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Order and disorder in electrochemical deposits of copper on graphite

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Abstract

Electrochemical deposition of copper on highly oriented pyrolytic graphite (HOPG) from aqueous 0.05M H₂SO₄ and 0.1M NaCl media has been studied using cyclic voltammogram (CV), single-pulse potentiostatic current vs. time (*i* vs. *t*) transient, and in situ scanning tunneling microscopic (STM) techniques. At potentials positive to the Nernst reversible potential, Cu(II) ions tend to adsorb on the HOPG surface. In the NaCl medium, the adsorbed Cu(II) ions form a stable, ordered layer. In this medium, the *i* vs. *t* transients indicate that the kinetics of bulk deposition is limited by planar diffusion, and the STM images reveal well-ordered bulk deposits. In contrast, in the 0.05M H₂SO₄ medium, the copper ions, even if adsorbed, do not form any stable or ordered layer on the HOPG surface. In this medium, the bulk deposition is a nucleated process, whose kinetics is limited by spherical diffusion, and the bulk deposit is disordered. It is inferred from these observations that the presence of an adsorbed and ordered layer of Cu(II) ions, prior to the onset of the bulk deposition, is responsible for the formation of ordered bulk deposits.

Keywords: Copper; Diffusion and migration; Electrochemical methods; Graphite; Growth; Nucleation; Scanning tunneling microscopy; Surface structure

1. Introduction

The two fundamental steps involved in the electrodeposition of a metal on a foreign substrate are nucleation and growth. Substrates such as oxide-covered platinum have pre-existing nucleation centers [1], where the foreign metal atoms deposit and grow. On substrates like mercury, anything that deposits must first generate its own nuclei before it grows [2]. In both cases, the nuclei have to reach a critical size before they become stable; nuclei that do

not reach the critical size will dissolve and disappear [3]. If the rate of nucleation is smaller than the rate of growth, then the growth will occur from a limited number of nuclei that are available, leading to disordered deposits [4]. In contrast, as the number of viable nuclei increases, the growth process is likely to be less disordered, following the order set by the nuclei. In an extreme case, if the entire surface of the substrate is completely covered by well-ordered nuclei, before the onset of growth, the deposit will also be well ordered. The nucleation process as the rate-limiting step on a defect-free single crystal surface was impressively demonstrated by Budevski and co-workers [5].

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Another step in the deposition process, apart from nucleation and growth, is diffusion [6]. The diffusion process has received ever-increasing attention, due to its potential role in the formation of dendrites and other diffusion-limited aggregates. A comprehensive review of early stages of modern-day concepts of metal deposition is provided by Fleischmann and Thirsk [7]. Three other articles, by Kolb [8], Juttner and Lorenz [9], and Adzic [10], cover more recent work on electrodeposition.

Apart from the three physical processes of nucleation, growth, and diffusion, metal deposition processes also involve two or three chemical steps. They are adsorption, charge transfer, and, in cases where the substrate metal is different from the one that is deposited, underpotential deposition (UPD). The UPD process involves either a partial or a complete charge transfer reaction, and occurs at electrode potentials that are much more positive than the Nernst reversible potential for the metal deposition reaction [8–10].

On graphite bulk deposition is not necessarily preceded by a UPD step [11], although cyclic voltammograms with peaks at potentials positive to the Nernst reversible potentials have been reported in some cases [12,13]. Such peaks may have been caused by adsorption of metal ions; unlike the UPD process, however, the adsorption process may not have been associated with transfer of charge between the adsorbed ions and the electrode. Whether due to adsorption with or without charge transfer, the order and stability of the first layer is critical for anything that deposits over it. There have been several recent studies on the effect of the UPD layer on the bulk deposit [14], but none with regard to adsorbed metal ions with no charge transfer. In the work reported here, we deposited copper on highly oriented pyrolytic graphite (HOPG) from aqueous electrolytes of two different ionic compositions, namely, 0.05M H_2SO_4 and 0.1M NaCl, both containing Cu(II) ions. We found no evidence of UPD in either media. However, before the onset of bulk deposition, copper ions appear to form a stable adsorbed layer in the NaCl medium, but not in H_2SO_4 . The results reported here describe how the adsorption step affects the kinetics and morphology of bulk deposition.

We employed cyclic voltammetry (CV), potentiostatic single-pulse current–time (i vs. t) transients,

and in situ scanning tunneling microscopy (STM) to study the copper deposition process on HOPG. The i vs. t transients data provided information on the kinetics and mechanism of bulk deposition; primary evidence regarding the presence or absence of nucleation was obtained from this data. Charge densities were calculated by integrating i vs. t transients. The in situ STM was used to identify the presence of adsorbed ions on the HOPG/electrolyte interface, and to image the morphology of the bulk deposit. The CV measurements were used only for qualitative identification of electrode potentials where various processes such as adsorption and deposition commenced or terminated.

2. Experimental procedure

All experiments were carried out at $21 \pm 1^\circ\text{C}$ from unbuffered aqueous solutions of 0.1M NaCl or 0.05M H_2SO_4 containing cupric ions. The Cu(II) ion concentration was kept at 0.2mM for the STM experiments, and at 1.0mM for all others. All experiments were conducted in a small Kel–F cell (electrolyte volume ~ 0.5 ml), and the electrolyte was not deaerated [15]. In all cases, “blank” experiments were conducted using the background electrolytes (in the absence of dissolved copper ions). The HOPG surface (0.283 cm^2 area) was prepared following a

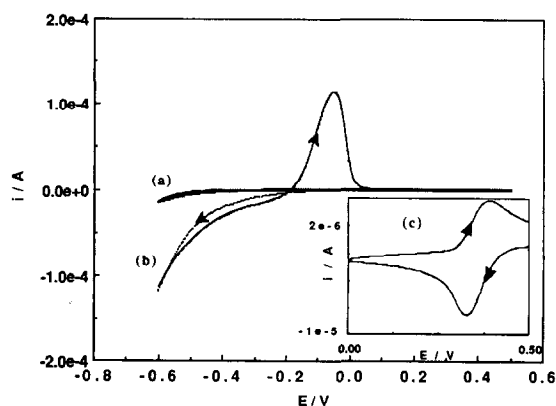


Fig. 1. CV of HOPG in aqueous electrolytes containing: (a) 0.05M H_2SO_4 ; (b) 0.05M H_2SO_4 + 1mM Cu(II); and (c) solution (b) with a higher amplification in the current axis. The cathodic current in the CV was taken as negative, scan direction was +0.70 to -0.40 to +0.70 V, and scan rate was 20 mV/s.

procedure described in our earlier work [16]. In the 0.1M NaCl medium, an Ag/AgCl wire in direct contact with the electrolyte was used as the reference electrode. In the 0.05M H_2SO_4 electrolyte, a silver wire was used as a quasi-reference electrode. The potentials reported in this work were converted to the Ag/AgCl, 0.1M NaCl scale for uniformity. A platinum wire was used as the auxiliary electrode in both electrolytes.

Cyclic voltammetry was used to identify the potential regions of ionic adsorption and bulk deposition reactions. The i vs. t transients were collected under potentiostatic control (EG & G PAR, Model 273) using a programmable waveform generator (Stanford Research Systems, Model DS345) and an FFT analyzer (Advantest R92211C with two 16-bit A/D converters) at the rate of 10 to 100 ms per data point. The working electrode was pulsed from 0.50 V to more negative potentials, which ranged from 0.40 to -1.0 V in intervals of 5 to 50 mV. During the course of the experiment, on several occasions, the pulsing potential was set to 0.40 V to verify the reproducibility of the transient at that potential. Any lack of reproducibility was taken as an indication of a modified surface, and the surface was cleaved again and the experiments repeated. The length of

the transients was set from 40 ms (double-layer region) to 8 s (faradaic region); the exact periods were decided after checking the transients for possible slow or fast transitions that might be associated with adsorption or other related interfacial processes. No filter was used while collecting the transients. Following each pulse, the potential was returned to $+0.50$ V for 1 min before applying the next pulse.

The interface was imaged using a Nanoscope II ECSTM (in situ STM) in the constant-height mode with a scan rate of 20 to 31 Hz. The STM tip (Pt–20%Ir) was electrochemically polished and insulated as described elsewhere [16]. The Z-offset distance was kept either at 1 nm (in the double-layer region) or at 35 nm (in the bulk-deposition region), and the tunneling current at 1 nA. Before adding the electrolyte, particular care was taken to polarize the HOPG electrode to $+0.50$ V in order to avoid accidental deposition of Cu without the potential control. The interface was imaged by STM first at $+0.50$ V. While imaging the interface, the potential was changed in steps of 50 mV toward -0.50 V. This procedure enabled us to image the interface before the onset of adsorption process, during the adsorption process, and during the bulk deposition process.

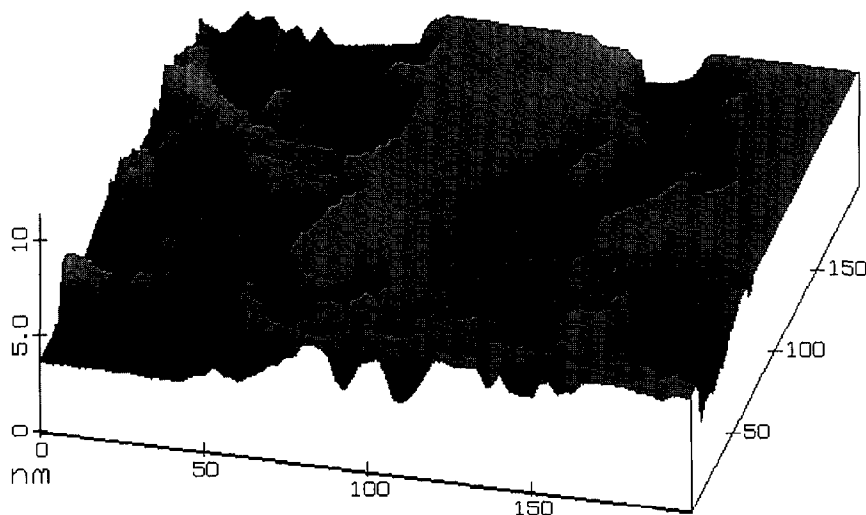


Fig. 2. An unfiltered STM image of the HOPG/aqueous electrolyte interface containing 1mM Cu(II) + 0.05M H_2SO_4 showing the bulk deposit of copper at -0.50 V. The “flat” surfaces are artifacts caused by the saturation of the tunneling current.

3. Results

The CV and in situ STM results are combined and presented as one set, thereby enabling the potential regions in the CV and the capacitance data to act as signposts to highlight the STM images. The i vs. t transient data are presented separately. The results are categorized based on the deposition of Cu from (i) 0.05M H_2SO_4 , and (ii) 0.1M NaCl.

3.1. CV and in situ STM data

HOPG / Cu(II) in 0.05M sulfuric acid: The cyclic voltammograms for the HOPG/0.05M H_2SO_4 system with and without Cu(II) ions are shown in Fig. 1. The peak related to the bulk deposition of copper can be seen around -0.40 V, with the cathodic and the anodic currents forming a large “loop” similar to those reported earlier [12,17]. The presence of the loop indicates that the bulk deposition is a nucleated process. A cyclic voltammogram taken in presence of Cu(II) ions, with a higher sensitivity for the current (Fig. 1c), shows yet another peak around 0.5 V. This is much more positive to -0.03 V, the Nernst reversible potential (E_{Cu}^{r}), for the reaction $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$ ($[\text{Cu}^{2+}] = 1.0\text{mM}$). Furthermore, no peak was observed at 0.50 V in the absence of Cu(II) ions in the electrolyte, suggesting possible adsorption of the Cu(II) ions on the HOPG surface.

Over most of the potential region between $+0.50$ and 0.0 V, STM images of the interface resembled the graphite surface. Even if Cu(II) ions were ad-

sorbed at the HOPG surface as suggested by results from the CV (Fig. 1c), they were not visible in STM images. At bulk deposition potentials (negative of -0.40 V), STM images showed a rough and disordered surface, with corrugations on the order of tens of nanometers. An example of this shown in Fig. 2 reveals nuclei of several different sizes growing simultaneously. The “flat” regions in some of the larger nuclei seen in this figure are artifacts caused by the saturation of the tunneling current, which was easily avoided by lifting the STM tip to 30 nm or above. Furthermore, when the potential was changed from -0.50 to $+0.60$ V (where copper deposits are expected to dissolve), these crystallites stayed on the surface for several minutes. Sequential images of this surface (not shown) confirmed a relatively slow dissolution process.

HOPG / Cu(II) in 0.1M sodium chloride: The cyclic voltammograms for the HOPG/0.1M NaCl system with and without Cu(II) ions are shown in Fig. 3. In Fig. 3b two deposition peaks can be seen during the cathodic scan, one at Ia (-0.175 V) and the other at IIa (-0.38 V). The corresponding dissolution peaks occur at 0.175 V (Ib) and -0.11 V (IIb), respectively. Note that E_{Cu}^{r} for the Cu(II) reduction reaction is -0.03 V, suggesting that the peak at Ia is likely due to the reduction of Cu(II) ions. The separation between the peaks at Ia and IIa suggests that the deposition of Cu occurred in two distinct layers. The onset of Cu(II) reduction at potentials negative to -0.03 V was further established through i vs. t transients (see Section 3.2).

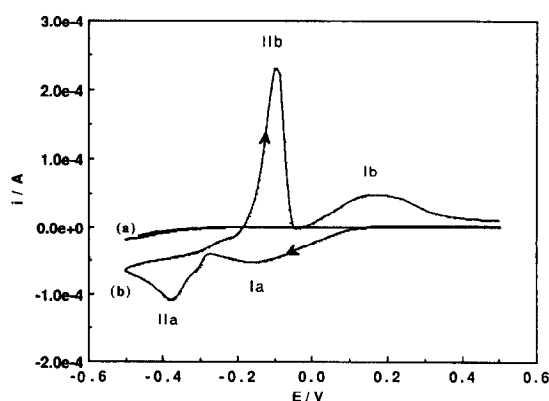


Fig. 3. CV of HOPG in aqueous electrolytes containing: (a) 0.10M NaCl; and (b) 0.10M NaCl + 1mM Cu(II). The cathodic current in the CV was taken as negative, scan direction was $+0.50$ to -0.50 to $+0.50$ V, and scan rate was 20 mV/s.

Also, the onset of the peak Ia occurs at +0.10 V, which is much more positive to E_{Cu}^{r} , suggesting possible adsorption of Cu(II) ions prior to the charge transfer reaction.

The in situ STM images of the HOPG/electrolyte interface (Fig. 4a) obtained between 0.45 and 0.25 V are close to those reported for the STM images of graphite atoms in the HOPG surface (0.246 nm, 60°)

[21]. At potentials negative to 0.25 V, a partially ordered adatom structure began to evolve, which became fully ordered around 0.0 V (Figs. 4b–4d). Since Cu(II) cannot be reduced to Cu(0) at potentials positive to E_{Cu}^{r} (–0.03 V), the ordered images seen in Figs. 4b and 4c can only be due to adsorbed and ordered copper ions. This ordered layer could be imaged even at potentials more negative than –0.03

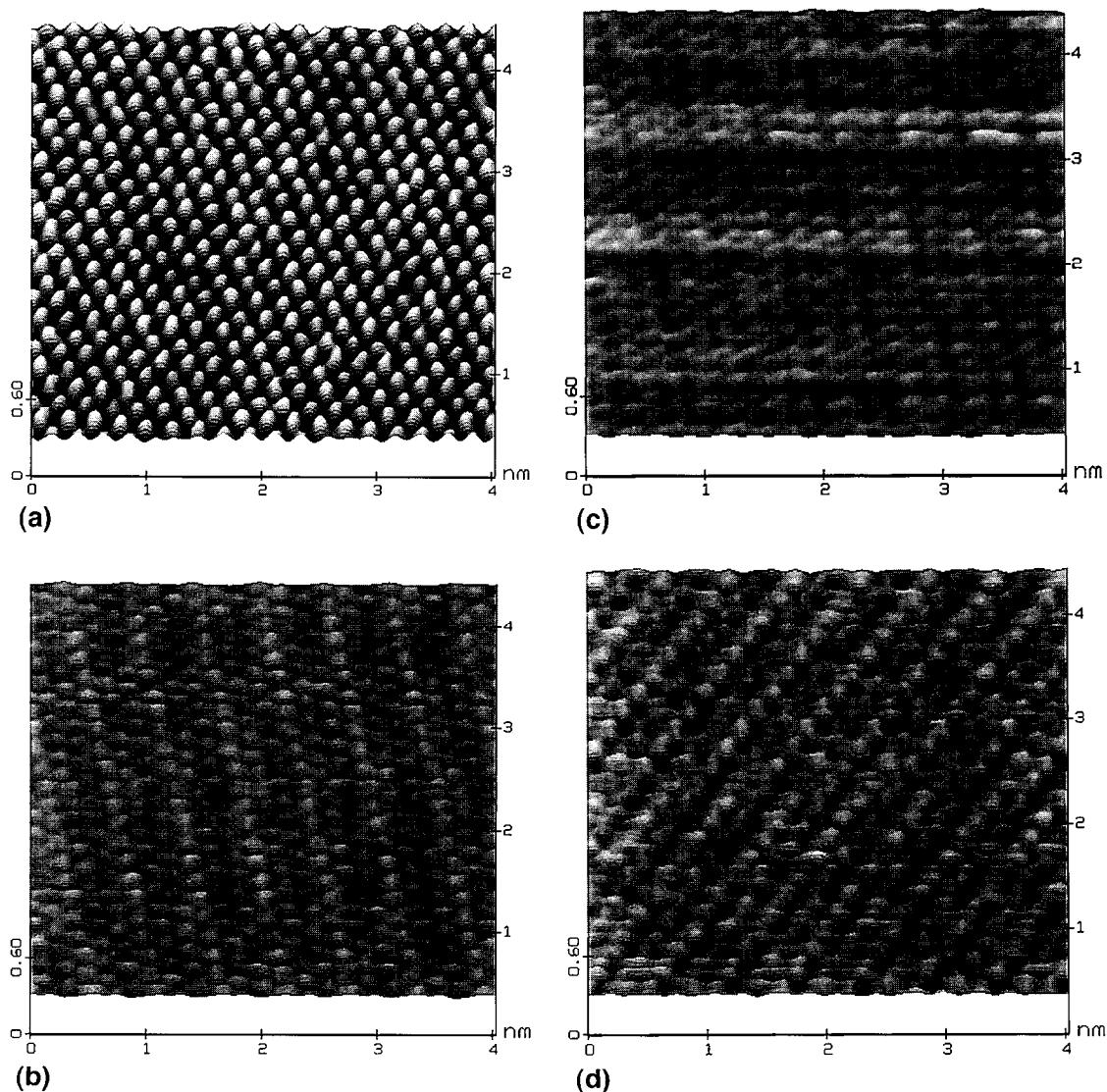


Fig. 4. The STM images of the HOPG/aqueous electrolyte interface containing 1.0mM Cu(II) + 0.1M NaCl at: (a) +0.40 V; (b) 0.05 V; (c) 0.0 V; and (d) –0.05 V. Using the FILTER/TWOFIT command in Nanoscope II, these four images were fitted to 2D FFT and the D. C. components filtered. Image (a) shows a graphite surface. Images (b)–(d) show an overlayer on the graphite surface, with a vertical column at every 0.57 nm. This overlayer was absent in the absence of Cu(II) ions in the electrolyte.

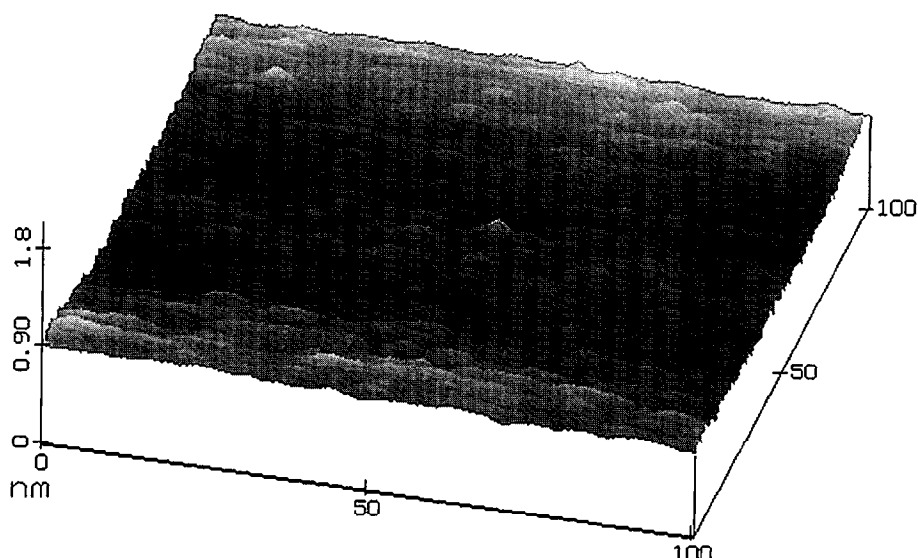


Fig. 5. An unfiltered STM image of the HOPG/aqueous electrolyte interface containing 1mM Cu(II) + 0.1M NaCl showing the bulk deposit of copper at -0.40 V.

V, where the bulk deposition was in progress. An example of such an image, taken at -0.05 V, is shown in Figs. 4d. To make sure that images obtained at potentials negative to 0.25 V were not artifacts, the in situ STM experiments were conducted on several freshly cleaved HOPG surfaces using 0.1 M NaCl with and without Cu(II) ions. In the absence of Cu(II) ions, the images resembled the graphite surface at all potentials. Only with copper ions in the solution could we reproduce images such as those shown in Fig. 4b–4d. Large-scale in situ STM images of the interface, taken while the bulk deposition reaction was in progress, showed a fairly smooth surface. An example of such an image, taken at -0.40 V, is shown in Fig. 5.

3.2. Current versus time transient data

Current vs. time (i vs. t) transients, based on potentiostatic single-pulse perturbations, were collected over the entire range of potentials where CV and STM data showed the possibility of either adsorption or (faradaic) charge transfer reaction due to bulk deposition. The i vs. t transients were integrated to get the total charge, enabling us to distinguish adsorption from either partial or total-charge transfer reactions. In the bulk deposition region, i vs.

t transients also served to distinguish planar from spherical diffusion.

HOPG / Cu(II) in sulfuric acid: Fig. 6 shows the charge vs. potential (q vs. E) for the HOPG/ 0.05 M H_2SO_4 system with 0 and 1.0 mM Cu(II). These charges were computed from the i vs. t transient by fitting them to a weighted least-square equation [18] of the form $\ln(i) = a + bt$, where a and b are constants. The q values shown in this figure could not be reproduced better than $\pm 5\%$ due to variations in

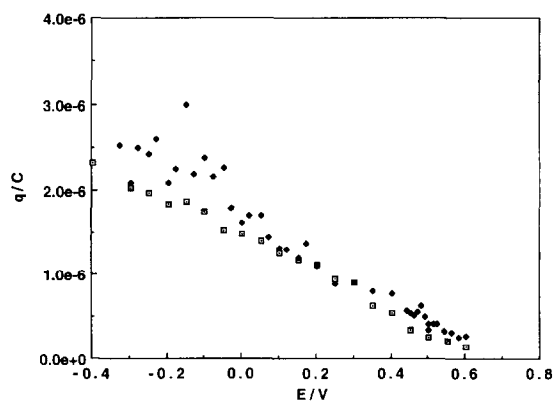


Fig. 6. Charge (q) vs. potential (E) in the double-layer region for the HOPG/aqueous electrolyte interface containing: (□) 0.05 M H_2SO_4 ; and (◆) 1.0 mM Cu(II) + 0.05 M H_2SO_4 .

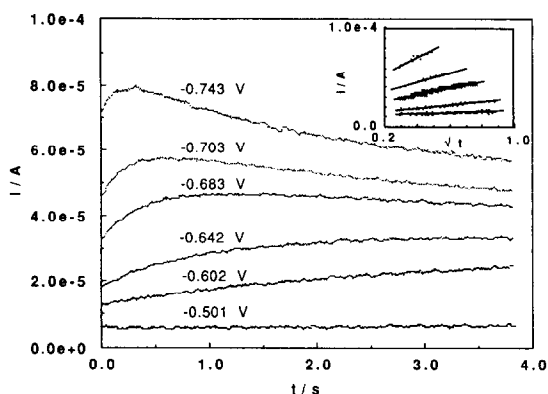


Fig. 7. Current (i) vs. time (t) transients obtained by potentiostatic single-pulse techniques for the HOPG/aqueous electrolyte interface containing 0.5mM Cu(II) + 0.05M H_2SO_4 , from a starting potential of 0.50 V. The pulsing potentials are indicated over each transient. The inset shows the i vs. $t^{0.5}$ plots for all the transients, except for the one at -0.501 V.

the surface area of the HOPG electrode between experiments. Note that between 0.60 and 0.0 V the charge varied linearly as a function of potential, and the presence or absence of Cu(II) in the electrolyte made very little difference in its values. In other words, in that potential range, all these charges were associated only with the charging of the double layer. The deviations in q at potentials more negative than -0.10 V are due to the reduction of Cu(II) ions (see Fig. 1b for the corresponding CV). The i vs. t transients obtained at and negative to -0.50 V are shown in Fig. 7. These transients are similar to

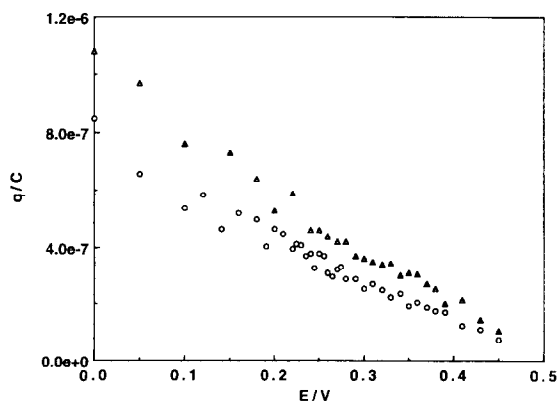


Fig. 8. Charge (q) vs. potential (E) in the double-layer region for the HOPG/aqueous electrolyte interface containing: (Δ) 0.10M NaCl; and ($\circ$) 1.0mM Cu(II) + 0.10M NaCl.

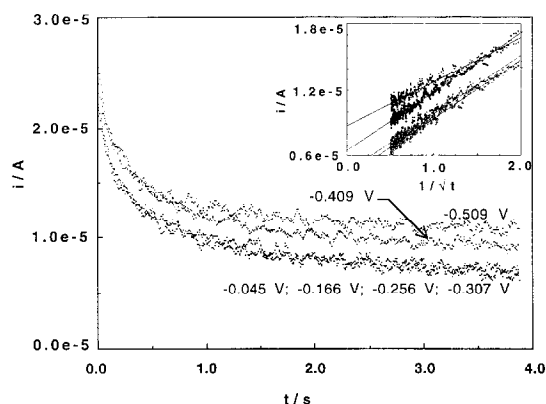


Fig. 9. Current (i) vs. time (t) transients obtained by potentiostatic single-pulse techniques for the HOPG/aqueous electrolyte interface containing 1.0mM Cu(II) + 0.10M NaCl from a starting potential of 0.50 V. The pulsing potentials are indicated over each transient. The inset shows the i vs. $t^{-0.5}$ plots.

those reported by Hills et al. for systems that undergo electrochemical nucleation in which the nucleation process is limited by spherical diffusion during the initial growth stages of the nuclei [19] (the rising part of the transients in Fig. 7). The latter part of these transients follows a semi-infinite linear diffusion to a planar surface.

HOPG / Cu(II) in sodium chloride: Fig. 8 shows the charge vs. potential (q vs. E) for an HOPG/0.1M NaCl system with 0 and 1.0mM Cu(II). As in the H_2SO_4 case, before the onset of bulk deposition (potentials positive to 0.0 V), q varied linearly with potential. The presence or absence of Cu(II) in the solution did not make much difference in the q values. Thus, in the 0.4 to 0.0 V range, the currents were only associated with the charging of the double layer; there is no evidence of transfer of these charges between the adsorbed ions and the HOPG electrode. The i vs. t transients for potentials negative of -0.045 V are shown in Fig. 9. Unlike the transients obtained in the H_2SO_4 medium (Fig. 7), these currents did not show any increase during the initial stages of the transient. They all appear to follow a semi-infinite linear diffusion equation [6,20]. Furthermore, at pulsing potentials between -0.045 and -0.31 V, the transients very nearly overlapped, accounting for charge values ranging from $1.14 \times 10^{-4} \text{ C} \cdot \text{cm}^{-2}$ to $1.32 \times 10^{-4} \text{ C} \cdot \text{cm}^{-2}$. In compar-

ison, for pulsing potentials negative of -0.40 V, the current and charge values were higher.

4. Discussion

The main focus of this discussion is on the influence of the adsorbed species on the kinetics and morphology of bulk deposits of copper on HOPG. Throughout the experiments, the metal deposited (copper) and the substrate used (HOPG) were the same. The parameter that varied and that was responsible for the observed differences in adsorption and deposition was the composition of the electrolyte. The CV, STM, and i vs. t characteristics were dependent on the composition of the electrolyte. However, within a given medium, the data obtained from the different techniques were consistent and complimentary.

The peaks seen in the cyclic voltammograms (Fig. 1 and Fig. 3) at potentials positive to the Nernst reversible potential, E_{Cu}^r , suggest that the Cu(II) ions may be adsorbed on the HOPG surface. However, there was no evidence of transfer of electric charge from the electrode to the Cu(II) ions (see Fig. 6 and Fig. 8). In other words, even if adsorbed, Cu(II) ions did not undergo underpotential deposition, where UPD is defined as a process associated with transfer of charge from the electrode to the ion at potentials positive to E_{Cu}^r . Further, in the H_2SO_4 medium, STM images of the electrode surface mostly resembled that of the graphite surface, suggesting that even if the Cu(II) ions were adsorbed, they were not permanently held on the surface. In the NaCl medium, STM images taken at potentials positive to E_{Cu}^r revealed stable structures (Figs. 4b and 4c), suggesting that the adsorbed ions were permanently held at the interface.

Note that in the NaCl medium, copper ions can exist as a complex with Cl^- , forming CuCl^+ or CuCl_2 . The images in Figs. 4b and 4c may correspond to CuCl^+ or CuCl_2 rather than Cu^{2+} . It is also possible that Cl^- ions may have co-adsorbed with the copper ions. However, it is difficult to confirm these possibilities from the STM data. The adsorbed species seen in these images are unlikely to be Cl^- ions (not associated with copper ions) since in situ STM images of the HOPG/electrolyte interface ob-

tained in pure NaCl medium (not shown) corresponded to a bare graphite surface. In all our discussions, we assumed that the images seen in Figs. 4b and 4c resulted from adsorbed Cu(II) ions.

The CV provided qualitative evidence regarding the nucleation-controlled deposition. The “loop” in the current seen in Fig. 1a, during the deposition of copper in the H_2SO_4 medium, indicates a nucleation-controlled process, while its absence in the NaCl medium indicates that the deposition process was not limited by nucleation.

Quantitative information regarding the kinetics of the deposition can be obtained from the i vs. t transients. In the NaCl medium, bulk deposition started at -0.045 V. At all potentials more negative to -0.045 V, these transients (Fig. 9) were potential-independent and followed a $1/\sqrt{t}$ behavior. When fitted to a planar diffusion equation [6,20],

$$i(t) = nFAcD^{0.5}/\pi^{0.5}t^{0.5}, \quad (1)$$

where nF is the molar charge of the depositing species, A is the area of the electrode, c is its concentration in $\text{mol} \cdot \text{cm}^{-3}$, and D is its diffusion coefficient, the transients in Fig. 9 (-0.045 , -0.166 , -0.256 and -0.307 V) yielded a D value of $1.288 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Since the basal plane of the HOPG is an ideal planar surface (except for steps between the basal planes that usually form during cleaving), the observed planar diffusion cannot be a total surprise. Further, the constancy of the charge (1.14×10^{-4} to $1.32 \times 10^{-4} \text{ C} \cdot \text{cm}^{-2}$) in the -0.045 to -0.31 V range suggests a constant amount of copper deposition in this range. With increase in overpotential (pulsing potential more negative than -0.4 V), the current values of the transients began to increase (for example, see transients at -0.409 and -0.509 V in Fig. 9), although they were still limited by semi-infinite linear diffusion. This may have been due to an increased surface area resulting from some degree of disorder in the deposit at those high overpotentials, but we cannot fully explain this behavior.

It is interesting that when the base electrolyte was changed from NaCl to H_2SO_4 , the kinetics of Cu deposition on HOPG switched from planar diffusion to spherical diffusion (Fig. 7). The behavior of the transients in Fig. 7 are consistent with the observed “loop” in the CV in Fig. 1a, and both suggest that

the copper deposition from H_2SO_4 medium is a nucleated process. A comprehensive theory of nucleation and growth controlled by spherical diffusion was developed and verified through the deposition of silver on platinum, silver on graphite, and mercury on graphite by Hills et al. [19]. They showed that

$$i(t) = nF\pi A(2Dc)^{3/2} M^{1/2} N t^{1/2} / \rho^{1/2}, \quad (2)$$

where M is the molecular weight and ρ the density of the metal that is being deposited, and N is the nucleation density or number of nucleation sites per unit area on the graphite surface. nF , A and c have the same definitions as under Eq. (1). Eq. (2) suggests an increasing current with time. As may be seen from Fig. 7, the rising part of the currents follows a $t^{0.5}$ behavior. Hills et al. explained the potential dependency of these transients as resulting from an increase in the number of nucleation sites that become active with an increase in potential. The transients in Fig. 7 were fitted to Eq. (2), and a series of N values were calculated as: $0.34 \times 10^6 \text{ cm}^{-2}$ at -0.682 V , $1.95 \times 10^6 \text{ cm}^{-2}$ at -0.763 V , and $4.28 \times 10^6 \text{ cm}^{-2}$ at -0.823 V ; the required D ($1.13 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) was obtained by fitting the latter part of a transient at -1.0 V to Eq. (1).

The observed spherical diffusion on a planar HOPG surface can be explained using the simple model in Fig. 10a. Here, the small discs indicate the viable nuclei growing by the addition of atoms along the perimeter as well as on the top surface of the nuclei. If the growth process is diffusion limited, it

can have the appearance of spherical diffusion [19]. Note that spherical diffusion does not necessarily refer to the morphology of individual nuclei, but to the hemispherical symmetry of the diffusion zones around each nucleus. At longer times, when the spherical zones overlap, the diffusion process changes from spherical to planar. This is the most probable scenario for the deposition of copper from the H_2SO_4 medium.

The model used in Fig. 10b helps explain the i vs. t transients obtained in the NaCl medium. Unlike the H_2SO_4 case, there was no rise in the current or maxima in the transients, suggesting the absence of spherical diffusion. In the NaCl case, since the adsorbed Cu(II) ions covered the surface almost uniformly (Figs. 4b and 4c), they were likely to have acted as nucleation centers. Following the model in Fig. 10b, these nuclei were coalesced prior to the bulk deposition, and the diffusion during growth was purely planar.

5. Conclusions

In this work, we have demonstrated that a stable layer of adsorbed Cu(II) ions is an important precursor to a well-ordered bulk deposit of Cu on HOPG. In situ STM images showed that the order and stability found in the adsorbed layer depended on the composition of the electrolyte. In the H_2SO_4 medium, even if Cu(II) ions were adsorbed, they were not permanently held on the HOPG surface. Consequently, once bulk deposition commenced, its growth occurred from a limited number of nucleation sites, which, when coalesced, formed a highly disordered three-dimensional layer. Cu(II) ions adsorbed from the NaCl medium were more stable. Potentiostatic single-pulse current–time (i vs. t) transients showed that in the H_2SO_4 medium the kinetics of the bulk deposition of Cu was limited by spherical diffusion, and in the NaCl medium it was limited by planar diffusion.

Note that the HOPG surface was prepared by cleaving, which is known to generate monoatomic steps on the surface. Those steps, in principle, could have acted as nucleation centers for the bulk deposition of copper. However, the contrasting results obtained from the H_2SO_4 and the NaCl media indicate

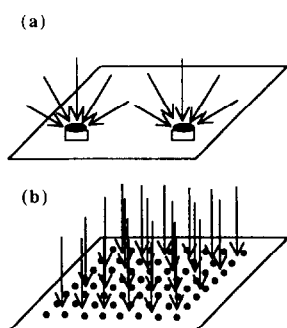


Fig. 10. Schematic representation of the growth of: (a) a small number of nuclei set far apart from each other, giving rise to spherical diffusion; and (b) a large number of nuclei set very close to each other giving rise to planar diffusion. The arrows indicate the direction of diffusion.

that those steps did not alter the kinetics or the mechanism of bulk deposition. Similarly, the presence or absence of oxygen in the electrolyte did not alter the spherical (in H_2SO_4 medium) and linear (in NaCl medium) diffusion behaviors of the Cu(II) ions [15]. Thus, oxygen in the electrolyte cannot have been responsible for the order and disorder found in the bulk deposits of copper.

In the recent past, there have been several reports describing the effect of UPD layers on bulk deposits on foreign metal substrates [14]. HOPG is a unique substrate in the sense that although it is a foreign substrate, there is no UPD layer formation on it, as shown by us in this work as well as by others in earlier reports [11]. However, metal ions can get adsorbed to the surface before the onset of the bulk deposition, without any transfer of charge between them and the substrate. The present study demonstrates how the adsorbed metal ions can bring about a dramatic change both in the kinetics and the morphology of the bulk deposit.

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