

Carbon and Mercury–Carbon Optically Transparent Electrodes

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A carbon optically transparent electrode (C OTE) has been prepared by vapor-depositing a thin carbon film (150–310 Å thick) on glass and quartz. The electrode properties are similar to those of a conventional graphite electrode with a higher resistance (1000–1700 Ω/\square). Optical transparency is good throughout the ultraviolet–visible region. Electrochemical and spectroelectrochemical measurements were made with ferricyanide and *o*-tolidine respectively. The C OTE serves as a good substrate for deposition of a thin mercury film (15–25 Å) to form a mercury film transparent electrode (Hg-C OTE). The Hg-C OTE exhibits electrochemical properties of conventional mercury film electrodes as evidenced by Pb^{2+} cyclic voltammograms. The Hg-C OTE enabled the spectroelectrochemical characterization of cysteine oxidation, which was shown to involve the oxidation of mercury to form mercurous cysteinate.

Optically transparent electrodes (OTEs) have proved useful in spectroelectrochemical studies of a variety of redox systems (1–3). Various types of OTEs have been prepared and characterized in the past several years (1). OTEs consisting of very thin conductive films of Pt, Au, SnO_2 , and InO_2 which are deposited on glass or quartz substrates have been used extensively; gold minigrids have proved to be especially adaptable to the thin-layer cell configuration; germanium plates have been used for infrared studies. OTEs with mercury characteristics have been formed by electrodepositing thin films of mercury onto Pt OTEs and Au and Ni minigrids.

One of the most useful electrode materials is carbon or graphite, which exhibits good positive and negative potential ranges (4, 5). Past attempts to prepare carbon/graphite OTEs have been thwarted by poor adhesion between the vapor-deposited carbon film and the substrate (6). Recently, an OTE consisting of a thin carbon film deposited on a germanium substrate was prepared and used successfully for infrared spectroelectrochemical measurements in aqueous solutions (7, 8). We report here the characterization of an OTE formed by depositing a thin layer of carbon onto a glass or quartz substrate (C OTE). This electrode enables ultraviolet–visible spectroelectrochemical measurements to be made on an electrode surface which is similar to that of the conventional graphite electrode.

Graphite and glassy carbon electrodes have been used extensively as substrates for mercury film electrodes, especially in anodic stripping voltammetry (9–11). The usefulness of graphite and carbon for this purpose is attributable to their inertness towards mercury. This minimizes contamination of the mercury film by a mercury-soluble substrate. The development of the C OTE has made possible the preparation

of a transparent mercury electrode by electrodepositing a very thin mercury film onto a C OTE. This Hg-C OTE minimizes the problems of substrate amalgamation which affect other mercury OTEs utilizing platinum (12), nickel (13), and gold (14) as substrates. We report here the preparation and characterization of such a Hg-C OTE and its use in a spectroelectrochemical examination of the mechanism of cysteine oxidation.

EXPERIMENTAL

Apparatus. Carbon film OTEs were prepared commercially (Lebow Company, 1407 Norman Firestone Road, Goleta, Calif. 93017) by evaporating carbon with an electron beam technique onto specially prepared glass and quartz microscope slides according to the procedure described by Mattson and Smith for deposition onto germanium (7). Electrodes with a film thickness of 150 to 160 Å were prepared by a single deposition of carbon (A and E in Table I). Electrodes with film thicknesses of 280 to 310 Å were prepared by two separate depositions of ca. 150 Å each. Electrodes were also prepared by deposition onto substrates at 450 °C (A, B, and C) and at room temperature (D and E).

The design and assembly of the optically transparent electrochemical cell has been described (12). The potentiostat used for electrochemical experiments was a Princeton Applied Research Model 173 potentiostat–galvanostat with a Model 179 digital coulometer. All potentials were measured vs. a saturated calomel electrode which was isolated from the solution by a thirsty glass plug. Spectra of the C OTEs were recorded on a Cary Model 14 spectrometer. Spectra of *o*-tolidine oxidation were taken with a Harrick Rapid Scanning Spectrometer, Model RSSB (Harrick Scientific Co., Ossining, N.Y.) and recorded on a Houston Instruments 2000 x-y recorder. Transmittance changes at a set wavelength were measured in a spectrometer consisting of a tungsten lamp source, a Schoeffel GM 100 miniature grating monochromator, and an Emitronics #T124 PMT connected to an operational amplifier current to voltage converter. Voltage output was monitored with a Digitec 261 Digital VOM and transmittance-current-potential curves were recorded with a Hewlett-Packard 136A X-Y,Y recorder.

Reagents. The 1.00 mM ferricyanide solution was prepared by dissolving potassium ferricyanide (Allied Chemical) in 1 M KNO_3 . The 1.00 mM *o*-tolidine in 0.5 M acetic acid, 1.0 M HClO_4 was prepared by dissolving the *o*-tolidine (Aldrich) first in concentrated acetic acid and then diluting almost to volume with distilled water before adding concentrated perchloric acid. Pb^{2+} solutions were prepared by the appropriate dilution of 1000 ppm Fisher atomic absorption standard in 0.5 M KNO_3 . The 3 mM mercurous ion solution was prepared by dissolving $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ (Baker Analyzed) in 0.5 M KNO_3 . Solutions of cysteine were prepared with L-cysteine hydrochloride hydrate (Aldrich) in 0.1 M HClO_4 .

Procedure. The carbon film OTE was thoroughly rinsed with 95% ethanol and then with distilled, deionized water immediately before being subjected to five minutes of radiofrequency discharge cleaning (Plasma Cleaner, Harrick Scientific Company, Ossining, N.Y.). The cell was then assembled as previously described (12). Deaerated solution was injected into the cell through the SCE port. The SCE, separated from the analyte solution by a thirsty glass plug (Vycor Glass, Corning Glass Company, Corning, N.Y.), was then placed in the cell. The area of electrode exposed to

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Table I. Characteristics of Carbon Film OTEs

Electrode ^a	No. of depositions	Substrate temperature, °C	Carbon film thickness, Å	Carbon film resistance, Ω/□	Absorbance at 540 nm	Cyclic voltammetry Δ <i>E</i> _p , mV ^b
A	1	450	150	1 700	0.472	112
B	2	450	280	1 000	0.625	110
C	2	450	280	1 000	0.602	120
D	2	~ 25	310	44 000	0.440	540
E	1	~ 25	160	51 000	0.300	

^a A, B, D, and E deposited on glass substrate. C deposited on quartz substrate. ^b 1.00 mM ferricyanide, 1.0 M KNO₃. Scan rate = 10 mV s⁻¹.

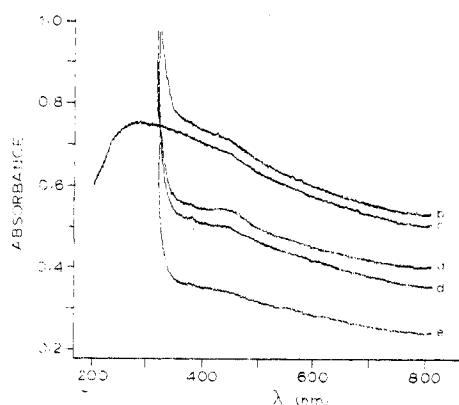


Figure 1. Absorbance spectra for C OTEs prepared by several procedures. See Table I for description of electrodes (A-E)

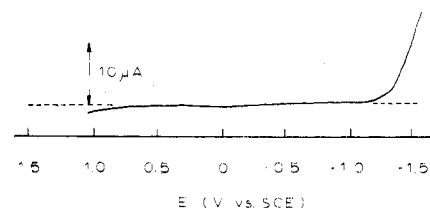
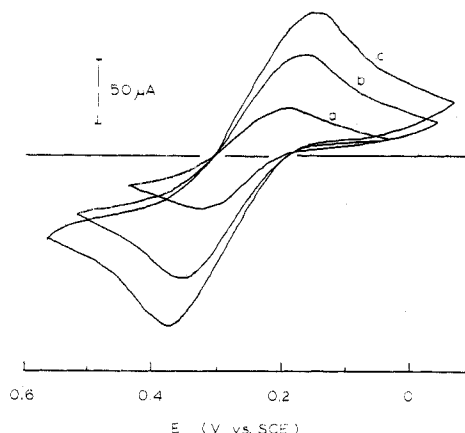
solution was approximately 0.8 cm². Before each new solution was added, the cell was thoroughly rinsed with distilled, deionized water.

The Hg-C OTE was prepared by depositing mercury from a 3 mM HgNO₃, 0.5 M KNO₃ solution onto a C OTE. Deposition was accomplished by stepping the potential to -0.7 V vs. SCE for ca. 2 min with the solution unstirred. The cell was then open-circuited and rinsed thoroughly with distilled water.

RESULTS AND DISCUSSION

Carbon OTE. Table I summarizes characteristics of several C OTEs. The electrodes were prepared on both glass microscope slides (electrodes A, B, D, E) and quartz (electrode C) substrates. The effect of substrate temperature during the deposition procedure was evaluated by preparing electrodes with substrates at room temperature (D, E) and at 450 °C (A, B, C). Comparison of the electrical resistance for the various electrodes shows that the resistance decreases as the thickness of the carbon film increases. However, the resistance of the electrodes prepared with the substrate at room temperature is ca. 50 times greater than those with the substrate at 450 °C. Evidently, deposition on a hot substrate is very important for minimizing electrode resistance. The resistances of the electrodes prepared with the hot substrate were 1000 to 1700 Ω/□, depending on the film thickness. This is substantially greater than the resistances of Pt, Au, SnO₂, and InO₂ film OTEs which are typically 5–20 Ω/□ (1). The resistances of the electrodes prepared for this study are within a factor of ×2 of the expected resistance for graphite films (490 Ω/□ for a 280-Å film) based on the resistivity of pure graphite.

The optical properties of the C OTEs depended upon film thickness and substrate. Spectra in the ultraviolet-visible range for several electrodes are shown in Figure 1. Electrodes with film thicknesses of 280 Å exhibit an absorbance varying from 0.5 to 0.7 over the optical range of 840 nm to 350 nm. Electrodes with glass substrates absorb strongly below 350 nm, whereas quartz substrates extend the optical range to below 200 nm. This transparency is comparable to that reported for Pt and Au film OTEs (1). With a quartz sub-

Figure 2. Current-potential curve at the carbon-film OTE; pH 10 carbonate-borate buffer, 0.5 M KNO₃; scan rate 20 mV s⁻¹Figure 3. Cyclic voltammograms of 1 mM ferricyanide, 0.1 M KNO₃ at C OTE. Film thickness = 280 Å. Scan rates (a) 10 mV s⁻¹, (b) 50 mV s⁻¹, (c) 100 mV s⁻¹

strate, the C OTE is useable throughout the ultraviolet-visible range.

Observation of the electrode surfaces by scanning electron microscopy revealed a smooth carbon surface with no observable pinholes or irregularities for both the singly and doubly deposited films on substrates at 450 °C.

The electrochemical properties of the carbon OTE were similar to those of bulk graphite electrodes. Figure 2 shows a current-potential curve for a pH 10.0 carbonate-borate buffer. The electrode exhibits low residual current throughout a wide potential window which extends well into both the positive and negative regions. The film was very stable under conditions of repeated potential cycling in aqueous media of varying pH. Mild hydrogen evolution did not disintegrate the film as in the case of Pt OTEs, although vigorous evolution of hydrogen led to separation of the film from the glass substrate around the edges. Generation of oxygen at large positive potentials caused immediate disintegration of the carbon film.

Typical cyclic voltammograms on a C OTE with a 280 Å-thick film for ferricyanide at various scan rates are shown in Figure 3. The voltammograms at slow scan rates are similar to those reported at the graphite electrode (15). The cathodic and anodic peak separation (Δ*E*_p) is greater than the expected 0.059 V, due to the resistance of the carbon film, and increases with faster scan rates because of the larger currents. The *E*^{o'}

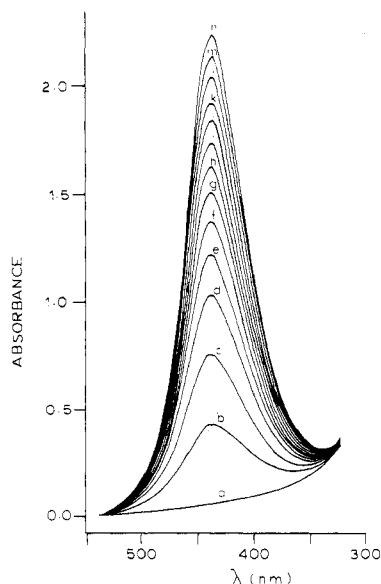


Figure 4. Spectra recorded during oxidation of *o*-tolidine at C OTE (280-Å film) by potential step to +0.8 V vs. SCE in quiescent solution. 1.00 mM *o*-tolidine, 0.5 M acetic acid, 1.0 M HClO₄. (a) 0, (b) 5, (c) 10, (d–n) 10-s intervals

(obtained by averaging the anodic and cathodic peak potentials) of +0.263 V vs. SCE agrees well with that obtained by other workers on bulk graphite (15). Values for ΔE_p obtained from ferricyanide voltammograms are shown in Table I for the various electrodes. Comparison of the values for film thicknesses of 150 Å and 280 Å shows only a small improvement for the thicker film. However, the greatly increased resistance of electrode D, which was deposited on room temperature substrates, gives a much larger ΔE_p value.

The utility of the C OTE for spectroelectrochemical measurements was demonstrated with *o*-tolidine, which undergoes a 2e[−] oxidation to form a yellow product (16, 17). Figure 4 shows a series of spectra recorded through a C OTE during generation of the yellow oxidation product by a potential step to +0.800 V vs. SCE. The optical transparency of the C OTE is sufficiently great that such spectral changes are easily measured. A plot of absorbance (at $\lambda_{\text{max}} = 438$ nm) vs. $t^{1/2}$ was linear over a range of 5 to >100 s, which indicates a diffusion-controlled oxidation of *o*-tolidine at the C OTE (1–3). The slope of the plot was $0.19 \text{ s}^{-1/2}$. A value for ϵ of $3.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, which was determined for the yellow product by thin-layer spectroelectrochemical techniques (18), gives a diffusion coefficient of $2.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for *o*-tolidine. A negative deviation from linearity occurred for times of less than about 4 s. This is attributed to the resistance of the carbon film. Quantitative response for faster times necessitated the use of positive-feedback iR compensation.

As illustrated by the results presented above, a stable carbon OTE can be prepared by the procedure described by Mattson and Smith for a carbon-germanium OTE. Optical transparency is sufficient for good spectroelectrochemical measurements in the ultraviolet-visible range. The rather large film resistance presented no difficulty in this characterization; however, it would certainly limit the usefulness of the C OTE in the spectroelectrochemical measurement of fast homogeneous chemical reactions where rapid charging of the electrode is essential (2, 3).

Mercury-Carbon OTE. Transparent mercury electrodes (Hg-C OTE) were prepared by electrodepositing thin mercury films on the carbon OTEs. The best Hg-C OTEs were prepared by deposition at −0.7 V vs. SCE with a solution of Hg₂²⁺ rather than Hg²⁺. In both cases the transmittance of the OTE decreased as the mercury film was deposited.

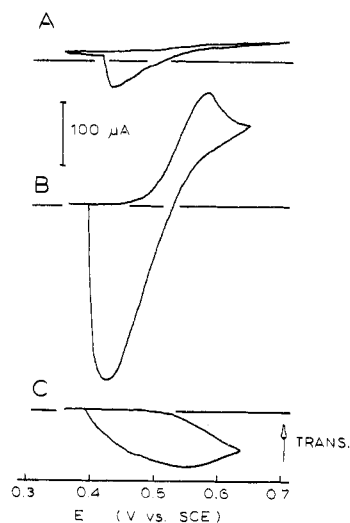
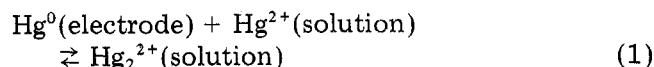


Figure 5. (A) Cyclic voltammogram of Pb²⁺ at C OTE. (B) Cyclic voltammogram of Pb²⁺ at Hg-C OTE. (C) Transmittance-potential behavior at Hg-C OTE during cyclic voltammogram of Pb²⁺. 2.42 mM Pb²⁺, pH 4.0 acetate buffer

However, in the case of Hg²⁺ reduction, the transmittance increased when the cell was open-circuited immediately after mercury deposition, indicating dissolution of some of the deposited mercury. This loss of mercury from the film occurred at a diffusion-controlled rate as indicated by linearity of an absorbance- $t^{1/2}$ plot (1). The mercury loss is attributed to the following reproporationation (19):



This reaction is controlled by the rate of diffusion of Hg²⁺ in the plating solution to the electrode surface for reaction with Hg⁰. The loss of the mercury film precluded preparation of a satisfactory Hg-C OTE by reduction of Hg²⁺. Consequently, deposition from a solution of Hg₂²⁺ was used to prepare all Hg-C OTEs used in this study.

The thicknesses of the mercury films on the Hg-C OTEs were typically 15–25 Å. This increased the absorbance of the OTE by only about 0.05 a.u. above the absorbance of the C OTE. Thus, good optical transparency was retained by coating with very thin mercury films.

Examination of the Hg-C OTE surface by reflectance microscopy revealed a mercury deposit existing as droplets, similar to that shown in Figure 2 of reference (20). These droplets could not be coalesced by the evolution of hydrogen, a procedure which is successful on bulk platinum (21).

The electrochemical characteristics of the Hg-C OTE are similar to those which have been reported for mercury films on bulk carbon and graphite substrates (20, 22). The negative potential range was less than that of pure mercury as a result of the exposed carbon between mercury droplets. The mercury film could be repeatedly stripped off and redeposited with no apparent damage to the carbon film.

The conversion from solid carbon to liquid mercury electrode behavior is evident by comparison of the two cyclic voltammograms for Pb²⁺ in Figure 5. The reduction wave for Pb²⁺ on the carbon OTE is very poorly defined and the Pb stripping wave greatly skewed (Figure 5A). By contrast the well-defined voltammogram on the Hg-C OTE (Figure 5B) is typical of that obtained on mercury film electrodes used for anodic stripping voltammetry [e.g., curve 1 in Figure 3 of reference (22)]. The accumulation of Pb in the mercury droplets could be monitored optically as shown by the transmittance-voltammogram in Figure 5C. All of the Pb⁰ is removed from the mercury during the positive potential scan

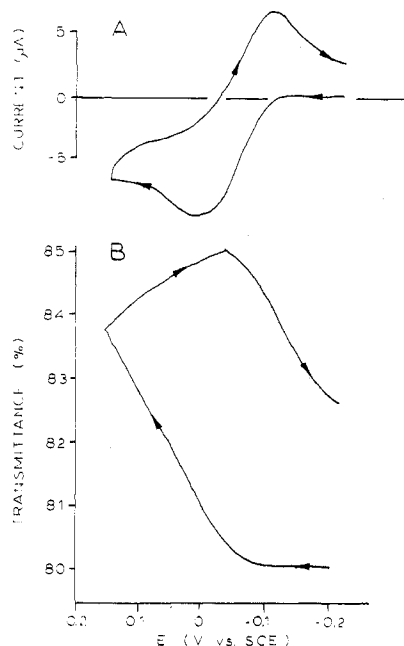
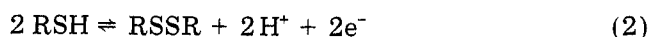


Figure 6. Spectroelectrochemistry of cysteine at Hg-C OTE. 2.00 mM cysteine, 0.1 M HClO₄; scan rate 10 mV s⁻¹. (A) Cyclic voltammogram. (B) Transmittance-potential response of Hg-C OTE during cyclic voltammogram

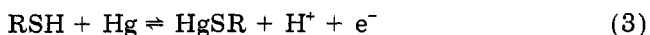
as evidenced by return of the transmittance to its original value.

The C OTE serves as a good substrate for a transparent mercury film electrode. The inertness of the carbon toward the overlying mercury film eliminates the time-dependent amalgamation of Pt, Ni, and Au substrates which contaminates the mercury with varying amounts of intermetallic compounds such as PtHg_x in the Hg-Pt OTE. The Hg-C OTE is also much more tolerant of hydrogen evolution than is the Hg-Pt OTE. It can be used not only to impart mercury character to the electrode, but also to investigate the participation of mercury itself in an electrochemical reaction as illustrated in the next section.

Cysteine Oxidation at the Mercury-Carbon OTE. The oxidation waves of certain organic and inorganic compounds at mercury involve the oxidation of the electrode itself rather than the compound. An example of this is the oxidation wave for cysteine which has been studied by Kolthoff and Barnum (23). At a platinum electrode, cysteine (RSH) undergoes oxidation to form cystine (RSSR) by the following mechanism:



However, at the dropping mercury electrode, the oxidation wave occurs at a potential which is 600 mV more negative than on platinum. To account for this large potential shift, the formation of soluble mercurous cysteinate by the following electrode mechanism was proposed:



The Hg-C OTE enables the participation of Hg in the oxidation mechanism of cysteine to be optically observed by light passing through the electrode. According to reaction 3, the optical transparency of the Hg-C OTE should increase because of loss of mercury as the electrode potential is positively scanned through the oxidation wave. Since liquid mercury attenuates light throughout the visible range, any visible wavelength is suitable for the optical experiment. Figure 6 shows the current and optical response as the potential is cycled through the oxidation peak and then back through the reduction peak. Indeed, the transmittance of the Hg-C OTE increases during the positive scan in which HgSR

is formed and then decreases during the negative scan after the potential for HgSR reduction is reached (ca. -50 mV) and mercury redeposits on the OTE. This directly confirms a mechanism which involves oxidation of the mercury electrode such as the one postulated by Kolthoff and Barnum in Equation 3.

This example illustrates the potential utility of the Hg-C OTE for investigating mechanisms of electrode reactions in which mercury is directly involved. Analogously, the Pt OTE and Au OTE could also be used to observe electrode mechanisms which involve oxidation of these materials.

CONCLUSION

The C OTE and Hg-C OTE are electrodes with good optical transparency, thereby adding to the growing number of OTEs available. The electrode properties are similar to those of bulk graphite electrodes and conventional mercury film electrodes deposited on bulk graphite or carbon substrates, although the resistance is higher. Because of the inertness of the carbon substrate, the Hg-C OTE is in many respects a superior mercury OTE compared to the Hg-Pt, Hg-Ni, and Hg-Au OTEs which are extensively amalgamated with the substrate. The cysteine oxidation illustrates the utility of OTEs for directly observing electrode involvement in a mechanism by optically monitoring the transparency of the electrode itself. This demonstrates a new aspect of OTE applicability which has not previously been utilized. The carbon OTE is potentially useful for spectroelectrochemical studies with chemically modified graphite and carbon electrodes (24-26).

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