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background levels in biological materials, but AV has many advantages for the routine analysis of blood samples. The AV method is more sensitive, uses less sample, is less expensive in terms of equipment and reagent costs, and is not affected by the salt content of the sample. After complete combustion of the organic matrix, it can be applied to a wide range of biological samples.

Registry No. Pt, 7440-06-4.

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Spectroelectrochemical Characteristics of the Reticulated Vitreous Carbon Electrode

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The spectroelectrochemical characteristics of reticulated vitreous carbon optically transparent electrodes (RVC-OTE's) are described with respect to both thickness and porosity of the RVC. RVC-OTE's with thicknesses between 0.5 and 3.5 mm and porosities of 100, 80, 60, 45, and 30 pores per linear inch are examined. Cyclic voltammetry and chronocoulometry on solutions of potassium ferricyanide indicate a trend from thin-layer behavior toward semilinear diffusion behavior as the size of the pores increases. Chronoabsorptometry and spectropotentiostatic experiments using solutions of *o*-tolidine give comparable results for all thicknesses and porosities studied, resulting in values of $n = 1.94$ and $E^{\circ'} = +0.639$ V vs Ag/AgCl. Therefore, thicker electrodes with larger pore sizes can be employed in experiments in which weakly absorbing species are monitored.

INTRODUCTION

Reticulated vitreous carbon (RVC), a porous, vitreous carbon foam material, is well-suited for various electrochemical applications (1). It was first utilized in UV-visible transmission thin-layer spectroelectrochemistry by Norvell and Mamantov (2) as an electrode material in the construction

of an optically transparent electrode (OTE). RVC is available in several porosities, ranging from 10 to 100 pores per linear inch (ppi), and can be easily sliced into various shapes and thicknesses. Nearly all spectroelectrochemical applications of RVC-OTE's, however, use solely the 100 ppi grade of RVC with 0.5 to 1 mm thicknesses (2-7), even though the optical characteristics and surface-area-to-volume ratio of the electrode can be controlled by appropriate choice of thickness and porosity of the RVC (2).

Hobart and co-workers (8) report that the light transmittance of a porous metal foam (PMF) electrode is dependent upon both electrode thickness and pore size. They also indicate that larger pore sizes result in increased electrolysis times for these electrodes, which are similar in structure and optical properties to RVC. In another application the effects of pore size and thickness of 45 and 100 ppi RVC substrates on the distribution of zinc in Zn-Br₂ batteries were reported (9, 10). However, the effects of different thicknesses and porosities of RVC on the electrochemical and spectroelectrochemical characteristics of RVC-OTE's have not been previously reported.

This paper evaluates the spectroelectrochemical characteristics of RVC-OTE's with porosities ranging from 30 to 100 ppi and with thicknesses varying between 0.5 and 3.5 mm, with respect to their cyclic voltammetric, chronocoulometric, spectropotentiostatic, and chronoabsorptometric behavior in

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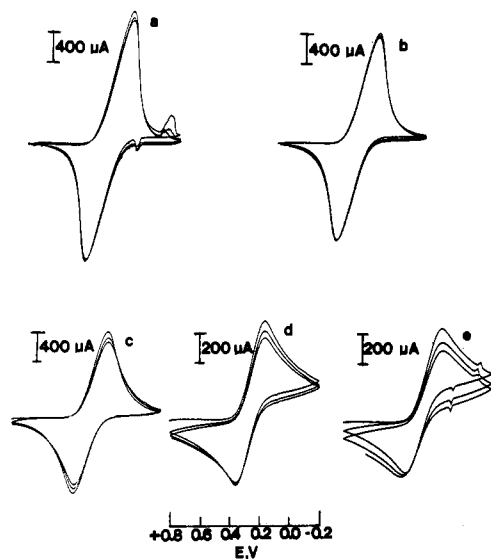


Figure 1. Cyclic voltammograms for 4.0 mM $K_3Fe(CN)_6$ in 1 M KCl at RVC-OTE's with thicknesses of 2.0 mm and porosities of (a) 100, (b) 80, (c) 60, (d) 45, and (e) 30 ppi: scan rate, 2 mV/s.

solutions of potassium ferricyanide and *o*-tolidine.

EXPERIMENTAL SECTION

Apparatus. Optically transparent cells were constructed with glass microscope slides in a similar fashion to those described by Norvell and Mamantov (2), using RVC (The Electrochemical Co., Inc., East Amherst, NY) with porosities of 30, 45, 60, 80, and 100 ppi, and thicknesses ranging from 0.5 to 3.5 mm. The minimum thickness to which the RVC could be sliced was dependent upon the pore size of the material. Electrical contact was made by attaching a thin copper wire to the RVC slice with silver-filled conducting epoxy (Epotek 410E, Epoxy Technology, Watertown, MA). Duplicate electrodes of each size were fabricated, one serving as the sample cell and the other as the reference cell for spectroelectrochemical studies.

Electrochemical experiments were carried out with a BAS Model CV-27 cyclic voltammograph and a Houston Instrument Model 200 X-Y recorder. A Ag/AgCl (3 M NaCl) reference electrode (BAS, Model RE-1) and a platinum wire auxiliary electrode were used in all experiments. For spectroelectrochemical studies a Perkin-Elmer Lambda 9 UV-Vis-NIR double beam scanning spectrophotometer was employed. Reference and sample cell holders were constructed from black-painted plastic thin-layer chromatography staining jars with holes machined in front and back to allow the light beam to pass through the RVC-OTE. Reference and auxiliary electrodes were positioned outside of the light path within the cell holder.

Reagents and Procedures. All solutions were prepared from ACS reagent grade chemicals and distilled, deionized water unless otherwise noted. Solutions of potassium ferricyanide for cyclic voltammetry and chronocoulometry were prepared in 1 M potassium chloride supporting electrolyte. *o*-Tolidine (practical grade, Sigma Chemical Co., St. Louis, MO) solutions were prepared in 0.5 M acetic acid and 1 M perchloric acid. All OTE's were flushed several times with distilled, deionized water and purged with nitrogen gas for 10–15 min prior to use.

RESULTS AND DISCUSSION

Electrochemical Characterization of the RVC-OTE's. Electrochemical experiments were conducted with solutions of 4.0 mM $K_3Fe(CN)_6$ in 1 M KCl. Cyclic voltammograms for RVC-OTE's with 2.0 mm thicknesses and varying porosities ranging from 30 to 100 ppi are shown in Figure 1. The relatively slow scan rate was required in order to minimize internal cell resistance and charging current contributions present at faster scan rates. For the RVC-OTE's with porosities of 100, 80, and 60 ppi, the current approaches zero after passing through an anodic or cathodic maximum, and

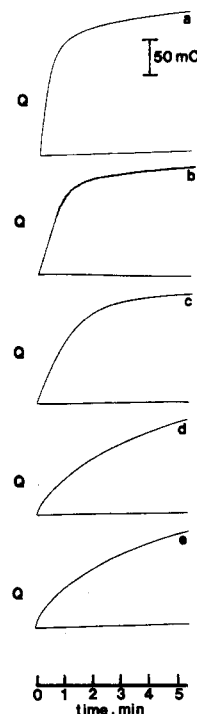


Figure 2. Chronocoulograms for the reduction of 4.0 mM $K_3Fe(CN)_6$ in 1 M KCl at RVC-OTE's with thicknesses of 2.0 mm and porosities of (a) 100, (b) 80, (c) 60, (d) 45, and (e) 30 ppi: potential step, +0.6 V to 0.0 V vs Ag/AgCl.

the anodic and cathodic peak currents are nearly the same, behavior which is characteristic of thin-layer cells (11). The currents for the 45 and 30 ppi RVC-OTE's, however, do not completely return to zero after passing through the anodic and cathodic peaks, indicating a trend toward semiinfinite diffusion behavior for these larger pore electrodes. Both the formal redox potential, $E^{\circ'}$, of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple (+0.27 V vs Ag/AgCl) and the peak potential separation ($\Delta E_p \approx 200$ mV) are found to be independent of both thickness and pore size of the RVC-OTE. The deviation from true thin-layer results, where $\Delta E_p = 0$, can be attributed to ohmic potential differences and less uniform current distributions at higher scan rates (11). The ΔE_p value of 200 mV found in the present study at a scan rate of 2 mV/s is consistent with values of 70 and 160 mV for scan rates of 0.2 and 1.0 mV/s, respectively, as reported by Ward and Hussey for a 100 ppi, 1.0 mm thick RVC-OTE (4). Faster scan rates result in much larger peak potential separation values, but do not affect formal potential values. Measured peak currents increase with both increasing porosity at constant thickness, which can be seen in Figure 1, and increasing thickness at constant pore size (results not shown). Both of these parameters correspond to increasing surface area of the electrode.

The trend from thin-layer behavior toward semiinfinite diffusion behavior with increasing pore size is also evident from chronocoulometric data, as shown in Figure 2. A solution of 4.0 mM $K_3Fe(CN)_6$ was reduced by stepping the potential from +0.6 V to 0.0 V vs Ag/AgCl. The time required for complete electrolysis in the RVC-OTE is a function of pore size, as was found for PMF-OTE's (8). For smaller pore sizes (100, 80, and 60 ppi) the electroactive material is always relatively close to some portion of the electrode surface, resulting in complete electrolysis in less than 10 min. For larger pore sizes, however, electrolysis times are longer: between 20 and 25 min for the 45 ppi electrode and nearly 30 min for the 30 ppi electrode. These longer times result because the electroactive material in the solution must diffuse through a longer distance in order to reach the electrode surface.

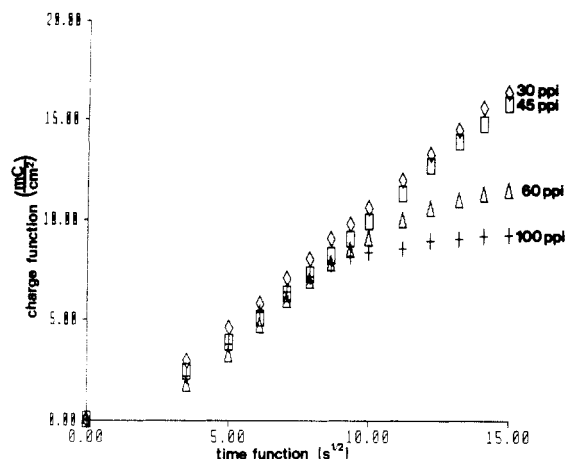


Figure 3. Charge-time data for the reduction of 4.0 mM $K_3Fe(CN)_6$ in 1 M KCl at RVC-OTE's with thicknesses of 2.5 mm and porosities of (+) 100, (Δ) 60, (\square) 45, and (\diamond) 30 ppi: potential step, +0.6 V to 0.0 V vs Ag/AgCl.

Table I. Calculated Surface Areas and Volumes of RVC-OTE's

thickness, mm	surface area, cm ²				
	100 ppi	80 ppi	60 ppi	45 ppi	30 ppi
0.5	6.05				
1.0	7.63	6.96	5.43		
1.5	11.0	10.4	8.80		
2.0	19.2	16.9	10.3	7.21	5.78
2.5	25.1	20.8	15.4	8.04	8.65
3.0			18.3	9.63	10.1
3.5			18.9	13.9	

thickness, mm	volume, μ L				
	100 ppi	80 ppi	60 ppi	45 ppi	30 ppi
0.5	92				
1.0	116	124	126		
1.5	166	186	205		
2.0	291	301	239	257	321
2.5	380	371	359	287	481
3.0			425	344	561
3.5			440	495	

Electrolysis times are independent of cell thickness.

Charge-time data for single potential steps of +0.6 to 0.0 V vs Ag/AgCl with 100, 60, 45, and 30 ppi electrodes (2.5 mm thickness) are plotted in Figure 3. At relatively short times all of these electrodes exhibit linear $Q-t^{1/2}$ behavior. However, at somewhat longer times the $Q-t^{1/2}$ behavior for the smaller-pored electrodes reaches a plateau, whereas the larger-pored electrodes continue to exhibit linear behavior during the time period studied, as would be expected for semiinfinite diffusion conditions. Electrode areas were calculated from the slopes of the linear portions of the $Q-t^{1/2}$ plots, and values range from approximately 5 cm² for the thinnest, larger-pored electrodes to about 25 cm² for the thickest, smaller-pored electrodes, as displayed in Table I. These areas correspond to electrode volumes ranging from approximately 100 to 500 μ L, as calculated from specified surface areas for the various grades of RVC (12).

Spectroelectrochemical Characteristics of the RVC-OTE. Table II shows the transmittance characteristics of RVC slices of various thicknesses and porosities. These results can be compared to transmittance values ranging from 22% to 82% for gold minigrid electrodes with mesh sizes ranging from 2000 to 100 lines per inch, as reported by Petek et al. (13). As can be seen in Table II, a 100 ppi, 1.0 mm thick slice of RVC, typically used in spectroelectrochemical studies using

Table II. Transmittance values of RVC-OTE's ($\lambda = 438$ nm)

thickness, mm	transmittance, %				
	100 ppi	80 ppi	60 ppi	45 ppi	30 ppi
0.5	48.2				
1.0	37.1	21.4	50.8		
1.5	11.3	8.18	29.8		
2.0	10.7	1.28	23.6	49.3	51.1
2.5	2.67	0.37	16.0	49.9	42.3
3.0	1.66	0.48	11.6	34.6	36.0
3.5		0.11	5.89	26.8	24.3
4.0				24.5	18.5

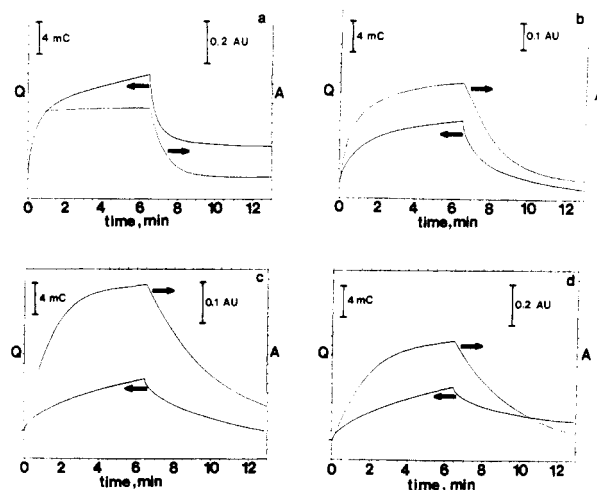


Figure 4. Chronocoulometry and chronoabsorptometry data for the oxidation of 100 μ M *o*-tolidine in 0.5 M HOAc, 1 M $HClO_4$ at RVC-OTE's with thicknesses of 2.0 mm and porosities of (a) 80, (b) 60, (c) 45, and (d) 30 ppi: potential step, +0.35 V to +0.85 V vs Ag/AgCl; wavelength, 438 nm.

RVC-OTE's, has similar transmittance characteristics to a slice of 45 ppi or 30 ppi RVC 3 times as thick. Therefore, longer path length RVC-OTE's could be employed when control of the optical characteristics of the electrode is desired, such as in situations in which electroactive products with low molar absorptivities are monitored.

Simultaneous charge- and absorbance-time results for the oxidation of a 100 μ M *o*-tolidine solution using 80, 60, 45, and 30 ppi RVC-OTE's (2.0 mm thickness) are shown in Figure 4. The potential was stepped from +0.35 to +0.85 V vs Ag/AgCl, and the absorbance of the oxidized form was monitored at 438 nm. The yellow color of the oxidized form was visible around the edges and throughout the surface of the electrode. The magnitude of the edge effect appears greater for the charge data than for the absorbance data, especially in the larger pore electrodes. Edge effects appear to be independent of cell thickness. Both absorbance-time and charge-time data indicate longer electrolysis times required with larger pore sizes.

Figure 5 shows the spectropotentiostatic behavior of a 100 μ M *o*-tolidine solution using 2.0 mm thick RVC-OTE's with porosities of 100, 80, 60, 45, and 30 ppi. The potential was held at each individual value until the current became steady or approached zero. These times ranged from 3–5 min for the smaller pore electrodes to 10–15 min for the larger pore electrodes. These absorption spectra were used to calculate $E^{\circ'}$ and n values for the oxidation of the *o*-tolidine. Plots of applied potential vs $\log [A_{red} - A]/[A - A_{ox}]$ for these spectra resulted in values of $n = 1.94$ ($n = 23$, relative standard deviation = 0.130) and $E^{\circ'} = 0.639$ V ($n = 23$, relative standard deviation = 0.0135) vs Ag/AgCl. These results compare favorably to those reported by DeAngelis and Heineman (14) in studies using a gold minigrid electrode.

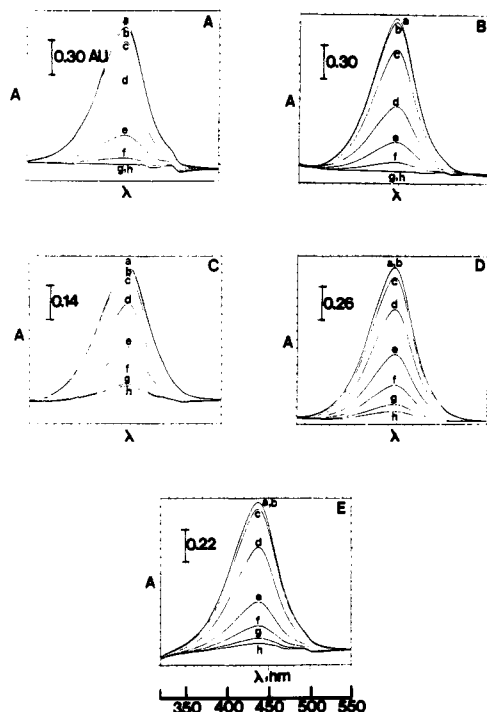


Figure 5. Spectropotentiostatic data for 100 μM *o*-tolidine in 0.5 M HOAc, 1 M HClO_4 at RVC-OTE's with thicknesses of 2.0 mm and porosities of (A) 100, (B) 80, (C) 60, (D) 45, and (E) 30 ppl: potential values, (a) 0.80 V, (b) 0.70 V, (c) 0.67 V, (d) 0.65 V, (e) 0.63 V, (f) 0.61 V, (g) 0.55 V, and (h) 0.45 V vs Ag/AgCl.

The choice of both thickness and pore size of RVC can permit greater control over both optical and electrochemical properties of RVC-OTE's in spectroelectrochemical experiments. As might be expected, smaller pore sizes tend toward

more optimal electrochemical properties, whereas thicker electrodes with larger pore sizes tend toward more optimal optical characteristics. Further investigation is continuing in order to adapt these electrodes as detectors in flow-through applications.

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