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OBSERVATIONS ON THE VOLTAMMETRY OF THE
Au(111) SINGLE CRYSTAL SURFACE IN ACID
AND THE EFFECT OF ANIONS

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INTRODUCTION

Unique voltammetric curves for Au(111) single crystal surfaces have been observed recently [1-4], which differ from one another with respect to features in the anodic potential regime. It is not clear as to whether any one factor, including (but not limited to) method of surface preparation, potentiodynamic pretreatment, and type of anion present is responsible for the differences. The voltammetry of ultrahigh vacuum (UHV) prepared Au(111) surfaces presented by us recently [1] were very different from those presented previously by Hamelin and co-workers [2], who used only conventional crystal polishing surface preparation and potential-cycling pre-treatment. In this report observations are presented concerning the voltammetry of the (111) surface prepared in UHV and the purported effect of anion [5]. Using Low Energy Electron Diffraction (LEED) it was determined that the (111) surface prepared initially is reconstructed to a ($\sqrt{3}\times 22$) real space incommensurate overlayer structure. Using a coupled UHV/electrochemistry system we were able to perform voltammetric experiments on surfaces that were well-defined and that required no electrochemical pre-treatment to obtain reproducible and invariant voltammetry.

EXPERIMENTAL

Electrode Surface Preparation

After following a specific recipe for electropolishing [6,7], the Au(111) crystals were transferred to UHV where the surfaces were subjected to the usual Ar^+ bombardment/thermal annealing cycles. Surface cleanliness was monitored by Auger electron spectroscopy and surface structure determined using LEED. Details are provided elsewhere concerning the specific surface pretreatments [1] and nature of UHV/electrochemical system [8].

Electrolyte Preparation

All electrolytes were prepared using ultrapure water (Harleco) and placed in a Teflon reservoir mounted in the system. HF electrolyte was made using Ultrex 48% hydrofluoric acid (J.T. Baker) and pre-electrolyzed using Au electrodes. To make HClO_4 electrolytes, 70% perchloric acid (either Ultrex from J.T. Baker or double distilled from GFS Chemicals) was used. Pre-electrolysis was not performed on HClO_4 electrolytes to avoid generation of other anions, especially chloride.

Equipment

An α Pd-H disk - Au ring assembly was used as the reference - counter electrode system. Potentials are quoted with respect to the reversible hydrogen electrode (RHE) in this paper. Electrochemical manipulations were performed using the

single crystal surfaces in a thin layer cell in the vacuum ante-chamber after backfill with ultrapure Ar (Matheson research grade) that had been passed through Ti sponge at 900°C. The contact area of the electrolyte drop with the center portion of the working electrode was approximately 0.3 - 0.4 cm². A commercial potentiostat (PAR 173D) was used to obtain the linear sweep cyclic voltammograms.

RESULTS AND DISCUSSION

Theoretical and experimental studies have revealed that the clean equilibrium surface structure on Au(111) is incommensurate with the bulk [9-11]. This real space structure denoted as " $\sqrt{3} \times 22$ " may be described briefly as comprising a compressed hexagonal atomic layer residing on a second normal hexagonal layer. The LEED patterns arising from this geometry are neither simple nor easily observed, but we have been able to observe these patterns on the surfaces we prepare in UHV [1,12].

A preliminary report [1] from our laboratory on the anodic potential window opening experiment with a freshly prepared reconstructed surface in HF yielded a voltammogram that was characterized by sharp oxidation/reduction waves. The steady state voltammetry was reached after the first cycle through a reversal potential of 1.75 V. This voltammetry remained stable for many cycles. The scan through the twentieth cycle was

virtually identical to that observed on the second. The twentieth sweep is shown in Fig. 1 where the anodic wave occurs at 1.42 V (FWHM = 50 mV) and the symmetric cathodic wave occurs at 1.08 V (FWHM = 75 mV). The anodic charge passed out to 1.75 V was determined by integration to be on the average about $250 \mu\text{C}/\text{cm}^2$. LEED studies have established that the surface structure present during potentiodynamic cycling is that of a (1x1) bulk termination surface lattice. In another study [12] we have described in detail the transitions that occur when dealing with the reconstructions on both Au (111) and (100) under a variety of conditions. It was our intention here only to report and compare the voltammetry observed with respect to presence of different ions and importance of local (short-range) order. We note, however, that contrary to our preliminary report [1] of stability of the reconstructed surface to contact with electrolyte, we have determined that on contact with electrolyte the incommensurate overlayer on (111) initially present in UHV was transformed to a (1x1) structure. The difference in atomic density between the ($\sqrt{3}\times 22$) and (1x1) structures is about 5% (higher in the latter), and the transformation to the (1x1) structure probably causes an atomic excess of 5% to be left on the surface as adatoms [12]. The effect of this disorder on electrode current-potential behavior was not discernible. In any event the surfaces on which linear sweep cyclic voltammetry were performed were (111)-1x1 with a high degree of local order.

Potentiodynamic cycling to anodic potentials in the 1.5 to 1.75 V range on (111) surface over 10 or 20 cycles duration in HF electrolyte did not significantly change the voltammetric curve. However, the LEED analysis indicated atomic-scale roughening of the surface commenced when the anodic limit exceeded about 1.65 V, corresponding to an anodic charge per sweep exceeding $275 \mu\text{C}/\text{cm}^2$. The observation of this characteristic structural change without a simultaneous change in voltammetry indicates that the Au oxide formation/reduction process is relatively insensitive to long-range order in the surface, i.e. the existence of frequent monoatomic steps. Another way in which this was seen was from experiments with sputtered surfaces. Two different types of voltammetric responses were observed from surfaces that had been Ar^+ sputtered but not subsequently thermally annealed. The voltammetry observed for a surface sputtered using an ion energy of $< 1 \text{ keV}$ was essentially identical to a surface that had been annealed after the sputter. On the other hand, a surface sputtered using $> 2 \text{ keV}$ beam of ions, which nearly obliterates the LEED pattern, gave a voltammetric response very similar to that observed for a polycrystalline surface. We found that even repeated oxidation/reduction cycling in either HF or HClO_4 could not induce either the extent of disorder or the polycrystalline voltammetry produced by 2 keV sputtering.

To study the sensitivity of linear sweep cyclic voltammetry to the combined effects of surface morphology and

anion, the UHV prepared surfaces were subjected to potentiodynamic cycling in HF in the presence of added perchlorate anion. Stepwise, addition of aqueous aliquots were made to the 0.3 HF electrolyte to achieve concentrations of 10 mM and 100 mM in ClO_4^- . These additions caused the anodic wave to become progressively broader with increasing amounts of ClO_4^- . Therefore we decided to monitor the voltammetry in HClO_4 alone.

Figure 2c illustrates the voltammetry of the (111) surface in 0.03 M HClO_4 . After UHV preparation of the single crystal, the surface was first cycled in the double layer region in 0.3 M HF with the result shown in Fig. 2a. The electrolyte was replaced by HClO_4 and cycling was continued. No difference was observed in the subsequent voltammetry shown in Fig. 2b. Extending the anodic potential limit of cycling gave the voltammetry shown in Fig. 2c. It is noted that this voltammetry is quite different than that given by Hamelin in HClO_4 [2], where two (or more) anodic waves were reported.

A striking result was achieved in the voltammetric response when Cl^- was added to HClO_4 electrolyte. The result is given in Fig. 3. This voltammetric curve is very similar to that reported by Hamelin [5]. In fact, the only way in which we could reproduce Hamelin's voltammetry was to add Cl^- to the electrolyte. However, we cannot say with absolute certainty that the presence of Cl^- is solely responsible for the effect. We cannot exclude the difference in surface structure as

influencing the voltammetry since we do not know the surface morphology of Hamelin's electrodes. The existence of adventitious Cl^- in the electrolyte from pre-electrolysis or potential cycling is suspected.

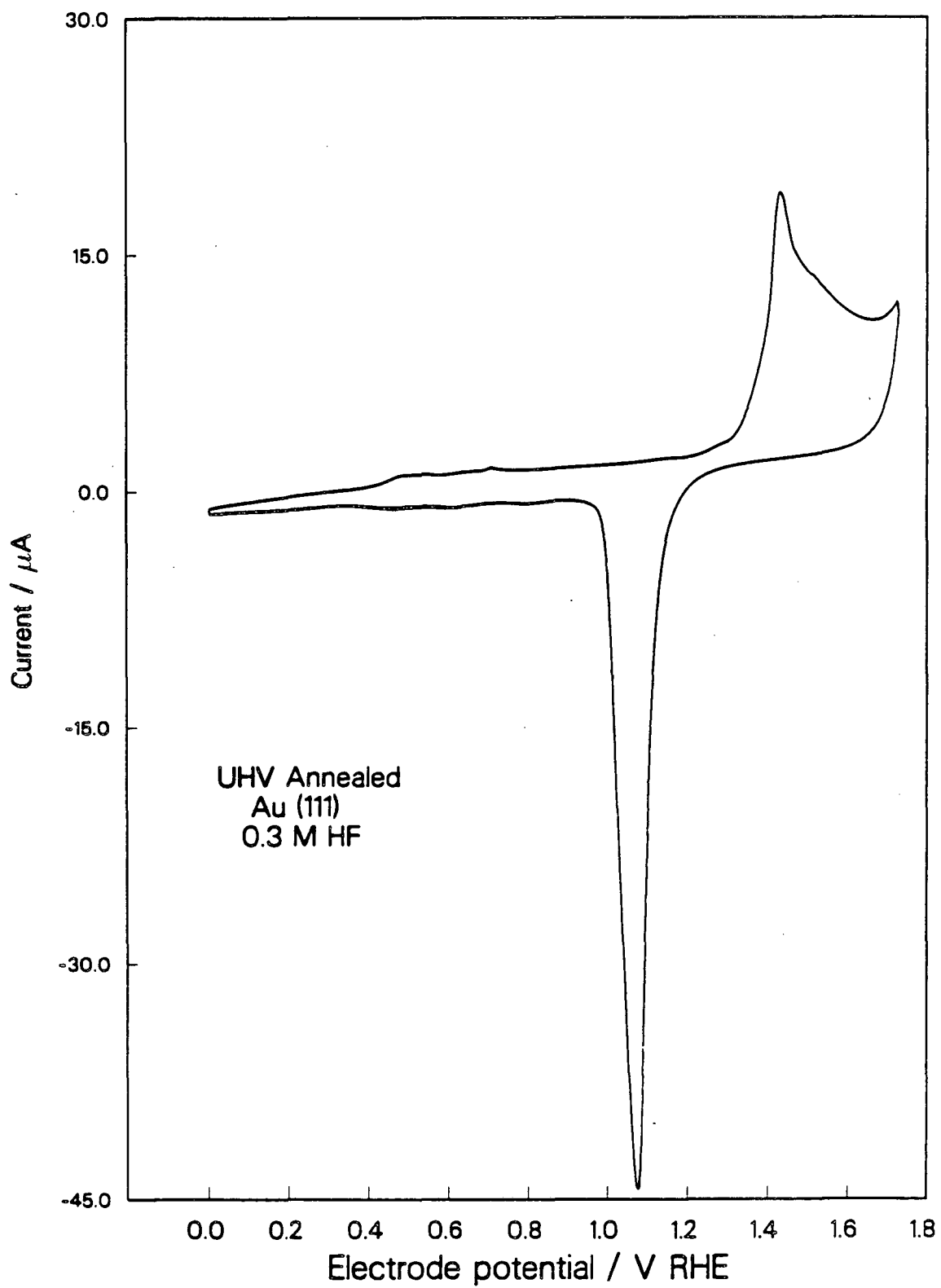
In concluding, we note that our results are consistent with the widely-held view that for the most part F^- and ClO_4^- electrolytes act "indifferently" on noble metal surfaces. Hamelin [5] reported that the voltammetry of Au in HF and HClO_4 are very different from the same crystal in the two electrolytes indicating a pronounced anion effect. We found it impossible to account for this effect without invoking the presence of Cl^- , possibly in combination with structural differences due to the difference in surface preparation. On the basis of experiments with Ar^+ sputtered surfaces and potentiodynamically cycled surfaces in HF and HClO_4 , it appears that the voltammetric features for Au oxide formation and reduction are insensitive to the degree of long-range order in the surface. Local order is clearly very important to oxide formation/reduction kinetics as the voltammetric peak shapes for even sputtered surfaces were dramatically narrower than that for polycrystalline surfaces.

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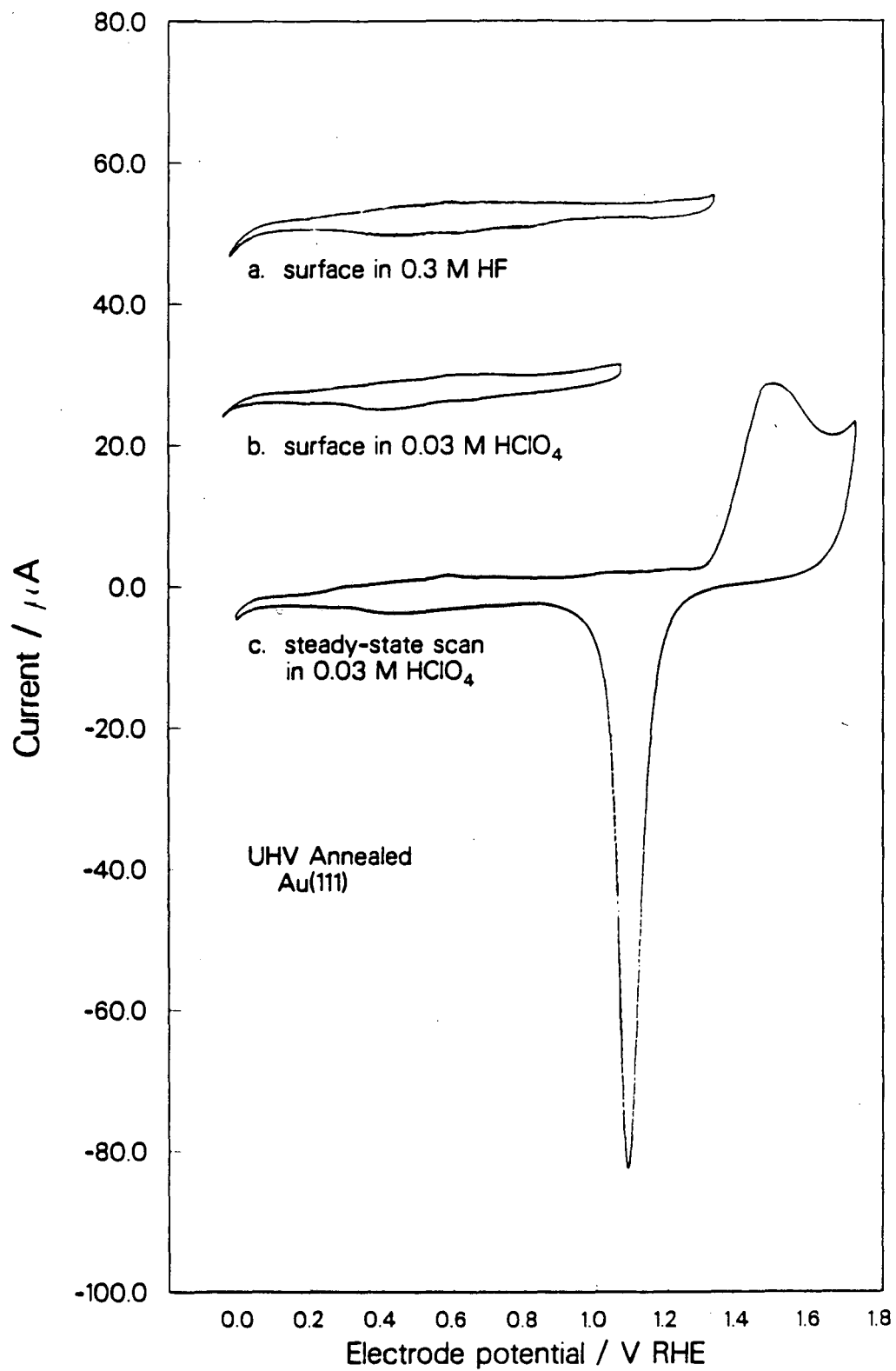
FIGURE CAPTIONS

1. Cyclic voltammogram of the (111) surface in 0.3 M HF recorded on the twentieth sweep at 50 mV/s. The steady state voltammetry was reached after the first cycle through the reversal potential of 1.75 V.
2. Cyclic voltammograms of the Au(111) single crystal surface a) in 0.3 M HF in the double layer region, b) after changing electrolyte to 0.3 M HClO_4 , c) including anodic potential region in 0.03 M HClO_4 . Sweep rate is 50 mV/s.
3. Addition of Cl^- to the electrolyte produced the voltammogram shown for the (111) surface. See text. Sweep rate is 50 mV/s.



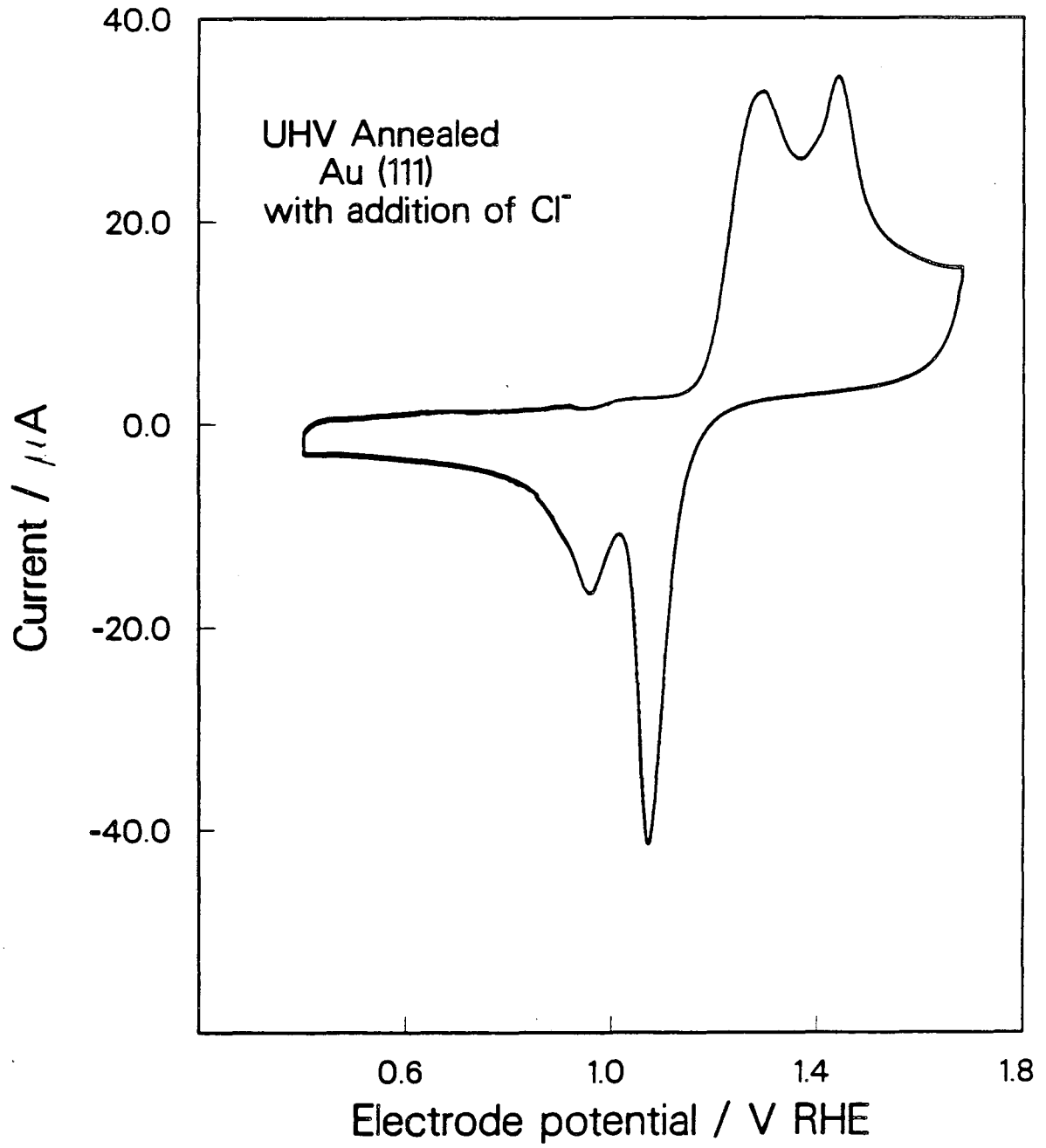
XBL 866-2256

Fig. 1



XBL 866-2265

Fig. 2



XBL 867-2556

Fig. 3

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