JOURNAL OF APPLIED ELECTROCHEMISTRY 10 (1980) 807–809

Correspondence

Three-dimensional nucleation of lead: a comment on the paper by F. Palmisano, E. Desimoni, L. Sabbatini and G. Torsi [1]

A recent paper [1] in this journal reports a study of nucleation reactions attending the electrodeposition of lead on to glassy carbon from aqueous hydrochloric acid. The authors come to two conclusions, one minor and one major, namely (a) that the results are difficult to reproduce and (b) that the growth of small nuclei is best described in terms of linear diffusion. We wish to refute both of these assertions and, most importantly, to reiterate that the growth of small, three-dimensional nuclei is always to be described in terms of hemispherical mass transfer.

A mass-transfer-controlled current to a hemispherical growth centre is well described by the equation [2]

$$I = \frac{nFAcD^{1/2}}{\pi^{1/2}t^{1/2}} + \frac{nFAcD}{r} \qquad (1)$$

where the first term is the linear term ($\perp$) and the second is the hemispherical term (⌓); r is the fixed radius of the centre, A is the hemispherical surface area and the other terms have their usual significance. It therefore follows immediately that the ratio of the two terms on the right-hand side is given by

$$I_{\perp}/I_{⌓} = r/\pi^{1/2}D^{1/2}t^{1/2}. \qquad (2)$$

At all ordinary values of nuclear radius and at all ordinary times (Palmisano *et al.* observed $r = 0.2\,\mu$m and their transients were typically 1 s) this ratio → 0. The dominant term is therefore $I_{⌓}$ which leads inevitably to the expression for the mass-transfer-controlled growth of instantaneously formed nuclei, first proposed by Hills *et al.* [3], namely

$$I = \frac{zFN\pi M^{1/2}(2Dc)^{3/2}t^{1/2}}{\rho^{1/2}} \qquad (3)$$

where N is the number density.

The validity of this equation has been confirmed by independent optical studies [4] and an even simpler practical proof is to be found in the work of Scharifker [5] who has grown *single* nuclei of several metals under potentiostatic conditions. Fig. 1 shows the potentiostatic transient for the growth of a single nucleus of mercury on a carbon fibre under conditions close to those used by Palmisano *et al.* and shows two important features, namely a delay time followed by a diffusion-controlled growth current. The corresponding rectilinear plot in Fig. 2 has, for the entire transient, precisely the slope predicted by Equation 3 with $N = 1$. The appropriate value of $cD^{1/2}$ is readily derived from falling current transients observed in a separate experiment at high overpotentials when $N \to \infty$ and

$$\frac{dI}{dt^{-1/2}} = \frac{nFA'cD^{1/2}}{\pi^{1/2}} \qquad (4)$$

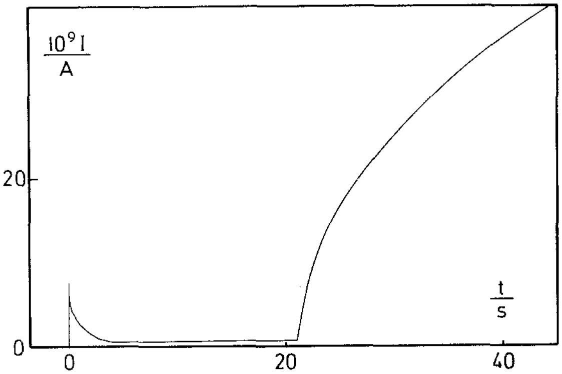

Fig. 1. Potentiostatic transient for the growth of a mercury single nucleus on carbon fibre from a 10×10^{-3} M solution of $Hg_2(NO_3)_2$ in KNO_3(aq) at − 200 mV.

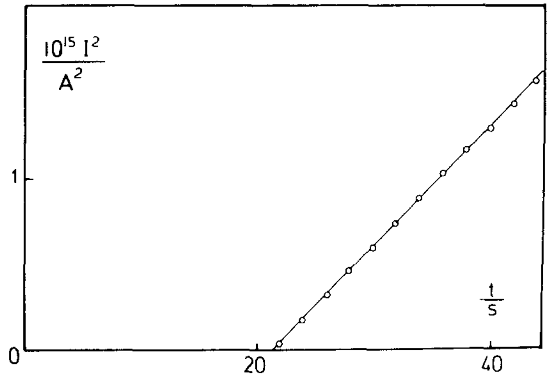

Fig. 2. Plot of I^2 versus t for the transient in Fig. 1.

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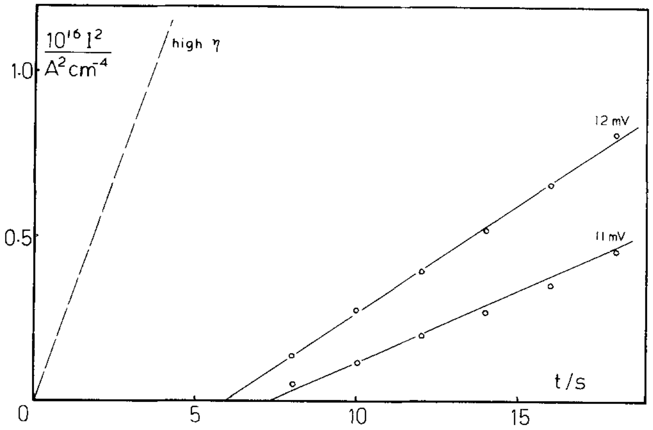

Fig. 3. I^2 versus t plots for the growth of a single nucleus of lead on to a platinum microelectrode from a solution of 8×10^{-3} M $Pb(NO_3)_2$ in 0.1 M HNO_3 at two different overpotentials as indicated. The slopes of these lines compare well with those predicted theoretically taking into account the Nernst factor. The broken line represents the theoretical result for a high overpotential.

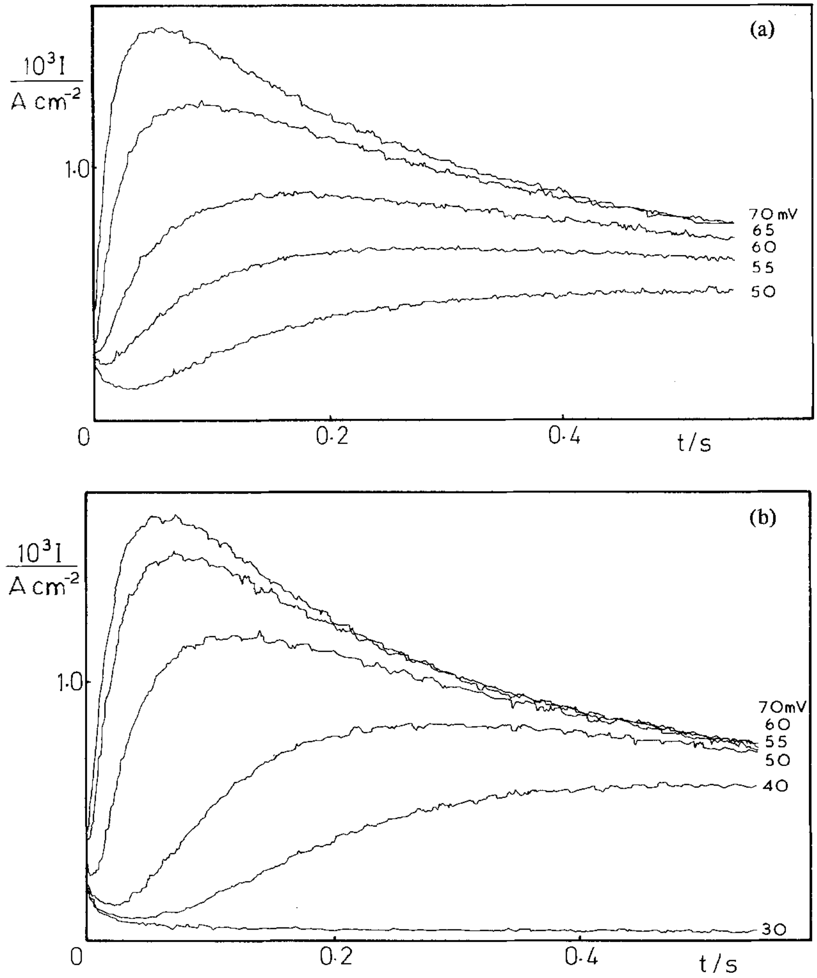

Fig. 4. Family of potentiostatic current transients for the deposition of lead on to vitreous carbon. (a) From an 8×10^{-3} M $Pb(NO_3)_2$ solution in 0.1 M HCl. (b) From an 8×10^{-3} M $Pb(NO_3)_2$ solution in 0.1 M HNO_3.

where A' is the total area of the electrode substrate.

There is no substance in the assertion by Palmisano *et al.* that their Equation 3 (taken from Reference [6]) is preferable to our Equation [3] and it should be refuted before regaining credence. It should also be emphasised that under conditions when the ratio in Equation 2 is small, the exact shape of the growth centre is immaterial and only the symmetry of the diffusion zone is important. The fact that the size of the growth centre increases with time is also unimportant and it has been shown that the contribution to the diffusive flux of the advancing electrode surface is very small [4].

There remains the authors' apparent confirmation of their Equation 3 by photomicrographic observation. The identity of the nuclear number densities must be an unfortunate coincidence and this may be deduced from several aspects. Firstly, from the exhibited distribution of nuclear sizes, it is evident that the nucleation is progressive and not instantaneous. Secondly, the comparison of number densities between two independent experiments, though laudable, is unwise because of the variability of the carbon surface.

There is unfortunately another shortcoming in the equations used by Palmisano *et al.* At low overpotentials, it cannot be assumed that the surface concentration c_i^σ, of electroactive species is negligibly small. From the Nernst relation

$$c_i^\sigma = c_i \exp \eta |z_i| F/RT \qquad (5)$$

it only approaches zero when the overpotential η is large. When this is not so, the bulk concentration c in Equation 3 must be replaced by $c - c^\sigma$. The effect of not taking account of Equation 5 is illustrated in Fig. 3 which compares two observed transients with that predicted by $\eta \to \infty$.

The authors' assertion that the experimental results for this system are not easily reproduced must also be questioned. With care, results in both chloride and nitrate solutions, such as those shown in Figs. 4a and b, are readily and accurately reproducible.

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Received 6 March 1980

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JOURNAL OF APPLIED ELECTROCHEMISTRY **10** (1980) 811–812

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Reply to a comment by G. Hills, I. Montenegro and B. Scharifker [1] *on our paper dealing with the three-dimensional nucleation of lead* [2]

The previous note [1] by Hills *et al.* comments on a paper [2] by our research group dealing with the three-dimensional nucleation of lead. It seeks to refute, 'before regaining credence', the model based on linear diffusion proposed [3] to describe the potentiostatic current–time transients for instantaneous three-dimensional nucleation. In our paper [2] we attempted to describe some experimental findings for the electrodeposition of lead on glassy carbon by using, without prejudice, theoretical models and equations reported in the literature. The comparability of the nuclear density numbers as calculated from the equation by Astley *et al.* [3] and as deduced by visual counting from our scanning electron microscope (SEM) observations led us to say that 'the equation proposed by Astley *et al.* better describes the system'.

We certainly agree with Hills *et al.* when they say that the growth of a single, small nucleus, as in the case of mercury on carbon reported by the authors, can be better described by a model based on (hemi)spherical [4] rather than linear diffusion [3]. Of course such a model can still be valid when the nuclear number density is sufficiently low to avoid, in the initial stages of nucleation, the overlap of the individual diffusion zones around each nucleus.

This seems not to be the case in our studies. The experimental nuclear number density is such that the distance between neighbouring nuclei is, under all our experimental conditions, more than one order of magnitude smaller than the diffusion layer thickness. This is perhaps the reason why this system seems better described by a model based on linear diffusion rather than a model based on localized spherical diffusion. On the other hand, from the equation based on the former a number of 10^9–10^{10} nuclei cm^{-2} can be obtained, while on the basis of the latter a number of 10^3–10^4 nuclei cm^{-2} is expected.

The scanning electron micrograph reported in our paper is, of course, representative of many observations performed after I–t transients were recorded and in the time interval for which the I–$t^{1/2}$ dependence was verified (see the caption of Fig. 8 in Reference [2]). The validity for our system of the I–$t^{1/2}$ dependence seems clearly indicative of an instantaneous rather than of a progressive nucleation; any contrary 'evidence' derived from the simple observation of a micrograph can only be a subjective opinion.

As to the minor point raised by Hills *et al.*, we did not say that our results were not reproducible but that it was impossible for us, as for other authors [4, 5], to confirm the dependence, $I \propto c^3$ (Astley *et al.*, model [3]) or $I \propto c^{3/2}$ (Hills *et al.*, model [4]). We tentatively ascribed this impossibility to difficulties in reproducing the glassy carbon surface. Now we are more inclined to think that the mutual interference between growing nuclei, not considered in both models, can influence in some way the concentration dependence of the growing current.

Finally we agree with Hills *et al.* that it is necessary to take into account that at low overpotentials the concentration at the electrode surface is not zero. However, when proper corrections are made one can see that the order of magnitude of the calculated density number does not change. For example, the density numbers (nuclei cm^{-2}) at an overpotential of -16.5 mV calculated from the equations of Hills *et al.* and Astley *et al.* are, after corrections, 6.88×10^3 and 3.70×10^9 instead of 9.43×10^3 and 9.76×10^9, respectively.

It can be concluded that to a first approximation our system seems better, but certainly not completely, described by Astley's model. Probably the kinetics of nucleation are more complicated than supposed in the formulation of either model [3, 4]; so, at present, an inflexible choice of either model to describe all the systems of growing nuclei is not quite justified. As is apparent from the present controversy more experimental and theoretical work is certainly needed for a better understanding of nucleation phenomena.

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Received 2 May 1980

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