Optically Transparent Electrodes

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Optically transparent electrodes (OTE) made from thin metal layers on glass were first used in electrochemical studies involving photovoltaic effects.[1] More recently, OTE made from "doped" tin oxide coated glasses were applied to electrode reactions where the products formed were followed by optical spectroscopy.[2] The use of these electrodes has now been extended to aid the elucidation of mechanism and kinetics of organic electrode reactions.[3]

The application of internal reflectance spectroscopy (IRS) with OTE for following processes involving absorbing species at a distance from the electrode surface well within the thickness of the diffusion layer has been experimentally demonstrated.[4] The advantages of OTE are quite clear. Normal transmission spectroscopy with the incident light passing normal to the surface of OTE allows spectral monitoring in a minimum of thickness of about 10^4 A, depending on concentration and molar absorptivity of the absorbing species. IRS lowers this minimum thickness by one or two orders of magnitude. IRS using germanium electrodes in the infrared region is also being pursued in various laboratories.[5]

Although some work has been done with thin metal films vapor deposited on glass substrates, most of our studies have employed OTE made from doped tin oxide coatings on glasses obtained from two commercial sources. Although the doping material can be varied, antimony is commonly used and the resulting tin oxide coating is a n type semiconductor with a broad band gap. The carrier density is high, the order of 10^{20} - 10^{21} cm^{-3}. The resistance varies considerably, depending on level of doping and thickness of the coating. Surfaces with resistances as low as 5-10 ohm-cm^{-2} have been prepared.

EXPERIMENTAL

For electrochemical studies, it is desirable to minimize the ratio of surface area to resistance, so a thin circular ring of conducting surface is used as shown in the cell design of Figure 1. A simple sandwich type cell is employed for spectral studies. A potentiostat utilizing solid state Philbrick operational amplifiers and a Hewlett-Packard Model 467A power amplifier is used. Spectral work is done on either a Cary Model 15 spectrophotometer or a Warner-Swasey Co. Rapid-Scanning millisecond spectrophotometer.

RESULTS AND DISCUSSION

Preliminary measurements of the differential capacitance of these tin oxide electrodes for various pH's and electrolytes have been made by superimposing a small oscillating voltage on a changing dc bias voltage. Since these electrodes behave quite inertly in most electrolytes, the potential range which can be examined is extensive in comparison to most other semiconductor electrodes. It is found that there is a potential region in which the differential capacitance remains fairly independent of electrolytes (e.g. KCl, Na_2SO_4, $KClO_4$, etc), their concentration and pH, and depends mainly on the particular semiconductor. For

example, a semiconductor with a resistance of 10 ohm-cm^{-2} gave a differential capacitance of 2.4 uF-cm^{-2} in KCl solutions 0.03 to 1.0 molar (pH = 6.5) over the potential range -0.3 to +0.4 V. vs SCE. Another semiconductor gave a capacitance between 10-15 uF-cm^{-2} in a potential range of +0.3 to -0.1 V vs SCE but at more negative potentials, C^{-2} varied linearly with electrode potential due to depletion of electrons in the space charge layer.

Using these electrodes, it is easy to follow the concentration of absorbing species formed during the course of an electrode reaction. For example absorbancy varies linearly with the reciprocal of the square-root of time during a chronoamperometric experiment as expected if the reaction is diffusion controlled and the product formed absorbs at the wavelength of the monitoring light. Similarly, electrochemical parameters for a variety of experimental techniques, i.e. chronopotentiometry, voltage-scan, etc., can be concurrently evaluated by spectral studies. However, in many cases there are complications due to the electrochemical parameters being affected by pH or by type or concentration of ions.

The oxidation of ferrocyanide has been extensively examined by cyclic voltammetry. Figure 2 gives examples of the changes in the current-potential (i-E) curves when KCl concentration or pH is varied. Since the saturation current for these semiconductors is high, the usual peak-type i-E curves, in which i_{max} is diffusion limited are observed. The overvoltage is affected by electrolyte concentration and pH. However, the quantitative aspects of the potential distribution throughout the semiconductor and the Helmholtz layer are complicated. Attempts are being made to further evaluate the electrical properties of these semiconductors and to relate them to the i-E characteristics. The situation appears promising since these electrodes behave quite inertly over a wide potential range.

In the oxidation of o-tolidine at pH 1.0, a one step, two electron i-E wave is observed with both OTE and platinum. Both amino groups are protonated at this pH, and the i-E curves with OTE show large overpotentials. At pH 4.0 with platinum, the wave splits into two peaks; with OTE, these waves are well developed and compare favorably to those obtained at platinum. At this pH, o-tolidine is monoprotonated and apparently, its interaction with the semiconcuctor surface is responsible for the lower overpotential. From optical studies during various electrochemical experiments, the electrode mechanism and associated reactions were determined to be:

$$RH^+ \longrightarrow S^{\cdot+} + H^+ + e^-$$

$$S^{\cdot+} \longrightarrow TH_2^{++} + e^-$$

and a disproportionation equilibrium:

$$RH^+ + TH_2^{++} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2\,S^{\cdot+} + H^+$$

where R, S· and T are the reduced, the free radical intermediate and the two-electron, fully oxidized molecule, respectively. The rate constant k_f has been evaluated under psuedo first order conditions. The rate constant for the slower hydrolysis reaction of TH_2^{++} has been measured.

Rate constants for some chemical coupling and dimerization type reactions which follow the charge transfer step have been also determined using OTE. The spectral examinations and results of these systems will be discussed.

The technique of IRS has been used to monitor surface concentration of species during oxidation at tin oxide coated OTE. The monitoring light was at a wavelength where the species absorbed. Determination of a spectrum is difficult, because simply taking the difference in optical absorbancy with and without absorbing species, does not give the correct spectrum for the species. Recent theoretical analysis[6] of the total IRS phenomenon has made possible the evaluation of changes occuring at the surface. Comments will be made about some results and the possible implications and direction of IRS at OTE.

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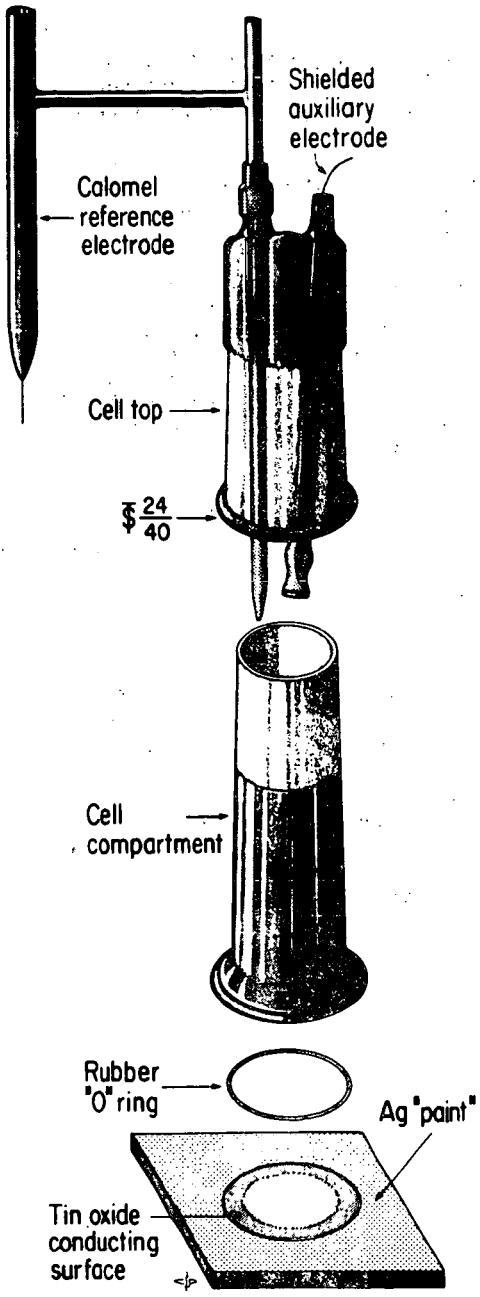

Fig. 1. Cell Design

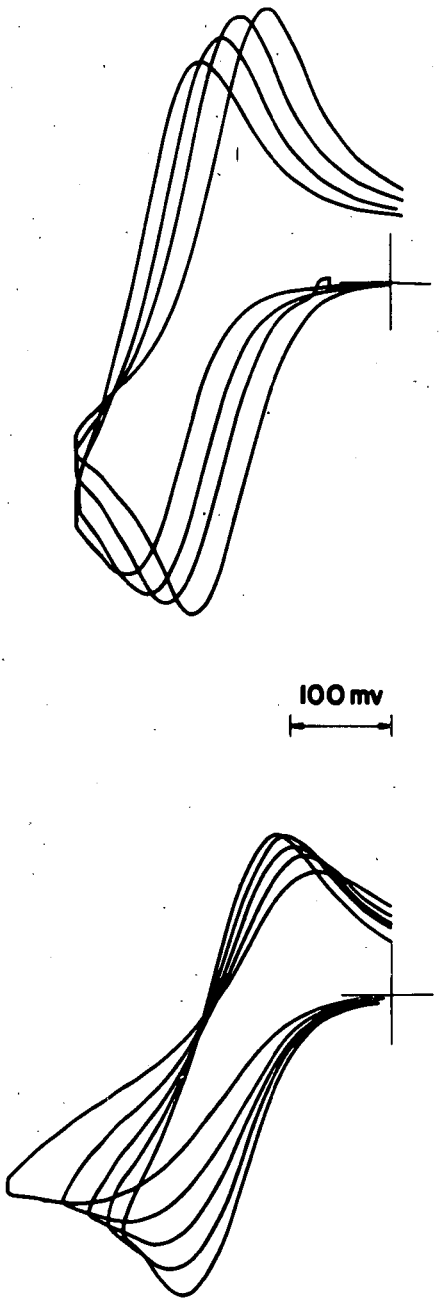

Fig. 2. Examples of i-E curves for ferrocyanid at OTE using cyclic voltammetry.

Top: (left to right) 0.03, 0.1, 0.3 and 1.0 M KCl.

Bottom: pH 6.8, 7.5, 8.4 and 10 (waves become less reversible with increasing pH).