Nucleation and growth of zinc on a glassy carbon electrode from a zincate solution

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NUCLEATION AND GROWTH OF ZINC ON A GLASSY CARBON ELECTRODE FROM A ZINCATE SOLUTION

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Abstract—The nucleation and growth of zinc on glassy carbon from a zincate solution, 6 M KOH + 0.25 M $K_2Zn(OH)_4$, was studied. Interaction effects between the electrode surface and deposited zinc were determined with voltammetric techniques. Current transients during growth at several potentials were compared with those predicted by nucleation and growth models. From these experiments it was concluded that deposition occurs *via* instantaneous nucleation following a 3-D-hemispherical growth model. Morphology, particle size and number of particles were investigated with scanning electron microscopy and prepulse techniques.

Key words: zinc deposition, glassy carbon, nucleation, morphology, voltammetry.

1. INTRODUCTION

The electrodeposition of zinc has been investigated from alkaline[1–4] as well as from acid electrolytes [4–8]. On metal substrates such as silver[1, 2], copper [3], gold[3, 8] and platinum[8], underpotential deposition (*upd*) is noticed, resulting in the formation of a well adhering monolayer or a new alloy phase. For all these materials the work function is higher than for zinc[3, 9, 10].

On inert materials such as glassy carbon[5, 6] and graphite[8, 11] but also on magnesium, tantalum and titanium[11] a crystallization overpotential (*cop*) has been observed; however, one investigation[12] presents a voltammogram of a graphite electrode in a zincate electrolyte without *cop* or *upd* features.

For deposition on a zinc electrode[3, 13] neither *cop* nor *upd* was observed voltammetrically. On zinc and on foreign substrates on which *upd* occurs, the further growth of zinc is mainly epitaxial. It is supposed[3, 9, 12] that on substrate materials with lower work functions than zinc, nucleation is inhibited and *cop* will be observed. This results in a granular deposit which adheres poorly[8], because the growth of nuclei is faster than the formation rate of new nuclei on this type of surface. It is also proposed that nucleation theories[14, 15] are particularly valid for *cop* cases, because no monolayer or new metal phases are formed. The further growth of the nuclei according to a 3-D model is described in the literature[14, 16]. The aim of this study is to investigate nucleation and further deposition of zinc on glassy carbon from an alkaline electrolyte with different techniques. Voltammetry was used to establish *upd* or *cop* behavior; potential pulses were applied for studying the growth model. The morphology and the number of particles were investigated with scanning electron microscopy.

2. EXPERIMENTAL

A standard three-compartment electrochemical cell with a volume of 100 cm³ was used for the experiments. The cell was filled with an alkaline electrolyte of 6 M KOH and 0.25 M $K_2Zn(OH)_4$ prepared by electrochemical dissolution of zinc powder. The zincate concentrations were measured *via* titration with $K_4Fe(CN)_6$ [17]. A Hg/HgO reference electrode and a platinum counter electrode of 6 cm² area were used. The working electrode was a rotating disk electrode (*rde*) of glassy carbon with a radius of 3 mm, which was polished with Al_2O_3 paste down to 0.05 μ m. The ohmic drop was 2.5 Ω . Potential pulses from a PAR 175 programmer were, *via* a Solartron 1286 potentiostat, applied to the electrochemical cell. Transient results were directly plotted with a Kipp BD-8 *x-t* recorder. During the experiments the *rde* was rotated with a speed of 16 rps and prior to each nucleation experiment the glassy carbon electrode (*gce*) was held for 5 min at a potential of -1.20 V *vs* Hg/HgO to remove all zinc traces. For morphology analyses and particle size measurements of zinc growth on glassy carbon, a scanning electron microscope (JEOL JSM-840A) was used.

3. THEORY

The nucleation theory for electrochemical deposition is analogous to the formation process from the vapor phase to a substrate and has been comprehensively treated by Fleischmann and Thirsk[14] and Harrison and Thirsk[15]. In case of a uniform nucleation probability, the number of nuclei, N^* , is proportional to the number of active sites, N_0 ,

$$N^* = N_0[1 - e^{-\eta}], \quad (1)$$

Table 1. Initial and prolonged current transient for instantaneous or progressive nucleation and 2-D or 3-D kinetic controlled growth process

Model	Initial transient		Prolonged transient	
Instantaneous 2-D cones	$I = \frac{2\pi nFM Ah N^* k^2 t}{\rho}$	(4)	$I = \frac{2\pi nFM Ah N^* k^2 t}{\rho} \exp(-\pi M^2 N^* k^2 t^2 / \rho^2)$	(5)
Progressive 2-D cones	$I = \frac{\pi nFM Ah W k^2 t^2}{\rho}$	(6)	$I = \frac{\pi nFM Ah W k^2 t^2}{\rho} \exp(-\pi M^2 W k^2 t^3 / 3\rho^2)$	(7)
Instantaneous 3-D cones	$I = \frac{\pi nFM^2 AN^* k^3 t^2}{\rho^2}$	(8)	$I = nFkA[1 - \exp(-\pi M^2 N^* k^2 t^2 / \rho^2)]$	(9)
Instantaneous 3-D hemispheres	$I = \frac{2\pi nFM^2 AN^* k^3 t^2}{\rho^2}$	(10)	$I = nFkA[1 - \exp(-2\pi M^2 N^* k^2 t^2 / \rho^2)]$	(11)
Progressive 3-D cones	$I = \frac{\pi nFM^2 A W k^3 t^3}{3\rho^2}$	(12)	$I = nFkA[1 - \exp(-\pi M^2 W k^2 t^3 / 3\rho^2)]$	(13)
Progressive 3-D hemispheres	$I = \frac{2\pi nFM^2 A W k^3 t^3}{3\rho^2}$	(14)	$I = nFkA[1 - \exp2(-\pi M^2 W k^2 t^3 / 3\rho^2)]$	(15)

where W is the nucleation frequency. For the initial time range and a small W value, the number of nuclei becomes

$$N^* \simeq W N_0 t, \tag{2}$$

while if W is large

$$N^* \simeq N_0. \tag{3}$$

Beyond the instantaneous or progressive nucleation, 2-D or 3-D growth processes can occur as described by Fleischmann and Thirsk[14], Harrison and Thirsk [15], Abyaneh[16] and Greef *et al.*[18]. Nucleation of cylinders with radius r and height h is proposed in these models. As a first approximation, a right-circular cone growth in the r -directions and h -direction will be assumed, with an equal growth rate, k ; secondly a hemispherical growth is also taken into account [19,20]. In Table 1, the corresponding initial and prolonged current transients are summarized for the case of kinetic limited currents, where M is the

molecular weight, n is the number of electrons, F is the Faraday constant, A is the area, ρ is the density and T is the absolute temperature. The current transients for diffusion limiting for hemispherical growth[20, 21] are presented in Table 2, where D is the diffusion coefficient and c is the concentration.

From the initial course of the experimental $I \simeq t^n$ relation and from morphology studies, the growth model can be determined.

Table 2. Initial current transient for instantaneous nucleation and 3-D diffusion controlled growth process

Model	Initial transient
Instantaneous 3-D hemispheres	$I = \frac{\pi nFM^{1/2}(Dc)^{3/2} AN^* t^{1/2}}{\rho^{1/2}}$ (16)
Progressive 3-D hemispheres	$I = \frac{4\pi nFM^{1/2}(Dc)^{3/2} AN^* t^{3/2}}{3\rho^{1/2}}$ (17)

Fig. 1. Voltammogram of a *gce* in 6 M KOH + 0.25 M $K_2Zn(OH)_4$, scan velocity 10 mV s⁻¹.

Fig. 2. Initial current transient for zinc deposition on a gce for potential pulse from $E = -1.200$ V to $E = -1.401$, -1.412 and -1.425 V.

4. RESULTS AND DISCUSSION

4.1. Growth model

Figure 1 shows the voltammogram of a gce in 6 M KOH + 0.25 M $K_2Zn(OH)_4$ at a scan rate of 10 mV s^{-1} and a rotation speed of 16 rps. During the scan in the cathodic direction a significant *cop* can be noticed before zinc deposition occurs. The backward anodic scan shows a steep decrease of the current in the potential region where zinc is deposited, the anodic peak at more positive potentials corresponds with zinc dissolution. The voltammogram is very similar to results in acid electrolytes[5, 6] and no interaction between the zinc deposit and the gce is supposed.

The zinc deposition process on the gce was further investigated by studying the initial and subsequent

current transients for potential pulses from -1.200 V to a range between -1.380 and -1.526 V. The curves show a potential dependent increase of current after an initial induction time (Fig. 2). Obviously there is a relation between the appearance of *cop* and the induction time. At more negative potentials, the induction time decreases. In Fig. 3 the transients of Fig. 2 are plotted as a function of $(t - t_0)^2$, where t_0 is the induction time. Testing of the transients as a function of $(t - t_0)^3$ does not result in a straight line.

The parabolic course for the initial deposition indicates either 2-D growth after progressive nucleation [equation (6)] or 3-D growth (cone or hemispherical) after instantaneous nucleation [equations (8) and (10)].

Further information can be obtained from the long time transients, for which equations (7), (9) or (11)

Fig. 3. I vs. $(t - t_0)^2$ plot for the transients of Fig. 2.

Fig. 4. Prolonged current-time transient for zinc deposition on glassy carbon at different potentials.

describe the subsequent transient. The experimentally found transients for the deposition potentials of -1.401 to -1.526 V are given in Fig. 4. The current plateaux at prolonged times indicate that the equations (9) and (11) give an acceptable description of the transient. Therefore, it is concluded that the growth is 3-D (cone or hemispherical) after instantaneous nucleation.

4.2. Morphology and particle size

The prolonged current transient at a potential of -1.380 V is given in Fig. 5. As shown before, the initial current is proportional to $(t - t_0)^2$. SEM pictures were taken of the zinc deposit at respectively 100, 200, 400, 600, 720 and 810 s and are shown in Fig. 6a-f.

These SEM observations indicate that at short deposition times and low nucleation potentials all zinc deposits are nearly identical in size, and that scarcely any nucleation beyond the instantaneous

nuclei formed by the potential step is observed. The deposit after 600 s is also seen in Fig. 7a and b; the SEM picture of Fig. 7b is made under an angle of 75° in order to obtain a better view of the shape of the deposit. A nearly spherical granular crystalline growth with different hexagonal crystal faces can be noticed. These photos suggest the hemispherical growth model. Therefore, equations (10) and (11) in Table 1 represent the initial and prolonged current transients.

From the slopes in Fig. 3 the product of crystal growth rate and number of nuclei, $N \cdot k$, is calculated for the three deposition potentials from equation (10); this is given in Table 3. Considering the low value current, which is of the order of 1 mA, the iR -drop during the initial curve is negligible.

Current plateaux calculated with equation (11) and the data of Table 3 are, however, lower than the measured values as presented in Fig. 4. This can be due to (a) limitation of the current due to depletion

Fig. 5. Current transient of zinc deposition on a gce for potential pulse to $E = -1.380$ V.

Fig. 6. SEM pictures of zinc deposition on a *gce* at $E = -1.380$ V after a deposition time of: (a) 100 s, (b) 200 s, (c) 400 s, (d) 600 s, (e) 720 s and (f) 810 s.

of the diffusion layer; (b) loss of larger particles from the electrode surface; (c) different morphologies of the deposit. Moreover these data are not corrected for ohmic drop which also affects the current plateau.

For several SEM pictures in Fig. 6 the particle size was measured as a function of time and was found to increase linearly with time as shown in Fig. 8.

After about 600 s deposition, a faster current increase is seen in Fig. 5 indicating a new growth mechanism. Beyond this time (Fig. 6e, f) the beginning of a mossy zinc deposit is observed on the already deposited zinc and the particle diameter increased strongly with time due to the very rarefied structure of the mossy deposit (Fig. 8). With time this deposition process results in a complete covering of the electrode surface with mossy zinc and the current reaches a plateau. Also Cachet *et al.*[22] noticed an enhanced formation of mossy zinc in the presence of electrochemical dissolved zincate.

Figure 7c presents the result of zinc growth at a more negative potential of -1.401 V after a deposition time of 100 s; and shows that the particle size now varies, indicating a more progressive nucleation process. The initial transient shows $I \approx (t - t_0)^2$ (Fig. 3) indicating instantaneous nucleation. However, at high currents and long deposition times diffusion will control the deposition process, which will result in a lower slope as seen in Table 2. Therefore, it is concluded that the deposition now occurs via a progressive nucleation process with diffusion control. In all cases a poor adherence of the zinc deposit to the glassy carbon substrate was noticed.

Table 3. Growth rate for zinc deposition

E vs. Hg/HgO/V	$N^*k^3 \times 10^{15}/\text{mol}^3 \text{ cm}^{-8} \text{ s}^{-3}$
-1.401	3.9
-1.412	53.9
-1.425	235

Fig. 7. (a) SEM-picture of zinc particle deposited at $E = -1.380$ V after 600 s; (b) same deposit as in (a) taken under an angle of 75° ; (c) SEM-photo of deposition at $E = -1.401$ V after 100 s.

Fig. 8. Particle diameter as function of time during deposition at $E = -1.380$ V.

4.3. Number of particles

For SEM pictures of zinc growth at -1.380 V the average number of particles per square μm was determined; it is assumed that this number is equal to N^* . Furthermore, the potential dependence of the number of particles was studied using prepulse experiments. After nucleation during a 100 ms prepulse from -1.200 V to a potential between -1.380 and -1.660 V, the growth of the nuclei was studied at a potential of -1.380 V. At this potential no further nucleation is assumed. In that case, equation (10) defines the initial growth process. This is confirmed by Fig. 9 where the results show a $I \approx (t - t_0)^2$ relation. From this figure, an increasing deviation of

Fig. 10. Number of particles as a function of the nucleation potential; (O) found from SEM-pictures, (x) found with the slopes of the $I \sim (t - t_0)^2$ relation.

the $I \approx (t - t_0)^2$ relation is noticed at higher nucleation potentials and subsequent times due to increasing coverage of the electrode area with zinc and increased diffusion limitation. The slope of the lines in Fig. 9 are, according to equation (10), proportional to N^*k^3 ; and N^* is measured at -1.380 V from the SEM pictures. Because the zinc growth for all these experiments occurs at -1.380 V, the same k value can be assumed; so the change of N^* with potential can be obtained from the slopes in Fig. 9; this number is presented in Fig. 10 as a function of the nucleation potential.

5. CONCLUSION

With cyclic voltammetry crystallization overpotential is observed during the zinc deposition on a

Fig. 9. I vs. $(t - t_0)^2$ plot for deposition at -1.380 V after different prepulse potentials during 100 ms.

glassy carbon electrode in an alkaline zincate solution. Therefore, no interaction between the electrode surface and the deposit occurs and a poor adherence of the deposit can be expected.

From current transients during growth and SEM pictures it was concluded that the instantaneous nucleation and 3-D hemispherical growth model gives a good description of the deposition process if an induction time is taken into account. The assumption of equal growth rate in three dimensions was confirmed by SEM pictures of the deposit.

Initially, a nearly spherical granular crystalline deposit with different hexagonal zinc faces is observed with the SEM, which changes into a mossy deposit after prolonged deposition. At longer deposition time and high deposition potentials, the process involves prolonged nucleation and diffusion control.

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