

Spectroelectrochemical Sensing Based On Multimode Selectivity Simultaneously Achievable In A Single Device. 12. Characterization Of A Channel Waveguide Sensor

Susan E. Ross¹, Carl J. Seliskar¹, William R. Heineman¹, Saroj Aryol², and Joseph H. Nevin²

¹Department of Chemistry
and

²Department of Electrical and Computer Engineering
University of Cincinnati, Cincinnati, Ohio 45221

A new sensor concept based on three modes of selectivity (chemical partitioning, electrochemistry, spectroscopy) has recently been demonstrated (1,2). In this concept, threefold selectivity for the analyte by the sensor was obtained by incorporation of a chemically-selective film, choice of the electrode potential, and choice of wavelength of the light. The concept has been successfully demonstrated using a prototype multiple internal reflection (MIR) optic and a planar slab waveguide, which consisted of a simple bilayer of an indium tin oxide (ITO) optically transparent electrode (OTE) deposited on either a 1 mm thick glass substrate or an ion-exchanged BK7 (IEBK7) slab waveguide. Analyte detection was enhanced by over-coating the sensor with a chemically-selective film and was based on the change in the attenuation of light guided through the sensor.

An important extension of our work is to evaluate planar waveguides as potential replacements for the MIR optic in the spectroelectrochemical sensors described to date. The potential advantages of waveguides (3-5) over MIR devices are several: 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.

Here, we report an ion-exchanged channel waveguide with optical fibers used for coupling. A channel waveguide design has certain advantages compared to the slab waveguide design reported previously (2). In a channel design, the electrodes can be metallic (gold) strips that are too thick to be transparent but have minimal iR drop, rather than (transparent) indium tin oxide for which iR drop can be substantial. In the channel design, the electrodes can be isolated from the light path and no baseline optical modulation results from modulating the potential. In the slab design, the modulation of indium tin oxide restricted the detection limit (2). On the other hand, the separation of the optical channel from the electrode introduces another dimension of analyte diffusion with electro-modulation into the response time of the sensor.

We have demonstrated the essential process of electro-modulation using a channel waveguide over-coated with a sol-gel processed anion-selective film which selectively preconcentrates the ferricyanide-ferrocyanide couple. The sensor consisted of a K⁺/Na⁺ ion-exchanged multimode channel waveguide with adjacent bi-metal electrodes – either gold locked with chromium (Au/Cr-CHIEBK7) or gold locked with titanium (Au/Ti-CHIEBK7) to the BK7 glass substrate. In choosing this design, several issues arose that required significant work to resolve. These issues included electrode shape and placement, electrode robustness, analyte diffusion, optical coupling, and selective film deposition within the channel.

The sensor design required an electrode and the chemically-selective film to allow efficient electrochemical modulation of the analyte. Cyclic voltammetry with these sensors in ferricyanide solution was performed to determine the attendant electrochemical behavior. Channel waveguides made with electrodes locked to BK7 with chromium were unsuitable because of severe degradation with use in solution. On the other hand, gold electrodes locked to BK7 glass with titanium were found to be robust.

In order for electro-modulation with a CHIEBK7 waveguide to be successful, the optical response must correspond to the electrochemical events at the film/electrode interface. Initially, electrochemistry with a PDMDAAC-SiO₂ coated channel waveguide in 5.0 mM Fe(CN)₆⁴⁻, 0.1 M KNO₃ using a triangular potential excitation waveform and a double step potential excitation waveform was performed and the results showed that the electrochemical portion of the system functioned properly. Next, electro-modulation of the waveguide was done with optical signal acquisition. Electrochemical modulation produced optical changes (ΔA_{ferri}) that corresponded to cycling between colorless ferrocyanide and yellow ferricyanide, which absorbs at the monitored wavelength of 442 nm. Overall, the ΔA_{ferri} values for electro-modulation were relatively small, $\Delta A_{\text{ferri}} = 0.067$, for a 5.0 mM Fe(CN)₆⁴⁻ solution. This was an unfortunate result of the PDMDAAC-SiO₂ film being necessarily thick (>1 μm), in order to stabilize the film near the channel, and of poor optical coupling. 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 fiber butt-coupling; optimization of the gold electrode configuration 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 at the waveguide surface.

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