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## EFFECT OF SURFACE PREPARATION OF Pt(111) ON Cu UPD

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### SUMMARY

The influence of surface preparation such as annealing, cooling, quenching of Pt(111) and the way of contacting to the electrolyte on characteristics of Pt(111) in 0.1M H<sub>2</sub>SO<sub>4</sub> and underpotential deposition (UPD) of copper on such treated surfaces have been investigated using cyclic voltammetry. Effects of Cu<sup>+</sup> and Cl<sup>-</sup> ions concentration on the UPD of copper have been monitored using coulometric data and the results are discussed in terms of coadsorptions of Cu<sup>+</sup> and Cl<sup>-</sup>.

### INTRODUCTION

Several phenomena such as adsorption - desorption of hydrogen and oxide formation-reduction occurring on metal electrodes during electrolysis generate useful information on the surface states of the electrodes. Typically, the results obtained on single crystal Pt(111) surfaces by different workers [1-4] vary considerably, specially as regards the adsorption-desorption of hydrogen and the hydrogen coverage. This variation may arise from the difficulty to obtain Pt(111) surfaces of identical properties (e.g. work function, dielectric constant, electronic and optical properties) or due to difference in surface states of the electrode as a result of pretreatment procedures. It is relevant to note from the literature [1,4-6] that Pt(111) surfaces behaves differently when different pretreatment routes was used. Clavilier [3] and others [1,2,4-6] have shown that

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a pretreatment procedure involving annealing, cooling, quenching, etc., can significantly alter the surface state of Pt(111) and yield a very clean surface [1-6]. However, the results are of preliminary nature and the role of time factor during pretreatment, which appears to play a vital role, has not been investigated in detail. Hence systematic investigations to understand the influence of this time factor (during pretreatment) on the final surface state and characterization of the 'treated' surface using Cu UPD reaction as a probe have been carried out and the salient features are presented here.

#### EXPERIMENTAL

The single crystal of Pt(111) orientation used in this experiment was a 3 mm diameter disc, prepared at Techn.Büro f. Kristallzüchtung Auftragsforschung Neuhausen, Germany. The crystal was mounted by spot welding with a thick platinum wire to the back of the crystal and bending it so as to allow the faces of the crystal to be parallel to the solution surface. This arrangement known as "dipping" technique [7] is useful and employed for finding the characteristic voltammograms of Pt(111) surfaces. Prior to bringing the desired Pt(111) surface into contact with the electrolyte, the electrode was pretreated by using standard procedures [8] by dipping in acetone, exposure to boiling aquaregia for 5 minutes, annealing at 950°C in hydrogen atmosphere followed by allowing to cool for 60 to 90 seconds in the vapour of deaerated ultrapure water and finally quenched for a few seconds.

Electrolytes were prepared from triply distilled water employing  $H_2SO_4$  (Merck, Suprapur),  $CuSO_4$  (Merck, p.a.) and HCl (Merck, Suprapur).

An all glass three electrode cell with separated compartments for counter and reference electrodes has been used. A platinum foil of  $4\text{ cm}^2$  area and Saturated Calomel Electrode (SCE) served as counter and reference electrodes respectively. Before starting the experiment electrolyte was purged with  $N_2$  gas of 5N purity to maintain the inert atmosphere on the surface and protect from contamination induced by atmospheric oxygen. A potentiostat (FHI ELAB G050-33 Model) along with an x-y-t recorder (Type BD 91901/901/901 made by Kipp and Zonen, Holland) used for recording the voltammograms. All potentials were quoted with respect to SCE.

#### RESULTS AND DISCUSSION

Before proceeding with experiments using "dipping" technique, an experiment in which the whole of the electrode area was exposed in the electrolyte, was carried out and cyclic voltammogram recorder in  $0.1M\ H_2SO_4$  in the potential range of  $-0.2$  to  $+0.6V$ , after pretreatment to the crystal as mentioned in experimental section. Cyclic voltammogram as shown in Fig.1a was observed, which is quite different than the reported by others [5,6,8,9] on Pt(111) surface. It may be seen that the crystal behaves no more as a Pt(111), because all faces of the crystal are in contact with the electrolyte. Thereafter  $10^{-3}M$  of  $CuSO_4$  was added to  $0.1M\ H_2SO_4$  to use copper UPD behaviour on this system as a further probe for investigating the above interface. Fig.1b shows the response observed. It confirms the contribution of poly surface states of the crystal rather than the contribution due to single crystal face. Further experiments were carried out using electrodes that were annealed for 20 minutes,

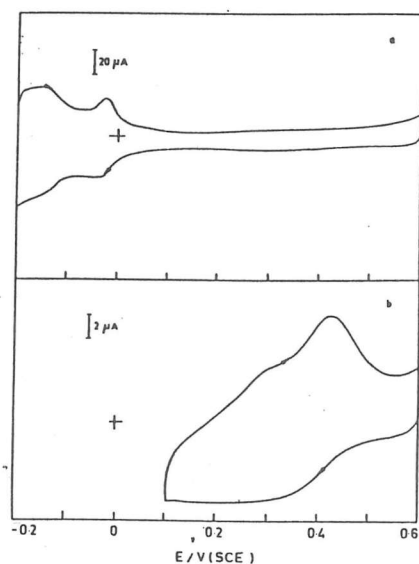


Fig.1 Cyclic voltammogram of the fully dipped platinum electrode in (a) 0.1M  $H_2SO_4$ ;  $v = 50 \text{ mVs}^{-1}$ ; (b) 0.1M  $H_2SO_4 + 1.0 \times 10^{-3} \text{ M CuSO}_4$ ;  $v = 10 \text{ mVs}^{-1}$  [Pretreatment conditions: 30 min. annealing, 70 S cooling, quenching time 1 S].

cooled for 60 seconds in a bubbler containing ultrapure water and purged with  $N_2$  gas and then contact to the electrolyte (0.1M  $H_2SO_4$ ) was made using dipping arrangements. Using this mode of contact to the solution, voltammogram of Pt(111) surface in 0.1M  $H_2SO_4$  and Cu UPD were recorded and shown in Fig.2a and 2b respectively. When compared to Fig.1a and 1b, it was noted that in Fig.2a, a reversible hump appears in between 0.1V to 0.3V, simultaneously a slight change in between -0.2 to 0.05V was also noted. It indicates that appearance of hump is associated with the hydrogen adsorption-desorption processes. A pronounced influence

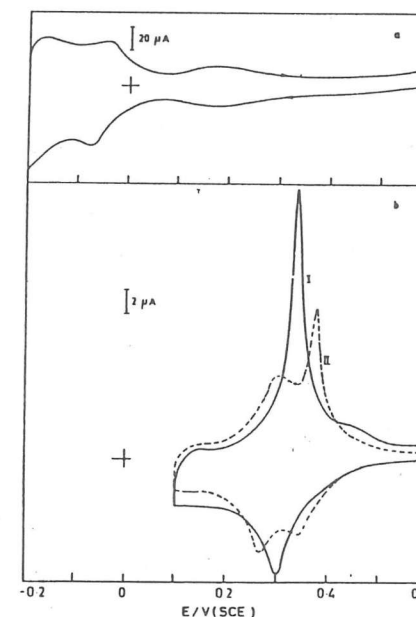


Fig.2 Cyclic voltammogram of the Pt(111) face in (a) 0.1M  $H_2SO_4$ ;  $v = 50 \text{ mVs}^{-1}$ ; (b) 0.1M  $H_2SO_4 + 1.0 \times 10^{-3} \text{ M CuSO}_4$  (I); 0.1M  $H_2SO_4 + 1.0 \times 10^{-3} \text{ M CuSO}_4 + 10^{-4} \text{ M HCl}$  (II);  $v = 10 \text{ mVs}^{-1}$ . [Pretreatment conditions: 20 min. annealing, 60 S Cooling, quenching time 1S]

due to the hump, on the Cu UPD is also seen in Fig.2b (Curve I). The effect of small concentrations of  $Cl^-$  ions on the current potential curve for Cu UPD on Pt(111) is also shown in Fig.2b (Curve II). The two desorption peaks of Cu UPD at around 0.33 V which are not seen in halide free solution (see Fig.2b, Curve I), become clearly separated in the presence of  $Cl^-$  ions (see Fig.2b, Curve II). Thus, addition of  $Cl^-$  ions leads to a complex structure of the voltammetry for Cu UPD, which arises due to the attractive interactions between  $Cu^+$  and the  $Cl^-$ , such that

deposition of Cu draws  $\text{Cl}^-$  to the surface. To understand the mechanism, studies employing a technique like AES and LEED are needed.

In the next set of experiments, the electrode was again annealed for 25 minutes, cooled for 65 seconds followed by quenching for 1 second. Cooling and quenching the electrode, thereafter transferring to the cell, avoids the problem of strain or any contamination induced by atmospheric oxygen. To observe further changes if any for Pt(111) surface, cyclic voltammogram in 0.1M  $\text{H}_2\text{SO}_4$  and Cu UPD were recorded and shown in Fig.3a and 3b respectively. There was an indication about the improvement as can be seen through a small sharp spike that appears reversibly at 0.21V (see Fig.3a).

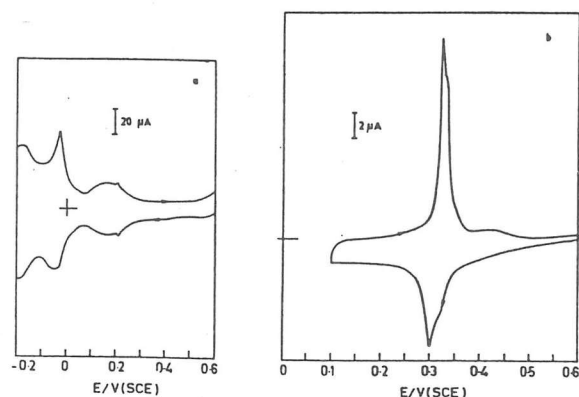


Fig.3 Cyclic Voltammogram of the Pt(111) face in (a) 0.1M  $\text{H}_2\text{SO}_4$ ;  $v = 50 \text{ mVs}^{-1}$ ; (b) 0.1M  $\text{H}_2\text{SO}_4 + 1.0 \times 10^{-3} \text{ M CuSO}_4$ ;  $v = 10 \text{ mVs}^{-1}$  [Pretreatment conditions: 25 min. annealing, 65 S cooling, quenching time 1 S].

This small spike apparently suggests the changed surface state on treatment accounts for the observed influence on Cu UPD structure

(Fig.3b). This is further evident from the shoulder which appears in Cu UPD on cathodic going scan (0.33V) and its dissolution on anodic going scan (0.34V). These results indicate that surface states of Pt(111) in 0.1M  $\text{H}_2\text{SO}_4$  (and Cu UPD structure) evolves with number of pretreatment cycles and with increasing time for the pretreatment steps. The spike, which seems to be the reason for improved surface states, has evoked different explanations by different authors [3, 9]. Clavilier [3] suggested unusual splitting of hydrogen adsorption-desorption process, while Scherson report [9] indicates that the spike to be associated with specifically adsorbed anions and responsible for the phase transition. One small but broad peak can also be seen on anodic scan in Fig.2b and in 3b, just after the copper dissolution peak. It may be attributed to the presence of some kind of impurity on the surface. Fig.4a and 4b also show the same trend but to a lesser extent in comparison to Fig.2b and 3b and the corresponding humps do not fully disappear with the number of treatments.

Efforts were made to optimize the pretreatment conditions for obtaining the "evolved surface" of Pt(111) by increasing the annealing time (30 minutes) and cooling time (70 seconds) followed by quenching for 1 second and recording cyclic voltammograms as described earlier. Results are shown in Fig.4a and 4b. These results (Fig.4a and 4b) were compared with the data reported by Clavilier and others [3,5], and was found fairly comparable. It is noted that annealing cooling and quenching times have important roles in getting the evolved surface. These time factors vary from crystal to crystal depending on the surface states.

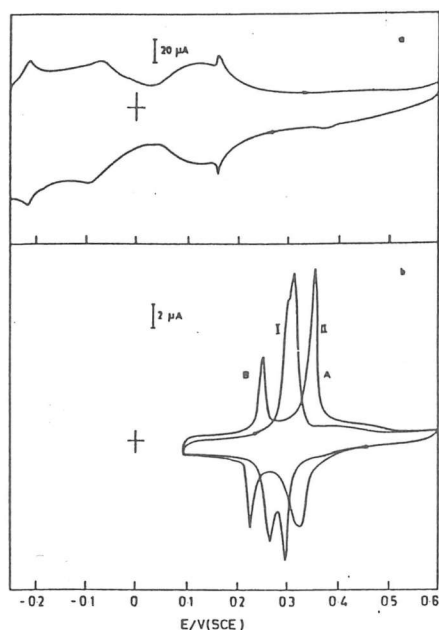


Fig.4 Cyclic voltammogram of the Pt(111) face in (a) 0.1M  $H_2SO_4$ ;  $v = 50 \text{ mVs}^{-1}$ ; (b) 0.1M  $H_2SO_4 + 1.0 \times 10^{-3} \text{ M CuSO}_4$  (I); 0.1M  $H_2SO_4 + 1.0 \times 10^{-3} \text{ M CuSO}_4 + 10^{-4} \text{ M HCl}$  (II);  $v = 10 \text{ mVs}^{-1}$   
 [Pretreatment conditions: 30 min. annealing, 70 S cooling, quenching time 1 S]

At low temperature, short time annealing will not be enough to produce evolved surface. Similarly cooling and quenching time have also their own effect on the surface. If sufficient time is not allowed to cool and crystal brought to the contact of electrolyte hurriedly, problem of strains will arise. Once when expected result was achieved on "evolved surface" of Pt(111) in 0.1M  $H_2SO_4$  and for Cu UPD, then different concentrations of HCl was added to study the effect of  $Cl^-$ . Effect of  $Cl^-$  concentrations on Cu UPD structure were studied because (see Fig.2b Curve II) it was

noticed that addition of  $Cl^-$  has strong influence on Cu UPD. The  $Cl^-$  influences the two Cu UPD peaks to shift in opposite directions, while the low coverage peak ( $\approx 0.30\text{V}$ ) moves to even higher binding energy in the presence of  $Cl^-$ . The high coverage peak which most likely corresponds to the formation of a monolayer  $400 \mu\text{C cm}^{-2}$  at 0.26V, is shifted to lower binding energy. A competition between  $Cu^+$  and  $Cl^-$  for adsorption sites seems to occur, at  $\approx 0.26\text{V}$  in Fig.4b, as a response of which UPD peaks shift to more negative potentials. This shifting behaviour of Cu UPD peak has been already noticed by Kolb et al [10]. Recent report by Markovic et al [5] indicates that in  $Cl^-$  free supporting electrolyte, Cu appeared to be deposited at underpotential in metallic islands having the platinum lattice constant. In the presence of  $Cl^-$  ions the Cu was deposited at underpotential into a CuCl adlattice [5] having a more favourable thermodynamic potential than Cu adatoms alone and thus lowering the activation energy for the initial deposition (peak A). The UPD peak (B) corresponds to the formation of Cu monolayer. The concentration of  $Cu \geq 0.1 \text{ mM}$  is reported [5] to suppress hydrogen adsorption and form a complete monolayer at UPD on Pt(111). Cyclic voltammograms were recorded with varying concentrations of  $Cu^+$  and  $Cl^-$  and corresponding charges were calculated and included in Table 1. We can see that charge for Cu UPD increases with increase in concentration of copper (from charge associated with anodic sweep). A monolayer formation ( $400 \mu\text{C cm}^{-2}$ ) was observed at a concentration  $\geq 7.5 \times 10^{-4} \text{ M}$ . Continuous decrease in charge with increasing concentration of  $Cl^-$  ions under the low coverage (peak A) and increase in charge under the high coverage (peak B) was observed. This perhaps suggests that  $Cl^-$  ions have strong influence on

TABLE I  
Cu UPD on Pt(111) in 0.1M H<sub>2</sub>SO<sub>4</sub>: Effect of Cu<sup>2+</sup> and Cl<sup>-</sup>  
on Coverage (Dissolution peak)

Cu <sup>2+</sup> Concentrations (M)	Cl <sup>-</sup> Concentrations (M)	Coverage, μC cm <sup>-2</sup>			
		Q	Q <sub>A</sub>	Q <sub>B</sub>	Q <sub>T</sub> =(Q <sub>A</sub> +Q <sub>B</sub> )
2.5 x 10 <sup>-4</sup>	--	320	--	--	--
5.0 x 10 <sup>-4</sup>	--	365	--	--	--
7.5 x 10 <sup>-4</sup>	--	400	--	--	--
1.0 x 10 <sup>-3</sup>	--	470	--	--	--
1.0 x 10 <sup>-3</sup>	1.0 x 10 <sup>-5</sup>	470	--	--	470
1.0 x 10 <sup>-3</sup>	5.0 x 10 <sup>-5</sup>	--	370	80	450
1.0 x 10 <sup>-3</sup>	1.0 x 10 <sup>-4</sup>	--	260	125	385

Q = Anodic dissolution charge of Cu UPD (μC cm<sup>-2</sup>); Q<sub>A</sub> = Charge under low coverage peak; Q<sub>B</sub> = Charge under high coverage peak; Q<sub>T</sub> = Total Charge (μC cm<sup>-2</sup>).

both the peaks A as well as B, but coadsorbed at a potential corresponding to the peak B, as a result of which charge increases. It was also observed that only the concentration of Cl<sup>-</sup> ions  $\geq 5 \times 10^{-5}$  M has influence on Cu UPD structure, as inferred from Table I. Here, in these experimental conditions, it is observed that threshold concentration of Cl<sup>-</sup> anions is  $5 \times 10^{-5}$  M unlike in the earlier report [5], where threshold concentration is  $1 \times 10^{-5}$  M. Charge integrated from the anodic peak of UPD (Fig.4b) was also found to be slightly higher than the reported value. Other characteristics are similar to those reported in literature [5]. The presence

of Cl<sup>-</sup>, appears to have a catalytic effect on Cu UPD causing the deposition of submonolayer (260 μC cm<sup>-2</sup>) Cu more reversibly and also produce a more strongly bonded state. However, completion of the deposition to form a monolayer is apparently impeded by the presence of Cl<sup>-</sup>, which is consistent with the stabilizing role of Cl<sup>-</sup> in the submonolayer state [11].

### CONCLUSION

Surface states of Pt(111) strongly depends on annealing and cooling time which was monitored using the electrochemical method. Appearance of a clear and sharp spike in the voltammogram characterises a clean surface, as revealed by subsequent effects on Cu UPD structures.

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## Electrochemical Behaviour of Zinc in Alkaline Carbonate Solutions

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### Abstract

Carbonation by atmospheric carbondioxide is a problem in affecting the performance of electrodes used in alkaline batteries. Zinc electrodes suffer loss of shelf-life, discharge capacity and cycle life when carbonates contaminate the electrolyte. Cyclic voltammetric studies on zinc in alkaline carbonate solutions revealed the formation of two types of passive films. Increase of carbonate and hydroxyl ion concentrations causes the dissolution of both these films. The enhanced dissolution is responsible for the loss of cycle life. Detailed mechanism of film-formation and dissolution is discussed.

### Introduction

Interest in the understanding of the passivation of zinc in alkaline carbonate solutions is raised, in particular with that of carbonate's deleterious effect in alkaline electrochemical cells while using zinc as a rechargeable anode. Carbonates slowly accumulate due to the absorption of atmospheric CO<sub>2</sub> or it is introduced with the tapping-up water. Excess amounts of carbonates in the electrolytes of Ni-Zn cells are known to have a detrimental influence on the cell performance; the cells become sluggish due to the decrease in conductivity [1]. However, a few studies were made on the effect of carbonates on the dissolution and passivation of zinc [2, 3, 4].

The chemical species likely to be formed by the oxidation of zinc in dilute alkali and alkaline carbonates solutions may be an amorphous form and six other crystalline forms designated as  $\alpha$ ,  $\beta_1$ ,  $\beta_2$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$ . The most stable one is  $\epsilon$ -Zn(OH)<sub>2</sub> or several basic carbonates may be formed in addition to ZnCO<sub>3</sub><sup>2-</sup> species in excess carbonate solutions. Zn<sub>5</sub>(OH)<sub>6</sub>(CO<sub>3</sub>)<sub>2</sub> is well characterised among other basic carbonates. It occurs naturally as hydrozincite among other basic carbonates. It occurs naturally as hydrozincite which consists of Zn<sup>2+</sup> in coordination with 6 and 4 in the ratio of 2:3 [5].

It is also important to establish whether the formation ZnCO<sub>3</sub> involves the direct formation of a solid state oxidation or dissolution-precipitation.