

Underpotential deposition of copper on electrochemically treated polycrystalline Au surfaces

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Abstract. Cyclic voltammetric responses of electrochemically treated polycrystalline gold surfaces have been examined using Cu-UPD probe reactions (UPD – underpotential deposition). The treatment procedure used appears to induce preferential crystal orientation of the Au surface with a very small roughness factor and affords a simple method to obtain well-defined surfaces for electrochemical studies.

Keywords. Cu-UPD; faceting; Au electrodes; anion effects.

1. Introduction

Cyclic voltammetric (CV) features associated with surface processes, for example underpotential deposition (UPD), can be profoundly influenced by the nature of the surface treatment procedures followed (Kolb 1978; Parsons 1986) and other ions present in the electrolyte solution (Zei *et al* 1987). The recent work by the Arvia group (Arvia *et al* 1986; Perdriel *et al* 1986) deals with electrochemical treatment procedures to achieve 'stabilised' CV responses using repetitive triangular potential sweep (RTPS) and repetitive square wave potential sweep (RSWPS) modes and in most cases preferential orientation of the polycrystalline surfaces, mainly of platinum and gold have been arrived at. However, most experiments are concerned with platinum surfaces and correlations have been made with responses from the single crystal surfaces of low-index planes. Work on treatment of gold surfaces is relatively limited in literature and gold electro-oxidation/reduction involves complex processes (Perdriel *et al* 1986).

The Cu-UPD presents a very strong sensitivity to the substrate surface structure. In the course of our experiments on Cu-UPD on polycrystalline gold surfaces, we have made some interesting observations, when the Au-electrode surface is subjected to a potential cycling treatment between the limits, +0.1 V and +1.5 V *vs mse* (Hg/HgSO₄ electrode); the potential cycling profile is shown in figure 1. We present these observations in this paper and discuss the results alongwith those obtained with electrodes subjected to the "faceting" (RTPS) treatment suggested (Arvia *et al* 1986).

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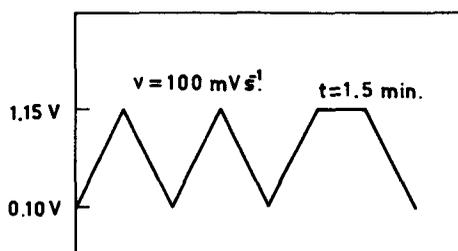


Figure 1. Potential cycling profile for electrochemical "treatment" of polycrystalline Au surface in 0.5 M H_2SO_4 .

2. Experimental

A conventional double-compartment cell with a provision for deoxygenation was employed. A large platinum foil, $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode (*mse*) and a polycrystalline Au electrode (supplied by Bio-analytical systems) served as counter, reference and working electrodes respectively. The system under study is $x\text{M CuSO}_4 + 0.5\text{M H}_2\text{SO}_4$. The solutions were purged and blanketed with dry nitrogen. All chemicals, which were of analytical grade, were recrystallised once and their solutions prepared from chloride-free triple-distilled water. All potentials mentioned in this paper are with reference to the *mse*.

Prior to each set of CV curves recorded, the Au surface was polished to a mirror-finish, on a fine grade (4/0) emery sheet, rinsed in acetone and triple distilled water several times. Electrodes subjected to the above mechanical treatment are referred to as "untreated" electrodes. Particular care was exercised in maintaining a memory-free surface; (prolonged) bulk deposition of copper was avoided to eliminate the effects of alloy formation with the Au-substrate. The electrode surface produced after the electrochemical treatment is referred to as "treated" electrode, which involves a potential cycling profile in 0.5 M H_2SO_4 solutions represented in figure 1.

The extent of roughening was determined by integration of the charge for oxide formation in an i vs E profile to the potential at which the O-adsorption current (diffusion tail) becomes minimum (Burnstein minimum). Cyclic voltammograms were recorded on a Wenking Potentiostat (LB 75L) and Voltage Scan Generator (VSG-72) coupled to a Rika Denki $X - Y/t$ recorder.

3. Results and discussion

On an "untreated" electrode, Cu exhibited a CV response shown in figure 2a typical for UPD (Lorenz *et al* 1971). The charge associated with the UPD stripping after accounting for the roughness is $\approx 460\ \mu\text{C cm}^{-2}$ corresponding to a monolayer coverage. An UPD shift (ΔU_p) of $\approx 250\ \text{mV}$ was observed (figure 2b) which is in consonance with the Kolb-Przasnyski-Gerischer (KPG) correlation (Kolb *et al* 1974). A linear relationship was observed (figure 3) for the stripping charge vs potential indicating that the UPD type process obeys the Temkin isotherm (Schultze 1970). The $\log i_{p,a}$ vs $\log v$ (v = sweep rate) plots (figure 4) yielded slope values of 0.95 ± 0.05 indicating a surface process to be operative. As can be seen from figure 2a, the cathodic

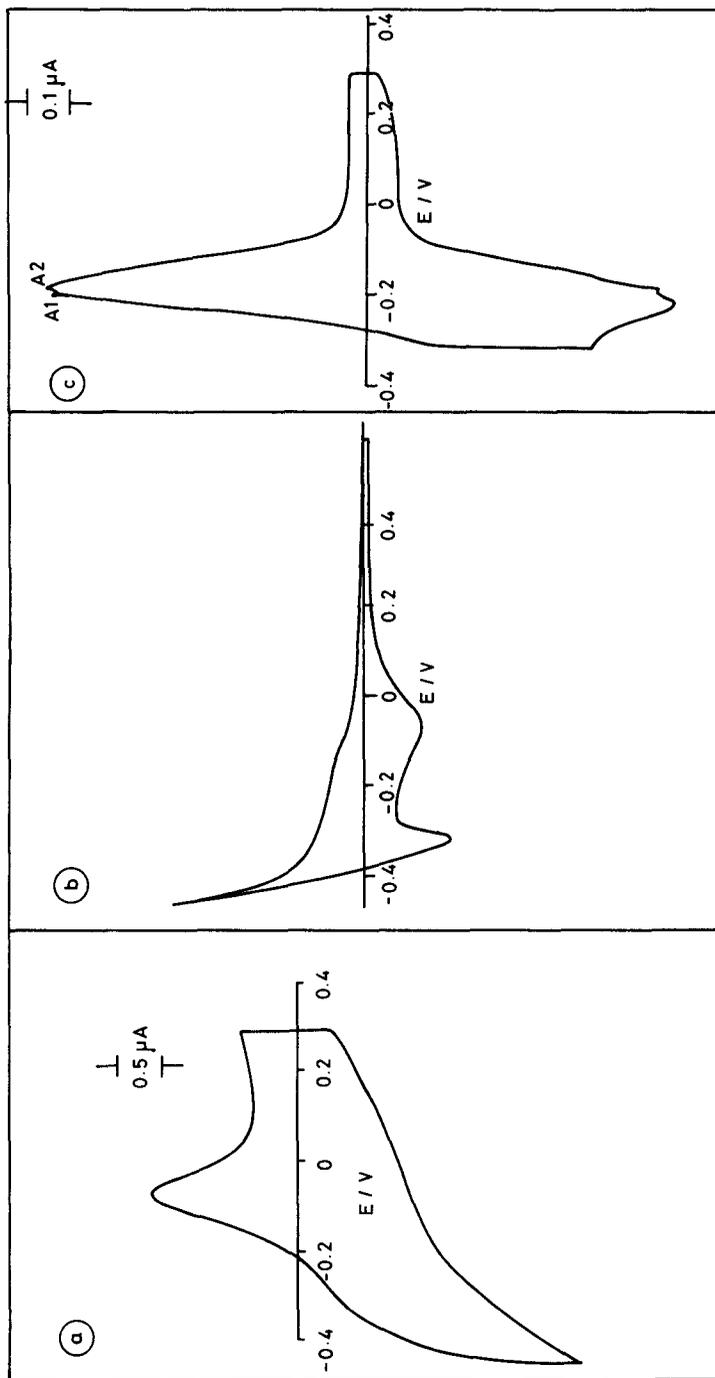


Figure 2. Cu-UPD CV responses (a) on "untreated" electrodes; (b) UPD and bulk deposition/stripping patterns; (c) on "treated" electrodes in $1 \times 10^{-3} M CuSO_4$ in $0.5 M H_2SO_4$.

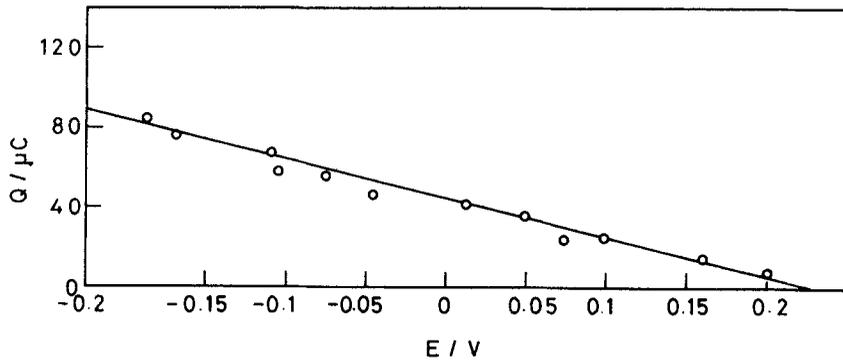


Figure 3. Stripping charge vs potential relationship for 1×10^{-3} M CuSO_4 in 0.5 M H_2SO_4 on both "treated" and "untreated" electrodes.

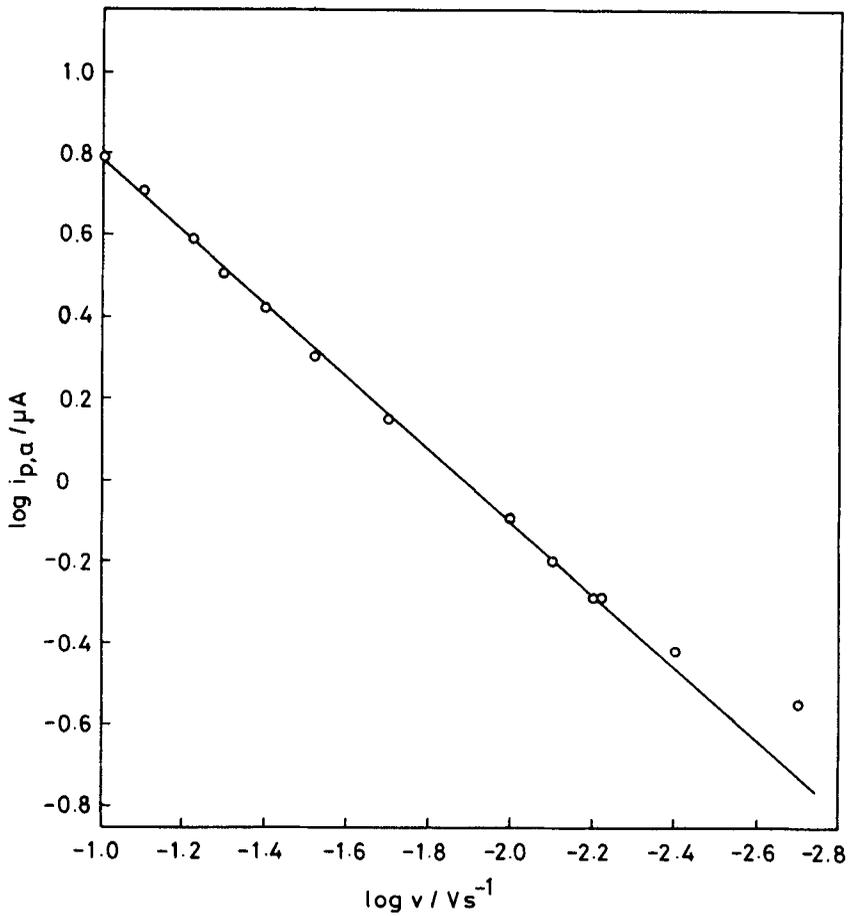


Figure 4. Log $i_{p,a}$ vs log v plot for UPD-stripping process.

portion of the CV is not so well-defined as to be amenable to analysis involving $i_{p,c}$ and $E_{p,c}$. However, on "treated" electrodes, the cathodic portion assumed a well-defined peak shape with a shoulder attached to it and now the $E_p (= |E_{p,a} - E_{p,c}|)$ is negligibly small and $i_{p,a} \approx i_{p,c}$ (figure 2c). After obtaining a stabilised Cu-UPD CV response, polarisation was carried out cathodically to more negative potentials to observe any changes that might occur in the Cu-OPD (overpotential deposition) peaks. However, no significant changes as regards the UPD shift were observed. The cathodic portion of CV after anodic treatment using a potential cycling profile presented in figure 1 has a shoulder (S_c) attached to it, whereas the single anodic stripping peak is split into two distinct ones, with peak potential differences between S_c and A_2 and C_1 and A_1 equal to zero ($\Delta E_p \approx 0$). These criteria are unmistakable signatures of surface-type processes. This is the first time that such a symmetrical (about the potential axis) response for the Cu-UPD is reported on Au-surfaces. These results indicate that the present treatment leads to an ordered surface in terms of crystal orientation. This is the result of the O-electrodesorption/desorption and the consequent restructuring and preferential orientation of the polycrystalline surface (Arvia *et al* 1986; Somarjai and Van Hove 1988). Incidentally, we verified the responses for Cu-UPD at electrodes subjected to an (RTPS) "faceting" treatment (Arvia *et al* 1986; Perdriel *et al* 1986) and the results are presented in the following.

3.1 Copper UPD on faceted Au electrodes

A freshly polished Au surface was subjected to RTPS treatment at $v = 2000 \text{ Vs}^{-1}$ for about 5 to 15 minutes between $+0.1$ and $+1.15 \text{ V vs mse}$ in $0.5 \text{ M H}_2\text{SO}_4$. The electrodes thus treated were transferred into a cell containing $0.5 \text{ M H}_2\text{SO}_4 + 10^{-2} \text{ M CuSO}_4$ and cathodically scanned between $+0.3$ and -0.3 V at $v = 50 \text{ mVs}^{-1}$. A CV response (figure 5) almost similar to the one obtained with our "treated" electrodes was observed without any significant roughness difference. Assuming the initial roughness factor to be 1.00 and using the area under the O-electrodesorption peak (figure 6) and/or the Cu-UPD stripping peak an increase of the factor by 0.07 units was observed.

A few remarks on what emerges on the macroscopic details of the gold electrode

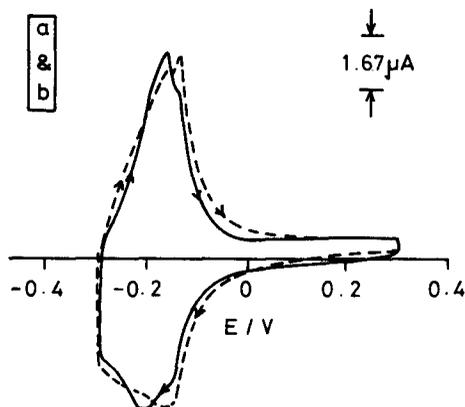


Figure 5. Cu-UPD CV response on "faceted" electrodes; (a) (—) first cycle; (b) (---) stabilised response: $1 \times 10^{-2} \text{ M CuSO}_4$ in $0.5 \text{ M H}_2\text{SO}_4$.

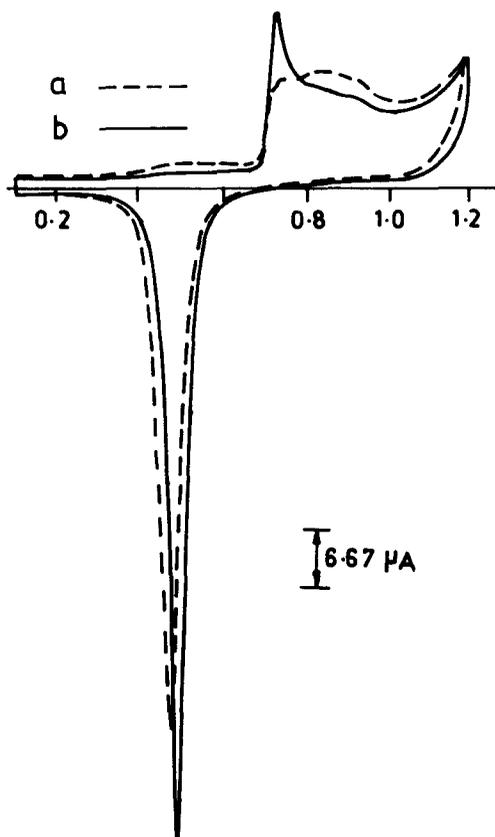


Figure 6. CV response of Au electrode in 0.5 M H₂SO₄ solutions: (a) before and (b) after "treatment" (using the profile in figure 1).

oxidation in sulphuric acid solutions and subsequent reduction may be in order at this juncture. After treating the electrode surface with a potential cycling profile (figure 1), the resultant O-electroadsorption/desorption CV response (figure 6) is more typical of that exhibited by an Au (110) surface. This suggests that a substantial portion of the electrode surface is now composed of facets oriented in the (110) direction, in good agreement with the results reported with an Au (110) single crystal and with RSWPS-treated Au surfaces (Twomey 1989). When the electrodes were subjected to "faceting" in 0.5 M H₂SO₄ solutions containing Cl⁻ ions, three peak couples (A1/C1, A2/C2 and A3/C3) with very sharp features were observed for Cu-UPD, all corresponding to three distinct surface processes. Similar observations were also made in the case of our "treated" electrodes. However, only in the case of "faceting" (RTPS) in the Cl⁻ containing 0.5 M H₂SO₄ solutions, substantial areas of the Au surface were found to be corroded and on optical microscopic examination, development of a pyramidal shape on the surface could be seen. Higher current magnitudes associated with the Cu-UPD response on these "faceted" (in Cl⁻ containing solutions) electrodes also confirmed that the faceting treatment has been accompanied by an increase in the roughness due to severe corrosion. This loss of gold was not observed in the case of our "treated" electrodes.

Hence, it is concluded that under the treatment conditions we have presented in this paper, preferential orientation occurs accompanied by only a small roughening. This is interesting in view of the simplicity of the method employed here. However, the real nature of the surface after the treatment is to be ascertained using more reliable surface analytical techniques. It may be useful to take into account the experimental findings in a recent study (Angerstein-Kizlowska *et al* 1989) on the stochastically gated surface processes in Au oxidation, wherein higher rates of anodic sweep have been reported to introduce some kinetic irreversibility in O-electroadsorption and hence methods using lower or moderate sweep rates may be preferable.

In addition, anion effects play an important role in these processes as described earlier and our future communication will deal with the effects of chloride and perchlorate ions on both the preferential orientation processes and metal-UPD. Microscopic examination of the "treated" surfaces in the context of the stochastically gated surface processes on Au-surface oxidation/reduction is warranted.

In our opinion, a precise control over roughening (dissolution/redeposition) could be achieved retaining the effects of preferential orientation by means of an interplay with the chemistry of Au oxidation/reduction, e.g. partially blocking the surface sites by hydrophobic substances. This aspect has been reported from our laboratory recently with a silver electrode in solutions containing tetraphenylborate anion (Bharathi *et al* 1990).

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