Sensors Based on Spectroelectrochemistry

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A sensor that combines electrochemistry, spectroscopy, and selective partitioning into a film to substantially improve selectivity for applications that involve complex samples has been demonstrated (1-9). The sensor consists of an optically transparent electrode (OTE) coated with a selective film. Sensing is based on the change in absorbance (ΔA) for attenuated total reflectance (ATR) at the OTE that accompanies electrochemical modulation of analyte that has partitioned into the film. Selectivity for the analyte relative to other solution components is obtained by choice of film material, electrolysis potential, and wavelength for optical monitoring.

One form of the sensor consists of an indium tin oxide OTE that has been coated with a thin film (typically <1 μm thick) of charge-selective material. The following films have been used: anionically charge-selective sol-gel derived composites PDMDAAC-SiO_2, PVTAC-SiO_2, and QPVP-SiO_2 [where PDMDAAC = poly(dimethyl diallylammonium chloride), PVTAC = poly(vinyl tetraammonium chloride, and QPVP = quaternized poly(4-vinyl pyridine)] and cationically charge-selective Nafion and sol-gel derived Nafion-SiO_2 composite.

Metal complexes have served as models of analytes that undergo optical changes in the visible region upon electrochemical modulation. For example, $Fe(CN)_6^{4-}$ is determined at a sensor with a film of PDMDAAC-SiO_2 by the ΔA at 420 nm when colorless $Fe(CN)_6^{4-}$ that has partitioned into the film is oxidized to $Fe(CN)_6^{3-}$, which is yellow. Sensors for $Ru(bipy)_3^{2+}$, $Ru(CN)_6^{4-}$, and $Re(DMPE)_3^{1+}$ [where DMPE = 1,2-bis(dimethylphosphino)ethane] have also been demonstrated.

Sensors are also being developed for analytes that do not undergo sufficiently large spectral changes in the visible range upon electromodulation. One approach is to use an electron transfer mediator that is immobilized in the film and that exhibits a large ΔA upon electromodulation. For example, ascorbate is detected indirectly by its reaction with an electron transfer mediator, $Ru(bipy)_3^{2+}$, which is immobilized in a film of Nafion-SiO_2 (7). Ascorbate is oxidized by electrogenerated $Ru(bipy)_3^{3+}$, and this reaction affects the optical change at 450 nm associated with electromodulation of $Ru(bipy)_3^{2+}$. Another approach is used for metal ions that undergo only weak optical changes upon electromodulation. Here a coordinating ligand that serves as a chromophore is immobilized in the film. When the metal ion partitions into the film it reacts with the ligand in the film to form a coordination compound that gives a much larger optical response when it is electrochemically modulated. An example is the determination of Cu^{2+} at a sensor with a film of Nafion-SiO_2 containing the ligand 2,9-dimethyl 1,10-phenanthroline (neocuproine).

Three waveforms for electromodulation have been examined: triangle, square, and sinusoid (6). Because the optical modulatioon signal is reproducible, ensemble averaging can be used to lower the limit of detection by improving the signal to noise ratio (4).

A small portable sensor unit including a virtual interface, control electronics and optics has been developed. This instrument was used to determine ferrocyanide in a sample of radioactive waste from a storage tank at the Hanford Site (9). This measurement provided a practical application of the sensor to a complex sample of high pH and ionic strength

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