte relative to other solution components is obtained by choice of coating material, electrolysis potential, and wavelength for optical monitoring.

The purpose of this new sensor is to significantly broaden the applicability of sensors to real samples by improving selectivity. This high level of selectivity is to be achieved without any fragile biocomponent. The concept is to be demonstrated with a sensor for ferrocyanide.

Progress in Year 1

Good progress relative to the goals for the first year has been made. Most importantly, the novel sensor concept has been clearly demonstrated using two different chemical systems. An OTE consisting of indium tin oxide coated on glass was coated with a sol-gel derived charge-selective thin film and was used as the basic sensor Attenuated total reflection (ATR) was the optical detection mode. The selective coating was either the anion-selective sol-gel derived **PDMDAAC-SiO_2** composite film, where PDMDAAC = poly(dimethyldiallylammonium chloride, or the cation-selective sol-gel derived **Nafion-SiO_2** composite film. **$Fe(CN)_6^{4-}$** was used as a model analyte with the **PDMDAAC-SiO_2** composite film to demonstrate that the change in transmittance of the ATR beam resulting from oxidation of **$Fe(CN)_6^{4-}$** to **$Fe(CN)_6^{3-}$** at the sensor can be used to quantitate an analyte (1). This was also demonstrated with **$Ru(bipy)_3^{2+}$** as a model analyte with a **Nafion-SiO_2** composite film (2). The work described in these two papers clearly describes the quantitative capability of the sensor.

The three modes of selectivity have also been demonstrated using mixtures of the model analytes **$Fe(CN)_6^{4-}$**, **$Fe(CN)_6^{3-}$**, **$Ru(bipy)_3^{2+}$**, and **$Ru(CN)_6^{4-}$** with the appropriate coating. The level of selectivity imparted by each of the three modes (coating material, electrolysis potential, and wavelength for optical monitoring) was demonstrated (3).

Work on the other model analytes, methyl viologen dication and **$Re(DMPE)_3^+$** where DMPE = 1,2-bis(dimethylphosphino)ethane, has begun. In the case of methyl viologen, we have found that the Nafion-sol gel composite functions as a good selective coating for the sensor. We have just demonstrated a spectroelectrochemical response for the electrogenerated methyl viologen radical cation. A good electrochemical response for **$Re(DMPE)_3^+$** at Nafion-sol gel composite has also been obtained.

The selective coating on the sensor surface is especially important since it provides the first level of selectivity. We have explored a variety of materials to find selective films that are also rugged and adhere well to the OTE surface (4-8). We have clearly shown that the selectivity properties of polymers such as Nafion and PDMDAAC can be imparted to sol-gels, which possess these properties (4,5,7,8). We have also shown that the same properties can be achieved by doping a polymer-based host (6).

Instrumentation is being developed to enable us to use signal averaging of repetitive optical response signals to achieve lower levels of detection. This instrumentation also enables us to evaluate various excitation signals for the sensor response such as a sinusoid.

We have worked out the laboratory conditions under which we can make K^+/Na^+ and Ag^+/K^+ ion-exchanged multimode planar waveguides in several types of sodium-rich glass. We have now made both slab and channel waveguides in optical crown (Schott BK7). In the latter case we have established the masking and polishing procedures to make channels of a variety of widths and depths ranging from single to multimode in size. The procedures for simultaneously making channel waveguides with electrodes placed next to the waveguide channel for spectroelectrochemistry 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 enhancement in optical signal compared to our prototype multiple reflection (ATR) sensor.

Since the immediate application of the sensor concept will be to the detection of ferrocyande in a highly radioactive environment, we have begun evaluating the effect of high doses of gamma radiation on various sensor components. This has proved to be a good project for two undergraduate students.

Papers resulting from support provided by this grant are listed as the References at the end of this proposal. Copies of those published and in press are included in Appendix I.

Our first conference paper on this work was presented at the Joint Meeting of the Electrochemical Society and the International Society of Electrochemistry in Paris. The abstract is included in Appendix II. Abstracts for several presentations at conferences during the second year of the grant have been accepted.

Personnel Supported

During the first year, support has been provided for the following personnel:

Faculty

William R. Heineman - overall project direction, electrochemistry, study of analytes

Carl J. Seliskar - overall project direction, selective coatings, waveguides
Thomas H. Ridgway - spectroelectrochemistry theory, instrumentation
Joseph Nevin - waveguides

Graduate Students

Letian Gao (5th year) - selective polymer coatings
Hongying Gao (5th year) - interaction of polymers with analytes
Yining Shi (4th year) - demonstration of sensor concept, development of waveguides, ferrocyanide analyte
Andrew Slaterbeck (4th year) - demonstration of sensor concept, development of instrumentation, $Ru(bipy)_3^{2+}$ analyte
Zhongmin Hu (4th year) - $Re(DMPE)_3^{+}$ analyte
Mike Clager (3rd year) - methyl viologen dication analyte
Mila Maizels (3rd year) - gamma radiation cross-linked polymer films, ferrocyanide analyte
Saroj Aryal (engineering) - waveguides
Liping Zhou (2nd year) - interaction of polymers with analytes

Undergraduate Students

Ian Rodway (senior) - effects of radiation on sensor components
Ryan Steinmetz (senior) - effects of radiation on sensor components

Expenditure of Funds

$74,000 of the funds budgeted for the first year were unspent. This budget surplus is due to several reasons. Funds were allocated to Engineering in support of a graduate student to develop waveguides. A student was not immediately found for the project, resulting in a 6-month delay in their initiation of spending. Two or our graduate students from the Department of Chemistry were awarded named fellowships for their excellent research and degree progress and hence needed no support from the grant for nine months each. This enabled us to add more student personnel to the project. It is anticipated that these funds will be spent during the first part of the 2nd year of the project as we support these additional students.

References

1. Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. **1.** Demonstration of Concept with Ferricyanide, Y. Shi, A. Slaterbeck, C. J. Seliskar, W. R. Heineman, Anal. *Chem.*, 69(18), 3679-3686 (1997).

2. Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device, A. Slaterbeck, Y. Shi, C. J. Seliskar, T. H. Ridgway,

W. R. Heineman, Proc. of the Symp. on Chemical and Biological Sensors and Analytical Electrochemical Methods, The Electrochemical Society, Inc., Pennington, NJ, A. J. Ricco, M. A. Butler, P. Vanysek, G. Horvai, A. F. Silva, Eds, Vol. 97-19, 50-60 (1997).

3. Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 2. Demonstration of Selectivity in the Presence of Direct Interferences, Y. Shi, C. J. Seliskar, W. R. Heineman, Anal. *Chem.*, 000, 0000-0000 (1997).

4. Electrochemical Behavior of Graphite Electrodes Modified by Spin-Coating with Sol-Gel Entrapped Ionomers, M. D. Petit-Dominguez, H. Shen, W. R. Heineman, C. J. Seliskar, *Anal. Chem.*, 69(4), 703-710, (1997).

5. Optically Transparent Polyelectrolyte-Silica Composite Materials: Preparation, Characterization, and Application in Optical Chemical Sensing, Y. Shi, C. J. Seliskar, ***Chem. Mat.,*** 9(3), 821-829 (1997).

6. Spectroscopic Sensing with a Highly Transparent, Ion-Exchangeable Polymer Blend, L. Gao, C. J. Seliskar, L. Milstein, *App. Spectrosc.*, 51(11), 0000-0000 (1997).

7. Electrochemical Behavior of Graphite Electrodes Modified with Nafion Sol-Gel by Spin Coating, B. Barroso-Femandez, M. T. Lee-Alvarez, C. J. Seliskar, W. R. Heineman, *Anal. Chim. Acta*, submitted 4/28/97.

8. Influence of Ionomers on Behavior of Sol-Gel-Ionomer Modified Graphite Electrodes, H. Shen, C. J. Seliskar, W. R. Heineman, *Anal. Chem.*, submitted 5/14/97.

Appendix I

Publications Describing Research Supported by this Grant

Published or In Press

1. Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 1. Demonstration of Concept with Ferricyanide, Y. Shi, A. Slaterbeck, C. J. Seliskar, W. R. Heineman, *Anal. Chem.*, 69(18), 3679. 3686 (1997).

2. Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device, A. Slaterbeck, Y. Shi, C. J. Seliskar, T. H. Ridgway, W. R. Heineman, Proc. of the Symp. on Chemical and Biological Sensors and Analytical Electrochemical Methods, The Electrochemical Society, Inc., Pennington, NJ, A. J. Ricco, M. A. Butler, P. Vanysek, G. Horvai, A. F. Silva, Eds, Vol. 97-19, 50-60 (1997).

3. Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 2. Demonstration of Selectivity in the Presence of Direct Interferences, Y. Shi, C. J. Seliskar, W. R. Heineman, *Anal. Chem.*, 000, 0000-0000 (1997).

4. Electrochemical Behavior of Graphite Electrodes Modified by Spin-Coating with Sol-Gel Entrapped Ionomers, M. D. Petit-Dominguez, H. Shen, W. R. Heineman, C. J. Seliskar, *Anal. Chem.*, 69(4), 703-710, (1997). Partial support.

5. Optically Transparent Polyelectrolyte-Silica Composite Materials: Preparation, Characterization, and Application in Optical Chemical Sensing, Y. Shi, C. J. Seliskar, *Chem. Mat.*, 9(3), 821-829 (1997).

6. Spectroscopic Sensing with a Highly Transparent, Ion-Exchangeable Polymer Blend, L. Gao, C. J. Seliskar, L. Milstein, *App. Spectrosc.*, 5l(11), 0000-0000 (1997). Partial support.