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Throwing Light on Electrodes

The following is a summary of one of the papers presented at a Joint Meeting of the Electro-analytical Group and the Electrochemistry Group of the Faraday Division held on February 27th, 1981, at Southampton University.

Analytical Applications of Spectroelectrochemistry

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There are many ways in which spectroscopic and electroanalytical techniques have been combined. Ellipsometry, ESCA and Auger electron spectroscopy have been used to monitor the electrode surface, UV, visible and IR absorption, NMR, ESR and luminescence spectrometry have been used to study the layers of solution adjacent to the electrode, and Raman, specular reflection and internal reflection spectroscopy have been used to study both solution and electrode. In conjunction with these, the electrochemical techniques of chronoamperometry (single and a double potential step), chronopotentiometry, coulometry and cyclic voltammetry have all been used. A variety of electrode - light beam configurations have been devised, of which possibly the most interesting are the optically transparent electrodes (made from a thin film on a substrate or from a minigrid), which have been used with both transmission normally through the electrode and total internal reflectance spectroscopy.

These spectroelectrochemical combinations have been used to determine E^0 and n values, rate constants, diffusion coefficients and reaction mechanisms and to study adsorbed species, oxide films and electrodeposits on electrode surfaces. There have been very few quantitative analytical applications reported.

Analytical Possibilities

The most promising candidates as analytical methods are those in which absorbance is measured whilst movement of species in solution is governed by semi-infinite linear diffusion. Starting from the Cottrell equation,^{1,2} a simple expression for absorbance (A) measured normal to the electrode surface may be deduced by a variety of methods,^{3,4} namely $A = \epsilon_R 2(D_0 t / \pi)^{1/2} C_0^*$ (for a reaction $O + ne \rightarrow R$) where ϵ_R is the molar absorptivity of the reduced species, t is time and D_0 and C_0^* are the diffusion coefficient and bulk concentration of the oxidised species. It should be noted that the units of C_0^* are mol l^{-1} , whereas in the Cottrell equation they are mol ml^{-1} . The potential analytical usefulness can readily be seen from the equation's similarity to the Beer - Lambert relationship, in which the path-length term

has been replaced by a function of time, $2(D_0 t / \pi)^{1/2}$. This function has, erroneously, been referred⁵ to as the diffusion layer thickness. However, it is not difficult to show that, by considering the expression for the variation of C_0 with distance (x) from the electrode surface [$C_0 = C_0^b \operatorname{erf}(x/2D_0 t)^{1/2}$], where erf is the error function] and by finding the slope, by differentiation, at $x = 0$, the diffusion layer thickness is $(\pi D_0 t)^{1/2}$. What the equation does indicate is that, as far as the absorbance is concerned, the concentration of the absorbing reduced species may be considered constant (equal to the bulk concentration of the oxidised species) up to a boundary, which moves out into the solution as a function of the square root of the time, beyond which the concentration is zero. Thus the term $2(D_0 t / \pi)^{1/2}$ represents a diffusion layer thickness (but not *the* diffusion layer thickness^{6,7}).

The problem of applying this spectroelectrochemical technique to any real system becomes immediately apparent when it is realised, for a value of D_0 of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (fairly typical of ions in solution), that after electrolysis for 10 s the path length is 0.1 mm and has increased to only 0.37 mm after 100 s. This means that for most applications a spectrometer equipped with signal-averaging facilities must be used to give meaningful signal to noise ratio characteristics, and makes the modification of a conventional ultraviolet - visible spectrometer for spectroelectrochemical work an unattractive proposition with any of the electrode - light beam configurations mentioned earlier.

Novel Electrode - Light Beam Configuration

If the configuration is changed so that a light beam of fixed height h is passed at grazing incidence over a plane electrode of length l then the equation for the absorbance becomes⁸ $A = (\epsilon_R - \epsilon_O) \times 2l(D_0 t)^{1/2} / h \pi^{1/2} C_0^b$, again for a reaction $O + ne \rightarrow R$ but allowing for the possible absorbance of the oxidised species as well. It can be seen that the previous equation has been modified by term l/h . Thus, for an electrode 1 cm long and a light beam of thickness 0.5 mm the path-length term becomes 0.2 cm after 10 s and 0.74 cm after 100 s. This configuration has been used to study the reduction of a number of metal ions⁹ and both the reduction and oxidation of a number of organic molecules.⁸ Results consistent with the equation given above were obtained and it should be noted that the spectra observed were indeed the difference between the oxidised and reduced forms, which means that care should be taken in interpreting a spectroelectrochemical spectrum as evidence of the existence of a single absorbing species at the electrode surface.

Advantages

This configuration has a number of advantages to offer. Firstly, all studies performed with optically transparent electrodes can be carried out but with freedom from the effects of the electrode transmission characteristics, and with considerably increased sensitivity, making the use of a conventional spectrometer a viable proposition. The sensitivity limit is set by the lowest value of h that can be tolerated, but the use of fibre-optic light guides or lasers (as has been reported recently¹⁰) may extend the system over the method in which the light beam of the conventional spectrometer is simply blanked off by the appropriate amount. The system is not only applicable to reactions of the types mentioned earlier but may be extended to more complex electrode reactions for which spectroelectrochemical equations have already been derived,¹¹ by modification of these equations to allow for the l and h terms.

Analytical Applications

The system can not only be used for any existing spectrophotometric method involving oxidation or reduction (the electrode surface substitutes for the redox reagent), but also extends the range of reactions available for analytical use as the stringent kinetic requirements for most spectrophotometric reactions can be relaxed, highly reproducible conditions being obtained in the diffusion layer. This is well illustrated by the fact that it was shown possible to use electrogenerated hydroxide ion as a spectrophotometric reagent for a number of metals.⁹ In addition, the configuration is being evaluated for use in the spectroelectrochemical analogue of anodic stripping voltammetry, whereby metal ions are pre-concentrated and separated from the remainder of the sample matrix by electrodeposition on to the electrode surface and then anodically redissolved in a solution containing a colorimetric

reagent. Preliminary investigations¹² have shown that there are a number of problems associated with the redox and pH behaviour of the colorimetric ligand to be overcome before the system will provide a viable analytical technique.

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