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Induced Adsorption Of Chloride And Bromide By Submonolayer Amounts Of Copper Underpotentially Deposited On Pt(111).

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Induced Adsorption of Chloride and Bromide by Submonolayer Amounts of Copper Underpotentially Deposited on Pt(111).

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Abstract

The underpotential deposition of submonolayer amounts of copper induces an enhanced adsorption of chloride and bromide on Pt(111) and is reflected in exceedingly sharp voltammetric peaks. The adsorbed anions are believed to be in contact with the platinum surface and in the vicinity of the electrodeposited copper. The electrosorption valency for chloride anions was estimated to be about one. This effect of induced adsorption was not observed on Pt(100) pointing to the sensitivity of the process to the surface structure. The advantages of working with low concentrations of metals in upd studies is illustrated.

Introduction

The adsorption of anions on platinum has very important effects on numerous surface electrochemical processes, including the upd of metals [1-11] and the oxidation of small molecules such as methanol or CO [12,13].

With regards to upd processes, it has been reported that the adsorption of either copper or cadmium on platinized platinum enhanced the coadsorption of chloride or bisulphate [14-16]. In the case of bisulphate and employing radiotracer techniques, Wieckowski and coworkers [17-19] have reported on this enhanced anion adsorption induced by both Cd and Cu adatoms on Pt(111).

The effects of halides on the upd of metals on Pt(111) single crystal electrode surfaces has been the subject of numerous studies. Hubbard and co-workers [6-8] have shown by electrochemical/UHV studies that in the presence of a chemisorbed layer of iodine, the upd of copper on Pt(111) takes place in a series of well-defined, coverage dependent ad-layer structures with the copper ad-layer in contact with the platinum and iodine as the top-most layer. These results were confirmed by x-ray standing wave measurements [20] and most recently by STM [21].

Kolb and co-workers [3] reported that the presence of chloride had a dramatic effect on the upd of copper on Pt(111), giving rise to two very sharp voltammetric features. More recently [10], and using electrochemical/UHV techniques, they demonstrated that whereas the most positive voltammetric peak was due to copper deposition/stripping, the second (voltammetric feature at less positive potentials) was due to chloride adsorption/desorption. Similar results were obtained for bromide. In addition, they concluded that similar to the case of iodine, the halides (chloride, bromide) were the outermost ad-layer.

Yee and Abruña [22,23] recently reported on in-situ surface EXAFS studies of copper upd on Pt(111) in the presence and absence of chloride and, again, found that the chloride is the top-most layer.

White and Abruña [9] reported on a comprehensive study of copper upd on Pt(111) in the presence of halides and pseudo-halides and their findings were consistent with partial charge transfer.

Recently, Markovic and Ross [11] performed voltammetric studies of Pt(111) and Pt(100) electrodes in the presence of low concentrations of copper in hydrofluoric, perchloric and sulfuric acid electrolytes. They observed a redistribution of charge in the hydrogen potential region and attributed this redistribution to a complex interaction between adsorbed hydrogen, upd copper and adsorbed anions (in this case bisulphate anions). They also suggested that the deposition of small amounts of copper enhanced the adsorption of chloride present in solution as an impurity. This was confirmed by ex-situ Auger measurements.

From the experimental conditions employed in all these investigations, it can be deduced that the anion adsorption monitored was taking place on the electrosorbed adlayer and not on the platinum surface.

The electrosorption of various anions on bare platinum single crystal surfaces has been studied recently [24,25] and it has been shown that in some cases, including bromide and chloride [25], this adsorption involves charge transfer and is thus reflected in voltammetric features. Thus, one can take advantage of this fact in order to follow the adsorption of these species by voltammetric means.

In this paper, we present our results on the enhanced adsorption of chloride and bromide on platinum induced by the presence of submonolayer amounts of copper adatoms. The observed behavior, which we report on, is distinct from that previously described in that the halide adsorbs directly on the platinum surface and its coverage is strongly coupled to the surface coverage of electrodeposited copper.

Experimental

Apparatus and cells have been described elsewhere [26]. All potentials were measured against a Ag/AgCl (sat. NaCl) reference electrode. A coiled platinum wire was used as a counter electrode. All experiments were made at room temperature.

The platinum single crystal electrodes used in these experiments were prepared following Clavilier's technique described in reference 27. Before each experiment, the single crystal electrode was subjected to a high temperature treatment [28] and then quenched in ultrapure water. In the case of Pt(100), the electrode was cooled in a mixture of hydrogen and nitrogen [29].

Solutions were prepared using ultrapure water (18 MOhms Millipore Milli-Q water). Aqueous acid solutions were prepared from high-purity (ULTREX) sulfuric acid. Copper ion solutions were prepared by dissolution of $CuSO_4.5H_2O$ (Aldrich Gold Label 5N5) in sulfuric acid solutions. Chloride and bromide containing solutions were prepared by dissolution of NaCl and NaBr (Aldrich Gold Label) in 0.1M H_2SO_4 solution.

Prior to introduction into the electrochemical cell, the solutions were degassed for at least 20 min with prepurified nitrogen gas which was passed through hydrocarbon and oxygen traps (MG industries).

Results And Discussion

1. Voltammetric characteristics of Pt(111) in acidic solutions containing chloride and bromide.

As a point of reference, the voltammetry of Pt(111) electrodes in the presence of the anions under study is presented. Fig 1 shows the voltammetric profiles of Pt(111) in 0.1 M H_2SO_4 in the absence (—) and presence (----) of 1×10^{-3} M NaCl. Comparing both profiles, one can observe that the main effect of the presence of chloride is the suppression of the so-called unusual adsorption states. Recently, it has been found that these states correspond to the adsorption of bisulphate (sulfate) [25]. Nevertheless, it is noteworthy

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that the presence of chloride does not induce the appearance of new well-defined adsorption features in the voltammetric response. This could be related to the fact that when adsorbed, chloride does not form an ordered overlayer [19]. The total coulometric charge in 1×10^{-3} M chloride amounts to 255 $\mu C/cm^2$ and, of these, about 95 $\mu C/cm^2$ would correspond to the adsorption of chloride on platinum with charge transfer [25].

Fig. 2 shows the voltammetric profiles of Pt(111) in 0.1 M H_2SO_4 in the presence (-----) and absence (—) of 1×10^{-3} M NaBr. As in the case of chloride, it is worth noting the strong modification of the unusual adsorption states and, therefore, the preclusion of the adsorption of sulphate/bisulphate. However, contrary to the case of chloride, in this case a couple of very sharp, although small, features appear at +0.02 V. The sharpness of these features probably indicates that when adsorbed, bromide forms an ordered overlayer on Pt(111), as observed previously, by Hubbard and co-workers [30]. As expected, because of its stronger adsorption, the presence of bromide causes a shift of the entire voltammetric profile towards more negative potentials (with a peak at about -0.07 V) in relation to the case of chloride. The whole coulometric charge after correction for the apparent double layer amounts to 270 $\mu C/cm^2$ and, of these, about 110 $\mu C/cm^2$ would correspond to the adsorption of bromide as bromine [25]:

$$Pt + Br^- \rightleftarrows Pt\text{-}Br + 1e^- \qquad (1)$$
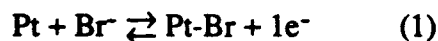
Although at first sight the charge densities would appear to be inconsistent with the adsorption of a monolayer of hydrogen, which on a Pt(111) surface amounts to 240$\mu C/cm^2$, they reflect the fact that halide adsorption is concomitant with and coupled to hydrogen desorption and vice-versa [25].

2.Voltammetric characteristics of Pt(111) in acidic solutions containing copper and either chloride or bromide ions.

Figures 3 and 4 present the voltammetric profiles corresponding to the deposition and stripping of one monolayer of copper at 1×10^{-3} M on Pt(111) in the presence of

chloride or bromide (1×10^{-3} M), respectively. As reported previously [3,9], the presence of strongly adsorbed anions induces the appearance of a new voltammetric peak. On a positive-going sweep, the peak potentials of these new processes are +0.33 V and +0.39 V for chloride and bromide, respectively. However in both instances, the main peak corresponding to the stripping of copper occurs at about +0.45 V, irrespective of the anion present in solution. As mentioned earlier, the peaks at less positive potentials are believed to be due to the adsorption of anions onto the copper adlayer and recent results from UHV investigations [10] as well as in-situ surface EXAFS [22,23], indicate that this is indeed the case.

Incidentally, in the case of chloride, two different behaviors can be distinguished for the upd peaks. The first peak in the positive going sweep is affected by the concentration of chloride, as expected from the aforementioned ascription, whereas the second peak, corresponding to the stripping of copper, is not. In the case of 1×10^{-4} M chloride the two peaks are not well separated. Nevertheless, it is striking that even for chloride concentrations as high as 0.1 M, a reversible behavior at 50 mV/s is not observed. However, much more reversible behavior is obtained at slow (e.g. 1 mV/s) sweep rates, as reported previously [9]. The reasons for the relatively fast sweep rate employed in this study (50 mV/s) are given below.

The coulometric charges, obtained by integration of the stripping peaks, amount to 470 $\mu C/cm^2$ in the case of chloride containing electrolytes and 570 $\mu C/cm^2$ in the case of bromide containing electrolytes. In the latter case, the value of charge density obtained is greater than that corresponding to the desorption of a full monolayer of copper (480 $\mu C/cm^2$), indicating that in order to evaluate coverages from charge measurements it is necessary to correct the net charge for the adsorption of anions on the bare platinum surface, as has been most recently emphasized by Kolb and co-workers [10]. That is to say, the voltammetric stripping peaks would correspond not only to the desorption of

copper but also to the coupled oxidative adsorption of anions (bromide) at the platinum surface sites that are being exposed upon stripping of the copper adlayer.

3.Experiments with low concentrations of copper ions

In order to investigate the effects of copper adatoms on the adsorption of anions on platinum, it is necessary to obtain submonolayer coverages of copper and to determine if there are variations in the voltammetric profiles, especially in the so-called hydrogen adsorption desorption potential region. Taking into account that copper is stable on the surface over a wide range of potentials, these experiments are feasible. Thus, we have performed studies with a low concentration of copper (10 μM) and several concentrations of both chloride and bromide (10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} M) in 0.10 M sulfuric acid solutions. In these studies the sweep rate was 50 mV/s. This relatively high value was employed so as to allow a significant time window during which the surface coverage of copper was below a monolayer.

Figure 5a shows the steady state cyclic voltammetric profile for a Pt(111) electrode in contact with a 1×10^{-2} M NaCl and 1×10^{-5} M Cu^{2+} solution in 0.1 M H$_2$SO$_4$ at a sweep rate of 50 mV/s. As can be ascertained, between -0.21 and +0.36 V, the adsorption/desorption of hydrogen and anions takes place in almost the same manner as in a copper-free electrolyte solution. The most characteristic peaks appear at 0.00 V along with a set of small peaks at +0.32 V, associated with the adsorption of chloride. At more positive potentials (+0.41 V) in the positive-going sweep, a peak corresponding to the stripping of the electrodeposited copper can be observed.

Figure 5b shows the effect of lowering the positive limit to +0.30 V. Under these conditions, copper is deposited (at a transport controlled rate) and accumulated on the surface over the entire potential range (+0.30 to -0.20 V) so its coverage progressively increases with time. Thus, we can monitor the effect of the fractional coverage of copper on the adsorption/desorption of hydrogen and anions. As can be seen in fig. 5b, a couple of

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exceedingly sharp peaks develop around -0.05 V when copper is present on the surface. It should be noted (as is clear from the figure) that the potentials of these peaks do not vary with height. Concurrently, a progressive blocking of the normal adsorption states can be observed. The maximum of these new peaks is attained when the fraction of the platinum surface uncovered by copper is about 0.5, as evaluated from the voltammetric charge. Also evident in fig. 5b are extremely sharp isopotential points. Since for surface processes isopotential points are observed when there is a simple equilibrium of species (adsorbed species in the present context) at a constant total coverage [31], this then represents compelling evidence of enhanced Cl^- adsorption induced by the electrodeposited copper.

As more copper is electrodeposited on the surface, the sharp peaks begin to decrease in amplitude as do the adsorption states corresponding to the bare platinum (fig. 5c). Finally, when copper is deposited over the entire surface (i.e. at full monolayer coverage), only the capacitive current corresponding to the copper adlayer can be observed. It is also worth noting the development of an oxidative peak at +0.28 V whose cathodic counterpart is somewhat broad. This is identified as the first peak appearing during the positive going sweep of a upd experiment under conventional (i.e. 1 mM copper and chloride) experimental conditions as discussed earlier (Figure 3).

In order to determine if, in fact, the results in fig 5c arose as a result of a surface completely covered by copper, a stripping experiment was performed by opening the window up to + 0.60 V (fig. 5d). In this case, the two peaks, characteristic of the desorption of one monolayer of Cu on Pt(111) in chloride containing media, can be clearly observed. As anticipated, the net charge involved during stripping is equal to 470 $\mu C/cm^2$. In the subsequent negative going sweep some copper is redeposited. The partial recovery of the adsorption capability of the platinum surface is also evidenced in figure 5d (curve 3) showing, anew, the very sharp adsorption/desorption peaks at -0.05 V.

The development of such a couple of reversible peaks could be due to the adsorption/desorption processes of any of the several species present in solution: Cl^-,

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H_3O^+, HSO_4^-/SO_4^{2-}, or Cu^{2+}. In order to rule out the possibility that neither H_3O^+ nor HSO_4^-/SO_4^{2-} are responsible for these peaks, an additional experiment, in the absence of chloride was performed. A steady state voltammetric profile for the Pt(111) electrode in 1×10^{-5} M Cu^{2+} + 0.1 M H_2SO_4 was obtained (figure 6, curve a). The so-called usual and unusual adsorption states as well as the peak corresponding to the desorption of the small quantity of copper accumulated on the surface during one voltammetric cycle at 50 mV/s can be observed. After recording this curve, the potential was held at -0.20 V for 5 min in order to obtain a partial coverage of copper on the surface. The subsequent voltammetric cycle, up to +0.27 V, is shown as well as the desorption process of copper around +0.45 V (curve b). It is evident from these experiments that there are no sharp peaks around -0.05V as seen earlier. Thus we can discard sulfate, bisulfate or H_3O^+ as responsible for this process. However it should be mentioned that we observe the same charge redistribution reported earlier by Markovic and Ross [11] and Yeager and co-workers [32] which could be tentatively ascribed to the enhanced adsorption of bisulfate in the presence of copper adatoms.

It is unlikely that copper is responsible for these adsorption states because of the sharpness of the peaks and their remarkable reversibility. Thus, these voltammetric characteristics cannot be fulfilled by a species which is not irreversibly adsorbed and whose bulk concentration is only 1×10^{-5} M. Thus, these experiments point to chloride, as anticipated, as being responsible for the observed response.

These observations imply that the presence of copper on the platinum surface has a strong influence and, in part, induces the coadsorption of chloride. Moreover, when copper adatoms are present, the adsorption of chloride occurs at a very well defined energy whereas in the absence of copper this adsorption is rather featureless, spreading over a wide range of potentials (fig.1). This would suggest the formation of a highly ordered halide or copper/halide adlayer at sub-monolayer copper coverages.

A question that needs to be addressed is the location, on the surface, of this unusually adsorbed chloride. In principle, the chloride anion could be located on the copper adlayer, or on the platinum surface at sites where copper is not deposited. In the latter case the sites could be near to or distant from the deposited copper. The first possibility; that is that the chloride anions are found on top of the copper ad-layer, can be ruled out because of the absence of the sharp peaks when the surface is completely covered by electrodeposited copper. It is also unlikely that these peaks are due to the adsorption of the anion on Pt(111) sites far away from the copper adatoms if we bear in mind that these peaks do not appear when the halide is present but copper is absent from the solution. Thus we conclude that these chloride anions are likely to be adsorbed on platinum sites in the vicinity of copper adatoms. The adsorbed chloride could be either in the periphery of the copper islands or there could be the formation of a mixed Cu-Cl adlayer as has been suggested by Markovic and Ross [11]. However, based on the present data we cannot unambiguously differentiate between these two models.

The fact that copper adatoms enhance the adsorption of chloride could be explained on the basis of electrostatic interactions. It has been shown that copper electrodeposited on the surface of platinum is partially charged [9,22,23,33-35]. Thus, the co-adsorption of chloride would give rise to charge compensation. Variations of the local work function could also be invoked. A lowering of the local work function at platinum sites neighboring the copper adatoms could induce an enhanced anion adsorption in the vicinity of copper adatoms as suggested by Markovic and Ross [11].

It is important to point out that the maximum development of the peaks associated with this enhanced anion adsorption is attained when the fraction of the surface free of copper is about 0.5. If the copper adlayer grows by forming 2-dimensional islands when increasing in coverage, one would expect the coalescence of these islands and a concomitant diminution of the number of boundary sites available thus leading to a decrease of these adsorption states. In addition, the stabilization energy of the anion on the surface

does not appear to depend on the coverage of copper adatoms as reflected by the invariance of the peak potential when the amplitude varies over a wide range.

It is also worthwhile pointing out the relation between this pair of reversible peaks and the anodic peak centered at +0.28 V. It appears that the development of this latter peak begins only after a threshold value of copper surface concentration is reached and coincides with the onset of the diminution of the sharp peaks associated with the enhanced adsorption of chloride. If the peak at +0.28 V corresponds to the adsorption of chloride on copper with an ordered adstructure [10,19], it is reasonable to suggest that a critical size of the copper islands is necessary for its development. This threshold size would be achieved by the coalescence of islands. If we assume the formation of a mixed adlattice, only when compact domains of copper are formed on the surface would the adsorption of chloride on copper (peak at +0.28 V) be possible.

From the stripping experiment shown in figure 5d two important points should be emphasized. First, the stripping profile clearly indicates that under the present experimental conditions a partial second layer of copper is not formed prior to the completion of the first. Secondly, after the stripping of the full monolayer of copper, the subsequent negative-going sweep shows a partial redeposition of copper and, anew, the presence of the sharp peaks at -0.05 V. This would imply that the halide adstructure corresponding to a submonolayer coverage of copper is the same irrespective of the way of creating the adlayer and/or the driving force of deposition. Similar behavior was found at other chloride concentrations. These data are presented in Table I and some salient features are discussed below.

Fig. 7 shows voltammetric profiles for submonolayer coverages of copper on Pt(111) at different concentrations of chloride from 1×10^{-4} to 1×10^{-1} M. It is clearly evident that, as expected, the peaks corresponding to the enhanced adsorption of chloride grow larger and sharper when the bulk concentration of the anion increases. In addition, the peaks shift towards more negative potentials as the bulk concentration of the anion

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increases. This fact confirms the assignment of chloride as the species linked to these adsorption/desorption peaks. Moreover, the observed potential shift is 59 mV per decade change in concentration as would be expected for the adsorption of an anion with an electrosorption valency of one. An exact determination of the electrosorption valency [36] is difficult since at the higher chloride concentrations, it is quite difficult to precisely subtract the background charge because of the coupled adsorption/desorption of hydrogen. However, it must also be pointed out that an electrosorption valency of one has been recently reported for the adsorption of chloride on platinum in the absence of copper adatoms [25]. On the basis of the data presented, and the above mentioned studies, we tentatively propose that the reaction associated with the sharp peaks is:

$$Cu-Pt + Cl^- \rightleftharpoons Cu-Pt-Cl + 1e^- \qquad (2)$$

Deviations of the expected shift are observed in the case of the 0.1 M NaCl solution. This is believed to de due to variations in the ionic strength in this case (supporting electrolyte was 0.1 M H_2SO_4) which would affect greatly the activity coefficients and therefore, the determination of the real electrosorption valency. Moreover, in this latter case, and as mentioned previously, the chloride adsorption process takes place at potentials where the desorption of hydrogen is taking place, with both processes probably being coupled.

The ΔE_p between the cathodic and anodic branches decreases with increasing concentration of the anion. This is because it is necessary to reach a minimum concentration of the anion in order to achieve the maximum degree of reversibility, taking into account that the sweep rate is relatively high (50 mV/s).

An analogous set of experiments was performed with bromide and similar results were obtained. Fig. 8a shows the steady state voltammetric profile corresponding to a Pt(111) electrode in contact with a 0.01 M NaBr solution in 0.1 M H_2SO_4 which additionally contains copper at a 10 μM concentration. The response is virtually identical to that obtained in the absence of copper. The main differences consist of the blocking of the

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small number of surface defects present in the well-ordered Pt(111) electrode and the appearance of a small peak at +0.38 V due to the desorption of the quantity of copper adatoms accumulated during one voltammetric cycle. We can identify the two most prominent voltammetric features for Pt(111) electrodes in bromide containing solutions; these being reversible spikes at -0.03 V, probably associated with a phase transition of the bromide adsorbed layer, and the main couple of peaks at -0.09 V associated with the desorption/adsorption of bromide coupled to the adsorption/desorption of hydrogen.

The same figure shows the effects of closing the potential window down to +0.30V which precludes the stripping of the electrodeposited copper layer. In this way, one can monitor the influence of the increasing amount of copper on the surface on the voltammetric profile, especially in the so-called hydrogen potential region. As in the case of chloride, a diminution of the charge involved in the normal adsorption states is found, that is, a progressive diminution of the height of the peaks at 0.03 V and -0.09 V. Concomitant with this is the appearance of new and exceedingly sharp peaks at -0.095 V in the positive going sweep and -0.12 V in the negative going sweep. As in the case of chloride, the maximum development of these peaks is attained when the fractional coverage of copper is about 0.5.

Further increments of the coverage of copper on the surface causes a diminution in the height of the induced sharp peaks and therefore a diminution in the amount of enhancedly adsorbed bromide (Fig. 8b). As in the case of chloride, sharp isopotential points are observed here, again consistent with the proposed mechanism. The virtually complete suppression of these adsorption states is reached when the entire surface is blocked by copper (fig. 8c).

Fig 8c also shows the stripping of the previously deposited monolayer of copper. Three overlapping peaks can be distinguished at +0.35, +0.425 and +0.45 V. The total amount of charge density involved in these peaks is equal to 420 $\mu C/cm^2$ (the surface is not fully covered by copper). As can be seen from a comparison with figure 4, the stripping peaks are essentially equal to those found with 1×10^{-3} M copper. During the subsequent

negative going scan, some copper is redeposited and the platinum surface is partially exposed showing, anew, the voltammetric characteristics of a Pt(111) electrode with a submonolayer amount of copper as well as the very sharp features associated with the anion adsorption/desorption reactions.

The same interpretation expounded in the case of chloride can be proposed for the case of bromide. The very sharp peaks are ascribed to the electrosorption of bromide on platinum in the vicinity of copper adatoms. The reasons for this enhanced adsorption could be ascribed to the partial positive charge supported by the copper adatoms and the lowering in the work function of platinum in the vicinity of copper. The reactions involved could be represented by:

$$Cu\text{-}Pt + Br^- \rightleftharpoons Cu\text{-}Pt\text{-}Br + 1e^- \qquad (3)$$
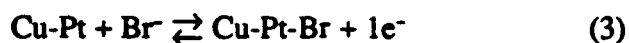
where Cu-Pt-Br is intended to imply that the bromide is in contact with the platinum surface and not below. From the stripping experiment, the same conclusions as in the case of chloride containing solutions are reached. In essence, a second copper layer is not formed prior to completion of the first monolayer irrespective of the potential range (as long as it is below bulk deposition) in which the deposition process is carried out. In addition, the structure of the submonolayer is also independent of the potential range of deposition.

However, there are some differences in the behavior of the two anions. First, it is worthwhile noting that in the presence of bromide, during the progressive blocking of the adsorption capability of bare platinum by copper, the spikes at -0.03 V are present. This probably means that there are relatively large domains of platinum free of copper. This assumption can be understood if we take into account that these spikes are not present in the voltammetric profile of Pt(s)[6(111)x(111)] which contains only small (111) terraces [32]. This result points to the formation of islands during the growth of the copper adlayer. Secondly, it is significant that in the case of bromide there is always a degree of irreversibility not present in the case of chloride.

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The behavior for the other concentrations of bromide studied parallels that presented above. Table II summarizes the peak potentials found for the sharp peaks and for the first peak appearing during the positive-going scan leading to the stripping of the copper monolayer. From the table, it can be seen that there is a shift towards more negative potentials upon increasing the bulk concentration of bromide as would be expected for the adsorption of an anionic species. The electrosorption valency could not be calculated because the desorption/adsorption process of the anion is strongly coupled with the adsorption/desorption process of hydrogen. In addition, there is always a degree of irreversibility which precludes the assignment of a specific value of coverage to each potential as can be seen in Fig. 9. It is also interesting to point out that the peaks are better developed and more reversible when increasing the bulk concentration of the anion.

As in the case of chloride, only the first desorption peak depends on the concentration of bromide. This peak is shifted towards more negative potentials upon increasing the concentration of the anions. This is in accord with assigning it to the desorption of bromide from the copper adlayer. However, the reasons for the irreversible nature of this process are not, at present, clear.

4.Studies on Pt(100) in the presence of halides at low concentration of copper.

In order to elucidate the possible structure sensitivity of these adsorption/desorption processes, experiments were performed with Pt(100) in the presence of either chloride or bromide at a low concentration of copper ions. These experiments revealed that the above mentioned adsorption processes depend on the structure of the substrate, since no further stabilization of the adsorption of chloride nor bromide was found for this orientation.

As an example, a typical experiment in the case of 10^{-3} M bromide and 10^{-5} M Cu^{2+} is shown in fig. 10. Fig. 10a shows the initial voltammetric profile which is characterized by a pair of reversible and sharp peaks at -0.07 V. This steady state voltammogram also presents a small irreversible peak in the positive going sweep. As in

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the case of the Pt(111), this peak is due to the desorption of the small quantity of copper accumulated during one cycle.

If the positive potential limit is fixed at +0.30 V, the electrodeposited copper is stable on the surface and one can monitor its effects on the reversible peaks characteristic of the blank voltammogram. As can be seen, only a monotonic decrease in the adsorption states of bare Pt(100) can be observed. It is also worth noting that there is no variation in the peak potential. This can be tentatively ascribed to the growth of the copper layer in the form of islands.

As in the case of Pt(111), the surface eventually becomes completely covered by copper adatoms and only capacitive currents exist in the so-called hydrogen potential range. Fig. 10b presents the voltammogram corresponding to the stripping of the monolayer of copper. Only one stripping peak at +0.535 V can be distinguished. It is worthwhile pointing out that the potential at which the stripping process takes place depends on the amount of copper on the surface. The higher the surface coverage of copper, the more positive the stripping potential. This implies that the copper adlayer is more stable at high coverage perhaps due to attractive interactions. The net voltammetric charge under this peak amounts to 350 $\mu C/cm^2$. The net charge obtained for the stripping of copper on Pt(100) in contact with a solution containing 1×10^{-3} M Cu^{2+} is 410 $\mu C/cm^2$. During the subsequent negative going scan some copper is redeposited and thus only a partial recovery of the bare platinum surface is attained as would be expected.

One can speculate on the reason(s) for the absence of enhanced halide adsorption on the Pt (100) surface when compared to Pt (111). For fcc metals, it is known that anions are generally more strongly adsorbed on (100) than on (111) faces [37]. Therefore, on the Pt (100) surface it would be very difficult to stabilize the halide adlayer further. However, such would not be the case for a Pt (111) surface. Thus, while there is clearly an enhanced adsorption of the halides on Pt(111), no such effect is seen on the Pt(100) surface. In

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addition, geometrical factors in the boundaries of the copper islands on Pt(111) could favor the interaction between copper adatoms and adjacent adsorbed anions.

We are continuing our investigations of enhanced adsorption of anions induced by electrodeposited monolayers and results of these investigations will be reported elsewhere.

Conclusions

We have demonstrated that partial monolayers of electrodeposited copper on Pt(111) give rise to an enhanced adsorption of chloride and bromide anions. The enhanced adsorption is reflected as a couple of exceedingly sharp peaks. Whereas the potential at which these peaks appear does not depend on the amount of copper on the surface, the height of the peaks is a strong function of the amount of copper deposited on the surface. The maximum development of the peaks is reached when the fraction of surface free of copper is about 0.5. In the case of chloride, this coincides with the onset of the development of the first upd peak in the positive going sweep. This enhanced adsorption/desorption process of chloride is reversible and we estimate its electrosorption valency to be one. In the case of bromide, the adsorption/desorption process exhibits some irreversibility.

The origin of this enhanced adsorption could be due to either the partial positive charge on the copper adatoms or to a decrease of the local work function of the platinum in the vicinity of copper.

We believe that the enhancedly adsorbed anions are directly bonded to the platinum atoms but only in the vicinity of copper islands. The presence of sharp isopotential points provides compelling evidence for the proposed mechanism.

Such enhanced adsorption was not observed in the case of the Pt(100) orientation indicating the structure sensitivity of these processes.

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Acknowledgments

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TABLE 1

Peak potentials for various processes at Pt(111) electrodes in contact with 0.1 M H_2SO_4 + 1×10^{-5} M Cu^{2+} and different concentrations of NaCl. E_p anodic: peak potential for the enhanced adsorption of chloride in the positive going sweep. E_p cathodic: peak potential for the enhanced adsorption of chloride in the negative going sweep. E_p stripping: peak potential of the first stripping peak of copper during the positive going sweep.

NaCl concentration (M)	E_p anodic (V)	E_p cathodic (V)	E_p stripping (V)
1×10^{-4}	0.090	0.045	0.340
1×10^{-3}	0.015	0.000	0.305
1×10^{-2}	-0.045	-0.055	0.280
1×10^{-1}	-0.080	-0.090	0.280

TABLE 2

As Table 1 for the case of NaBr.

NaBr concentration (M)	E_p anodic (V)	E_p cathodic (V)	E_p stripping (V)
1×10^{-4}	0.020	-0.050	-
1×10^{-3}	-0.055	-0.080	0.350
1×10^{-2}	-0.090	-0.115	0.350
1×10^{-1}	-0.105	-0.130	0.335

Figure Captions

Fig. 1. Voltammetric profiles for a Pt(111) electrode in 0.1 M H_2SO_4 in the absence (—) and presence (----) of 1×10^{-3} M NaCl. v = 50 mV/s.

Fig. 2. Voltammetric profiles for a Pt(111) electrode in 0.1 M H_2SO_4 in the absence (—) and presence (----) of 1×10^{-3} M NaBr. v = 50 mV/s.

Fig. 3. Voltammograms for UPD of copper on Pt(111) from 1 mM Cu^{2+} in 0.1 M H_2SO_4 in the absence (----) and presence (—) of 1×10^{-3} M NaCl. v = 50 mV/s.

Fig. 4. Voltammograms for UPD of copper on Pt(111) from 1 mM Cu^{2+} in 0.1 M H_2SO_4 in the absence (----) and presence (—) of 1×10^{-3} M NaBr. v = 50 mV/s.

Fig. 5. a. Steady state voltammetric profile for a Pt(111) electrode in contact with a 0.1 M H_2SO_4 solution containing 1×10^{-2} M NaCl and 1×10^{-5} M Cu^{2+} **b.**Successive voltammetric profiles after lowering the positive limit to +0.30 V. **c.**Subsequent voltammetric profiles after b. **d.: curve 1.** Blockage of the voltammetric features corresponding to the bare platinum. **curve 2.** Stripping of the copper monolayer previously electrodeposited. **curve 3.** Subsequent voltammetric profile showing a partial recovery of the adsorption states corresponding to bare platinum. v = 50 mV/s.

Fig. 6. curve a. Steady state voltammetric profile for a Pt(111) electrode in contact with 1×10^{-2} M NaCl and 1×10^{-5} M Cu^{2+} in 0.1 M H_2SO_4. (----) Voltammetric profile in the so-called hydrogen potential region after holding the potential at 0.20 V for 5 min. **curve b.** Subsequent stripping of the copper previously electrodeposited.

Fig. 7. Profiles showing the maximum development of the sharp peaks corresponding to the enhanced adsorption of chloride on Pt(111) in 0.1 M H_2SO_4 + $1x10^{-5}$ M Cu^{2+} and different concentrations of NaCl. (----) $1x10^{-1}$ M; (———) $1x10^{-2}$ M; (-•-•) $1x10^{-3}$ M; (••••) $1x10^{-4}$ M. v = 50 mV/s.

Fig. 8.a. Successive voltammetric profiles for Pt(111) in contact with $1x10^{-2}$ M NaBr and $1x10^{-5}$ M Cu^{2+} in 0.1 M H_2SO_4. b.Subsequent voltammetric profiles showing the progressive blocking of the surface. c.: **curve 1.** Blockage of the voltammetric features corresponding to the bare platinum. **curve 2.** Stripping of the copper previously electrodeposited. **curve 3.** Subsequent voltammetric profile showing a partial recovery of the adsorption states corresponding to bare platinum. v = 50 mV/s.

Fig. 9. As fig. 7 for the case of NaBr. (———) $1x10^{-1}$ M; (----) $1x10^{-2}$ M; (-•-•) $1x10^{-3}$ M; (••••) $1x10^{-4}$ M. v = 50 mV/s.

Fig. 10.a. Successive voltammetric profiles for Pt(100) in contact with $1x10^{-2}$ M NaBr and $1x10^{-5}$ M Cu^{2+} in 0.1 M H_2SO_4, showing the progressive inhibition of the adsorption processes corresponding to bare Pt(100). **b.:curve 1.**Blockage of the voltammetric features corresponding to the bare platinum. **curve 2.**Stripping of the copper previously electrodeposited. **curve 3.**Subsequent voltammetric profile showing a partial recovery of the adsorption states corresponding to bare platinum. v = 50 mV/s.
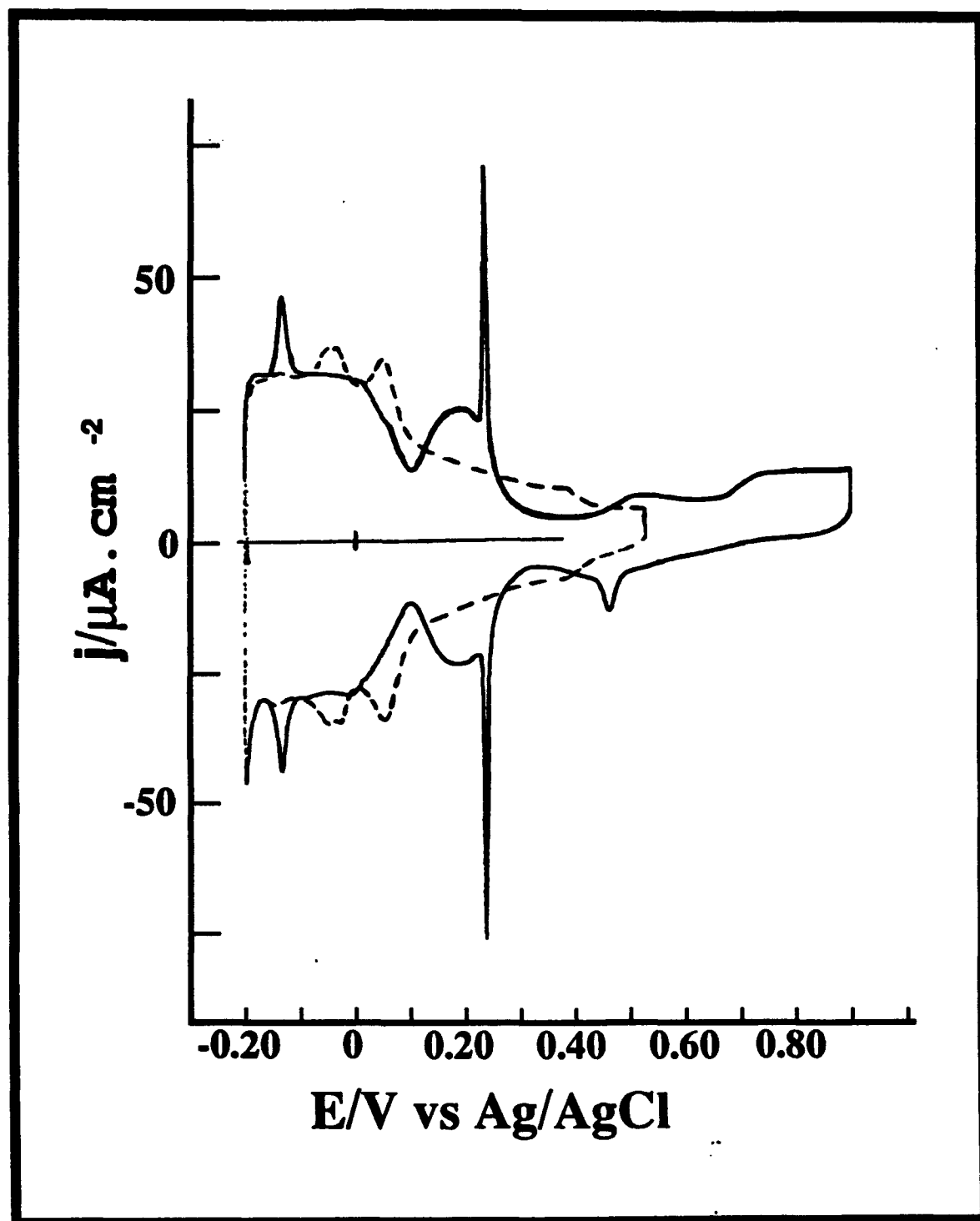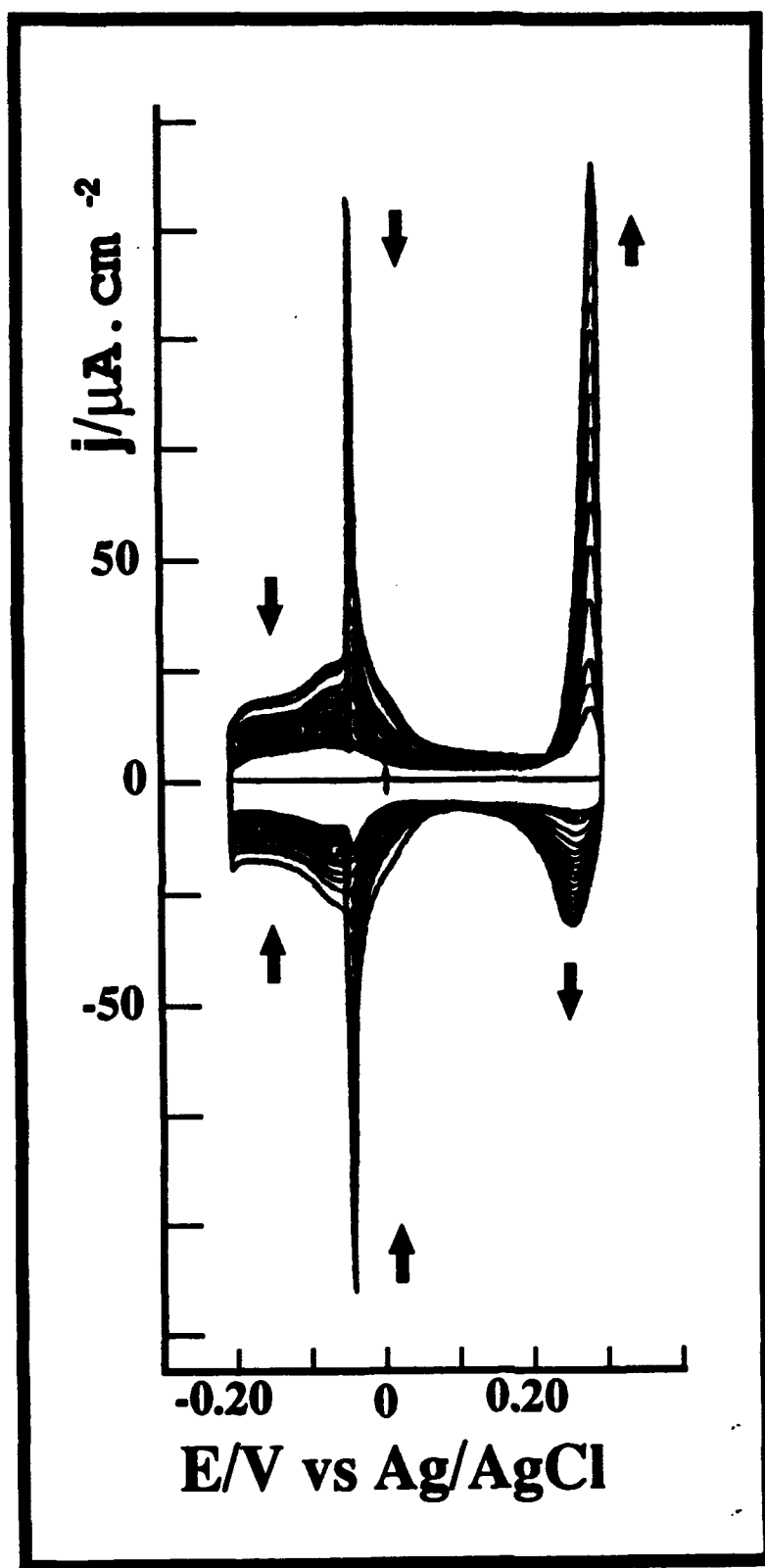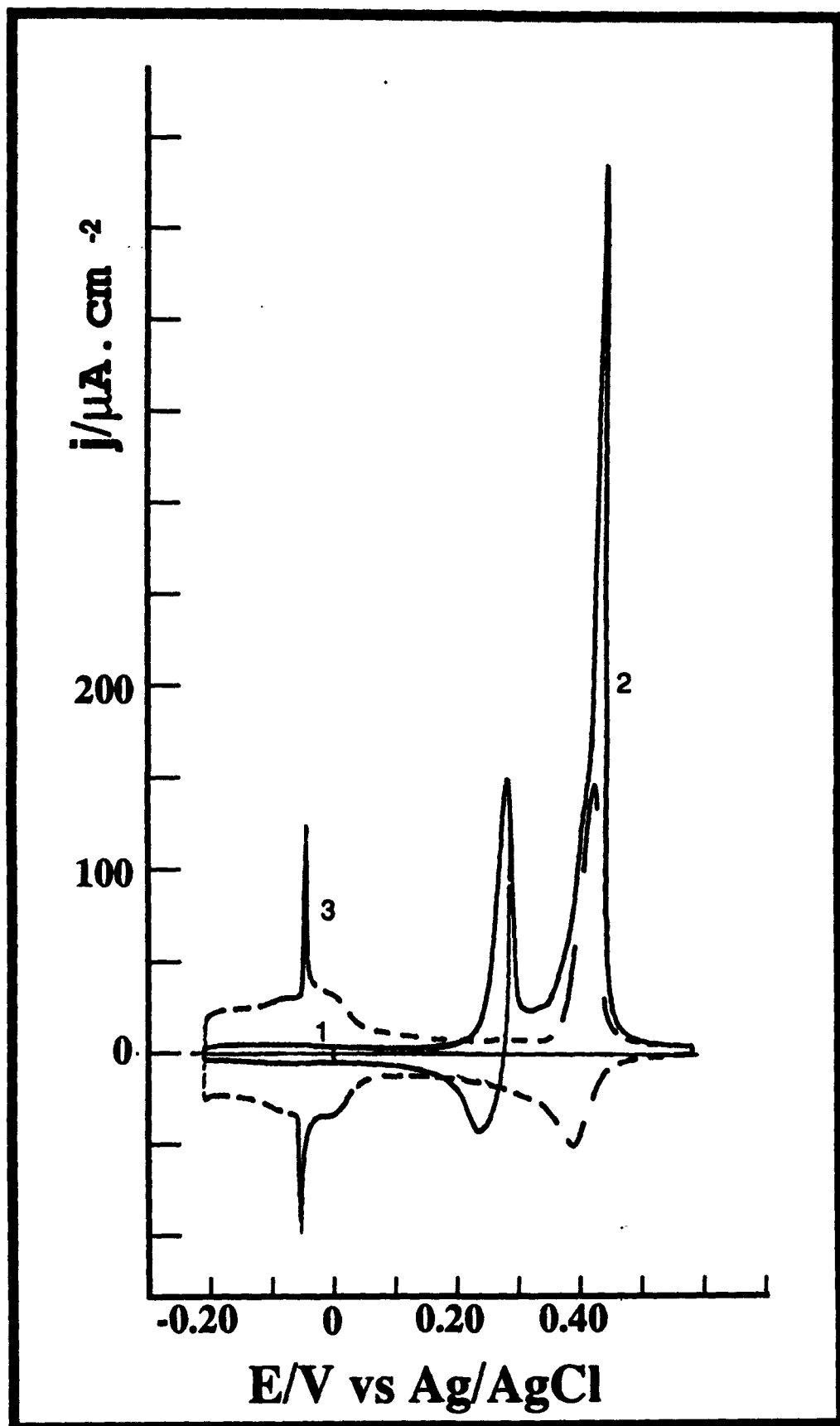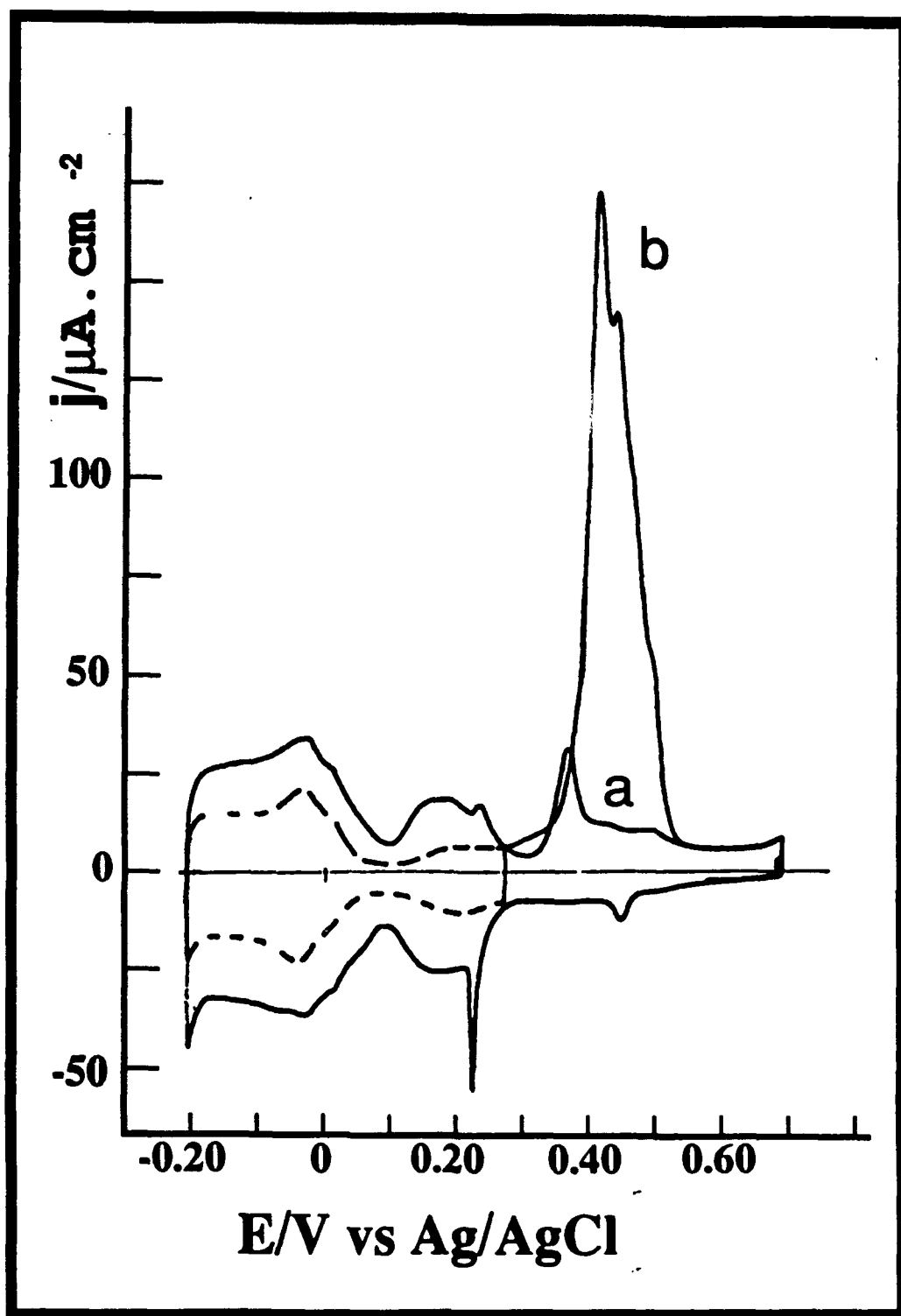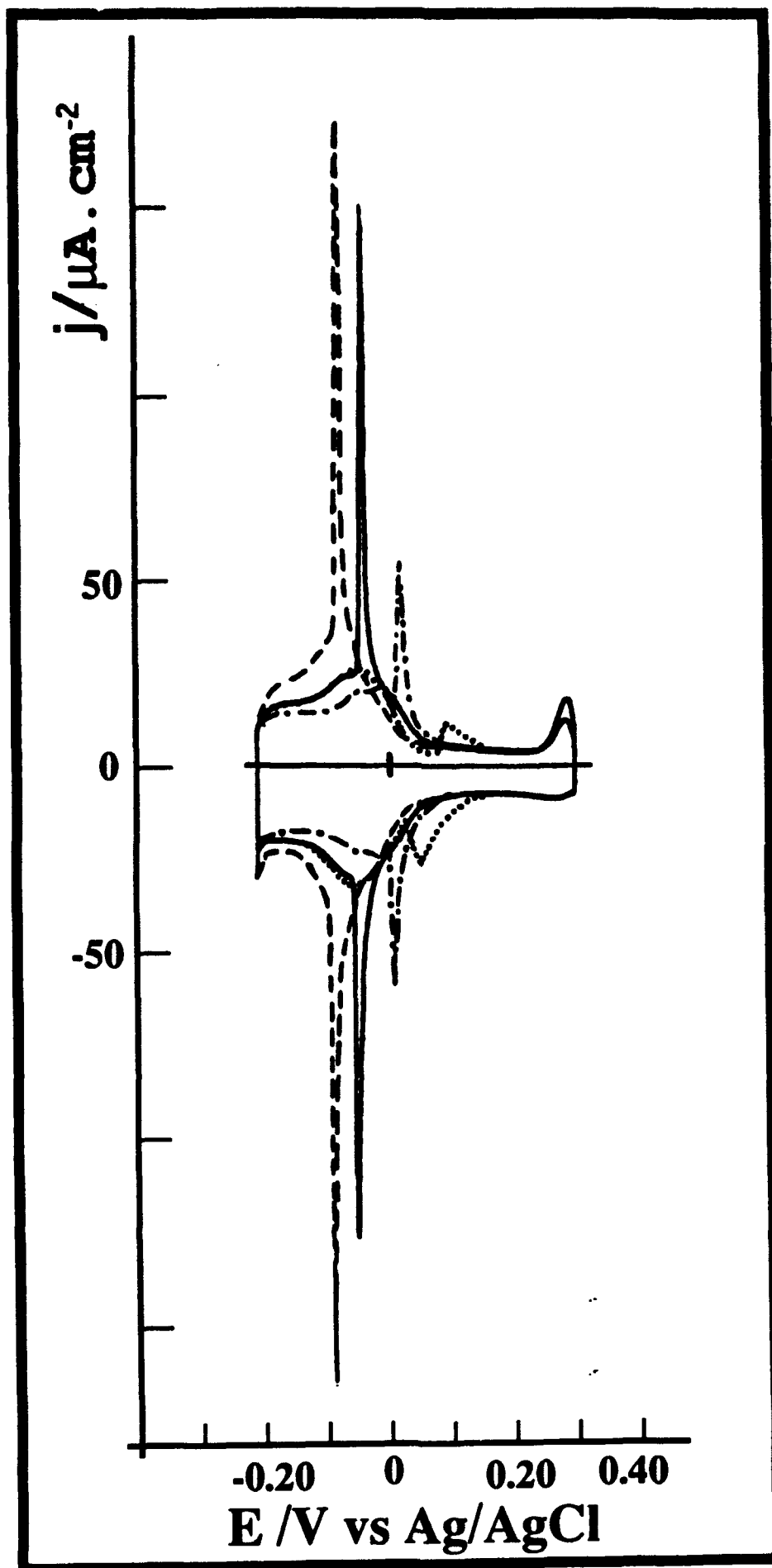
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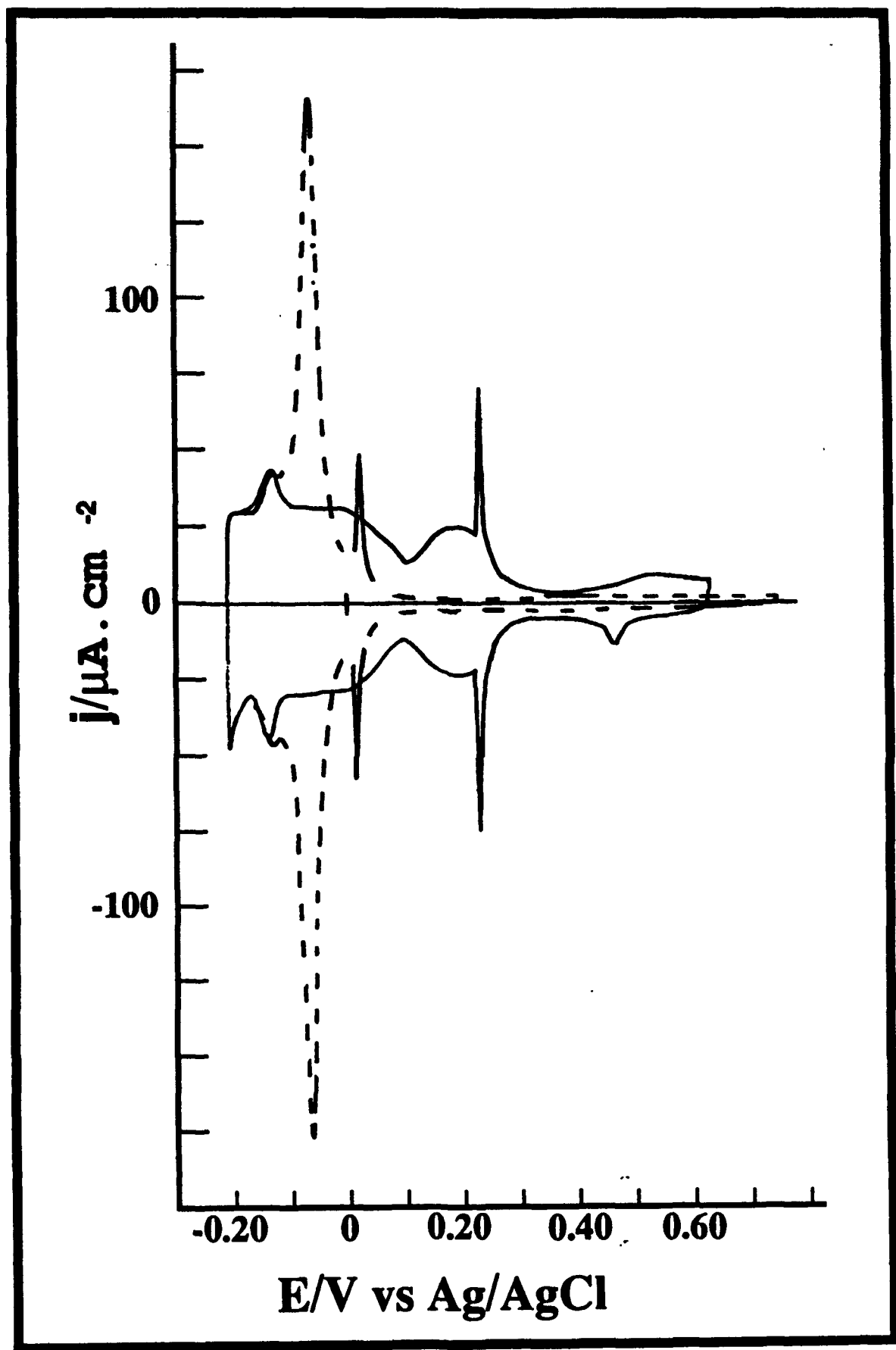
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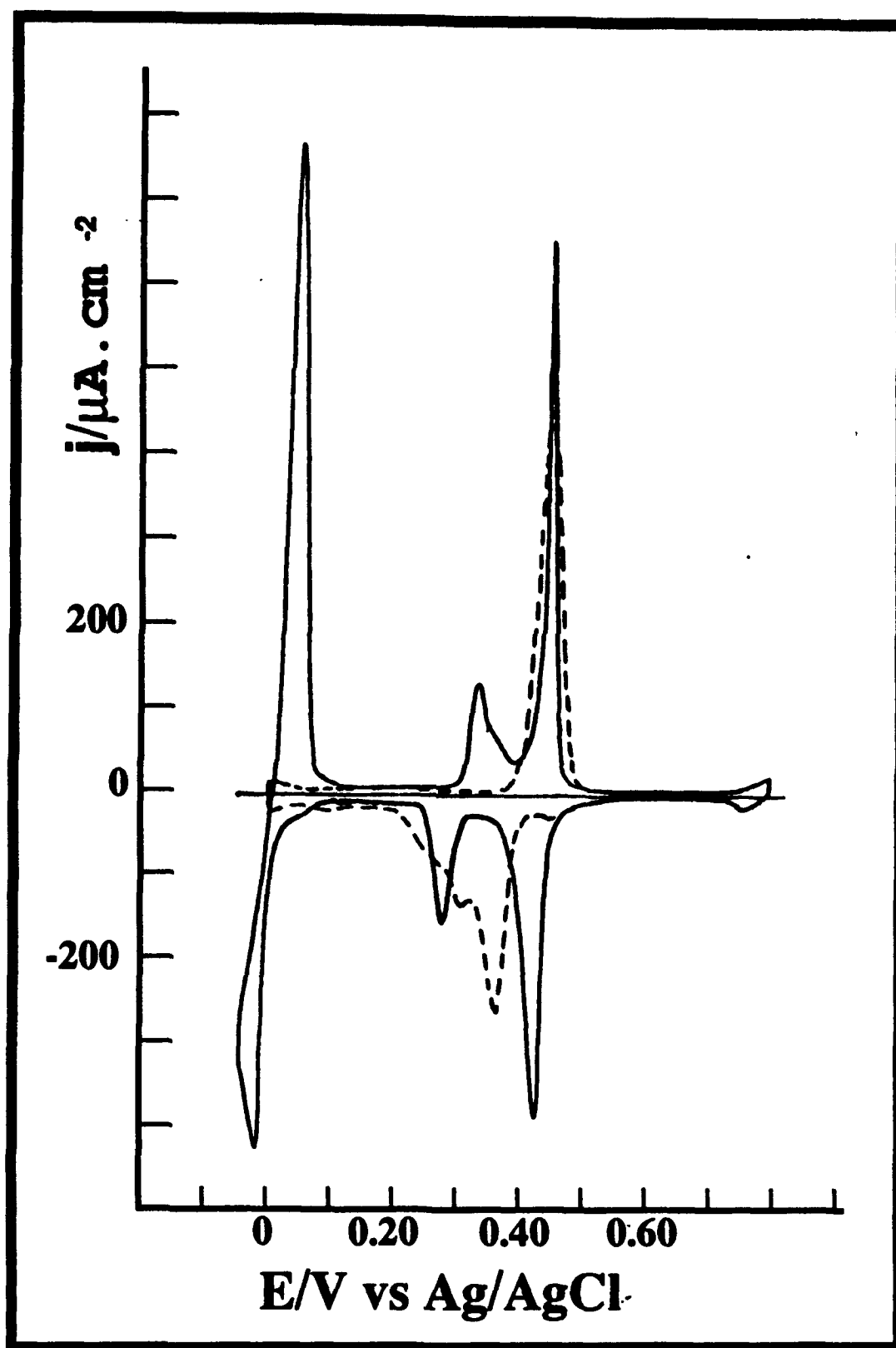
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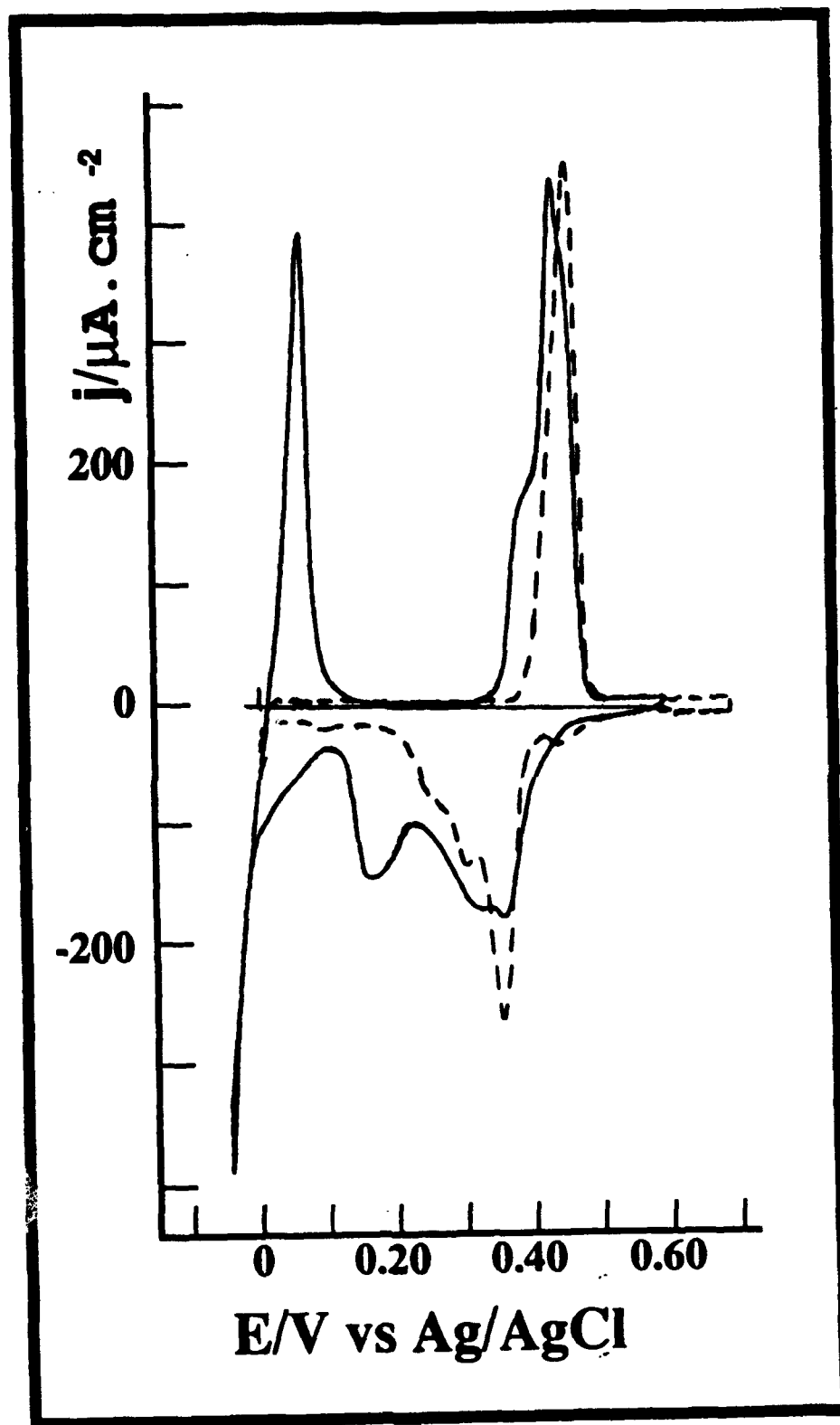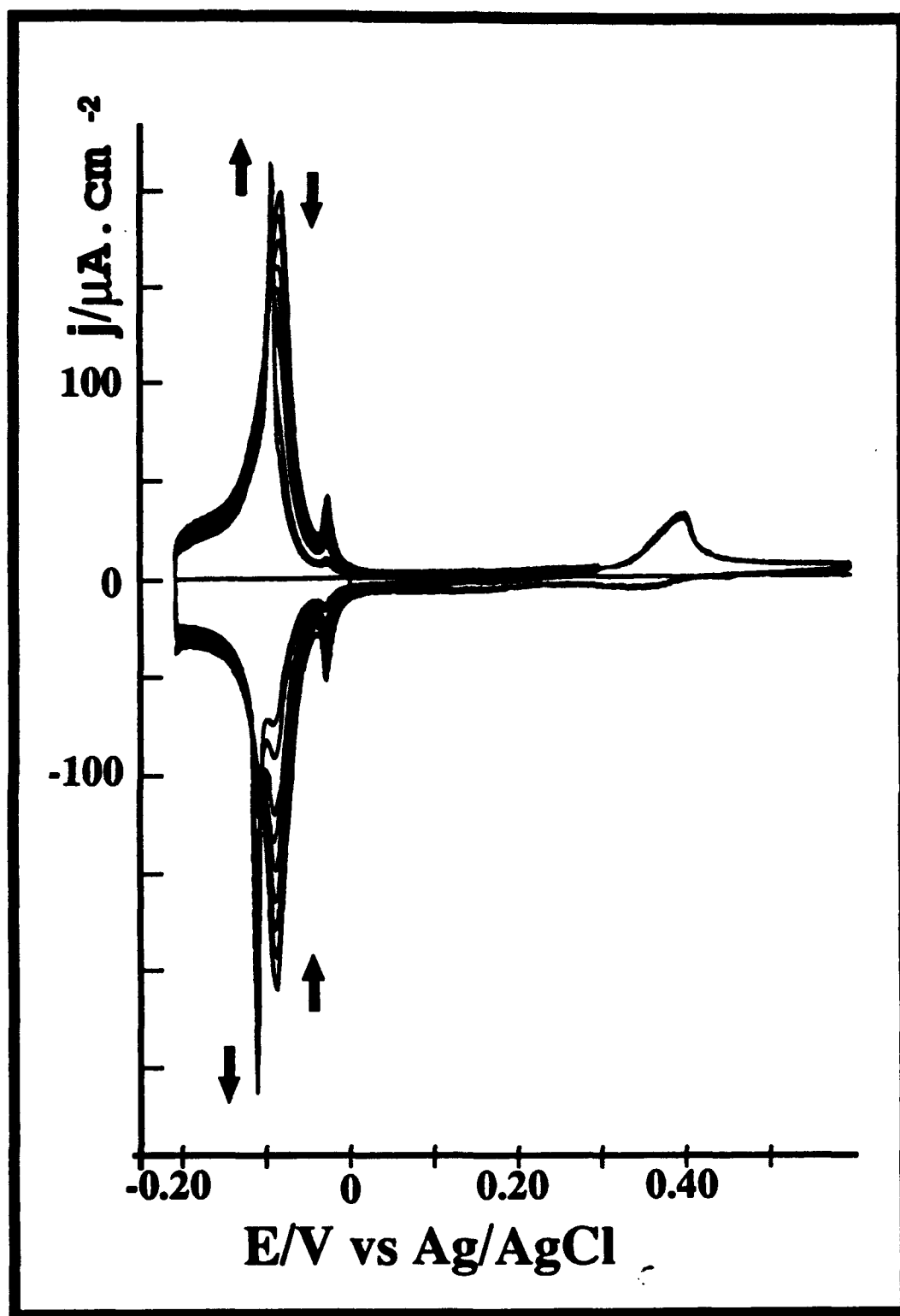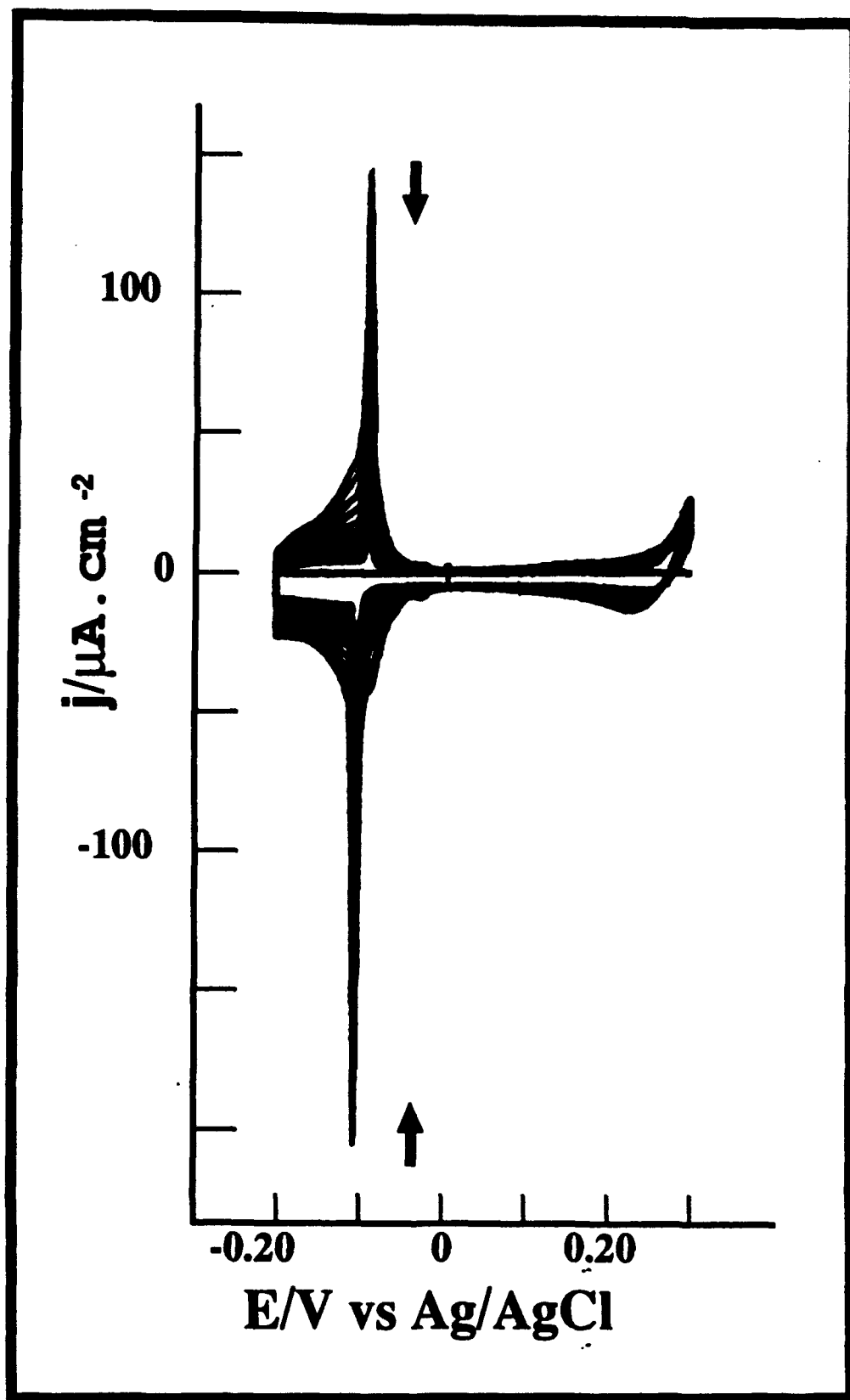
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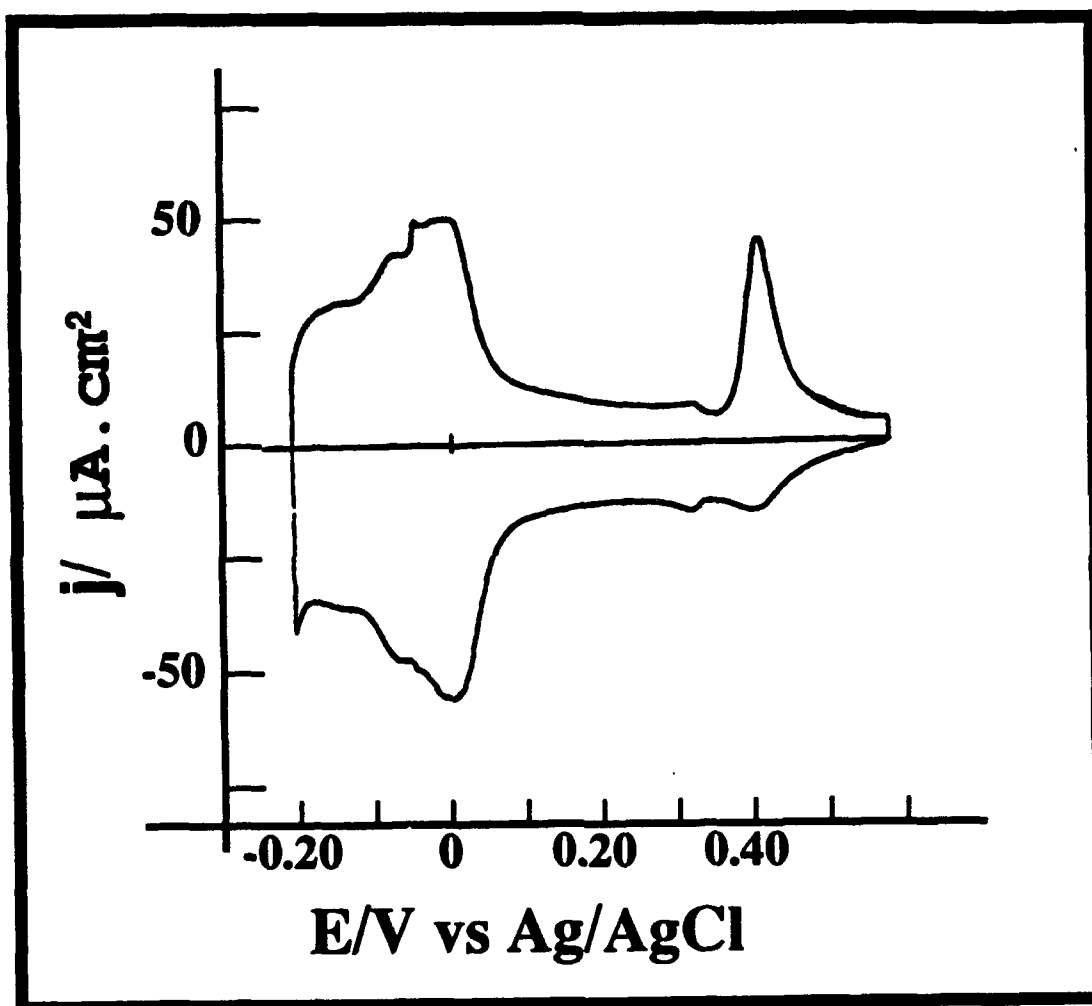
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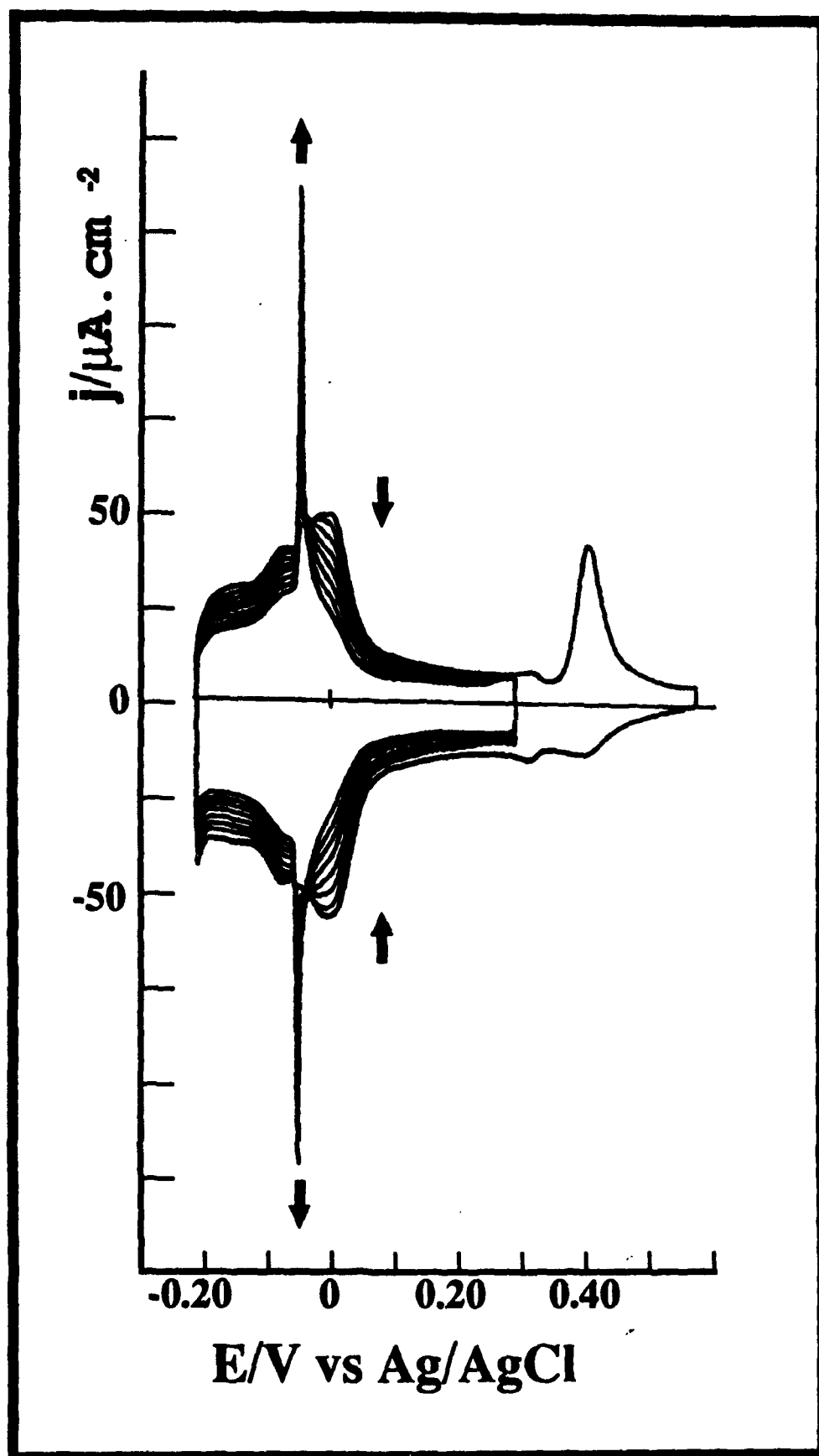
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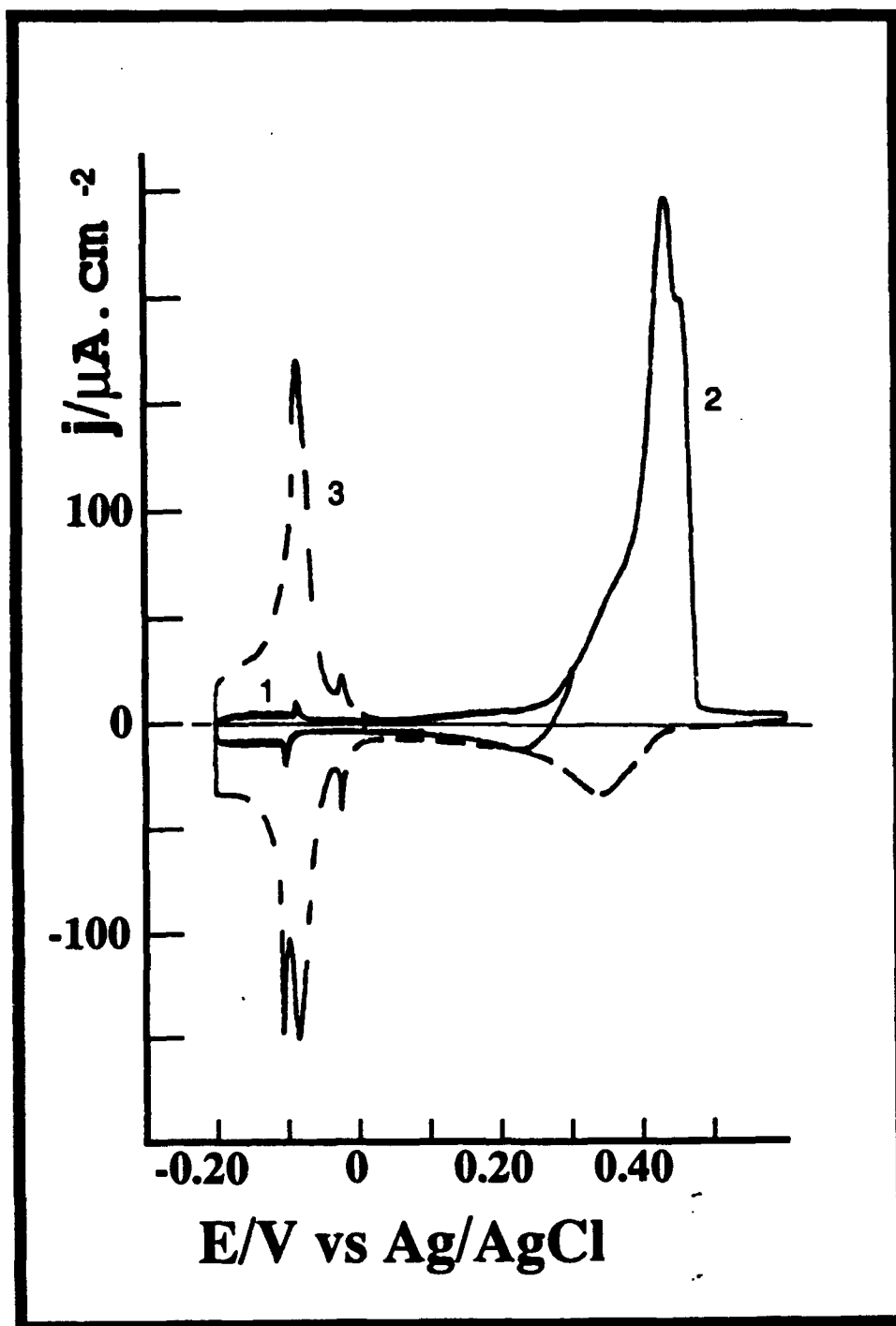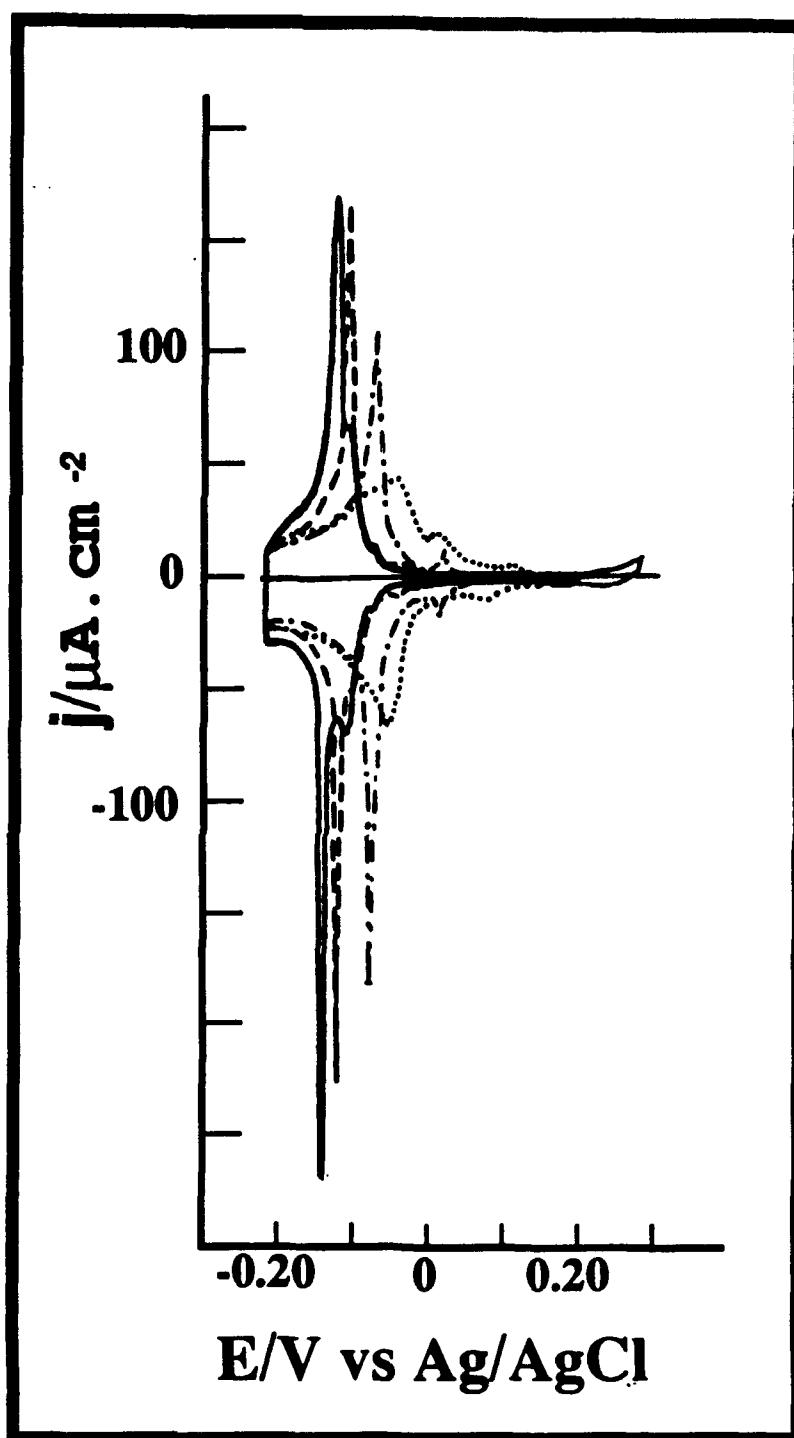
Figure 5c

Figure 5d

Figure 6

Figure 7

Figure 8a

Figure 8b

Figure 8c

Figure 9

Figure 10a

Figure 10b