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Ultramicroelectrode Ensembles V. Sealing Defects Between the Ensemble Elements and the Host Membrane with Octadecyltrichlorosilane

by

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<p>We have recently developed a new procedure for preparing ensembles of ultramicroelectrodes (1-4). This procedure entails filling the pores of a microporous host membrane with a conductive material. Nuclepore filters, with linear, cylindrical pores, were used as the host membranes. We have used this approach to prepare ultramicroelectrode ensembles based on Pt (1,2) and carbon paste (3,4) electrode elements.</p> <p>The Pt-based ensembles were prepared by electrochemically depositing the metal into the pores of the host membrane (1,2,5). This was accomplished by attaching the Nuclepore membrane to an electrode surface, immersing this electrode into a solution of chloroplatinic acid, and repeatedly scanning the potential of this electrode through the PtCl<sub>6</sub><sup>2-</sup> reduction wave (1,2). Deposition was continued until Pt was deposited through the pores, and well past the membrane/solution interface. The membrane surface was then sealed by vacuum-impregnating with molten polyethylene and polished to reveal the disk-shaped Pt ultramicroelectrode elements (1,2).</p> <p style="text-align: right;">(Continued on reverse)</p>						
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The sealing step proved necessary because electrolyte crept between the Pt elements and the host membrane; this caused the capacitive currents at the unsealed ensembles to be spuriously high (1). Unfortunately, even the sealed ensembles showed excessive capacitive currents, because the polyethylene contracted upon solidification (1).

An analogous problem is observed when fine metal wires are sealed in glass to prepare single ultramicrodisk electrodes (6); Wehmeyer and Wightman attempted to solve this problem by coating the electrode surface with chlorodimethyl silane (6). The surface was then lightly repolished to remove the silane from the active electrode area. Capacitive currents at the silane-coated electrode were smaller than at the uncoated electrode, indicating that this procedure blocked a portion of the defects at the glass/metal interface.

Wehmeyer and Wightman did not indicate whether their sealing procedure reduced the capacitive currents to the theoretically-predicted values. Furthermore, they do not indicate how long the chlorodimethyl silane remained attached to the defect sites. This is an important point because, in order to be an effective solution to the sealing problem, the silane derivative must remain attached for prolonged periods. Since the work of Wehmeyer and Wightman (6) a considerable amount of effort has been devoted to producing stable silane coatings at electrode surfaces (7).

We have used an approach similar to Wightman's to seal the elements in our Au ultramicroelectrode ensembles. We have, however, used a silane derivative which has been shown to yield stable films on Au electrode surfaces (octadecyltrichlorosilane, OTS) (7). Treatment of the ensembles with OTS yields active electrode areas which are identical to the areas measured from electron micrographs of the host membrane and to areas obtained from an independent electrochemical evaluation (Table I). We describe the results of these investigations in this correspondence.

Ultramicroelectrode Ensembles. V. Sealing Defects Between the Ensemble  
Elements and the Host Membrane with Octadecyltrichlorosilane

I. Francis Cheng, Jane M. Schimpf, and Charles R. Martin\*

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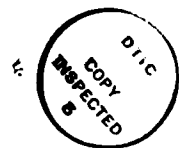
## INTRODUCTION

We have recently developed a new procedure for preparing ensembles of ultramicroelectrodes (1-4). This procedure entails filling the pores of a microporous host membrane with a conductive material. Nuclepore filters, with linear, cylindrical pores, were used as the host membranes. We have used this approach to prepare ultramicroelectrode ensembles based on Pt (1,2) and carbon paste (3,4) electrode elements.

The Pt-based ensembles were prepared by electrochemically depositing the metal into the pores of the host membrane (1,2,5). This was accomplished by attaching the Nuclepore membrane to an electrode surface, immersing this electrode into a solution of chloroplatinic acid, and repeatedly scanning the potential of this electrode through the  $\text{PtCl}_6^{2-}$  reduction wave (1,2). Deposition was continued until Pt was deposited through the pores, and well past the membrane/solution interface. The membrane surface was then sealed by vacuum-impregnating with molten polyethylene and polished to reveal the disk-shaped Pt ultramicroelectrode elements (1,2).

The sealing step proved necessary because electrolyte crept between the Pt elements and the host membrane; this caused the capacitive currents at the unsealed ensembles to be spuriously high (1). Unfortunately, even the sealed ensembles showed excessive capacitive currents, because the polyethylene contracted upon solidification (1).

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We have used an approach similar to Wightman's to seal the elements in our Au ultramicroelectrode ensembles. We have, however, used a silane derivative which has been shown to yield stable films on Au electrode surfaces (octadecyltrichlorosilane, OTS) (7). Treatment of the ensembles with OTS yields active electrode areas which are identical to the areas measured from electron micrographs of the host membrane and to areas obtained from an independent electrochemical evaluation (Table I). We describe the results of these investigations in this correspondence.

#### EXPERIMENTAL.

Reagents and Materials. Gold plating solution (Oroatemp 24) was purchased from Technics Inc. Nuclepore membranes (Nuclepore Corp. Pleaston, CA) with 3 and 5  $\mu\text{m}$ -dia. pores were used. Polyethylene (M.Wt. = 1000) and octadecyltrichlorosilane (OTS) were obtained from Polysciences and Petrarch, respectively. Purified water was prepared by passing house distilled water through a Milli-Q water filtration system. All other reagents were used without further purification.

Electrodes, Cells, and Equipment. The Nuclepore membrane-coated Pt working electrodes were prepared as described previously (1,2). A conventional single-compartment cell, with a Ag/AgCl reference and a Pt flag counter, was used for all studies. A "macro-sized" working electrode (area = 0.178 cm<sup>2</sup>) was prepared by sealing a Pt disk into Kel-F (8); the Pt disk was coated with Au by potentiostatic deposition (-0.9 V vs. Ag/AgCl) for 30 min. The electrochemical equipment has been described previously (1,4).

Ensemble Fabrication. Ensembles were prepared by potentiostatic deposition (-0.9 V vs. Ag/AgCl) of Au into the pores of the Nuclepore host membranes. As before, metal was deposited through the membrane and well beyond the membrane/solution interface (1,2). The membrane surface was then impregnated with polyethylene and polished (1,2).

A schematic representation of an Au ultramicroelectrode element, after sealing with polyethylene and polishing, is shown in Figure 1A. While some of the gap between the element and the membrane has been sealed with polyethylene, portions of the sides of the fibers are still exposed (1,2). At this point the membrane surface was exposed to neat OTS, in an Ar-filled glove bag, for 30 minutes. The surface was then rinsed with toluene; this procedure should leave a monolayer of OTS on all exposed metal surfaces (7) (Figure 1B).

The final step is the removal of the OTS from the active area. This was accomplished by polishing the surface of the ensemble. The following procedure was used: 0.05  $\mu$ m alumina was wetted with water to form a slurry. A small quantity of this slurry was applied to the index finger (covered by a latex glove). The surface of the ensemble was then lightly rubbed, in a circular motion, with the index finger. Rubbing was continued for 2 min. If the pressure applied with the finger is too high, the host membrane will tear.

Measurement of Active Electrode Areas. The success of the OTS-coating procedure was ascertained by determining the active electrode areas of the Au-based ultramicroelectrode ensembles. The procedure used is based on measurement of the voltammetric capacitive currents and is described in (1).

## RESULTS AND DISCUSSION

Figure 2 shows background cyclic voltammograms for the ultramicroelectrode ensembles after impregnation with polyethylene and polishing but before coating with OTS. An analogous background voltammogram for a macrosized Au disk electrode of equivalent geometric area ( $0.178 \text{ cm}^2$ ) is also shown in Figure 2 (top curve). If only the disk-shaped Au elements were exposed to the electrolyte solution, the active electrode areas for the 3 and 5  $\mu\text{m}$  element-diameter ensembles would be 8.0 % and 22.0 %, respectively, of the geometric area (Table I). The large background currents at the ultramicroelectrode ensembles show that the active electrode areas are, in fact, much larger than these theoretically-predicted values.

Figure 3 shows background cyclic voltammograms after coating with OTS and repolishing. Now the background currents at the ensembles are significantly smaller than at the Au macroelectrode, indicating that the OTS treatment reduces the active electrode area (7).

Have the active electrode areas been reduced to the appropriate levels? Table I compares active electrode areas, for the Au ultramicroelectrode ensembles (after OTS treatment), with active electrode areas obtained for the same Nuclepore membranes using two alternative methods. The first alternative method is based on electron microscopic evaluation of the sizes and densities of the pores (4). The second method is based on an analysis of voltammetric data at carbon paste-based ultramicroelectrodes prepared from the same

membranes. This method is described, in detail, in (4). We have shown that the carbon paste-based ensembles do not leak (4).

Table I presents the active electrode area data in terms of  $f_e$ , the fractional active electrode area (1-4);  $f_e$  is the active electrode area divided by the geometric area (1-4). The  $f_e$  values obtained at the Au ultramicroelectrode ensembles are identical to the values obtained by the electron microscopic method and by the electrochemical method involving the carbon paste ensembles (4). These data indicate that OTS treatment reduces the active electrode areas to the appropriate levels.

Finally, cyclic voltammograms for ferrocyanide, obtained at an OTS-sealed Au-element ultramicroelectrode ensemble, are shown in Figure 5. These voltammograms show characteristics between the "pure radial" (4) limiting case (sigmoidal voltammograms) and the "total overlap" (4) limiting case (conventional peak-shaped voltammograms).

#### CONCLUSIONS

In order for this approach to be a practical solution to the sealing problem, the OTS must not desorb from the extraneous Au surfaces during use. Rubinstein has found that monolayers of OTS are extremely stable (7); this is why we chose this material. In preliminary investigations we have found no evidence for loss of OTS after eight hours of exposure to 0.2 M NaCl.

Acknowledgements. This work was supported by the Office of Naval Research and the Dow Chemical Company.

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Table I. Fractional electrode areas<sup>a</sup> for the ultramicroelectrode ensembles.

Element Diameter ( $\mu\text{m}$ )	$f_e$		
	Electron micro- scopic method <sup>b</sup>	Electrochemical method Carbon paste elements <sup>b</sup>	Present study Au elements
3.0	$0.10 \pm 0.02$	0.08	0.08
5.0	-----	0.22	0.20

<sup>a</sup>See text. <sup>b</sup>See reference (4).

## Figure Captions

Figure 1. Schematic representation of the procedure used to seal the Au-element ultramicroelectrode ensembles.

Figure 2. Background cyclic voltammograms at an Au disk electrode (TOP) and at the Au-element ultramicroelectrode ensembles. The ensemble data were obtained before treatment with OTS. The MIDDLE curve is for the ensemble with 5.0  $\mu\text{m}$  elements. The BOTTOM curve is for the ensemble with 3.0  $\mu\text{m}$  elements. Scan rate = 200  $\text{mV s}^{-1}$ . Electrolyte = 0.2 M NaCl. All electrodes had geometric areas of 0.178  $\text{cm}^2$ .

Figure 3. Background cyclic voltammograms at an Au disk electrode (TOP) and at the Au-element ultramicroelectrode ensembles. The ensemble data were obtained after treatment with OTS. The MIDDLE curve is for the ensemble with 5.0  $\mu\text{m}$  elements. The BOTTOM curve is for the ensemble with 3.0  $\mu\text{m}$  elements. Scan rate = 200  $\text{mV s}^{-1}$ . Electrolyte = 0.2 M NaCl. All electrodes had geometric areas of 0.178  $\text{cm}^2$ .

Figure 4. Cyclic voltammograms for ferrocyanide at the 5.0  $\mu\text{m}$ -element diameter ultramicroelectrode ensemble. The scan rates are indicated to left. Solution was 10 mM  $\text{K}_4\text{Fe}(\text{CN})_6$ , 1 M KCl.

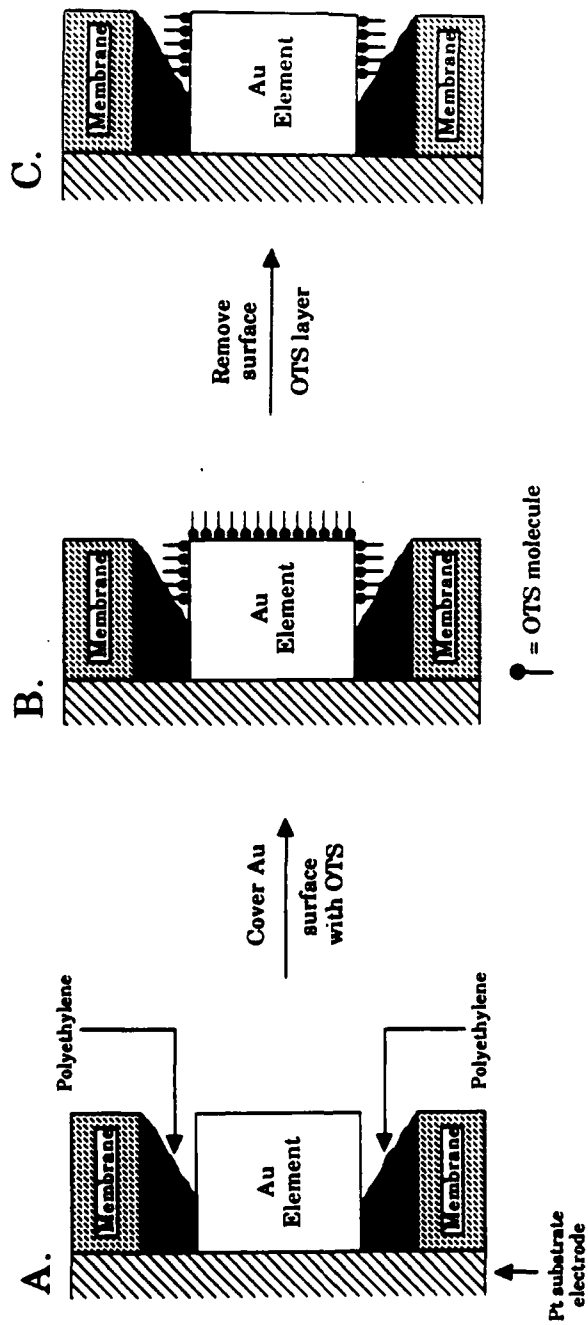


Fig 1

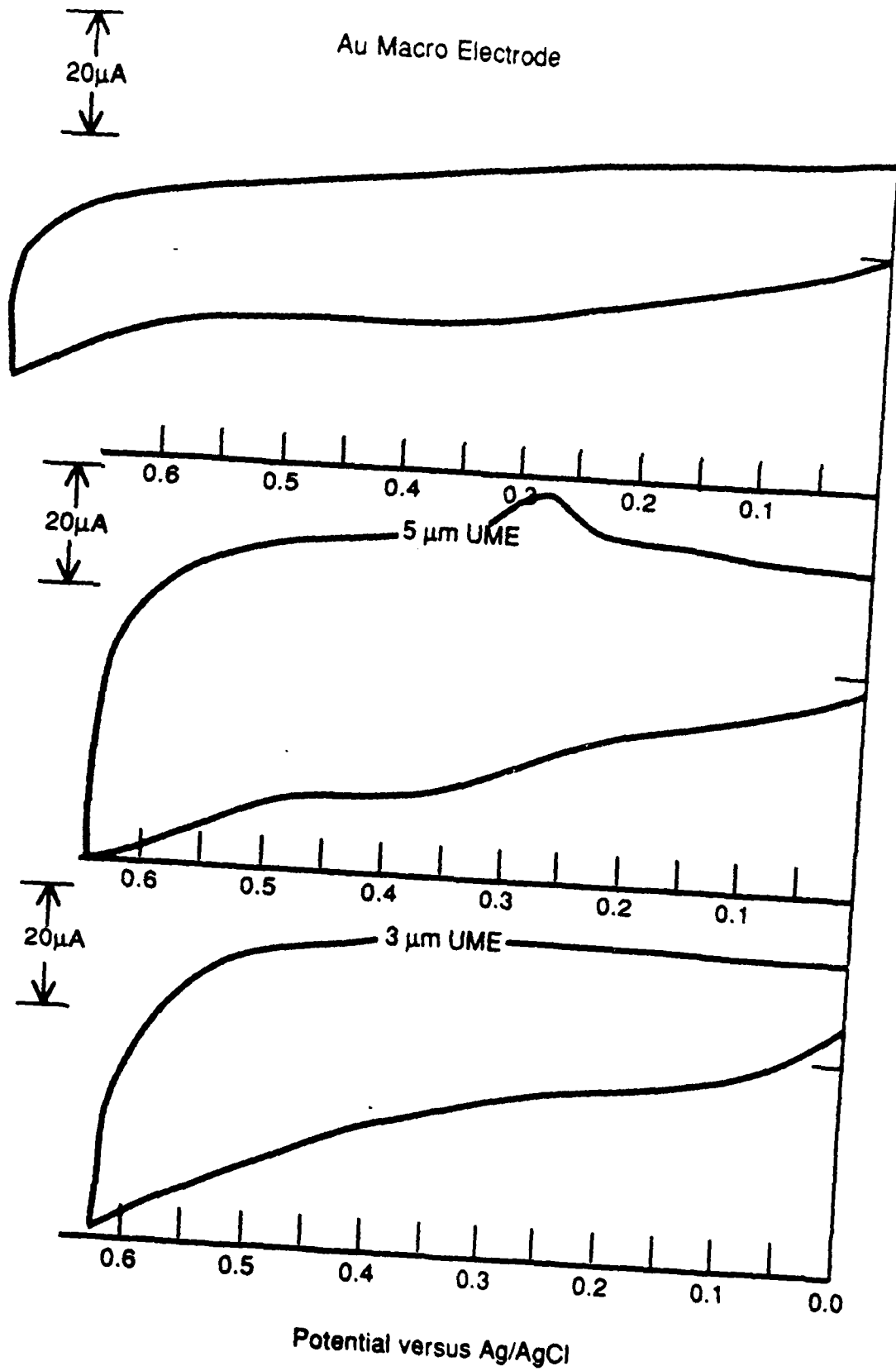


Fig 2

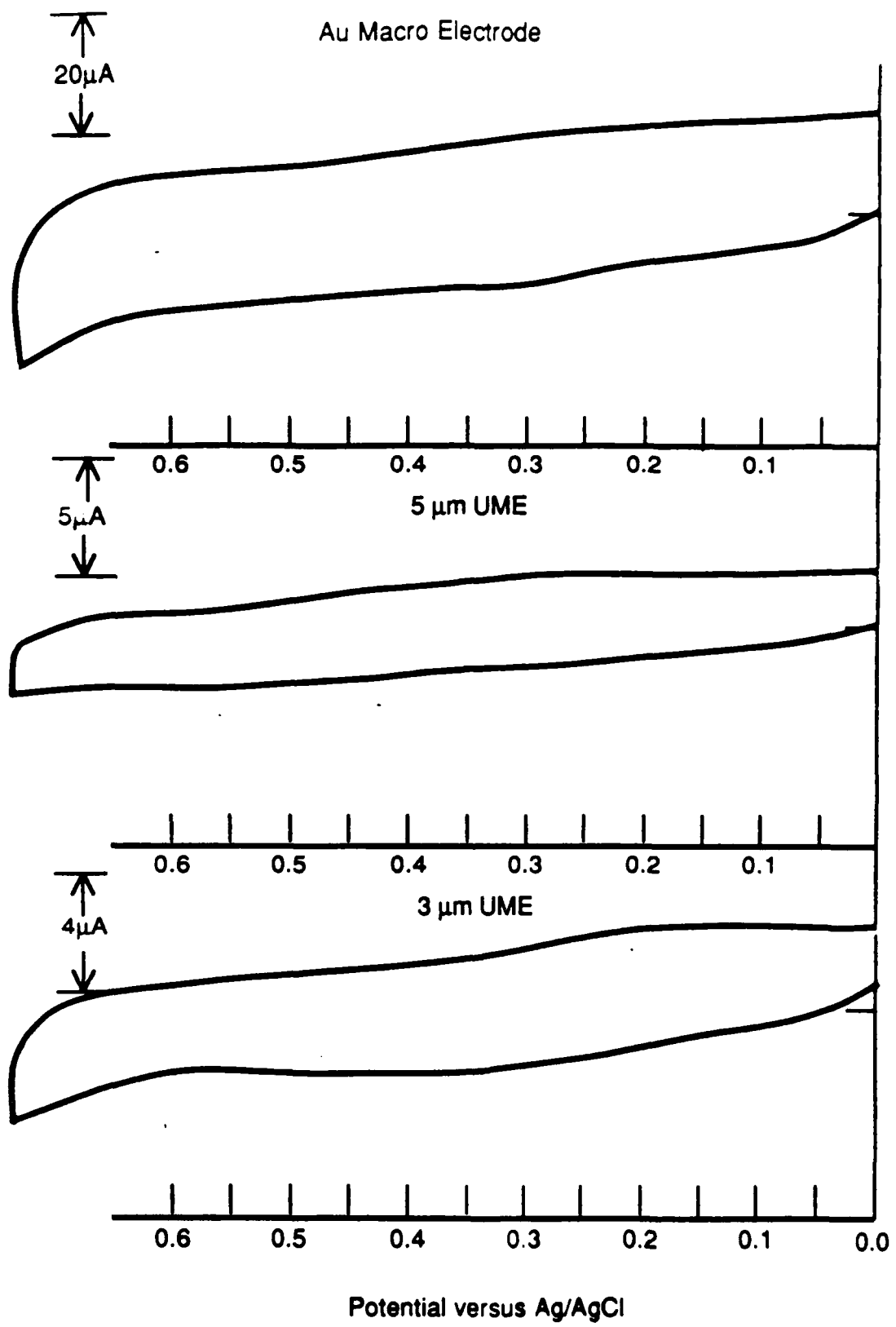


Fig 3

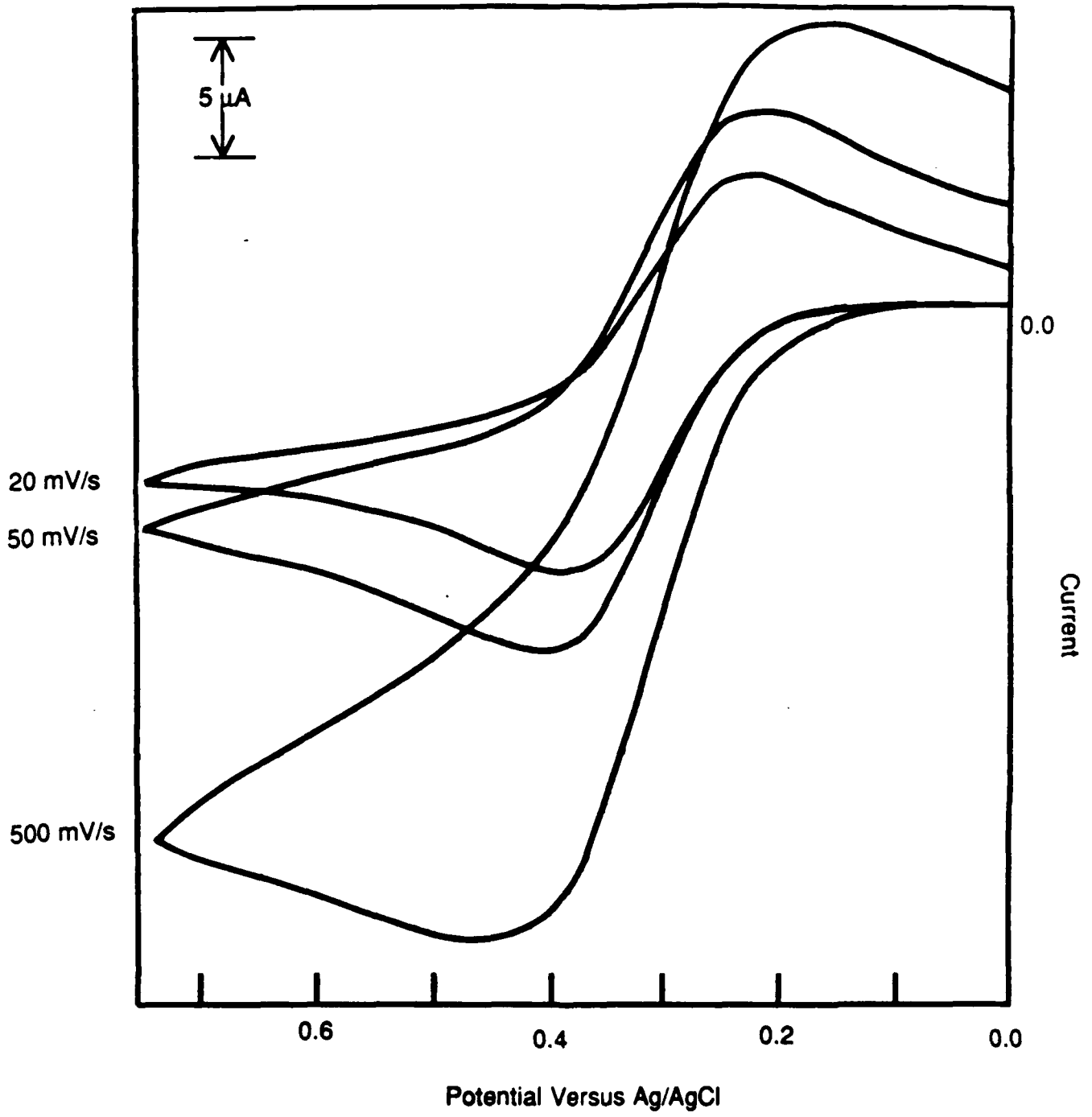


Fig 4