

## An Optically Transparent Thin Layer Electrochemical Cell

SIR: Considerable interest has been evident recently in methods for *in situ* spectral observation of the products of an electrochemical process. Successful application of the attenuated total reflectance technique with the optically transparent electrodes tin oxide-glass (1, 2) and painted Pt (3) have been reported. This approach has great promise, as it allows direct monitoring of the surface concentration of an absorbing electrode reaction participant, and further developments are expected.

The transmission spectral observation of the entire electrode diffusion layer has also received attention, but on a more limited scale. Kuwana (4, 5) has used the tin oxide electrode to observe *o*-tolidine oxidation product. This study employed infinite diffusion conditions, an arrangement which in general will pose difficulties when reactant as well as product absorbs. A more general capability for transmission measurements should result from incorporation of an optically transparent electrode into a thin layer cell (6, 7). Not only would interfering reactant absorption be eliminated, inasmuch as reactant is exhaustively electrolyzed in a few seconds, but also the capability of spectrally observing subsequent product reactions on time scales inconveniently slow for diffusion-based methods is generated. Furthermore, the *n*-value for the electrode process is simultaneously acquired. The ideal optically transparent thin layer cell should possess none of the difficulties of fabrication and use of currently employed micrometer-based cells (7, 8). A number of workers have previously suggested that an optically transparent thin layer electrode would be very useful (2, 6, 7), and reference has been made to unpublished data (2), but as yet no description of such an electrode is available.

This report describes a preliminary study of a simple optically transparent thin layer electrode designed for transmission spectral observations during and after electrolytic consumption of the cell reactant. The fixed-thickness cell employs a gold minigrd (1000 wires/inch) as the optically transparent electrode. The minigrd is sandwiched between two glass or quartz slides with an adhesive material serving also as spacer. All materials required are commercially available, and a cell can be fabricated in 10 to 15 minutes. Application of the cell will be illustrated by spectral-electrochemical data on *o*-tolidine oxidation in aqueous 1M HClO<sub>4</sub>-0.5M acetic acid.

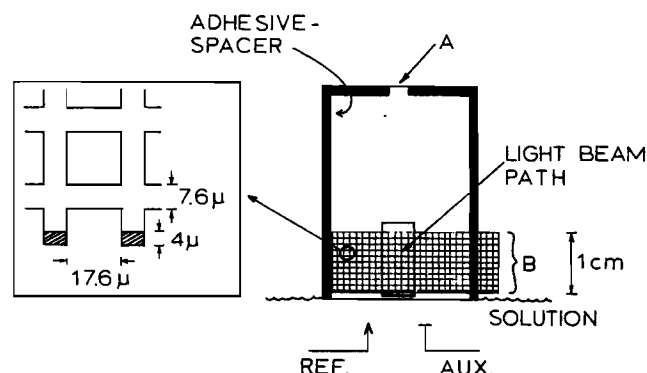


Figure 1. Optically transparent thin layer minigrd electrode cell. Inset shows minigrd dimensions

### EXPERIMENTAL

The 1000 wire/inch gold minigrd was purchased from Buckbee Mears, St. Paul, Minn. The inset of Figure 1 gives the manufacturer's grid dimensions; microscopic observation indicates a very high uniformity of the holes. The minigrd transparency is about 45%. Other minigrds of different dimensions are also available, such as 500 and 2000 wires/inch (% *T* = 60, 22; wire-to-wire spacing = 39, 6.3 microns, respectively).

The construction of a simple cell is shown in Figure 1. A minigrd cut to about 1 × 3 cm is placed between two optically flat glass or quartz slides, each previously painted with a narrow strip of adhesive-spacer around its periphery as shown, and gentle pressure is applied. Extra adhesive is painted on the slide edges to ensure sealing, and the cell is set aside for a drying period before use. Although the minigrd by itself is rather fragile, once mounted in this manner it provides a reasonably rugged cell. The open bottom of the cell allows contact with the sample reservoir solution and the reference and auxiliary electrodes; electrical connection to the minigrd is made at point B. Suction applied at A allows replenishment of the solution thin layer from the reservoir. The adhesive-spacer used here is a Tygon paint (Carboline K-63 white, Carboline Co., St. Louis, Mo.). Nonaqueous studies in progress have shown Teflon tape spacers to be equally satisfactory materials.

Experiments were performed on *o*-tolidine (Eastman Kodak) in aqueous 1M HClO<sub>4</sub>-0.5M acetic acid electrolyte. The HCl medium used in previous study of this reversible two-electron oxidation (2) was avoided because of proximity to the gold oxidation potential in chloride medium. The cell was positioned in a Cary Model 14 spectrophotometer so that the light path was that indicated in Figure 1. The *o*-tolidine oxidation product was monitored at 4380 Å as the minigrd potential was stepped or cycled with electrochemical apparatus previously described (9, 10). Charge- and absorbance-time curves were recorded simultaneously. Prolonged cycling on a given thin layer of solution caused formation of some black precipitate in the cell, the exact nature of which is not known, and concurrent attenuation of the quantity of cell reactant. It could be readily removed by flushing with electrolyte solution.

- (1) W. N. Hansen, R. A. Osteryoung, and T. Kuwana, *J. Am. Chem. Soc.*, **88**, 1062 (1966).
- (2) W. N. Hansen, T. Kuwana, and R. A. Osteryoung, *ANAL. CHEM.*, **38**, 1810 (1966).
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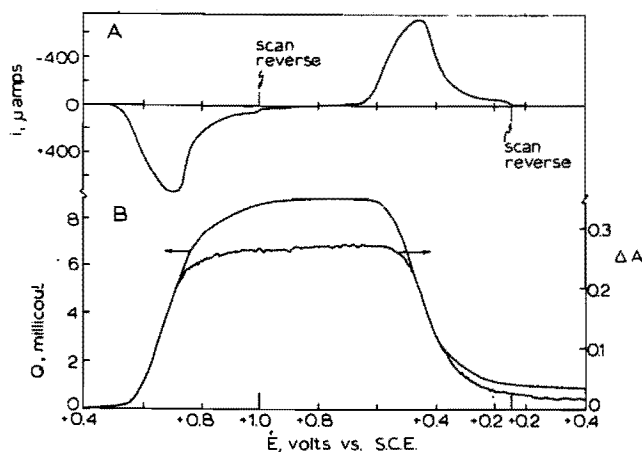


Figure 2. A. Current-potential  
B. Charge-potential and absorbance-potential curves for cyclic potential sweep

Total minigrid area 2.50 cm<sup>2</sup>, Electrode A, 2mM *o*-tolidine, 0.018 V/sec

The thickness of a new cell was calibrated by potentiostatic oxidation of a standard *o*-tolidine solution. A small correction for the minigrid volume is necessary. The manner of preparation of these cells (Tygon paint) precludes obtaining an exact premeditated thickness; however, cells could be prepared to within about 5 microns of a specified value in the range 20–100 microns by practiced variation of the number and/or thickness of coats of adhesive-spacer.

The cell thickness calibration can also be accomplished colorimetrically with a standard solution of absorbing species; measurements on the cells used here gave thicknesses agreeing with the potentiostatic ones to about 2%.

### RESULTS

Inasmuch as the grid-to-wall distance exceeds the minigrid wire-to-wire distance in the 70- to 90-micron cells discussed here, the gold minigrid diffusively approximates a transparent gold foil in the thin layer cavity. That is, the rate determining factor in a potentiostatic electrolysis of the thin solution layer is the diffusion of reactant from the cell wall to the minigrid rather than diffusion within the minigrid holes. This condition is desirable for the attainment of rapid electrolysis. This property of the minigrid was confirmed in chronopotentiometric experiments performed under infinite diffusion conditions where (except at very short transition times)  $i\tau^{1/2}$  was found to be proportional to the gross minigrid area (actual 2.00 cm<sup>2</sup>, measured 2.05 cm<sup>2</sup>) rather than to the microscopic wire area.

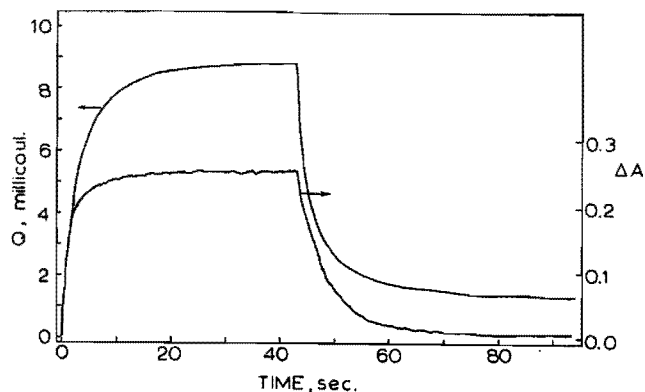


Figure 3. Charge-time and absorbance-time curves for application of a potential step from +0.2 V to +0.9 V to +0.2 V vs. SCE

Total minigrid area 2.50 cm<sup>2</sup>, Electrode A, 2.00mM *o*-tolidine

Current-potential curves obtained on the minigrid thin layer cell by slowly cycling the potential through the *o*-tolidine-active region are shown in Figure 2A. As pointed out by Anson (11), the cessation of current flow following the peak is a characteristic behavior of thin layer cells, indicating exhaustive electrolysis of cell reactant. This is observed both on the anodic cycle for the *o*-tolidine oxidation and the reverse cycle for reduction of the product. Several successive cycles produce quantitatively identical curves before the precipitation noted above causes attenuation of the peak current.

Integrals of the current-potential curves, with corresponding absorbance-potential curves, are shown in Figure 2B. These are typical of those obtained in an extended series of experiments. Both charge and absorbance curves level off as expected on the anodic cycle, and return to base line as the colored oxidized product is consumed on the cathodic cycle. Charge- and absorbance-time curves for potential stepping experiments show similar behavior, as shown in Figure 3. The flatness of these curves after depletion indicates minimal edge diffusion effects in this thin layer cell design.

Table I summarizes electrochemical data taken for two minigrid cells. The anodic potentiostatic charge data for electrode B shows good reproducibility in the measured cell thickness,  $l$ , in a series of experiments. Reproducibility was even better within a given experiment; extensive handling of the minigrid cell between experiments can cause some fluctuations in thickness due to the sponginess of the adhesive-spacer material. (Such fluctuations are lessened when using the Teflon tape spacer.) The measured charge is propor-

(11) A. T. Hubbard and F. C. Anson, ANAL. CHEM., 38, 58 (1966).

Table I. Electrochemical Data for *o*-Tolidine Oxidation in Minigrid Thin Layer Cell  
Potentials for  $E_{step}$  and  $E_{sweep}$  given in Figures 2 and 3

Electrode	[ <i>o</i> -tol], mM	$E_{step}$		$l^b$ , microns	$E_{sweep}$	
		$Q_{anod}^a$	$Q_{cath}^a$		$Q_{anod}^a$	$Q_{cath}^a$
A	2.00 <sup>c,d</sup>	8.14	6.93	86	8.16	7.43
B <sup>e</sup>	2.00	7.51	7.36	80	...	...
	2.00 <sup>c</sup>	7.26	6.98	77	...	...
	0.40 <sup>c</sup>	1.45 <sup>g</sup>	1.37 <sup>g</sup>	78	...	...

<sup>a</sup> Charge in millicoulombs, corrected for background.

<sup>b</sup> Corrected for minigrid, ~2 microns.

<sup>c</sup> Electrode previously fouled with precipitate.

<sup>d</sup> In spectrophotometer.

<sup>e</sup> Average  $l$  over all determinations  $79.0 \pm 2$  microns.

tional to sample concentration; the  $Q_{anod}/(o\text{-tol})$  ratio for 2.0 and 0.4mM solutions is 3.69 and 3.64 mcoulombs/mM, respectively. Good recovery of product upon reversal of the potential step is also found. It is better with a fresh electrode (see first entry for electrode B) than with one previously fouled with the precipitate. Electrode A was employed in concurrent spectrophotometric-electrochemical measurements; the electrochemical results are in general similar to those obtained with electrode B. Best results are obtained when solution is drawn through the cell immediately prior to the determination; this minimizes thermal gradients set up by the light beam.

## DISCUSSION

The results obtained in this preliminary examination of the minigrid thin layer cell demonstrate a rather satisfactory performance as a device for concurrent spectral-electrochemical measurements. The simplicity of construction and use experienced in this study is a highly valuable characteristic of the cell. Discussed below are some of the advantages and limitations of the minigrid thin layer cell, and of optically transparent thin layer cells in general, which are of significance.

As is the case with any thin layer cell utilizing an external reference electrode, the ohmic resistance of the thin layer of solution can lead to appreciable potential gradients in the cell. This was found to be true in the minigrid cell, particularly in cells with minigrids 2 cm high or with the grid not situated in close proximity to the open bottom of the cell. The resistance effect could actually be visually observed; in an anodic scan experiment on the 2-cm high minigrid a front of yellow color of oxidized product could be seen moving up the minigrid. Only when the color front reached the top of the minigrid did the current abruptly cease. This effect was much less severe in the 1-cm high minigrid used in the cells discussed above, but slight inflections in the current-time traces of potentiostatic experiments show that it is not completely absent. To minimize the effect of the  $iR$  drop on the absorbance curves, the light beam was placed to straddle the minigrid, as shown in Figure 1. The geometry of the minigrid thin layer cell should permit insertion of the reference electrode into the thin layer at central point(s) in the cell, and investigation of a cell thus designed to alleviate  $iR$  effects is in progress. It is also evident that, using a small light beam, one could spectrophotometrically follow the electrochemical process on various parts of a minigrid cell having unfavorable resistance properties and thus perhaps attain a more advanced understanding of the nature of the  $iR$  effect on the net electrochemical response.

The transmission measurement of the spectrum of the electrolysis product is not complicated by spectral distortions and peak-shifting which can occur in the ATR mode. This was found to be the case for the oxidized *o*-tolidine spectra observed in the minigrid thin layer cell, and is useful in dealing with cases of unknown product identification.

Optically transparent thin layer cells could obviously be prepared for tin-oxide or painted Pt electrodes using the adhesive-spacer construction. These could be of advantage for accessibility to different potential regions when thin layer diffusional properties better defined than those for the mini-

grid cell are desired or when examination of twin electrode cells is desired. When the electrode process leads to metal deposition or extensive adsorption, precipitation, etc., of product, the behavior of the tin oxide electrode would be basically different from that of the gold minigrid (and perhaps the painted Pt, which is a minigrid of sorts). This difference could be used to avoid transparency complications or, conversely, to study them.

It should be emphasized that for the most part the applications of optically transparent thin layer cells are complementary to those of the infinite diffusion ATR approach (2, 3). The thin layer transmission experiment offers the advantages of simplicity of construction and use (at least for the minigrid cell design) and of interpretation of the spectra of products. It should be valuable for routine investigations of new chemical systems where simultaneous acquisition of the charge to evaluate  $n$  and of the product spectrum is of aid in formulating the electrode reactions. The time scale of the thin layer approach is also more adaptable to study of slow subsequent reactions of the initial electrolysis product and of any effects this may produce on the apparent value of  $n$ . Because the ATR method responds only to the first 1000–2000 Å of the diffusion layer, rather than the entire diffusion layer response of the transmission measurement, ATR experiments may on the other hand prove to be better suited for study of reactions of more transient nature.

The relatively small quantity of spectrally observed solution in the ATR and thin layer transmission methods imposes limitations on both for observation of weakly absorbing materials. If an absorbance variation of 0.02 is the smallest reliably measured value on an expanded scale instrument and 5mM is the largest convenient concentration for the species under study, a product of thin layer thickness and absorbance coefficient  $\geq 4$  is required. For the 80-micron cells used here, an absorbance coefficient  $>500$  is required.

Edge effects in the thin layer cell can be eliminated altogether from the absorbance response by appropriate placement of the light path. This should allow a more quantitative evaluation of such effects on the electrochemical response than has been previously possible.

Further studies of the characteristics of the minigrid thin layer cell and its application to spectro-electrochemical problems are in progress and will be discussed in future reports.

ROYCE W. MURRAY  
W. R. HEINEMAN  
G. W. O'DOM<sup>1</sup>

Department of Chemistry  
University of North Carolina  
Chapel Hill, N. C. 27514

<sup>1</sup> Present address, TRW Systems, One Space Park, Redondo Beach, Calif. 90278

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