

Underpotential deposition studies of copper on glassy carbon

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Abstract. Studies on the deposition and dissolution of copper from 0.5 M sulphuric acid solutions onto glassy carbon (GC) using potential sweep techniques indicated that an additional peak occurs at higher positive potentials than the bulk stripping peak. This peak is identified as due to the stripping of underpotential deposited (UPD) copper. Results of investigations on the effect of sweep rate, deposition potential and time of deposition on the peak characteristics of UPD and bulk deposited copper are also reported.

Keywords. Underpotential deposition of copper; glassy carbon; potential sweep technique; bulk stripping peak; deposition potential.

1. Introduction

A large number of studies pertaining to the underpotential deposition (UPD) of various metals on solid electrodes have appeared in the literature for understanding the electrochemical and electrocatalytic properties of such systems (Kolb 1978). Very few studies were made on carbonaceous electrodes (Morcos 1975; Brainina *et al* 1972; Kiekens *et al* 1983) inspite of their widespread use in analytical and technical chemistry. The UPD of copper on polycrystalline graphite by using X-ray fluorescence technique (Vassos and Mark 1967) revealed that copper starts growing as three-dimensional nuclei at specific sites after the completion of a monolayer. The occurrence of an UPD peak was observed during the studies on deposition of mercury on glassy carbon (GC) by correlating the potential difference between the bulk and monolayer peak potentials to the difference in work functions of substrate and depositing metal (Kiekens *et al* 1983). However, no detailed studies have appeared on the deposition of mercury or other metals on GC. This paper reports the results of UPD studies of copper on GC by using potential sweep techniques.

2. Experimental

Experiments were carried out in 0.5 M sulphuric acid solutions prepared by diluting 98% sulphuric acid (BDH, AR) in conductivity water. Copper sulphate (BDH, AR) was added to the 0.5 M H₂SO₄ supporting electrolyte corresponding to 10⁻⁶ – 10⁻⁴ M range in UPD studies of copper. The working electrode is a polycrystalline GC (Tokai & Co., Japan) with a geometric area of 0.0707 cm². The

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electrode surface was polished with various emery papers of increasing fineness ($\frac{1}{6}$ to $\frac{4}{6}$). A bright platinum foil counter electrode and NCE (1 M KCl) as the reference electrode were employed in a three-electrode cell assembly.

3. Results and discussion

The cyclic voltammetric curve for the deposition and dissolution of 10^{-3} M copper in 0.5 M sulphuric acid solution on GC shows peaks corresponding to the bulk deposition of copper (-0.05 V) and its stripping (0.03 V). However, new peaks appear when the potential scan is limited to 0 to 0.5. The peaks at 0.4 and 0.3 V are due to deposition and dissolution, respectively.

3.1 Underpotential deposition of copper on GC

The cyclic voltammetric peak currents appearing at ~ 0.4 and 0.3 V are too small to be analyzed to elucidate the reason for their occurrence. To overcome this, sensitivity enhancement has been achieved by running anodic sweep voltammograms on samples of deposits of copper obtained by prior cathodic deposition of GC under varied conditions in all subsequent experiments. Hence, further studies were conducted by carrying out experiments in which the potential of the electrode is held at the cathodic limit for varying times followed by a potential sweep in the anodic direction to follow the anodic peaks for the above purpose. The electrodeposition of copper from x M copper sulphate ($10^{-6} \geq x \leq 10^{-4}$ M) in 0.5 M H_2SO_4 onto GC is achieved by holding the potential in the range -0.1 to -0.5 V for a certain time (t_d). Figure 1 shows typical cases wherein copper ($x = 10^{-5}$ M) was deposited at a potential (E_d) of -0.5 V for 2, 4 and 10 min, following which the deposits were anodically stripped. It is clear from the figure that there are two stripping peaks corresponding to the oxidative dissolution of copper at -0.05 V (peak 1) and 0.220 V (peak 2). Of these, peak 1 is identified as being due to the oxidation of bulk deposited copper as copper (II) (Stulikova and Vydra 1973). Peak 2 is characterised as the one arising from the stripping of underpotentially deposited copper as copper(II), as described below.

The possibility of peak 2 occurring at 0.22 V due to the oxidation of bulk deposited $\text{Cu}(0)$ to $\text{Cu}(1)$ is ruled out as $\text{Cu}(0)/\text{Cu}(1)$ peak is expected at potentials ~ 0.05 V (Stulikova and Vydra 1973). Hence the large potential shift in the positive direction to bulk deposition potential can be ascribed to the UPD of copper or the stripping of the first layer (monolayer) of deposited copper.

After examining the underpotential shifts of various metals deposited on different substrates, a relation was proposed (Kolb *et al* 1974) between the underpotential shift ($\Delta E_p = E_m - E_b$) and the difference in electronic work function ($\Delta\phi$) of the substrate and adsorbate,

$$E_p = 0.5 \Delta\phi.$$

Since, the work function of carbon and copper are 5.0 (Weast 1978) and 4.45 electron volts (Trasatti 1971), respectively, the monolayer stripping peak is expected to appear at 0.27 V higher positive values to bulk stripping peak. Hence, peak 2 with an observed shift of 0.27 V to the bulk stripping peak may presumably

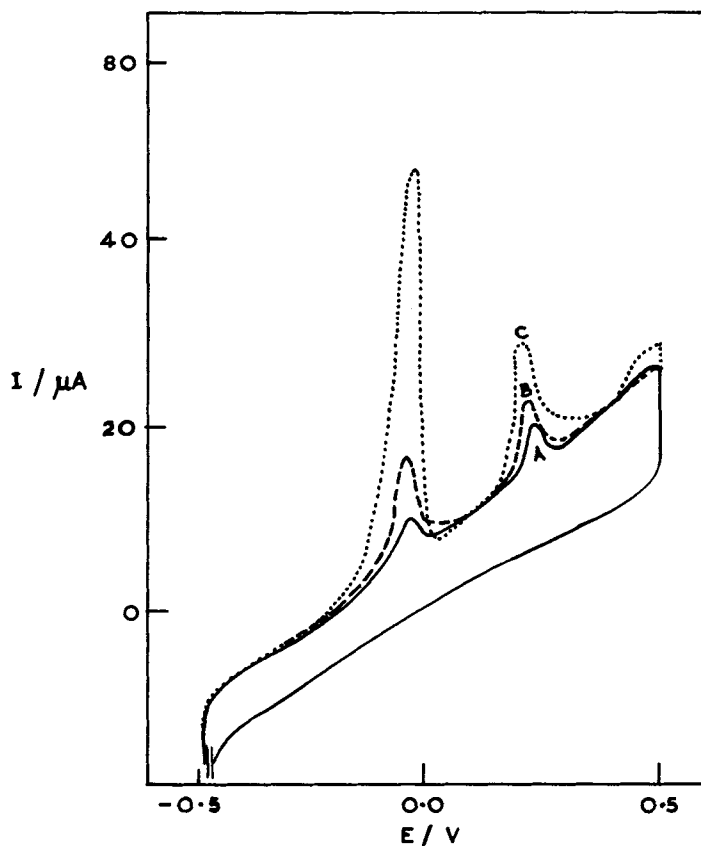


Figure 1. Potentiodynamic I - E profile at 11 mV/s obtained in 0.5 M H_2SO_4 + 10^{-5} M CuSO_4 . Anodic scan is effected after holding for 2, 4 and 10 min at -0.5 V on GC (curves A, B and C respectively).

be due to the stripping of the UPD monolayer of copper. This view is further confirmed by the fact that the charge associated with this peak corresponds to $10 \mu\text{C}$ and is varied over a range of $0.63 \mu\text{C}$ to $10 \mu\text{C}$ under all the experimental conditions studied but always less than the charge expected for stripping of the fully covered monolayer i.e. $24.5 \mu\text{C}$ for the area of the electrode employed (Bowles 1966; Furuya and Motoo 1979). Systematic studies were then carried out to understand the effects of copper concentration, time of deposition, sweep rate and deposition potential on the stripping pattern of bulk and underpotentially deposited copper.

3.2 Effect of copper concentration

Table 1 shows the stripping peak potentials of UPD and bulk deposited copper as a function of concentration of copper in solution. It is interesting to note from the table that with increase in the concentration of copper, the UPD and bulk stripping peaks are shifted in the anodic direction by around 30 mV per decade change in concentration while retaining the ΔE_p value constant. This shows that the peak potentials of UPD and bulk deposited copper obey the Nernst equation.

Table 1. Effect of concentration of copper on underpotential shifts. $(E_d = -0.5 \text{ V}; t_d = 4 \text{ min}; V = 11 \text{ mV/s}).$

Concentration of Cu^{2+} (M)	E_b	E_m	ΔE_p
5×10^{-6}	-0.08	0.190	0.270
10^{-6}	-0.065	0.200	0.265
10^{-5}	-0.050	0.220	0.270
10^{-4}	-0.025	0.245	0.270

 E values in volts (NCE); ΔE_p values in volts.**Table 2.** Effect of time of deposition on underpotential shifts and on charges associated with UPD and bulk stripping peaks. $([\text{Cu}^{2+}] = 10^{-5} \text{ M}; E_d = -0.50 \text{ V}; V = 11 \text{ mV/s}).$

t_d (min)	E_m	E_b	ΔE_p	Q_m	Q_b
2	0.220	-0.050	0.270	2.10	2.05
4	0.220	-0.050	0.270	4.00	3.85
6	0.220	-0.045	0.265	8.00	7.90
8	0.230	-0.035	0.265	10.00	9.90
10	0.230	-0.040	0.270	10.40	34.30

 E values in volts (NCE); ΔE_p values in volts; Q values in μ Coulombs.

3.3 Effect of time of deposition

The effect of time of deposition on electrooxidation charges of UPD and bulk deposited copper and their stripping peak potentials was then carried out and results are furnished in table 2. From table 2, it is clear that the charges associated with UPD and bulk deposition of copper increase with increase in time of deposition as per expectations. On the other hand, the increase of time of deposition has no appreciable effect on UPD peak potential (E_m) and bulk peak potential (E_b). It is also significant to note that the underpotential shift (ΔE_p) is practically unaltered (cf. figure 1 and table 2).

3.4 Effect of sweep rate

Typical results obtained during the sweep rate variation studies on the stripping behaviour of underpotential and bulk deposited copper are shown in table 3. The increase in sweep rate from 6 to 270 mV/s shifts both monolayer and bulk stripping peak potentials towards more positive potentials while retaining a constant ΔE_p value, as observed in the case of the deposition of thallium onto silver (Kolb 1978). The charges corresponding to the stripping of the monolayer and bulk deposited copper are practically constant over the entire sweep rate range studied suggesting the complete stripping of both the UPD and bulk deposits.

Table 3. Effect of sweep rate on underpotential shifts and charges associated with UPD and bulk stripping peaks.
 ($[Cu^{2+}] = 10^{-5}M$; $E_d = -0.50V$; $t_d = 4$ min).

Sweep rate (mV/s)	E_m	E_b	ΔE_p	Q_m	Q_b
6	0.21	-0.06	0.270	4.00	3.85
11	0.22	-0.05	0.270	4.00	3.90
30	0.22	-0.05	0.270	3.95	4.00
50	0.23	-0.03	0.260	4.00	4.00
100	0.24	-0.02	0.260	4.00	3.95
188	0.25	-0.015	0.265	3.90	3.95
270	0.26	-0.005	0.265	4.00	3.95

E values in volts (NCE); ΔE_p values in volts; Q values in μ Coulombs.

Table 4. Effect of deposition potential on stripping characteristics of UPD and bulk stripping peaks.
 ($[Cu^{2+}] = 10^{-5}M$; $t_d = 4$ min; $V = 11$ mV/s).

E_d (V vs NCE)	E_m	E_b	ΔE_p	Q_m	Q_b
-0.20	—	—	—	—	—
-0.25	—	—	—	—	—
-0.30	0.22	-0.050	0.270	0.63	0.60
-0.35	0.22	-0.045	0.265	1.88	1.90
-0.40	0.22	-0.050	0.270	3.25	3.25
-0.45	0.22	-0.050	0.270	2.88	2.85
-0.50	0.22	-0.050	0.270	4.00	4.00

E values in volts (NCE); ΔE_p values in volts; Q values in μ Coulombs.

3.5 Effect of deposition potential

The dissolution behaviour of copper was studied as a function of deposition potential (E_d) by holding the potential in the range -0.25 to -0.5 V in steps of 0.05 V for 4 min in 10^{-5} M copper sulphate in 0.5 M sulphuric acid solution. As is clear from table 4, the UPD and bulk deposition of copper occur only when E_d is maintained at potentials more negative than -0.3 V. With change of E_d from -0.3 to -0.5 V, the charges corresponding to the stripping of UPD and bulk deposited copper increase while retaining the expected constancy for E_m , E_b and E_p values.

4. Conclusions

All the above described results clearly establish the formation of UPD of copper with less than monolayer coverages on glassy carbon. The potentials of stripping peaks of UPD and bulk deposited copper and the underpotential shift remain unaltered on change of time of deposition or deposition potential. On the other hand a shift of the E_m and E_b to more positive values while retaining ΔE_p value as

constant is noticed with increase in concentration of copper in solution and sweep rate.

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