Sweep Rate and Concentration Effects on Metastable Structures Formed in the Underpotential Deposition of Silver on Pt(111)

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INTRODUCTION

The process of underpotential deposition (UPD) of metals on foreign metal substrates continues to be the subject of intense investigation [1] through the use of electrochemical (especially cyclic voltammetry) methods, surface spectroscopic techniques [2] and most recently scanned probe microscopies [3]. The use of electrochemical techniques such as cyclic voltammetry provides a means of probing the energetics of the system and also allows for an indirect characterization of the processes taking place. Features in the voltammetry can be sensitive to the mechanism of deposition and as a result, can provide information regarding structural transitions as well as interactions between the surface and the UPD layer. The underpotential deposition of silver on polycrystalline as well as single crystal Pt(111) surfaces is one system that has received considerable attention [4-16].

There are several parameters involved in the underpotential deposition of metals which may affect the growth mechanism of the metal overlayer. Of particular importance are the solution concentration of the metal to be deposited and the rate of potential sweep. As the concentration is varied, the mass transport of the species to the electrode is changed and this may affect the kinetics and/or the mechanism of the deposition process. This may lead to the formation of different surface structures at different concentrations. Changes in voltammetric features, which arise as the scan rate of the experiment is varied, typically reflect kinetic limitations in the growth of the deposited layer. Although the importance of these parameters is

clear, only limited examples of studies where these variables have been systematically changed have been carried out.

We report on the effects of concentration and scan rate on the underpotential deposition of silver onto a Pt(111) surface. We note that the voltammetry at a silver concentration of 0.10 mM is highly dependent on the scan rate whereas it is virtually unchanged at a silver concentration of 1.0 mM. We believe this may be due to the formation of different structures of the electrodeposited layer as a function of concentration. These results are then compared to those where after deposition, the electrode was rinsed (at constant potential) with clean supporting electrolyte containing no silver ions in solution. Results from these experiments suggest different interactions between the first and second silver monolayers with the substrate when deposited from silver solutions of different concentration.

EXPERIMENTAL

The working electrode was a 1 cm diameter Pt single crystal disk prepared at the Materials Preparation Facility of Cornell University. The crystal was grown from the melt, oriented by Laue photography, and cut in the (111) direction. Chemical and metallographic polishing were performed until a finished mirror surface was obtained on both faces. The crystal was supported by two 0.020-in Pt wires spot-welded to the sides in such a way as to allow only one face of the crystal to come in contact with the solution. Thus the response obtained is characteristic of a single Pt(111) face. Prior to experiments, the crystal was immersed in hot nitric acid for 10 minutes.

The electrode pretreatment consisted of heating the crystal to approximately 1000°C in a gas/oxygen flame for three minutes and then allowing it to cool for 60 s in the vapor of deaerated supporting electrolyte before quenching in the same solution. The waiting time was necessary to avoid strains induced by rapid quenching. Surface cleanliness was determined by cyclic voltammetry in 0.1 M H_2SO_4, which produced the characteristic "butterfly" pattern described by

Clavilier [17]. The electrode was then brought into contact with the solution. The rinsing experiments were performed as follows: (1) the potential was scanned in the negative direction at 2.0 mV/s from a starting potential of 0.850 V to a pre-determined value, (2) the solution was removed from the cell at a controlled potential, (3) the electrode was rinsed three times with pure supporting electrolyte at the same potential, and (4) the potential was subsequently swept in the positive direction.

All solutions were prepared with pyrolytically distilled water (PDW). Water from a Millipore Milli-Q system was distilled through a heated Pt gauze (700°C) to remove traces of organic species. Aqueous 0.10 M sulfuric acid (ULTREX, J. T. Baker) was used as the supporting electrolyte. Silver solutions of 1.0 mM and 0.10 mM were prepared by dissolving Ag_2SO_4 (Aldrich Chemical Co., 99.999%) in the supporting electrolyte. Impurities in the Ag_2SO_4, stated by the manufacturer, were Na (7 ppm) and Zn (0.5 ppm) as determined by ICP/MS.

Cyclic voltammetry was performed using either a BAS CV-27 potentiostat or a PAR model 173 potentiostat in conjunction with a 175 universal programmer. Data were recorded using a Soltec X-Y recorder. All potentials are referenced to a Ag/AgCl (1 M NaCl) electrode without regard to the liquid junction. A large area Pt foil was used as the auxiliary electrode.

Charges for silver deposition and stripping were determined after correction for the background charge measured under identical conditions except in the absence of silver ions in solution. Conditions and assumptions for these calculations have been previously addressed [5].

RESULTS AND DISCUSSION

As a point of reference, we consider (Figure 1) the UPD of Ag on a Pt(111) electrode from a 1mM solution of silver and at a sweep rate of 2mV/sec. As we have previously reported [5], the deposition of silver under these conditions takes place over four regions with the potential regions and the corresponding coverages being: (1) +0.85 to +0.69 V (1.25

monolayers); (2) +0.69 to +0.45 V (0.20 monolayers); (3) +0.45 to +0.36 V (0.75 monolayers) and finally bulk deposition of silver at potentials below +0.36 V. When the potential sweep is reversed prior to bulk deposition, two peaks (denoted 4 and 5 in Figure 1) corresponding to the removal of the deposited silver are observed. The potential regions and the corresponding charges for these processes are: (4) +0.39 to +0.45 V (0.67 monolayers) and (5) +0.70 to +0.92 V (1.54 monolayers); respectively. This behavior will be compared and contrasted to that observed when varying the silver ion concentration in solution and the rate of potential sweep.

The cyclic voltammograms for the underpotential deposition of silver from a 0.10 mM Ag^+ solution onto a clean and well-ordered Pt(111) electrode at various scan rates are shown in Figure 2. At a scan rate of 2.0 mV/s (Figure 2A), the deposition of silver is similar to that described above for a 1.0 mM silver solution [3] and again takes place over four regions: (1) the deposition of 1.2 monolayers from +0.850 to +0.635 V, (2) the deposition of 0.1 monolayers from +0.635 to +0.450 V, (3) the deposition of 0.4 monolayers from +0.365 to +0.265 V, and the deposition of bulk silver at potentials lower than +0.265 V. When the potential sweep is reversed prior to bulk deposition, two peaks (denoted 4 and 5) corresponding to the removal of the deposited silver are observed. The most positive stripping peak consists of a shoulder at +0.740 V and a peak at +0.795 V and is believed to represent the dissolution of the silver deposited in the first two underpotential regions. In contrast to the behavior observed in a 1.0 mM silver solution (Figure 1), the deposition peaks at a silver concentration of 0.10 mM are significantly broader, possibly suggesting kinetic limitations in the deposition process at this lower concentration. This may be responsible for the more defined peaks that are observed as the scan rate is lowered.

As the scan rate is reduced to 1.0 mV/s (Figure 2B), a new stripping peak at a potential of +0.875 V appears, becoming more prominent as the scan rate is further lowered to 0.5 mV/s (Figure 2C). It is evident from Figure 2 that the growth of the more positive peak with decreasing scan rate is accompanied by a diminution of the peak at +0.795 V. Assuming that both peaks represent the stripping of the silver adlayer from the Pt electrode, this might indicate a

time dependent rearrangement of the silver atoms on the surface. For comparison, Table 1 presents a compilation of the charge associated with all deposition and stripping peaks under the various experimental conditions investigated. Whereas it is clear from Figure 2 that the shape of region 5 is strongly dependent on the sweep rate, the data in Table 1 indicate that the total charge under the peak remains virtually the same. This strongly suggests a structural transformation in which the most positive peak is related to kinetically hindered sites on the Pt(111) surface which can only be occupied after some rearrangement has taken place.

It has recently been suggested that the mechanism of the underpotential deposition of silver on a Pt(111) surface favors cluster formation at low concentrations, e.g. 0.005 mM Ag^+ [4]. At this concentration, a splitting of the most positive stripping peak, similar to that observed here for a 0.10 mM silver solution, has been observed when the time scale of the experiment was increased. In such a case, a rearrangement from a 3-dimensional structure to a 2-dimensional structure was suggested to occur over time. This would enhance the Ag-Pt interactions at the surface, leading to a more stable structure for the silver adlayer. It is plausible then, that at a silver concentration of 0.10 mM the first monolayer of silver may form a metastable 3D structure which undergoes a 3D to 2D transition with time. Such a change may then give rise to the splitting observed.

Further evidence in support of such a transition is provided by overlaying the voltammetric scans at the three sweep rates in the regions of peaks 1 and 5 (Figure 3). In here clearly defined isopotential points (see arrows in Figure 3) are observed. Since for surface processes isopotential points are observed when there is a simple equilibrium of species (sites in the present context) at a constant total coverage [18], this then represents compelling evidence in support of the proposed mechanism. Recent work by Itaya and co-workers [19] on an in-situ ESTM study of silver UPD on Pt(111) provides additional evidence. Although in their study the solution concentration of silver was 1mM, they noted that the silver electrodeposited after the first deposition peak appeared to have a high surface mobility. Such a high mobility could provide a mechanism for the transition described here.

Voltammetric experiments have also been performed at a silver concentration of 1.0 mM. At a scan rate of 0.5 mV/s, shown in Figure 4A, the most positive stripping region develops a shoulder at a potential of 0.875 V. If the potential is held at 0.380 V after the third deposition peak for a period of twenty minutes (Figure 4B), no further change in the voltammetry occurs. Thus while the voltammetry in a 0.10 mM silver solution shows significant changes as a function of the length of time of the experiment, a corresponding change in the voltammetry is not observed with a 1.0 mM silver solution. As in the previous case, the total charge associated with the most positive stripping peak remains virtually constant (see Table 1). If the response obtained at a lower concentration indicates some structural rearrangement, then the data at 1.0 mM Ag^+ may indicate that a more stable structure is being formed at this concentration. The formation of such a well-defined monolayer would then preclude the movement of silver atoms on the electrode surface. Again, the results of Itaya support the formation of a well defined and rotationally commensurate silver monolayer, consistent with our observations.

It could be argued that the presence of *iso-potential points could indicate that there is* indeed a re-arrangement of the surface bound species but that such a re-arrangement is between two different two-dimensional surface structures. However, the fact that the coulometric charges correspond to a full monolayer, and that they are virtually the same under all conditions (see Table I) would preclude such a process. In essence, it would be difficult to envision two different 2-D surface structures at a constant coverage equivalent to a full monolayer. However, no such difficulties arise when one considers a change from three-dimensional clusters to a full two-dimensional monolayer.

Additional information is provided by rinsing experiments performed at silver concentrations of 0.10 mM and 1.0 mM, shown in Figure 5. It has been observed that silver layers on a Pt substrate are not removed by a washing of the electrode [20]. However, when the electrode is held at a controlled potential after the third deposition peak in a 1.0 mM Ag^+ solution and the electrode rinsed three times with pure supporting electrolyte, the peak corresponding to the removal of the second silver adlayer is not present in the reverse scan

(Figure 5A). If this procedure is carried out at a concentration of 0.10 mM Ag$^+$, the stripping peak is clearly present (Figure 5B). Since the second silver layer is retained during this rinsing procedure at lower concentrations but is not at a concentration of 1.0 mM, this might indicate that a more stable second layer (or clusters) is formed when the deposition takes place from a 0.10 mM solution. The fact that during the rinsing process we are dramatically decreasing the solution activity of silver (to essentially zero) would give rise to shifts in the potential of deposition/stripping. Although this could explain why the second monolayer is not retained (upon rinsing) when the deposition is from the 1.0 mM solution, a similar behavior would be expected from deposition from the 0.1mM solution. However, this is not the case since stripping of the second monolayer is clearly observed. Thus, there must be other factors at play. It should also be reiterated that the stability to rinsing of silver monolayers on platinum has been previously reported.[20]

An additional point to be considered is that of work function variations. It has been found that in UPD processes the work function changes from that of the substrate to that of the deposited metal as the coverage reaches a full monolayer. If the first equivalent monolayer formed by silver deposition from a concentration of 0.10 mM has some three-dimensional character, then there will still be exposed Pt atoms so that a work function difference will still exist and this may provide some stability towards cluster formation.

Furthermore, Becker et.al. [21] very recently reported on He scattering studies of silver deposited (under UHV) on Pt(111) at sub-monolayer coverages. They observed clustering induced by elastic strain of the deposit.

In summary, it has been observed that the voltammetry for the underpotential deposition of silver onto Pt(111) electrodes from a 0.10 mM silver solution is a strong function of the sweep rate. A similar response is not noted when deposition occurs from a 1.0 mM silver solution. This may suggest the formation of different overlayer structures based upon concentration, with a tendency toward 3-dimensional structures at lower concentrations. In addition, these observations suggest that care should be taken when making structural assignments based upon

voltammetry performed at high sweep rates as kinetic limitations in the underpotential deposition process may create metastable structures which are dependent on the time length of the experiment and the scan rate employed.

ACKNOWLEDGMENTS

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Table 1.
Charges for Various Potential Regions (mC/cm^2)

Peak Number	1	2	3	4	5
0.1 mM Ag$^+$ (2.0mV/s)	282 ± 13	24 ± 1	102 ± 5	185 ± 8	335 ± 16
0.1 mM Ag$^+$ (1.0mV/s)	244 ± 7	23 ± 1	121 ± 4	190 ± 6	332 ± 10
0.1 mM Ag$^+$ (0.5mV/s)	245 ± 10	30 ± 1	180 ± 7	200 ± 8	332 ± 14
1.0 mM Ag$^+$ (2.0 mV/s)	286 ± 16	29 ± 1	162 ± 7	179 ± 8	362 ± 17
1.0 mM Ag$^+$ (0.5mV/s)	278 ± 14	53 ± 3	172 ± 7	189 ± 9	380 ± 19
1.0 mM Ag$^+$ (0.5mV/s -hold)	268 ± 8	45 ± 7	164 ± 5	193 ± 6	373 ± 11

FIGURE CAPTIONS

Figure 1. Deposition of silver from a 1.0 mM solution in 0.1 M H_2SO_4 onto a Pt (111) electrode starting at +0.85 V. Numbers denote regions previously specified in the text. Scan rate = 2.0 mV/s, A = 0.78 cm^2.

Figure 2. Deposition of silver from a 0.10 mM solution in 0.1 M H_2SO_4 onto a Pt (111) electrode as a function of sweep rate starting from +0.85 V. A = 0.71 cm^2.

Scan rates: A: 2.0 mV/s; B: 1.0 mV/s; C: 0.5 mV/s.

Current scales: A: S=2µA; B: S=1µA; C: S=0.5µA

Figure 3. Overlay of regions one and five for silver deposition from a 0.10 mM solution at various scan rates. (————), scan rate = 2.0 mV/s; (- - - -), scan rate = 1.0 mV/s; (··········), scan rate = 0.5 mV/s. A = 0.71 cm^2. Arrows indicate isopotential points.

Figure 4. Deposition of silver from a 1.0 mM solution in 0.1 M H_2SO_4 onto a Pt (111) electrode (A) continuously scanning at a rate of 0.5 mV/s, (B) at a scan rate of 0.5 mV/s and with the potential held at 0.380 V for twenty minutes. A = 0.71 cm^2.

Figure 5. (A) Deposition of two Ag layers from a 1.0 mM silver solution. The electrode is held at a controlled potential after the third deposition peak, the electrode rinsed three times with pure supporting electrolyte, and the potential sweep resumed in the anodic direction after rinsing. Scan rate = 2.0 mV/s, A= 0.71 cm^2.

(B) Deposition of two Ag layers from a 0.10 mM silver solution followed by rinsing the electrode. Procedure and experimental parameters were the same as in figure 5A.
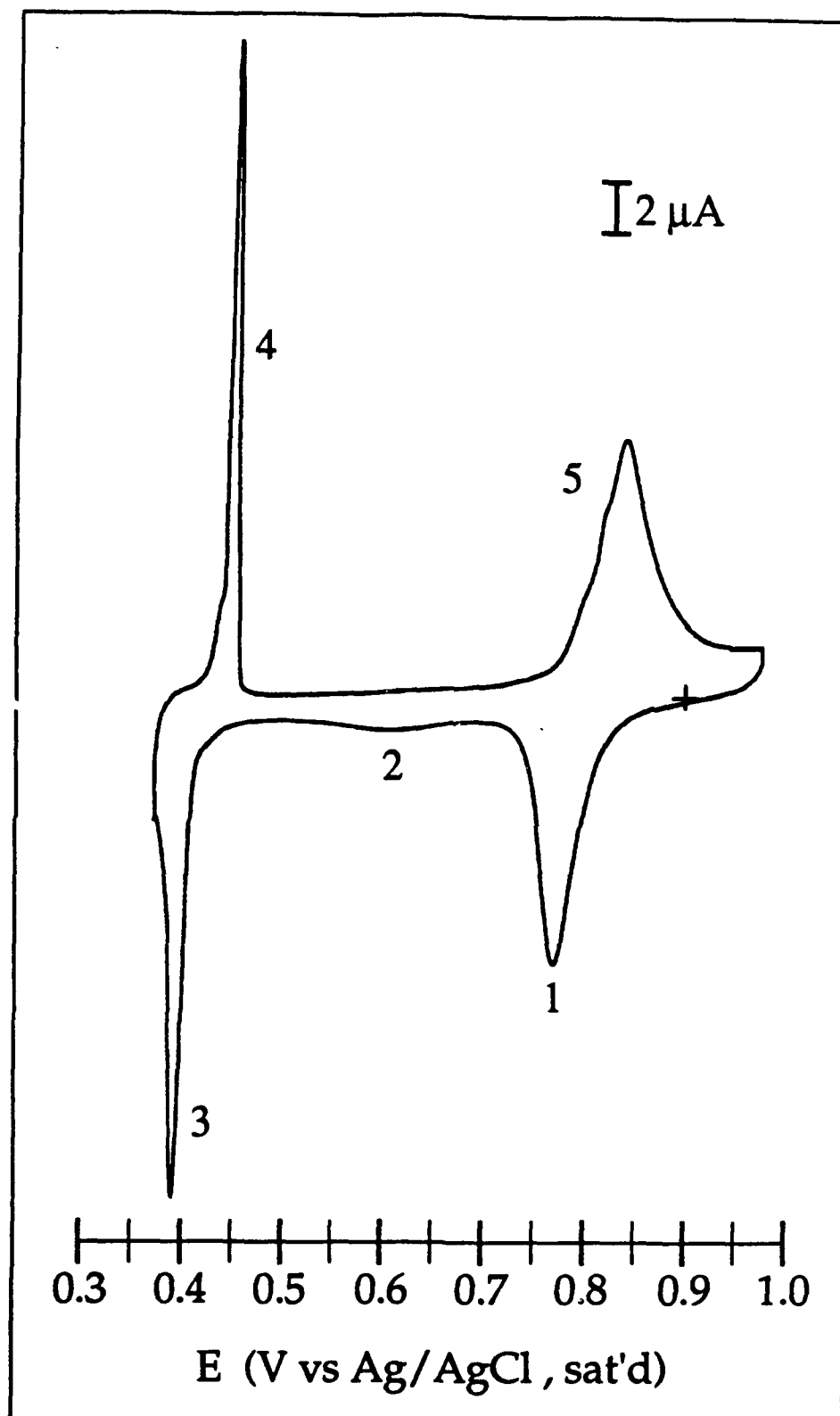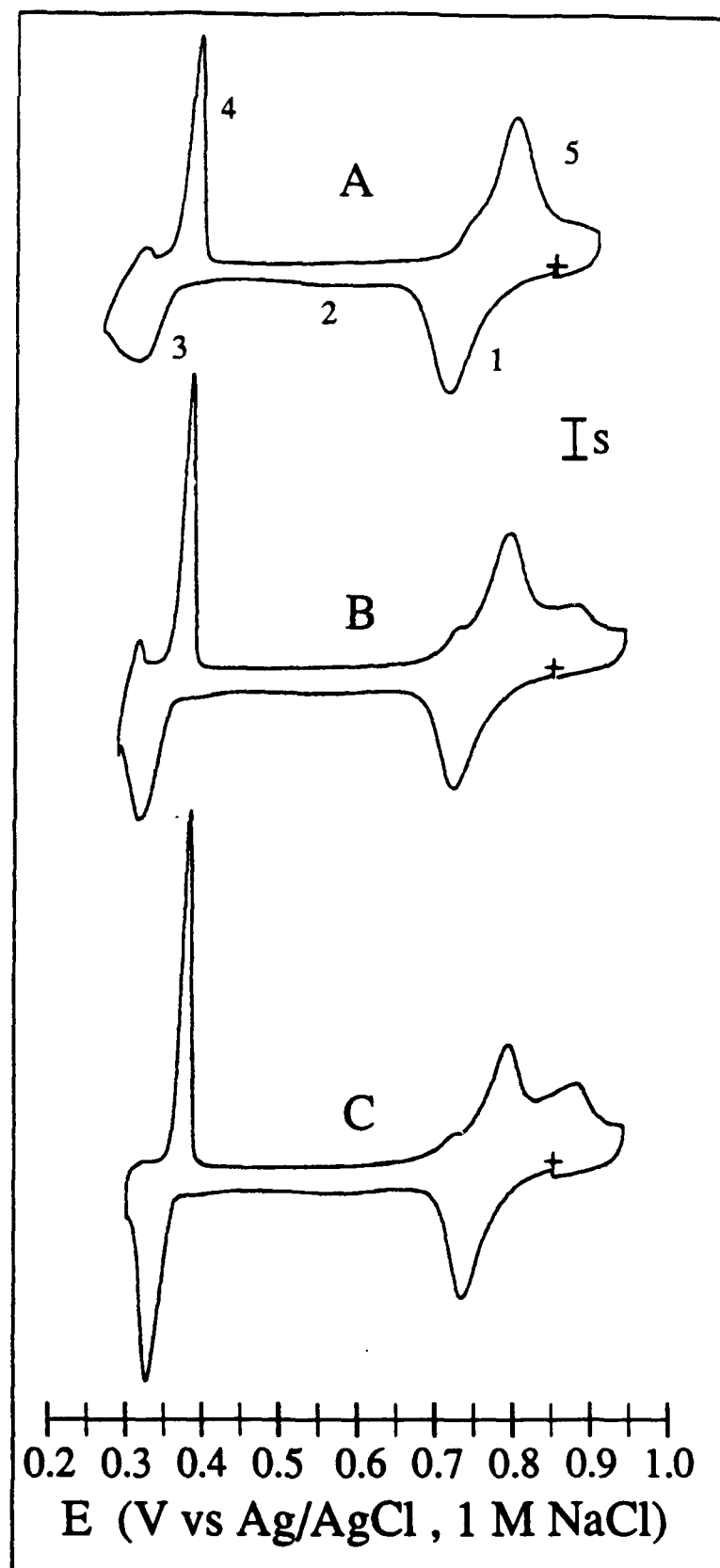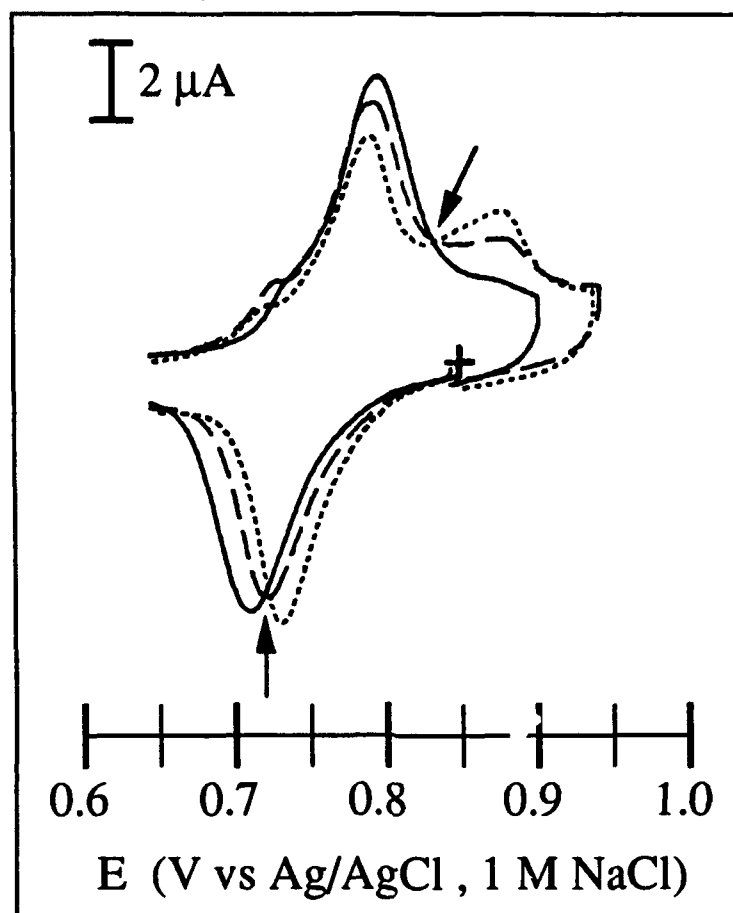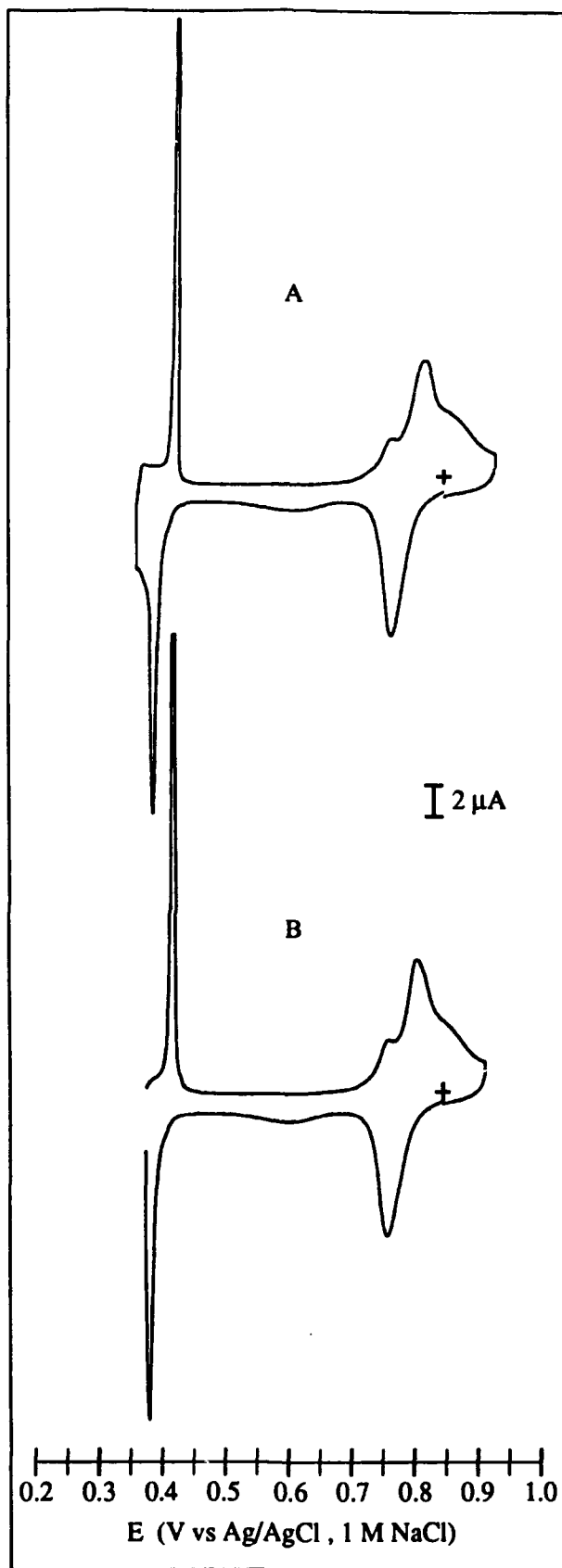
Figure 1

Figure 2

Figure 3

A

B

I 2 μA

0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

E (V vs Ag/AgCl , 1 M NaCl)

Figure 4

A

B

$I\,2\,\mu A$

E (V vs Ag/AgCl , 1 M NaCl)

Figure 5