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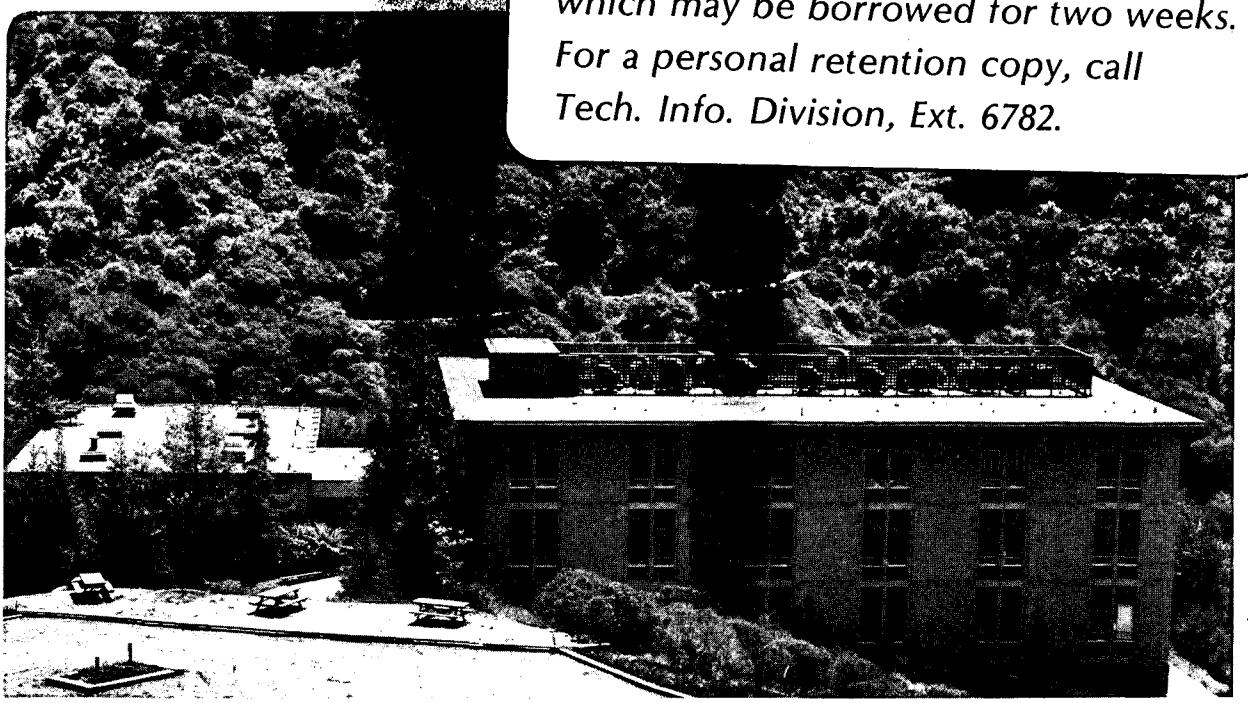

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THE UNDERPOTENTIAL DEPOSITION OF Cu ON Pt SINGLE CRYSTALS PREPARED IN AN ULTRA-HIGH VACUUM SYSTEM

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Recent studies of Pt single crystal electrodes prepared under ultra-high vacuum (UHV) conditions[1] have indicated that the cyclic voltammogram in acid posessed anomalous features which were not observed when the single crystal electrodes were prepared by conventional procedures[2] nor with any type of polycrystalline electrode. These anomalous features were first observed with electrodes prepared using an innovative technique[3] for surface preparation but the surfaces produced by this technique were not examined by Low Energy Electron Diffraction (LEED) or with Reflection High Energy Electron Diffraction (RHEED) and must be regarded as being of undetermined atomic structure.

The distinction of UHV-prepared single crystal electrodes is that they are atomically clean as determined by Auger Electron Spectroscopy (AES) and well-ordered as determined by LEED. A consequence of cleanliness on an atomic scale is that the need of extensive cycling of the Pt electrode into potentials anodic enough to oxidize any carbonaceous impurities that may exist on the electrode surface is eliminated. This is very important in

view of the fact that this procedure effects restructuring of the surface as results from this Laboratory[1] have indicated. The formation and reduction of the anodic film leads to a loss of long-range ordering which coincides with the gradual disappearance of the anomalous features in the voltammogram.

It is of considerable fundamental interest to determine whether electrode processes in general respond uniquely to long-range order on the surface. Because it is difficult to preclude the existence of impurities in experiments of this complexity[1], we decided to examine electrode processes that we expect to be relatively insensitive to traces of (unknown) impurities. The underpotential deposition (UPD) of Cu on Pt offers several advantages which are essential for a fundamental study of this nature. The existence of appreciable amounts of Cu(II) in the electrolyte appears to suppress chemisorption of other species onto the Pt surface, and Cu deposition and stripping occur before the onset of anodic layer formation and place exchange which breaks the long-range order of the surface[1]. As a result, any electrochemical process on a UHV-prepared Pt single crystal electrode at the potential interval 0 - 0.6 V vs. a Cu(II)[$a_{Cu(II)} = 10^{-3}$ M]/ Cu(0)[$a_{Cu(0)} = 1$] electrode can be reasonably attributed[4] to the UPD of Cu on a highly ordered substrate. It should be noted that in other studies of electrodeposition on UHV-prepared Pt single crystals[5] the electrodes were "protected" by an Iodine layer adsorbed from the gas phase prior to electrochemical experimentation. Since we believe that the presence of a third component such as Iodine in the Pt - Cu interaction may seriously limit the generality of our results in connection to the physical processes underlying the UPD, we took extraordinary precautions to prevent contamination and conducted

all experiments on clean Pt.

A detailed description of the experimental apparatus has appeared elsewhere[1,6]. Briefly, it consists of a UHV chamber (operating pressure 2.5 x 10^{-10} Torr) equipped with LEED, AES, and Mass Spectrometry facilities where the specimen can be cleaned by ion bombardment, O_2 - dosing, and annealing; the UHV chamber is coupled with a transfer chamber which can be evacuated to a pressure of 2 x 10^{-9} Torr and backfilled to atmospheric pressure with purified Ar. After satisfactory preparation in the UHV chamber, the single crystal is positioned in the transfer chamber where the electrochemical experimentation is carried out. In effect, the electrode is never exposed but to an atmosphere of purified Ar for a relatively short time. Evacuation of the transfer chamber and back-tranfer into the UHV allows post-electrochemical structural and chemical analysis of the surface. The electrochemical cell consists of an electrolyte drop sandwiched between the working Pt single crystal electrode and a PTFE-embedded Pd-disk Pt-ring arrangement accomodating the reference and counter electrodes, respectively[6].

In previous work with this apparatus[1,6] the electrolyte was a 0.3 M HF solution which allowed electrochemical charging of the Pd disk with H_2. In the present experiment, the same solution was used to which Cu(II) ions were added at a concentration of 7.8 x 10^{-4} M by anodic dissolution of a high purity Cu wire; the dissolution was effected by galvanodynamic pulses and mild stirring. The presence of Cu(II) in the electrolyte prohibited the electrochemical charging of the Pd disk with H_2. In experiments conducted outside the apparatus it was found that if Cu was deposited onto the Pd without the simultaneous evolution of H_2, the Pd could be converted to a Cu reference electrode in the same solution. The potential of the Cu(II)/Cu

reference electrode thus constructed was found to agree with the expected value by direct measurement against the SSCE*.

Preparation of the single crystal electrodes has been described elsewhere[1]. In brief, the crystals were first cut, mechanically-polished, and annealed at 1200°C in air in an outside furnace for 24 hrs. They were then mechanically polished again and etched in aqua-regia, the last step accompanied by boiling in ultra-pure H_2O. Before introduction in the UHV chamber they were Au brazed onto a Ta cap and holder. Auger spectra taken immediately after introduction into the UHV chamber indicated Carbon contamination. This was removed by Ar^+ sputtering followed by annealing and O_2-dosing typically at 650°C and $p_{O_2} = 8 \times 10^{-8}$ Torr. Once the Auger spectrum indicated the removal of Carbon, further annealing at 800°C was done with repeated LEED determinations until a stable LEED pattern for the face under consideration was obtained. Post-annealing Auger spectra were indicative of no chemical element other than Pt.

Experiments were conducted with the three low index planes of Pt, namely (100), (110), and (111). The LEED pattern obtained in UHV for the Pt(100) crystal indicated the existence of the "5 X 20" reconstruction; as reported elsewhere[1], the reconstructed surface reverts back to the 1 X 1 structure upon exposure to Ar at atmospheric pressure and contact with the

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* All potentials in this paper are referred against this Copper electrode taken to be Cu(II)[$a_{Cu(II)} = 7.8 \times 10^{-4}$ M]/Cu(0)[$a_{Cu(0)}$=1] except in Fig. 1b where $a_{Cu(II)} = 10^{-3}$ M. The symbol Cu(II)/Cu is used for it throughout with the implicit understanding that the activities of the species involved are the ones reported above. Since this electrode is ca. 240 mV positive against the SHE, the potential scales can be read against the SSCE without loss of accuracy.

electrolyte. On the contrary, the Pt(110) - 2 X 1 reconstruction appears to be stable after electrolyte emersion. It should be pointed out that the (110) - 2 X 1 surface is not atomically flat and consists of rows of (111) microfacets as confirmed by recent scanning tunneling microscopy results[7]. The LEED pattern obtained in UHV for the Pt(111) crystal corresponded to the ideal (111) - 1 X 1 structure.

Considerable effort was made to establish the exact shape of the voltammogram of Cu UPD on polycrystalline Pt. Special emphasis was paid to the structure of the cathodic portion and to the position of the cathodic peaks relative to the anodic peaks. We found that potential cycling of the electrode at 100 mV/s for 1 hr into the region of Pt oxidation and reduction followed by recording of the Cu UPD voltammogram at 10 mV/s resulted in patterns shown in Fig. 1. These were obtained in HF with a polycrystalline Pt wire and in H_2SO_4 with a stationary disk electrode. The two patterns are similar, indicating the existence of 3 peaks which appear at approximately the same potentials on both cathodic and anodic sides. It can be concluded that the processes that give rise to these peaks are reversible at this sweep rate. Experiments conducted in H_2SO_4 with a Pt wire which had been previously oxidized electrochemically for several hours and reduced resulted in the same pattern but with different relative peak heights and some further refinement appearing as "shoulders" on the principal peaks. Our preliminary conclusion was that the reaction was so sensitive to the details of the electrode surface structure that the quest for a unique voltammogram would presuppose the preparation of reproducible polycrystalline surfaces. However, in all cases the variable was the relative height of the peaks and not their position on the potential axis, nor their reversibility

at 10 mV/s. It should also be noted that in all cases the most anodic peak is at around 0.4 V, a value coinciding with the underpotential shift computed on the basis of the work function difference between Cu and Pt, according to the Kolb - Przasnyski - Gerischer (KPG) correlation[8], which we shall refer to as the "KPG peak".

The voltammograms obtained for the Cu UPD on the three Pt low index planes are shown in Fig. 2. It can be seen that their structures are simpler than the one obtained for the polycrystalline substrate and are characterized by the extreme sharpness and reversibility of the processes that give rise to the passage of current. In agreement with the KPG correlation, the UPD process begins at around 0.4 V. This is evidenced by a sharp symmetric peak in both (100) and (111) voltammograms* and on (110) by symmetric doublets centered at ca. 0.4 V. Due to the experimental arrangement an accurate determination of the electrode area wetted by the electrolyte is difficult. As a result, we report here only the deposition or stripping charge relative to the total charge on a complete sweep. In the case of Pt(111), the KPG peak contains one-half of the total charge; on (100) it contains ca. one-third the total charge; on (110) the doublet peaks at ca. 0.4 V contain ca. one-half of the total charge.

Probably the most striking feature of these voltammograms is that the KPG peak is followed by a second process of similar or grater sharpness. It is this process which exhibits a very strong sensitivity on the substrate structure, to the point that in the case of (100) it is separated

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* Experiments conducted in 0.3 M HF + 7.8 x 10^{-4} M Cu(II) + 10^{-3} M H_2SO_4 with the Pt(111) yielded identical results, indicating negligible anion effect.

from bulk deposition by only a few millivolts. Interpretation of this result at this point can only be speculative and there are several possibilities that can be put forward as tentative explanations. One possibility is that the KPG peak represents the formation of epitaxial Cu islands on the Pt surface and that the second process reflects the formation of a second layer on top of these islands. Another is the formation of an intermediate Cu superlattice (e.g. 2 X 2 or 3 X 3) of special stability which exhibits relative weak structure specificity followed by deposition into the empty superlattice which exhibits strong structure specificity due to lateral interactions between the deposited Cu atoms arising at the higher coverages. Still another is the selective action of an impurity which shows preferential electrochemical affinity towards Cu rather than Pt. Although the island formation hypothesis is favored by recent results on the deposition of Cu on Pt from the vapor phase[9], the present state of UPD theory as well as of the relations between electrochemical and gas phase adsorption and phase transitions do not allow the conclusive adoption or rejection of any of the above hypotheses, except probably the one involving impurities which was included here because it is always difficult to discount.

It is possible to interrupt the UPD process after the occurrence of one of its major stages and subsequently use the LEED facility to determine the structure of the Cu deposit. However, since the emphasis of the present stage of the work was to establish the basic electrochemistry of Cu UPD on Pt single crystal surfaces, we cannot present the LEED analysis of the Cu UPD states in this preliminary communication. We can, however, report LEED analysis of the Pt substrate surface restructuring effected through potential cycling into oxide formation and reduction and report to what

extent the Cu UPD process followed these changes.

Figure 3a shows anodic window opening for the Pt(111). It is to be noted that one of the anomalous peaks at around 0.65 V[1,3] is visible and is apparently unaffected by the presence of Cu(II) in the electrolyte. Figure 3b shows the voltammogram of Pt(111) after 10 cycles to 1.0 V. The oxide reduction is superimposed on the Cu UPD and the resulting shape reflects both processes. However, if after the 10 cycles the anodic reversal potential is brought back to 0.6 V, Cu UPD can be isolated and the effects of restructuring observed. Figure 3c reveals that the original Cu/Pt(111) voltammogram has changed significantly. The KPG peak still predominates but the second transition has lost its sharpness and a third process has appeared. Further cycling for 10 times to 1.1 V yields the Cu UPD pattern of Fig. 4c, which differs from the polycrystalline electrode only in the relative height of the peaks. Similar effects were observed for the originally (100) and (110) surfaces. On the (100) face, the KPG peak loses its sharpness, the second process of Fig. 2a merges indistinguishably with bulk deposition, and secondary processes appear at 0.1 - 0.3 V. The cycled single crystal electrodes were emersed under potentiostatic control at 0.6 V after anodic stripping of the Cu underpotential deposit. Post-electrochemical Auger analysis indicated the absence of Cu from the surface thereby establishing independently that potential as the anodic limit of the UPD process. LEED patterns of the Pt substrate after anodic cycling and Cu stripping were characterized by alternate spot broadening with incident beam energy as described in detail previously[1,6] for solutions not containing Cu ions. The real space structure corresponding to these LEED patterns is a correlated island - hole structure in which the island

(and hole) size and spacing vary as a function of the anodic potential limit.

There are two aspects to these structural modifications of the originally highly ordered Pt surface that appear to be directly related to the Cu UPD process: long-range low index order in the surface is broken; numerous (e.g. > 10^{14} per cm^2) atomic step and kink sites appear in the surface. The broadening of the single UPD peaks seems directly related to the loss of long-range order, and the new features cathodic to the KPG peak that develop upon anodic cycling seem directly related to Cu UPD at step and kink sites. The latter conclusion may appear to contradict the generally observed relation between adsorption energy and site coordination (step and/or kink sites ≡ high adsorption energy)[11], but this apparent contradiction should underscore the essential difference between the metal UPD process and molecular chemisorption. These results, even in their preliminary stage, suggest that electrode surfaces posessing long-range low-index order exhibit uniquely different behavior from less well-ordered surfaces.

In writing this note we have avoided comparing our results with the ones existing in the literature[10] for the Cu/Pt(hkl) system. We did so because we believe that these results are unique in that it is for the first time that a UPD reaction was studied on well-ordered and atomically clean single crystal Pt electrodes. We have made extensive efforts to reproduce the features of Fig. 2 with single crystal electrodes prepared outside the UHV chamber using conventional methods[2] but these efforts have failed. This points to the conclusion that UHV preparation and subsequent limited exposure of the electrode to an inert atmosphere is the only possible way we know to achieve the features of Fig. 2.

Acknowledgement

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References

1. F. T. Wagner and P. N. Ross, Jr., J. Electroanal. Chem., 150(1983)141.

2. Such as those described by J. L. Gland and G. A. Somorjai, Surface Sci., 38(1973)157, prior to transfering into ultra-high vacuum. In our experiments outside the UHV system, the crystals were annealed in Ar first at 650°C and then at 300°C for several hours. The purpose of the annealing step was to emulate annealing into the UHV chamber.

3. J. Clavilier, J. Electroanal. Chem., 107(1980)211.

4. M. W. Breiter, J. Electrochem. Soc., 114(1967)1125; G. W. Tindall and S. Bruckenstein, Anal. Chem., 40(1968)1951; 40(1968)1637; S. H. Cradle and S. Bruckenstein, Anal. Chem., 43(1971)932; 43(1971)1858.

5. J. L. Stickney, S. D. Rosasco, D. Song, M. P. Soriaga, and A. T. Hubbard, Extended Abstracts, 83-1(1983)1037, The Electrochemical Society, Pennington, New Jersey, and references therein.

6. P. N. Ross and F. T. Wagner, in Advances in Electrochemistry and Electrochemical Engineering, Vol. 13, H. Gerischer and C. W. Tobias, eds., to be published.

7. G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Surface Sci., 131(1983) L379.

8. D. M. Kolb, M. Przasnyski, and H. Gerischer, J. Electroanal. Chem., 54(1974)25.

9. R. C. Yeates and G. A. Somorjai, Surface Sci., 134(1983)729.

10. D. M. Kolb, R. Kotz, and K. Yamamoto, Surface Sci., 87(1979)20; C. L. Scortichini and C. N. Reilley, J. Electroanal. Chem., 139(1982)233; 139(1982)247; 139(1982)265; 152(1983)255.

11. G. A. Somorjai, Chemistry in Two Dimensions: Surfaces, Cornell University Press, Ithaca, 1981, pp. 176-282.

Figure Captions

Fig. 1. Cyclic voltammogram at 10 mV/s for Cu UPD on a) polycrystalline Pt wire in 0.3 M HF + 7.8 x 10^{-4} M Cu(II) and b) polycrystalline Pt stationary disk electrode in 0.5 M H_2SO_4 + 10^{-3} M Cu(II). The current density is accurately known for the disk electrode only and has been computed on the basis of its geometrical area; the roughness factor as determined from Hydrogen adsorption in the same electrolyte without Cu(II) is ca. 1.9. The charge consumed by Cu UPD at the end of the cathodic sweep is twice the charge for Hydrogen adsorption. The Cu(II)/Cu reference electrode is in the same solution (for details see text).

Fig. 2. Cyclic voltammograms at 10 mV/s for Cu UPD on UHV-prepared Pt single crystals in 0.3 M HF + 7.8 x 10^{-4} M Cu(II). Note the differences in the current scale indicating the sharpness in each transition displayed. The contact area is the same for each electrode (of the order of 0.3 cm^2) but is not accurately known and can vary by as much as 30%. Arrow in a) indicates the beginning of "bulk" deposition; if the sweep is extended in the cathodic direction by ca. 20 mV, the resulting diffusion-controlled bulk deposition peak is approximately equal to the UPD peak at this sweep rate.

Fig. 3. Cyclic voltammograms at 10 mV/s of the Pt(111) surface in 0.3 M HF + 7.8 x 10^{-4} M Cu(II) a) window opening in the anodic direction b) 10th sweep with an anodic reversal potential of 1.0 V c) Cu UPD after Pt(111) has been cycled to 1.0 V for 10 times.

Fig. 4. Cyclic voltammograms at 10 mV/s for Cu UPD in 0.3 M HF + 7.8 x 10^{-4} M Cu(II) on a) Pt(100) cycled to 1.35 V for 10 times b) Pt(110) cycled to 1.2 V for 10 times and c) Pt(111) cycled to 1.1 V for 10 times. Dotted line in a) is a magnified version of the solid line plot indicating the similarity of the cycled electrode to the polycrystalline.

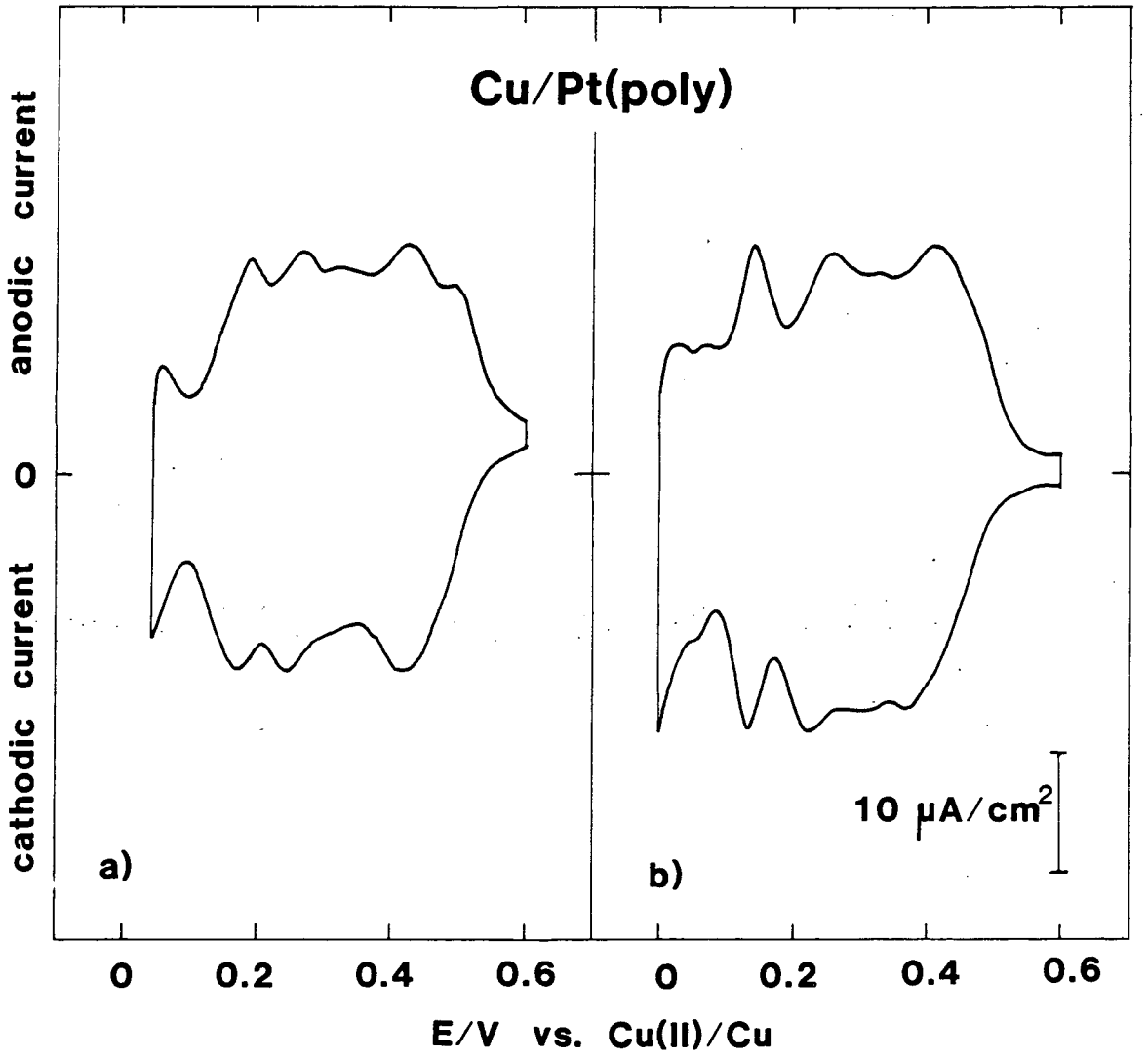

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Fig. 1.

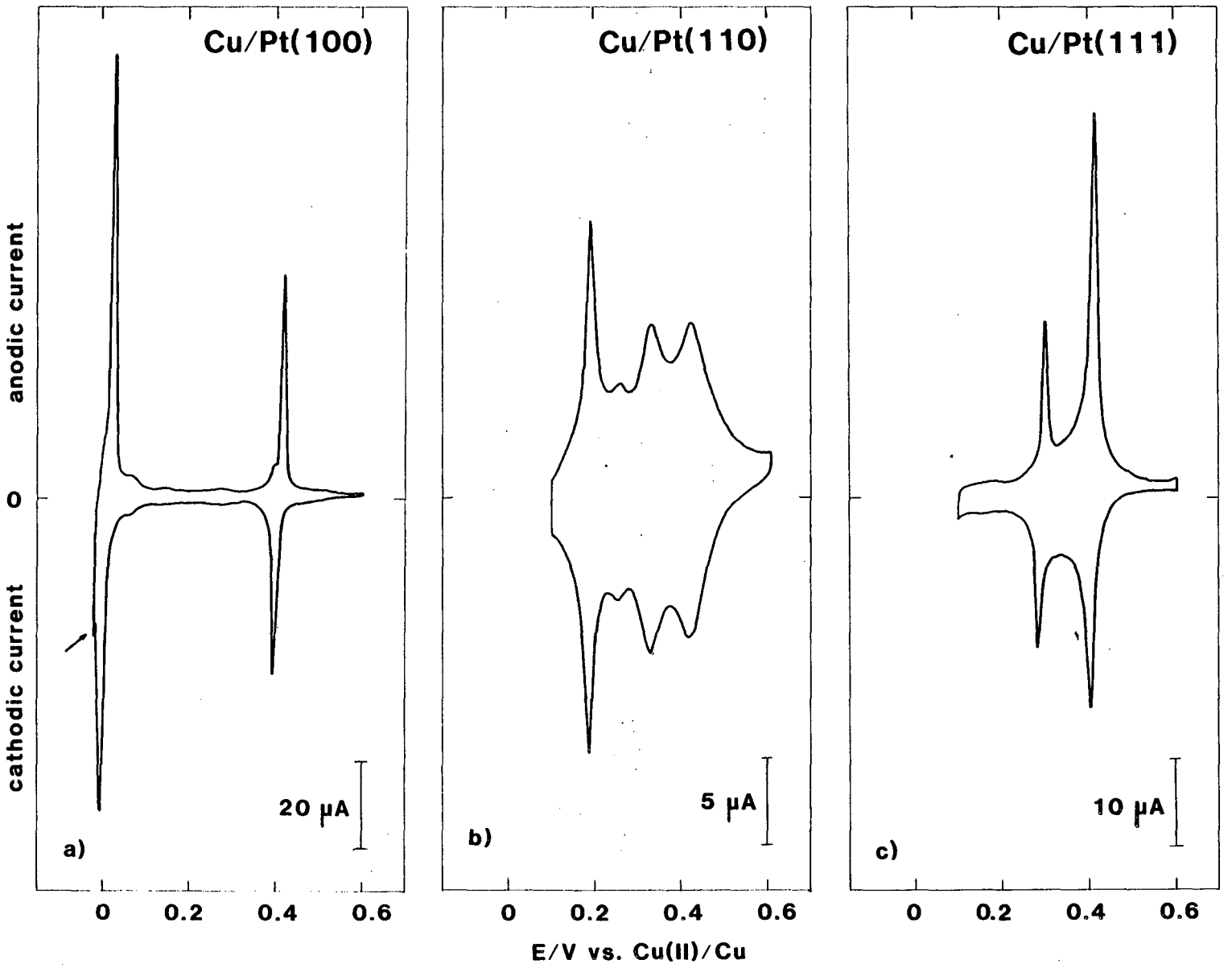

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Fig. 2.

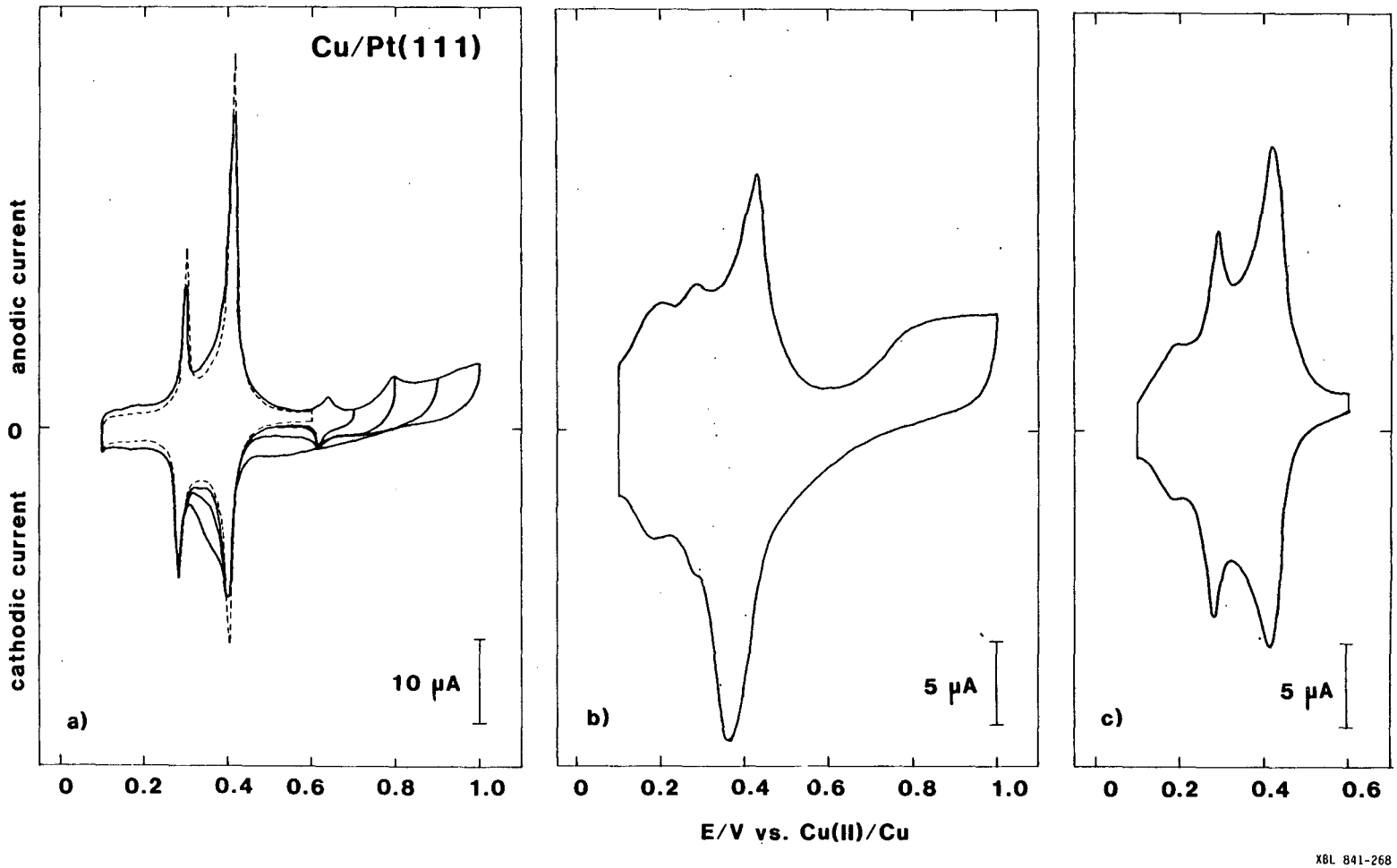

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Fig. 3.

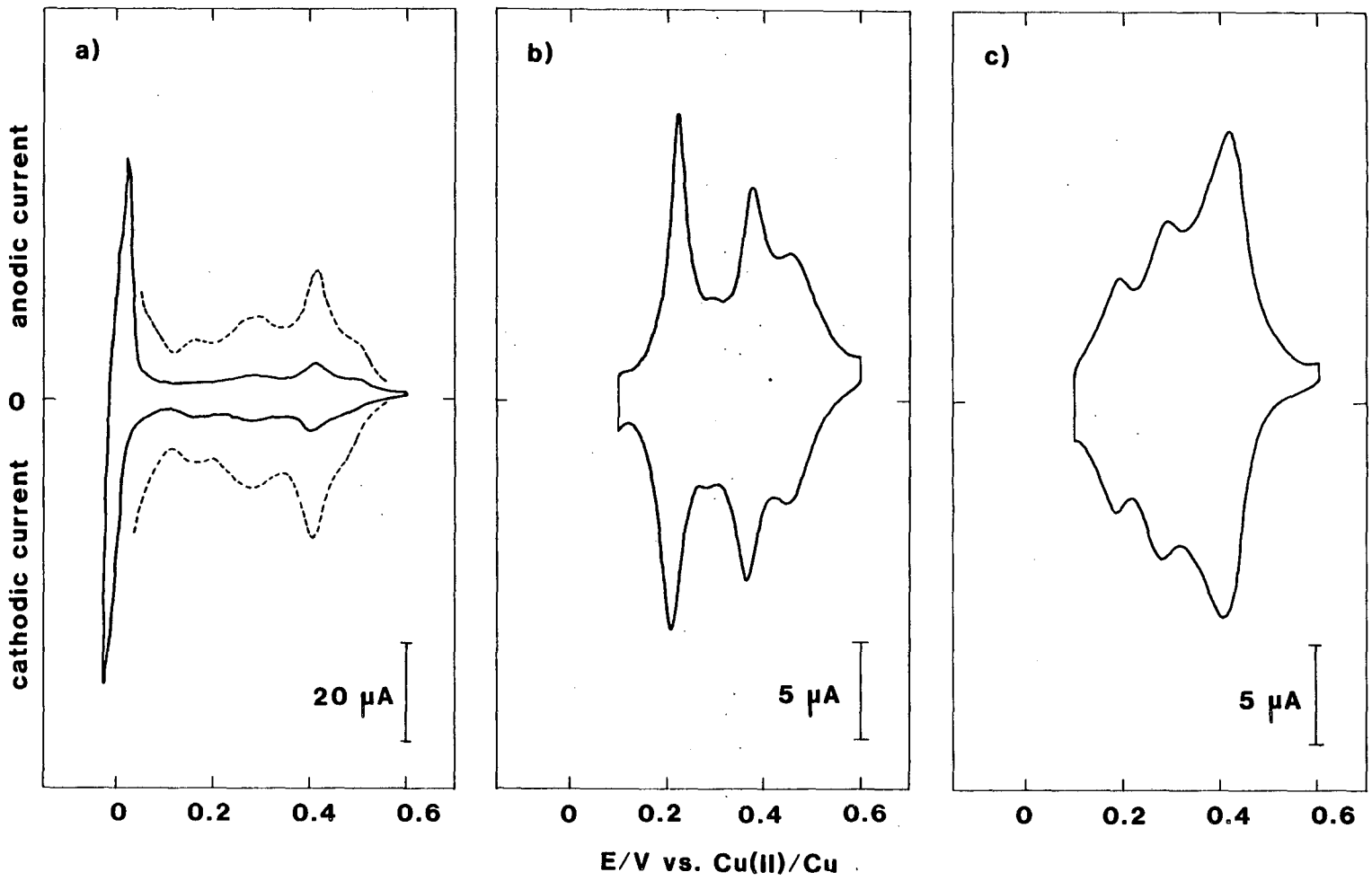

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Fig. 4.

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