APPLICATION OF DEPOSITED THIN METAL FILMS AS OPTICALLY TRANSPARENT ELECTRODES FOR THE INTERNAL REFLECTION SPECTROSCOPIC OBSERVATION OF ELECTRODE SOLUTION INTERFACES

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The feasibility of using Internal Reflectance Spectroscopy (IRS) as a method for monitoring electrochemical reactions spectrophotometrically at the electrode surface has been demonstrated previously (3,7). Since that time, it has been found that it would be highly advantageous to produce IRS crystal-electrodes which have surfaces with better electrochemical characteristics than those used previously [i.e., those which employed doped tin oxide in the visible range of the electromagnetic spectrum (3) and germanium in the infrared region (7)]. The semiconductor properties of tin oxide and germanium make these materials quite unsuitable for many experiments as their electrode properties are quite complex (5,10). This, therefore, makes the characterization of this combination electrolysis-spectrophotometric technique extremely difficult. Experimentally, it has been observed that the absorption baseline of tin oxide coated glass electrodes does not remain constant from one electrolysis to the next (5,10). Other investigators have also observed the same changes in the optical properties on electrolysis (6,9) which indicates that the surface is changing in some way.

For these reasons, the possibility of using thin platinum and palladium metal films on optically transparent substrates which can then be employed as IRS electrodes has been investigated.

We would like to report a relatively rapid and inexpensive method of producing such films and present some preliminary electrode-optical characteristics of these electrodes.

EXPERIMENTAL

Platinum-Glass IRS-Electrode

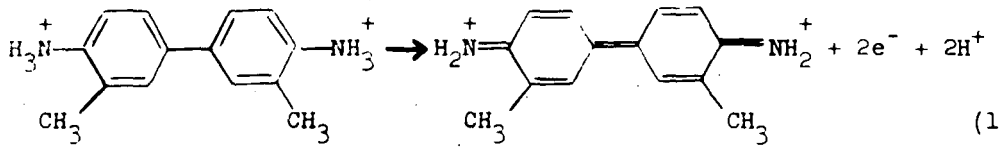
The method of producing the platinum-glass IRS-electrode employs the use of a solution of an organic ligand complex of platinum, (Liquid Platinum No. 1, Engelhard Industries Inc., Hanovia Liquid Gold Division, East Neward, N. J.) which is readily reduced to platinum metal on an inert substrate, such as glass, at sufficiently high temperatures.

To lessen the viscosity of the available Liquid Platinum (which enables a thin platinum film to be produced), a small amount (0.1 to 0.2 ml, depending on the thickness of film desired) is dissolved in 3 ml of dichloromethane, and the resulting solution is painted on to the IRS plate using brush strokes parallel to the light path. Several

coatings may be applied, again depending on the thickness of film desired. The plate is then allowed to cure in air for about one hour at room temperature. It is then fired in an open oven for about four hours. The firing temperature for Pyrex plates is between 650°C and 680°C (approximately the fusion point of the glass).

The cell was essentially the same as employed by Hansen et al. (3,9).

Constant current chronopotentiometry was carried out on the previously characterized (3) o-tolidine system. The apparatus is similar to those described earlier (2,3). A 5 millimolar solution of o-tolidine in a pH 2.00 KCl-HCl buffer was placed in the reaction cell, and on electrolysis the following reaction occurs:



I

II
(yellow)

Species I is colorless in the visible range, but II absorbs at 4,380 A (λ_{max}). The Cary Model 14 was set at this wavelength and simultaneous absorbance-time and potential-time plots of the oxidation reaction were carried out. The results are shown in Figure 1.

Christie (1) and Hansen et al. (3) have shown for forward current chronopotentiometry that the absorbance observed is proportional to the $\sqrt{t}$ provided that the penetration depth of the electric field vector is small compared to the diffusion layer. Figure 2 shows a typical absorbance $-t^{1/2}$ plot. These plots are linear over a wide range of current densities and reactant concentrations. They have also been found to be reproducible for successive runs with no shift appearing in the baseline which is what was originally desired. This is an absolutely necessary condition for scanning wavelength during an electrolysis to obtain a spectrum of the electrolysis product or intermediate.

Typical IRS spectrum scan results during the electrooxidation of o-tolidine are shown in Figure 3. A 5.0×10^{-3} M o-tolidine and 0.22 M chloride (pH = 2.0) solution was potentiostated at +0.60 V vs SCE. Curve 1 represents the spectrum (baseline) of the solution at zero applied voltage and Curve 2 represents the spectrum obtained during actual electrolysis. A very pronounced absorbance peak is observed which has a maximum at 4375 Å. This corresponds almost exactly to the normal transmission peak (λ_{max} = 4380 Å) observed for the oxidation product (species II of equation 1) of o-tolidine (Curve 3 of Figure 3 actually shows the transmission spectra of this compound prepared during electrolysis). It should be noted at this point that the IRS-spectra obtained during electrolysis at platinum film electrodes as several orders of magnitude better, with respect to both ΔA and resolution, than any obtained with tin-oxide conducting glass electrodes (1, 6, 9, 10). A replicate IRS cell containing supporting electrolyte was placed in the reference beam of the Cary 14 during all runs.

Experiments were also carried out varying the applied potential with cells containing only supporting electrolyte solution to see if the IRS absorption baseline was effected or varied in any way (a possible change in refractive index in the solution at the electrode surface might occur as the concentrations of the anions and cations of the supporting electrolyte in the compact and diffuse double layer vary with potential). As expected, however, no significant change in the baseline with potential was observed. The penetration or effective path length into a solution of the electric field vector is approximately 1000 Å in the visible range and the slight change in concentration of the various ions in the double layer (approx. 100 Å) predicted by Guoy-Chapman theory does not appreciably alter the integrated or average environment seen by the electric vector in the 1000 Å thick solution volume. However, whenever the potentials were sufficient to reach solvent or electrolyte breakdown large shifts in absorption are observed, especially with the halide solutions where corrosion of the film was found at anodic breakdown.

In designing an IRS-Electrode, such as the metal film type described above, it is desired to have the film as thin as possible yet thick enough to have good electrical conductivity. Transmission measurements on the above IRS cells have shown that the film is not completely uniform in thickness in some small areas but appeared to be covered to the eye. The average optical absorbance of the films was about 0.40 absorbance units which would indicate an average thickness of about 75 Å (11). The electrical resistance of such a thin film would be exceedingly high, however. Actual measurements of the contact resistance of the actual films was about 25 Ω-cm. To resolve this discrepancy, electronphoto micrographs were made of the surface of the films. Two distinct characteristics were observed that offer a possible explanation as to the operation of these plates. Figure 4a is a portion of the enlarged (45,000 diameters) surface which shows that there are a large number of small holes (estimated to be about 1.5×10^{-5} cm in diameter on the average). These holes appear to penetrate to the glass surface which explains why the film has such good optical transparency. They are made up essentially of bare areas and thick opaque interconnected areas of metal. The size of the holes is small compared to the diffusion layer thickness, of course, so all IRS measurements appear diffusion controlled to a plane electrode.

The second anomally in the optical behavior of these films is the experimental fact that absorbances obtained using these electrodes are an order of magnitude larger than those observed at conducting glass IRS Electrodes [compare Figure 3 to Figure 16 of Reference (2)] even though the cell geometries were essentially the same number of internal reflections. Figure 4b shows a second type of structure of the films. These are long parallel tunnels [rather than grooves as can be distinguished by the shadowing and other features of the picture] (11) in the film which are also parallel to the brush strokes. It is postulated that these tunnels, perhaps formed in some way by the initial entrapment of solvent, act as tiny "wave channels" (8). The light beam entering one of these "wave channels" will undergo an extremely high number of reflections because of the small dimension in traveling down the tunnel. Thus, the overall effective number of "reflections" is very large compared to those calculated from the gross geometry of the crystal. The average width of these "tunnels" was about 1×10^{-5} cm. This concept is further substantiated by the fact that IRS-Electrode made in the exact manner except

that the film was applied with brush strokes perpendicular to the light path were essentially opaque with respect to the solution phase. At present this theory is only speculation; however, detailed investigations of the film construction and the optical theory of these "wave channels" is being investigated and will be reported in the near future.

CONCLUSIONS

It is felt that these results show that it is possible to produce suitable thin metal surfaces on glass that are optically transparent as far as IRS is concerned and that enable one to study the IRS-electrochemical technique and electrode reaction mechanisms without serious changes of the electrode itself or the absorbance background during electrolysis. This conclusion is supported by the fact that the data in the visible region of the spectrum was reproducible and fitted theory well. Further investigation of other metal surfaces, methods of film deposition, characteristics of the deposited layer, and optical characteristics of the film are in progress and will be reported at an early date. Also, metal film deposits on quartz plates are being studies in the ultraviolet region and on AgCl and KRS-5 are being studied in the IR region (preliminary experiments have shown that Palladium films on KRS-5 crystals have a much broader IR window (5 to 16 microns) than conducting Germanium crystals (2 to 10 microns) used in previous *in situ* IRS-electrolysis studies (7).

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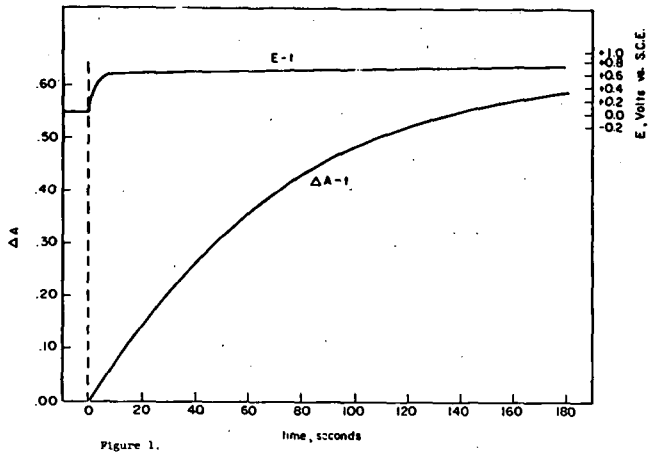


Figure 1.

Absorbance-time and potential-time curves for the chronopotentiometric electrolysis of 5 millimolar o-tolidine in a pH 2.00 HCl-KCl solution. The current was 1.00 milliamperes. The electrode area is approximately 6 cm^2.

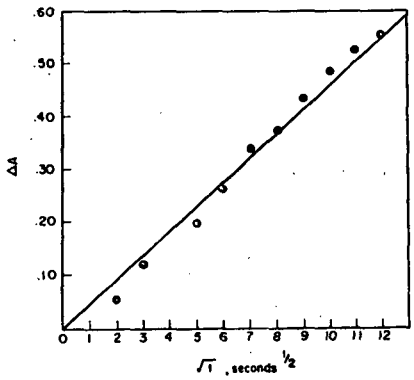
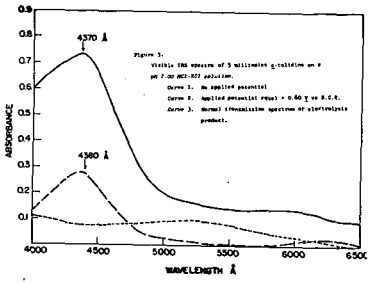
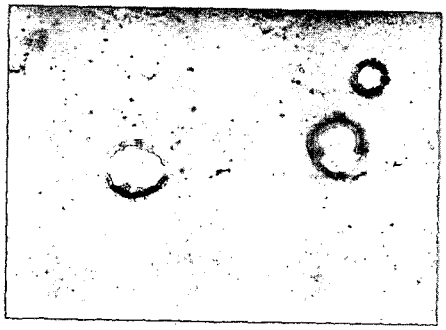


Figure 2.

Absorbance $-t^{1/2}$ plot of a typical chronopotentiometric electrolysis of the o-tolidine system at pH 2.00.





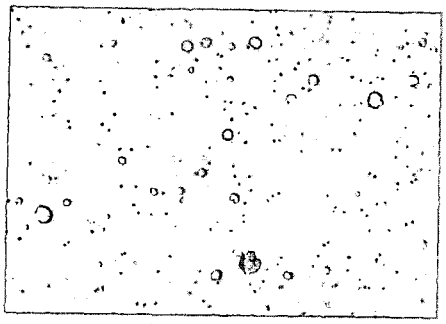


Figure 4.
Electron photomicrographs of the platinum coated IRS electrode

a) 45,000 Diameters, showing hole penetration of surface

b) 7,000 Diameters, showing one of the "wave channels"