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ELECTRODEPOSITION AND ANODIC STRIPPING OF SILVER ON
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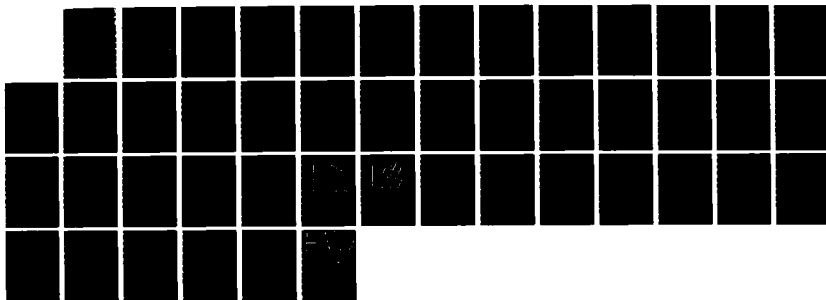
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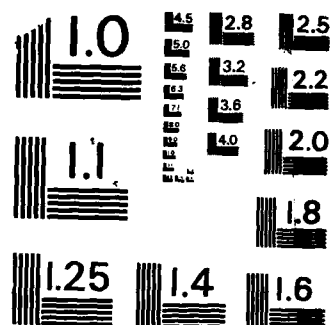
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**Electrodeposition and Anodic Stripping of
Silver on Single Carbon Fibers**

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SUMMARY

Silver is deposited electrolytically on carbon fibers from acetate buffer (1.25 M KOAc/1.70 M HOAc) in the potential range -0.3 to -0.8 V vs SCE. Chronoamperometric and cyclic voltammetric measurements confirm that the mechanism of deposition is nucleation; the rate is higher than at large circular glassy carbon electrodes. The silver deposits are more stable, especially with respect to oxidation by air, than are similar deposits of mercury. Preliminary results on codeposition of silver and mercury are also reported.

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INTRODUCTION

Carbon fibers have been used to make microelectrodes for voltammetric or amperometric studies [1-6]. The two features important in applications of such electrodes are the complicated chemistry and electrochemistry of the electrode material itself [7] and the geometry and size of the electrode. Attempts to control the capacitative and catalytic properties of carbon microelectrodes for direct voltammetric studies generally involve time-consuming, inconvenient procedures which are not necessarily well-defined [8,9]. At the present state of knowledge it is not clear what approaches might ameliorate this situation [10,11]. On the other hand, it appears that quantitative results can be obtained for metal depositions without special pretreatment.

Aoki, Tokuda, Matsuda, and coworkers have developed detailed theory for voltammetry at cylindrical electrodes [12-16]. The response depends in a complicated way on the radius of the cylinder and time scale of the experiment. The problem of deposition and stripping of a solid of variable activity at a cylindrical electrode has not been treated. O'Dea, et al. have investigated the voltammetric response for square wave voltammetry at cylindrical carbon fiber electrodes and suggested that peak shape and position depend only weakly on size and shape of the electrode [17]. Aoki, et al. have shown theoretically the ranges of parameters over which this observation applies and extended the treatment to restricted diffusion [18]. Thus square wave voltammetry appears from the fundamental point of view to be a good voltammetric technique for characterizing phenomena for which adequate theory is not available.

The cylindrical geometry is attractive from the practical point of view because the quality of the seal between insulator and conductor is much less

important in determining electrode performance than for a disk. In addition, the area is adjusted conveniently by choosing the length, independent of the radius, the latter of which alone determines the non-planar diffusional properties. Of course the cylinder cannot be polished by the usual mechanical means, and thus an important component of most electrode pretreatment procedures is unavailable. On considering the art of polishing, one may conclude this is not a drawback.

In the analytical context these electrodes can be used as substrates for anodic stripping voltammetry at mercury films [2,3, 19-21]. Under easily accessible experimental conditions the rate of accumulation of analyte by cylindrical diffusion during the plating process is equivalent to that at a rotating disk with a rotation rate of ca 1000 rpm [13,22]. Although the chronoamperometric current at a cylinder does not reach a steady state, the time dependence of the current is slight enough that the amount accumulated during deposition is linear with deposition time over reasonable ranges of parameters within the overall accuracy of the experiment [22].

Several papers have dealt with deposition of mercury on carbon fibers [2,3,20]. Silver is also an attractive candidate for quantitative electrodepositions. Perone has reported on the electrodeposition of silver at a large graphite disk electrode [23]. The mechanism of deposition on glassy carbon substrates at high concentrations of Ag(I) , which involves nucleation, has been studied in detail by Milchev, et al. [24-26] and by Gunawardena et. al [27]. Deposition under more analytically-pertinent conditions has been examined by Eisner and Mark [28] and by Brainina [29]. Using these results as a starting point we have examined the deposition of Ag on cylindrical carbon fiber electrodes. We should expect the process to

only the size and shape but also the surface of the carbon fibers is different. Some preliminary observations are also reported on co-deposition of silver and mercury.

EXPERIMENTAL SECTION

A three electrode system was used with a carbon fiber indicator electrode and platinum wire counter and saturated calomel reference electrodes. The reference electrode was placed in a salt bridge containing 1M KNO_3 . All potentials are reported versus this electrode. Voltammetric measurements were performed with a computer-controlled potentiostat based on a Digital Equipment Corp. PDP-8/E minicomputer [30]. In the case of square wave voltammetry the current was sampled during the last 1/3 of each pulse. Coulometric results were obtained with an EG&G PARC Model 173 Potentiostat and a Model 179 Digital Coulometer. Electron microscopy was carried out with a mini JSJ Model II electron microscope and optical microscopy employed a Leitz Epivert metallograph.

For all measurements the same microelectrode was used. It was prepared as described previously [19,20]. A carbon fiber was sealed into tygon tubing and this was connected to a teflon holder by thermally shrinkable tubing, so that one end of the fiber contacted mercury inside the holder and the other end was exposed as the active electrode. The length of the exposed part was 9.1 mm, and the carbon fiber used (AESAR, Johnson Matthey Inc.) had a diameter of 8 μm . For one series of measurements an electrode of a different length was used as specified below. A micrograph of such an electrode is presented in Figure 1.

After making the electrode, it was treated in an ultrasonic bath in sequence with "Alconox" solution, water, dilute (1:3) HNO_3 , and finally water. The only other conditioning procedure was to polarize the electrode at +0.55 V for at least 1 min. in the working solution before each voltammetric measurement. The working solution was chosen to be 1.25M KOAc/1.7M HOAc acetate buffer (pH=4.6), which was recommended by Eisner and

Mark [28] for deposition of silver on glassy carbon. According to our experience it also is reasonably good for deposition of mercury [20]. The working solutions were prepared freshly before each experiment by proper dilution of 0.05 M stock solutions of silver nitrate and mercuric nitrate.

Solutions were purged with argon before measurement and blanketed with argon during measurement. For all anodic stripping experiments square wave voltammetry was used with the parameter values of $E_{sw} = 24$ mV, $f=100$ Hz, $\Delta E_s = 4$ mV. All depositions (and stripping voltammograms) were carried out in quiet solution.

RESULTS AND DISCUSSION

A series of depositions of silver was performed in which the concentration of silver was varied. The deposition time was limited in most experiments to two minutes. Under this condition there is no stripping current for Ag if the concentration of Ag(I) is lower than $\sim 5 \mu\text{M}$. The range of concentration investigated was 5-100 μM . Typical anodic stripping peaks are presented in Figure 2.

Curves 1 and 2 in Figure 2 display a small shoulder at more positive potentials. Calculated values of amounts deposited for these conditions [22] combined with the bulk density of silver yield thicknesses of one and two monolayers, respectively, assuming a uniform deposit. Coulometric stripping in separate experiments gave amounts of charge equivalent to 1/3 and two monolayers, respectively. This phenomenon is familiar in stripping of solid deposits. Eisner and Mark have reported similar behavior on spectrographic pyrolytic graphite [28]. But in their case two well-separated peaks are observed, the more positive at ca +0.02 V vs SCE. This peak was attributed to stripping of the first monolayer. In the present case the shoulder appears when less than a monolayer has been deposited, and

it is more pronounced for a given concentration and deposition time when deposition is carried out at more negative potentials. Gunawardena, et al. [27] have shown that at short times the number density of nuclei increases exponentially with increasingly negative potential under conditions of high concentration (≥ 0.01 M) and relatively low overpotential (≥ -350 mV). Under the present conditions of low concentration (< 80 μ M) even with large overpotential (≤ -1 V) nucleation may also be observed, as shown below. It therefore appears that the shoulder is due to stripping of silver bound to carbon, which may have penetrated beneath the carbon surface [27].

Under the experimental conditions of Figure 2 the stripping peak current was found to be linear in silver concentration (correlation coefficient 0.98, $n=3$).

The nature of the electrodeposition process was investigated further using chronoamperometry and chronocoulometry. Figure 3 shows the chronoamperometric response at various deposition potentials. The slowly increasing current transient at short times for $E_{\text{dep}} \geq 0$ V is characteristic of nucleation. At lower concentrations the maximum of current (most clearly visible in curve 5) persists to more negative values of potential. For curves 6 and 7 of Figure 3 the currents are two to three times those predicted for diffusion-controlled currents [13]. Curve 6 corresponds to an overpotential of about -380 mV. At much higher silver concentration (0.05 M) for an overpotential of -340 mV Gunawardena et al. report a current maximum at 270 ms at a large carbon disk. Thus the nucleation process is much faster at the microcylindrical carbon fiber than at the large glassy carbon disk. More quantitative conclusions are beyond the scope of this initial survey.

Charge consumed during deposition and stripping peak current were measured for a range of deposition potentials ($-0.4 \text{ V} \leq E_{\text{dep}} \leq -1.0 \text{ V}$), concentrations of silver ($10\text{--}40 \text{ }\mu\text{M}$), and deposition times ($10\text{--}120 \text{ s}$). Typical stripping voltammograms are shown in Figure 4. The peak width at half-height is constant with value 110 mV over the range of conditions employed. Therefore peak height should be proportional to amount deposited. Note parenthetically that this is a reasonable hypothesis, but that theories for square wave stripping of solid deposits have not been worked out.

Consider first how the amount of charge required during deposition depends on potential and concentration. Representative values are given in Table 1. The values of charge are in the range predicted for accumulation under diffusion-control. Results at -0.4 and -0.7 V are about the same whereas the values obtained at -1.0 V are much larger. The charge appears to depend roughly linearly on concentration at higher concentrations. As predicted, the charge increases linearly with deposition time at -0.4 and -0.7 V , but at -1.0 V it increases with deposition time at a faster than linear rate. The increased charge at -1.0 V may be due to concomitant reduction of hydrogen ion which proceeds at a faster rate on the silver-covered surface than at the bare carbon substrate [31].

The efficiency of stripping, expressed by the ratio of peak stripping current to charge deposited, decreases with increasing deposition time. For example, for $E_{\text{dep}} = -0.4 \text{ V}$ and $C = 20 \text{ }\mu\text{M}$, the efficiency decreases from 1.4 A/C to 0.5 A/C on increasing t_{dep} from 10 s to 120 s . It is possible that at very negative potentials large dendrites form and fall off during deposition, thus increasing the charge (and decreasing the stripping current). Over the potential range -0.4 to -0.7 V where the deposition process is well-behaved, the efficiency of stripping still is not constant

with deposition time. The expected linear dependence on concentration and deposition time is only observed for the narrow range of conditions producing the equivalent of up to a few monolayers of silver.

The deposition of silver on carbon fibers is much better behaved and more reversible than deposition of mercury [20]. These processes are compared directly in Figures 5 and 6. The voltammograms presented there are for Ag(I) in acetate buffer and for Hg(II) in thiocyanate solution which are the recommended conditions for each. The concentrations of mercury and silver were both 160 μ M. The series of normal pulse voltammograms (Figure 5) for Ag(I) shows well-defined waves for which the plateau improves with increase in pulse width. For a pulse width of 200 ms the parameters of the wave are $E_{1/2} = +0.095$ V; $i_L = 1.02$ μ A. (Under these conditions the anodic stripping square wave peak of silver appears at $E_p = +0.305$ V.) In order to obtain a visible wave for reduction of Hg(II) using normal pulse we had to extend the pulse duration to 800 ms. Even then the limiting current ($i_L = 0.09$ μ A) was approximately ten times less than that for silver; and the difference between half wave potential ($E_{1/2} = -0.425$ V) and anodic stripping square wave peak ($E_p = -0.015$ V for $t_d = 40$ s) was twice as large as for silver.

The current-potential curves at various times in Figure 5 are explicable in terms of the current-time curves at various potentials in Figure 3. For silver nucleation is apparent as displayed by an increasing current transient only in a narrow potential range. In the limiting current region for the conditions of Figure 5, the response does not depend significantly on the nucleation process and consequently the shapes of the normal pulse voltammograms are quite reasonable. It should be noted that the currents are about twice as large as predicted [13]. For mercury the

pulse width had to be extended to 800 ms to obtain a reasonable, though very small, wave. For shorter pulse width the current was sampled from the increasing part of the current-time curve. These results suggest that nucleation of silver is much faster and more wide spread than that of mercury.

This generalization is also supported by cyclic voltammetry (Figure 6). For both elements we see the crossover of the cathodic branch due to forming a solid deposit. The cathodic wave of silver is flatter than that observed on a large disk electrode, but has the shape expected for very small cylindrical electrodes. The cathodic branch for mercury is poorly defined and shifted towards much more negative potential values. Comparison of the anodic peaks of silver and mercury shows clearly that deposition of silver is much more reversible.

The next question we address is that of stability of silver deposits. Our previous experience with mercury films is that a short time (tens of seconds) of exposure to the air is sufficient to destroy the deposit almost completely. Stability was determined by comparing anodic stripping voltammograms recorded right after deposition and after periods of time during which the electrode was either disconnected but kept in the solution or disconnected and exposed to the air. We performed this type of experiment for silver deposits on carbon fiber microelectrodes. For this particular set of experiments a carbon fiber electrode of different length was used (1-8.1mm). Typical results are presented in Table II.

The least stable deposit is that formed at -1.0 V, whereas the most stable are those deposited at -0.4 and -0.7 V. In all cases the oxidation potential shifts towards more positive values with increasing time. A similar effect was observed with increasing deposition time (see Figure 4).

i.e. the longer the deposition time, the more positive the anodic stripping peak potential. This might be due to penetration of silver into the bulk of carbon [27].

The data in Table II also confirm our previous observation concerning the efficiency of deposition for different potentials. For $E_{\text{dep}} = -0.4, -0.7, -1.0$ V the anodic peak heights are approximately equal, whereas for $E_{\text{dep}} = -0.1$ V, the peak height is about 20-25% smaller. Also for this electrode the charge consumed for deposition at -1.0 V was about twice that used at -0.4 or -0.7 V.

The stability of the silver deposit enables us to take electromicrographs of carbon fibers with quantitatively deposited silver. Pictures 7A and B show carbon fibers on which have been deposited coulometrically the equivalent of 10 and 100 monolayers of silver, respectively. The bare carbon surface is clearly visible in 7A, confirming that nucleation and growth occurs at active sites rather than uniformly across the surface. In 7B, the surface appears to be covered with silver, but the deposit is rough and irregular, reflecting different rates of deposition at different sites.

Finally, we consider codeposition of silver and mercury. The literature of this subject has been reviewed recently by Wrona and Galus [32] and discussed in more detail by Vydra, et al. [33]. The solubility of silver in mercury is ca 0.0007 mol Ag/mol Hg, but supersaturation and two-phase systems are observed commonly. For all of the results presented below the ratio of the molar concentration of Ag(I) to that of Hg(II) in solution far exceeds the solubility of Ag in Hg. The separate experiments for Ag(I) and Hg(II) [20] in acetate buffer yielded stripping peaks at about the same potential ($\sim +0.30$ V for Ag and $\sim +0.25$ V for Hg), the deposition and stripping of silver is much more reversible than that of mercury, and the

stripping peaks for Ag are about ten times larger than those for Hg under comparable conditions. The following observations are intended to illustrate the influence of each metal on the other in the deposition and stripping steps.

In Figure 7, stripping voltammograms for silver are shifted to more positive potential and diminished in height when the deposition is carried out at -0.1 V, where Hg(II) is not deposited on a bare carbon substrate. Changing the deposition potential to -1.0 V, where Hg(II) is deposited, increases the stripping peak for silver as expected in the absence of mercury (cf. Table II) but also results in a second peak at more negative potential. The silver stripping peak is shifted about 35 mV to less positive values and the second peak is about 70 mV less positive than would have been observed were silver absent. These investigations are not detailed enough to identify specific phases, but for brevity we refer to the more positive peak as the silver peak and to the other as the mercury peak.

Both concentration and concentration ratio are important determinants of stripping behavior, as shown in Figure 8. As the ratio of concentration $[\text{Hg(II)}]/[\text{Ag(I)}]$ is increased, the mercury peak finally appears. Under these conditions the mercury peak height doubles when the solution concentration is doubled at constant ratio, whereas the silver peak increases by only ca. 20% . Note that the conditions of curve 5 correspond to the saturation region for deposition of mercury alone, in which peak height becomes independent of concentration.

The narrow range of conditions giving rise to two stripping peaks was investigated more closely with the results displayed in Figures 9 and 10. It is seen that the potential of mercury oxidation remains constant, whereas the peak of silver, while forming, approaches the values of anodic peak

potential for silver deposited in the absence of mercury (see also Figure 2). Also important in this experiment is the fact that longer deposition time improves deposition of mercury significantly in both cases. This is probably due to formation of amalgam and silver, both of which form a better substrate for further deposition of mercury.

CONCLUSIONS

Silver can be deposited on carbon fiber surfaces. The relation between concentration and square wave stripping peak current is linear at constant deposition time, provided the total amount deposited is not more than a few equivalent monolayers. The suitable range of deposition potential is -0.3 to -0.8 V. At the lowest coverages there is evidence for stripping of a first layer, and the current-time and current-potential behavior are those characteristic of the deposition mechanism of nucleation and growth. This process is much faster than reported at large glassy carbon disk electrodes. It is not clear to what extent this is attributable to the high current densities which can be achieved at small cylindrical electrodes. Silver films are stable even when exposed to air, the worst case exhibiting a 30% decrease in stripping peak current after five minutes exposure. This permits simple experiments in which the fiber is plated in one solution, then transferred to another for voltammetric studies. In all respects the deposition of silver is better behaved than that of mercury. The codeposition of silver and mercury is quite complex, but deserves further study, for it presents the possibility of achieving substrates with favorable surface properties for analytical voltammetry.

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Figure Captions:

- Figure 1. Micrograph of a single carbon fiber microelectrode made by sealing a carbon fiber (8 μm diameter) into tygon (inner tubing) and thermally shrinkable tubing (outer tubing).
- Figure 2. Anodic stripping square wave voltammograms of silver deposited on a carbon fiber microelectrode. Silver concentration: (1) 10; (2) 20; (3) 40; (4) 80 μM ; 1.25 M KOAc/1.7 M HOAc. (SW: $E_{\text{sw}} = 24 \text{ mV}$; $f = 100 \text{ Hz}$; $\Delta E_{\text{s}} = 4 \text{ mV}$; $E_{\text{d}} = -1.0 \text{ V}$; $t_{\text{d}} = 30 \text{ s}$)
- Figure 3. Chronoamperometric curves for deposition of silver on a carbon fiber at different potentials. 160 μM Ag^+ in 1.25M KOAc/1.7M HOAc, pH=4.6. $E_{\text{dep}} = 1)+0.100$; 2)+0.075; 3)+0.050; 4)+0.025; 5)0.00; 6)-0.050; 7)-0.100 V. Electrode polarized at +0.055V for the first 50 ms. Current sampled instantaneously every 5 ms.
- Figure 4. Anodic stripping square wave voltammograms of silver deposited on a carbon fiber at $E_{\text{dep}} = -0.4 \text{ V}$. 20 μM Ag^+ in 1.25M KOAc/1.7M HOAc, pH 4.6. $t_{\text{dep}} = 1)10$; 2)20; 3)40; 4)80; 5)120 s.
- Figure 5. Normal pulse voltammograms of Ag(I) (160 μM in 1.25M KOAc/1.7M HOAc, pH 4.6) (curves 1-3) and Hg(II) (160 μM in 0.1M-KSCN) (curve 4-6) on a carbon fiber microelectrode. Delay before pulse: 2 s; pulse width: $t_{\text{p}} = 1)50$; 2)100; 3) and 4)200; 5)400; 6)800 ms.

Figure 6. Cyclic staircase voltammograms of Ag(I) (160 μM in 1.25 M KOAc/1.7M HOAc, pH 4.6) (curve 1) and Hg(II) (160 μM in 0.1 M KSCN) (curve 2) on a carbon fiber microelectrode. Sweep rate: 0.2 V/s (step height 4 mV, frequency 50 Hz).

Figure 7. Electron micrograph of 8 μm -diameter carbon fiber with silver deposited at -0.4 V in acetate buffer. Equivalent thickness of the deposit A) -10 layers, B) -100 layers.

Figure 8. Anodic stripping square wave voltammetry of silver in the presence of mercury at a carbon fiber microelectrode. $t_d = 30$ s, 1.25 M KOAc/1.7 M HOAc, pH 4.6. E_{dep} V; [Ag(I)], μM ; [Hg(II)], μM : Curve 1)-0.1, 10, 0; 2) -0.1, 10, 80; 3) -0.1, 20, 80; 4) -1.0, 20, 80.

Figure 9. Anodic stripping square wave voltammetry of silver in the presence of mercury at a carbon fiber microelectrode. 1.25 M KOAc/1.7 M HOAc, pH 4.6; $E_{\text{dep}} = -1.0$ V; $t_{\text{dep}} = 30$ s. [Ag(I)], [Hg(II)], μM : 1) 10,0; 2) 10,20; 3) 10,40; 4)10,80; 5) 20,160.

Figure 10. Anodic stripping square wave voltammograms of silver and mercury. 80 μM Hg(II) in 1.25 M KOAc/1.7 M HOAc, pH 4.6; $E_{\text{dep}} = -1.0$ V; $t_{\text{dep}} = 30$ s (A), 90 s (B). [Ag(I)] = 0 0; 1) 3; 2) 6; 3) 10 μM .

Figure 11. Anodic stripping square wave voltammograms of silver and mercury. As Figure 10 but [Hg(II)] = 160 μM . [Ag(I)] = 1) 10; 2) 20; 3) 30 μM

Table I. Charge used for deposition of silver on a carbon fiber microelectrode.

		Q, μC		
[Ag(I)], μM	E_{dep} , V	-0.4	-0.7	-1.0
0		0.1	0.1	0.2
10^b		0.6	0.9	0.8
20^b		2.5	2.6	4.1
40^b		4.6	4.5	9.5

a) 1.25 M KOAc/1.7 M HOAc, pH 4.6; $t_{\text{dep}} = 60$ s.

b) Total charge less charge for [Ag(I)]=0.

Table II. Peak currents and potentials for anodic stripping square wave voltammetry of silver deposited on a carbon fiber microelectrode.^a

E_{dep}, V	-0.1		-0.4		-0.7		-1.0	
Stripping:	$i_p, \mu\text{A}$	E_p, V	$i_p, \mu\text{A}$	E_p, V	$i_p, \mu\text{A}$	E_p, V	$i_p, \mu\text{A}$	E_p, V
b	8.76	0.365	11.40	0.360	11.39	0.350	11.72	0.350
c	7.06	0.405	9.60	0.395	10.15	0.400	8.82	0.395
d	7.39	0.410	8.40	0.395	8.30	0.390	7.10	0.380

a) $t_{\text{dep}} = 60 \text{ s}$, $[\text{Ag(I)}] = 40 \mu\text{M}$.

b) immediately after deposition

c) after 5 min. at open circuit in solution

d) after 5 min. in air

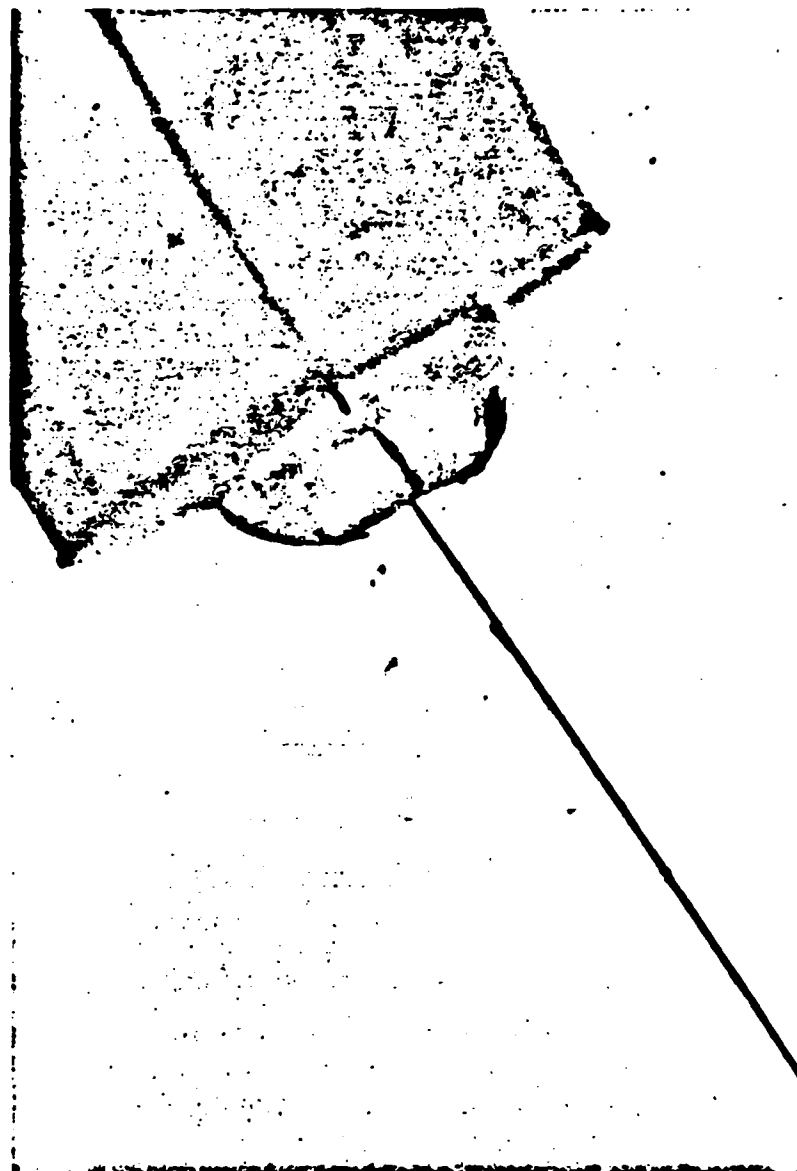


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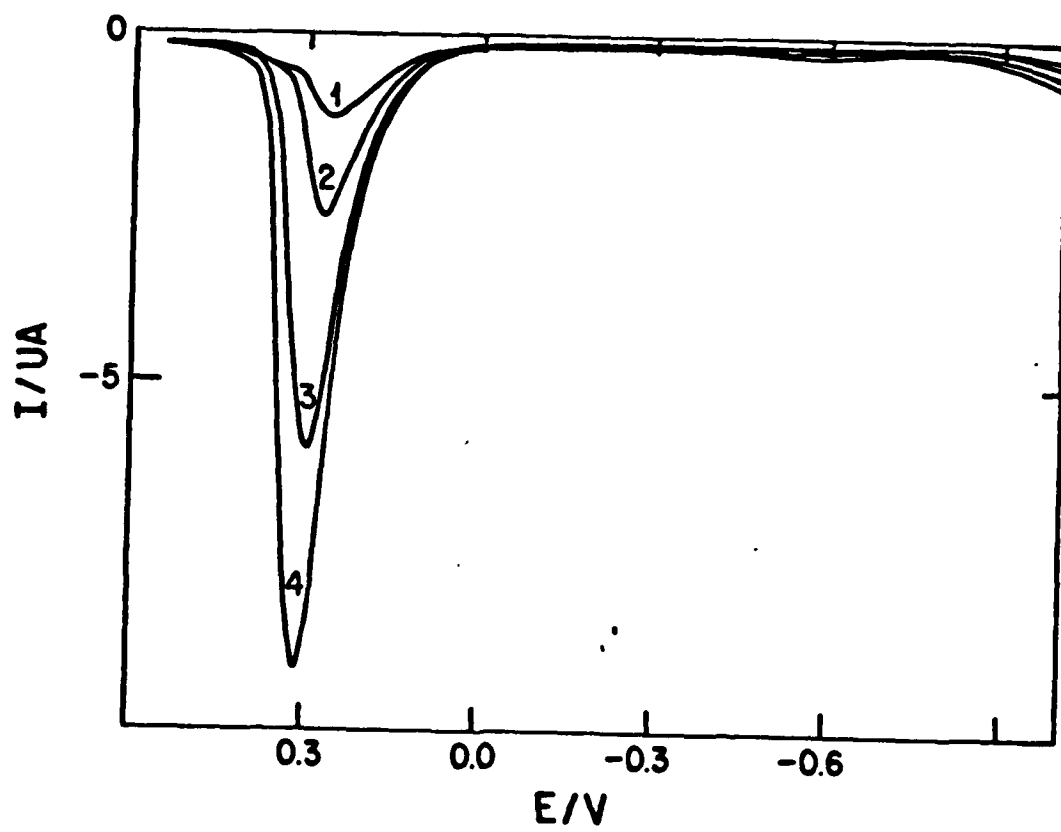


FIGURE 2

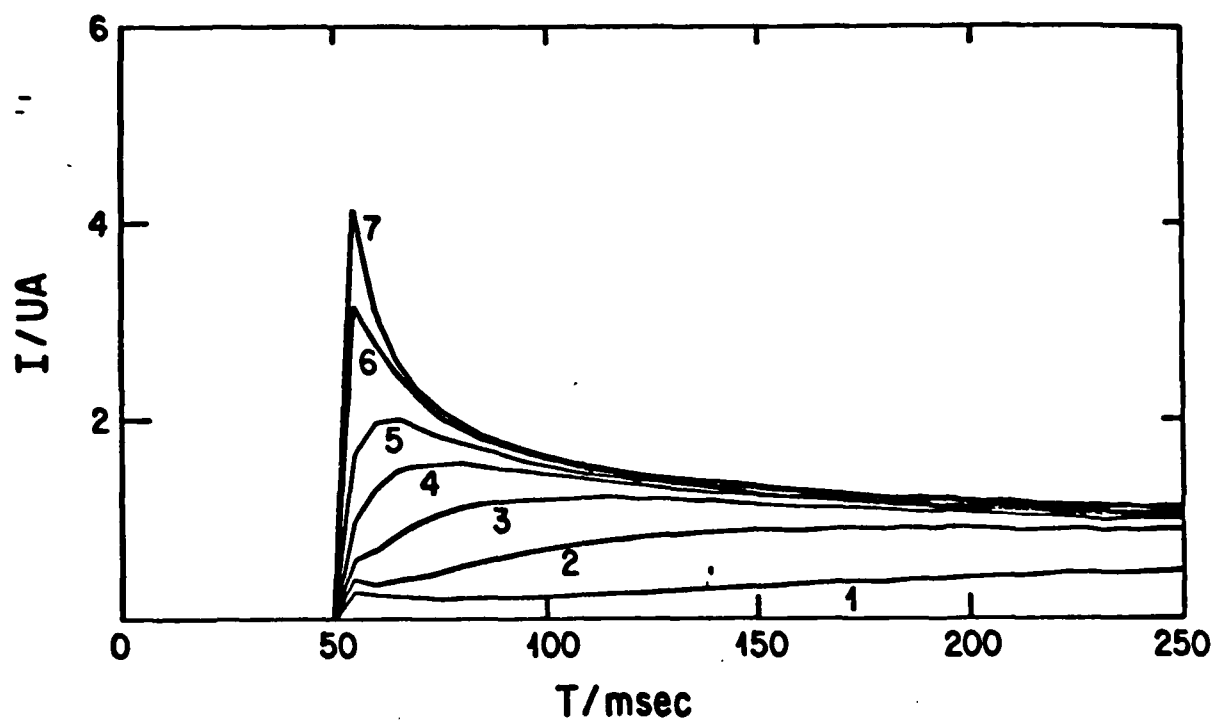


FIGURE 3

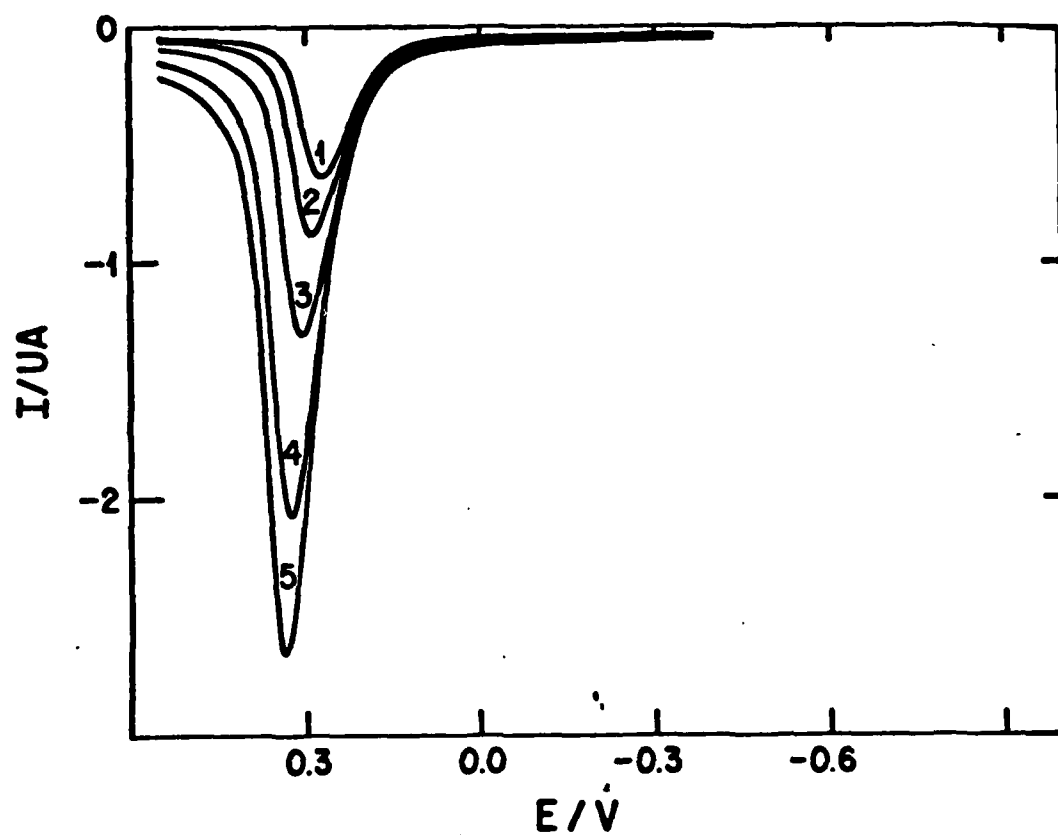


FIGURE 4

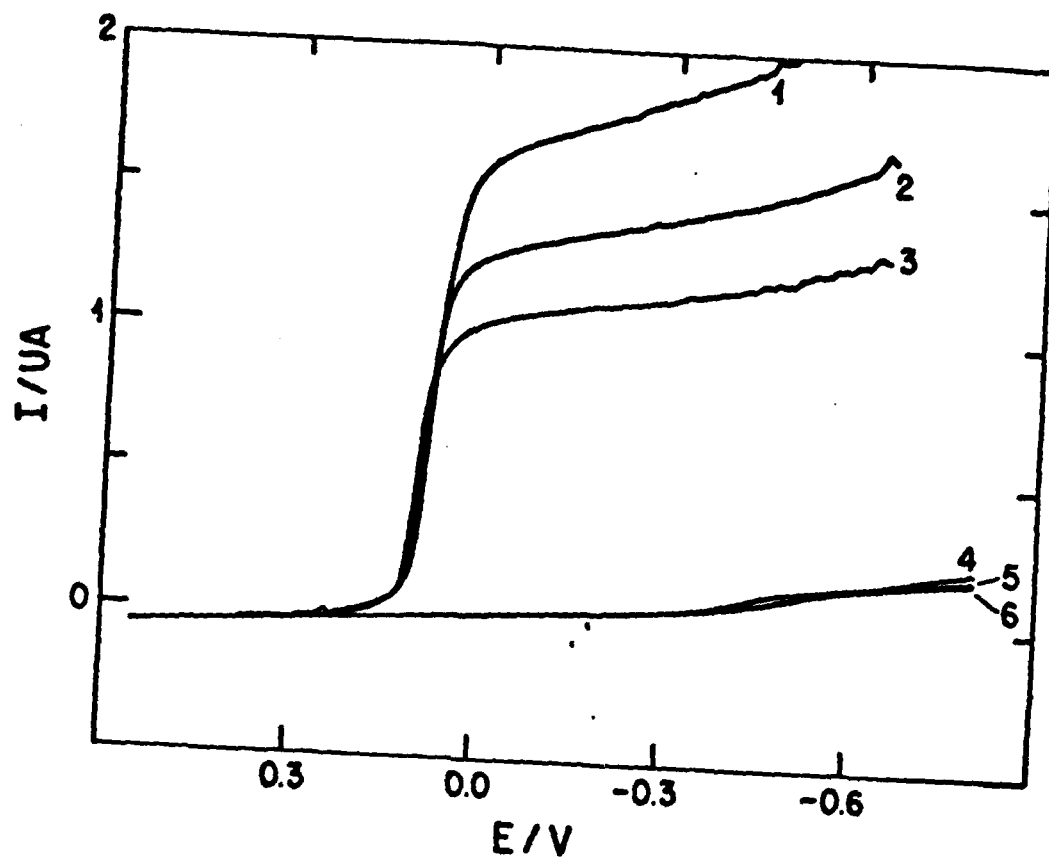


FIGURE 5

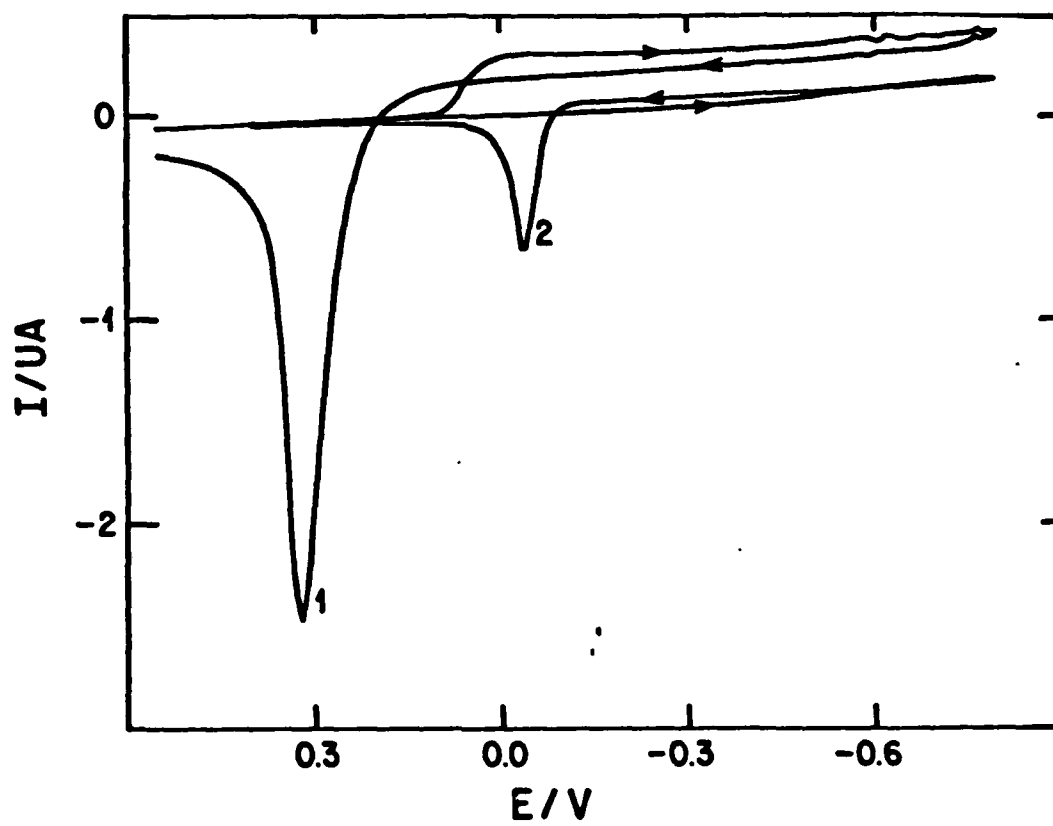


FIGURE 6

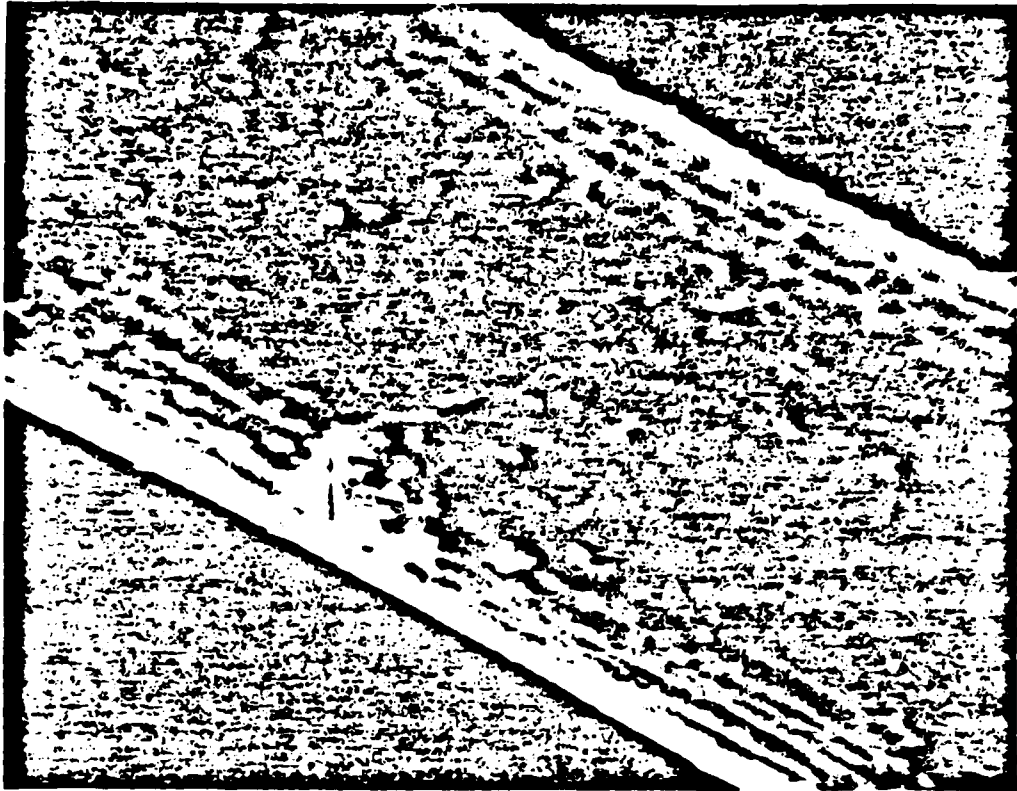


FIGURE 7A

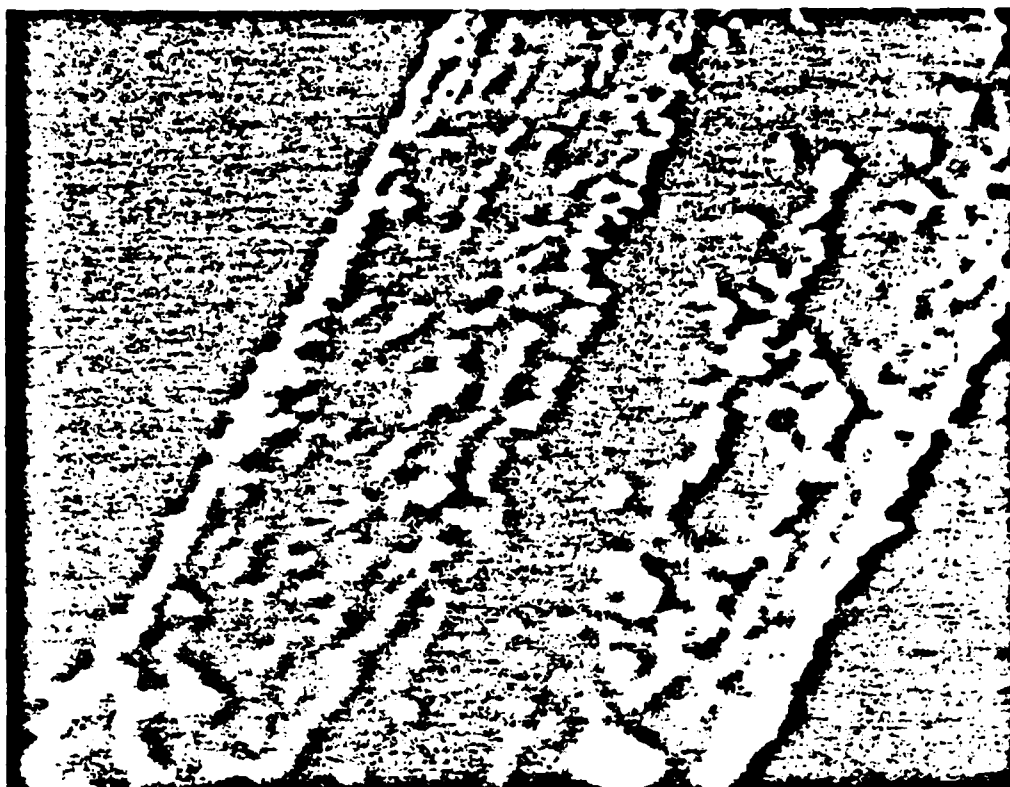


FIGURE 7B

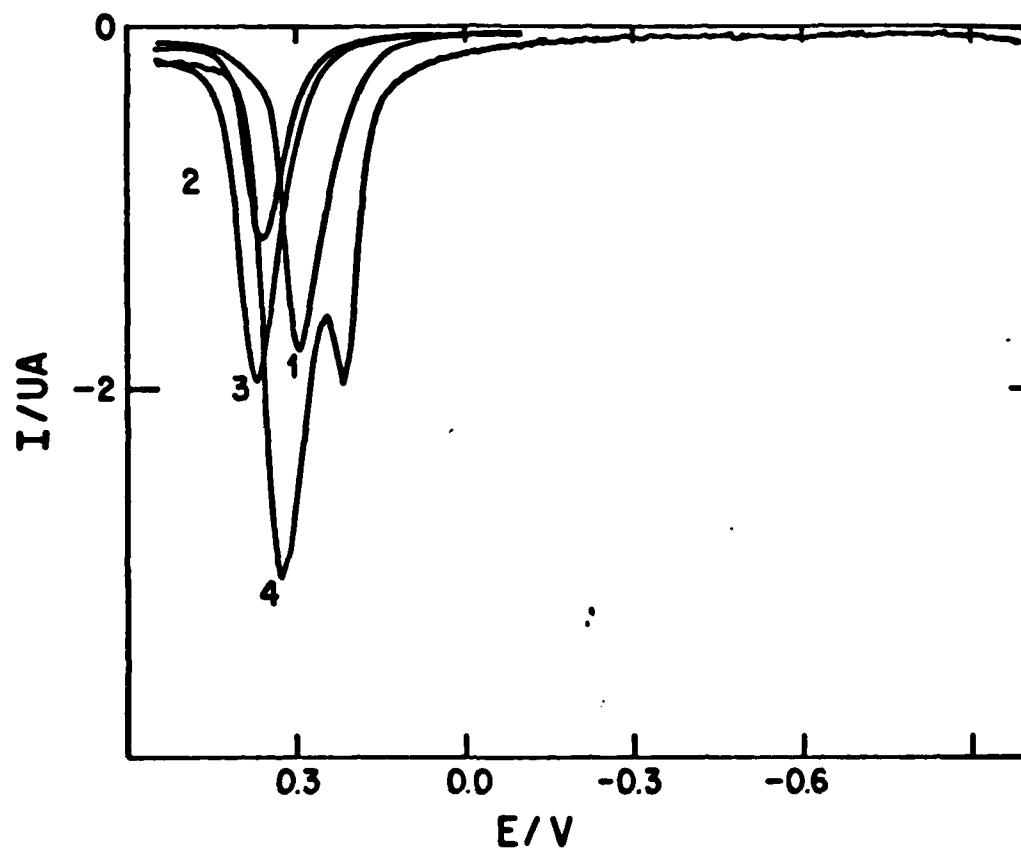


FIGURE 8

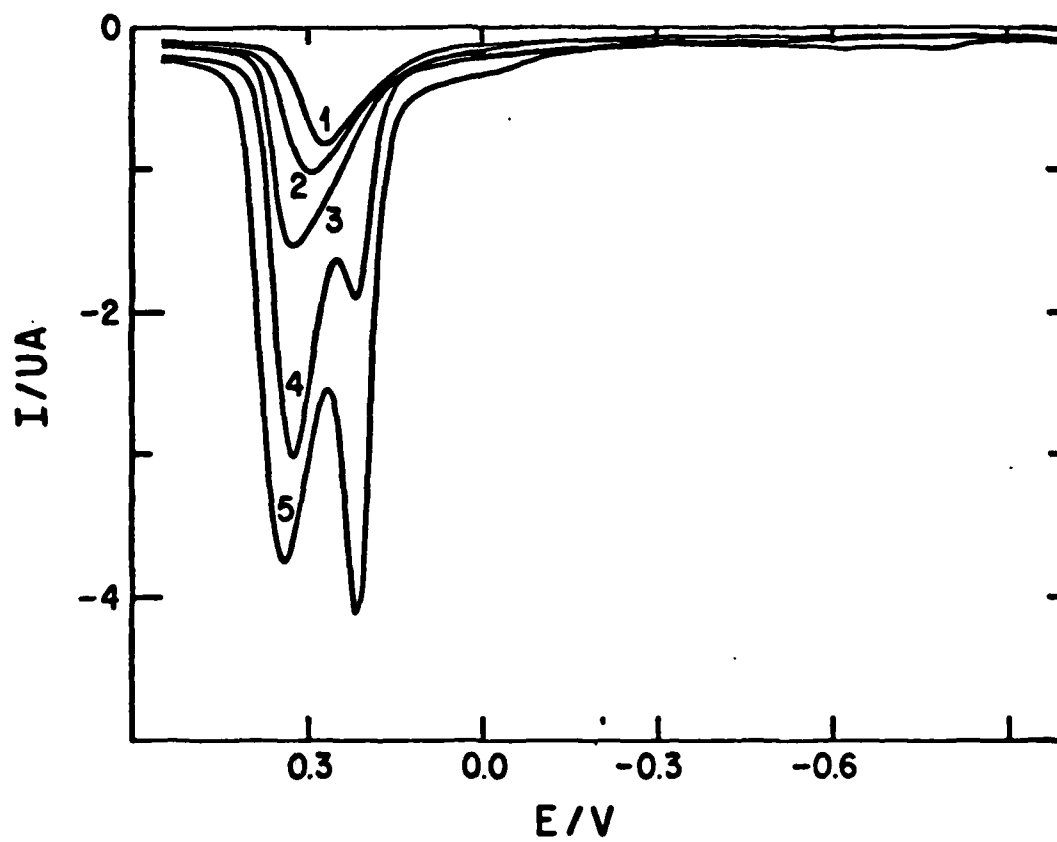


FIGURE 9

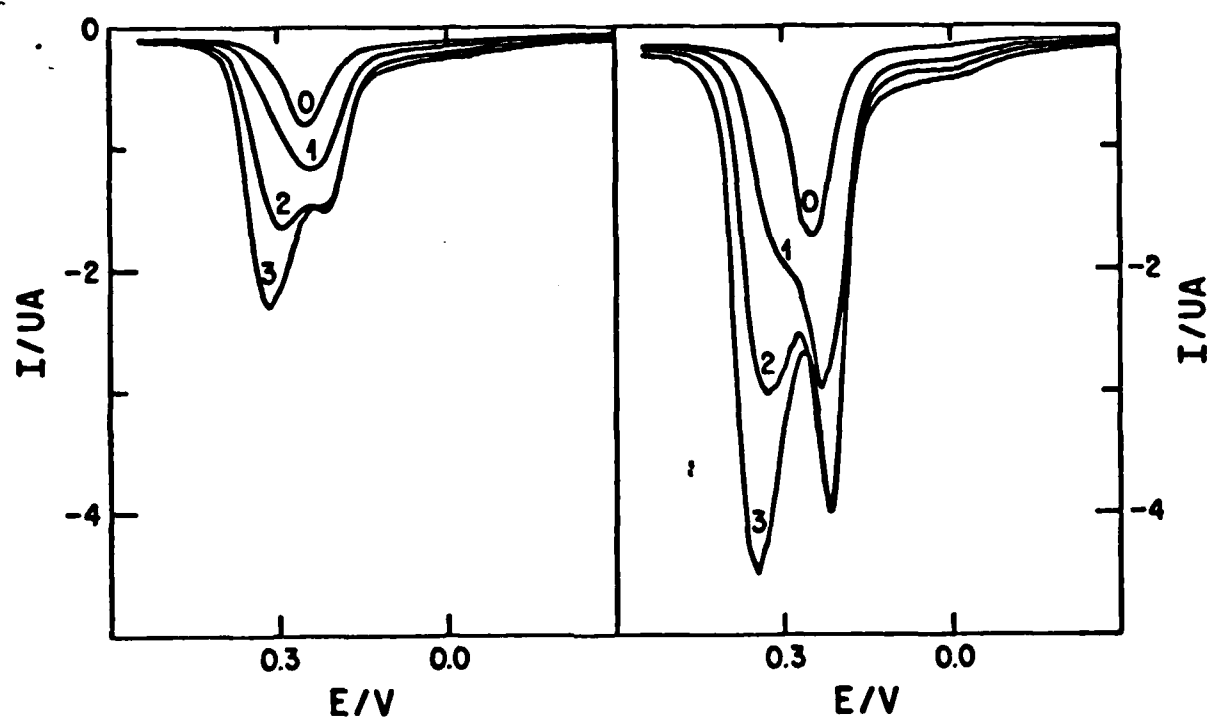


FIGURE 10

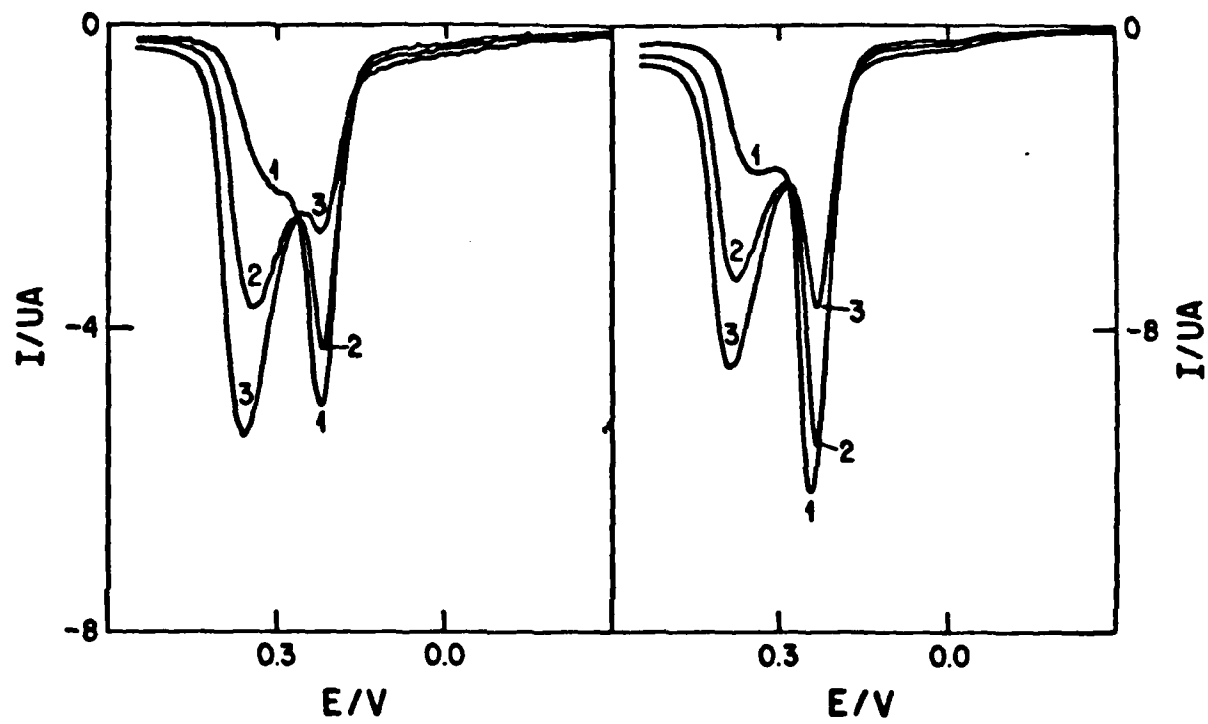


FIGURE 11

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