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Effect of an organic additive on the electrocrystallization of cadmium in alkaline solution

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The electrocrystallization of $Cd(OH)_2$ in KOH solution was studied on a solid cadmium electrode using the potential step method. An organic additive, polyvinyl alcohol (PVA), sometimes considered for use as an additive in nickel–cadmium batteries, was found to inhibit the nucleation process. A two-dimensional instantaneous nucleation and growth was found to take place in the absence of the expander, whereas deviation occurred when PVA was present. The general effect of adding PVA was to lower i_m and increase t_m.

1. Introduction

For many years expanders (usually organic acids or alcohols) have been considered as additives to the negative plates of nickel–cadmium batteries. The well-known result of this process is to inhibit crystal growth of the cadmium hydroxide which would thus lead to a lowering in the surface area available for electrochemical processes to take place. However, little information is available concerning the use of organic additives to control the morphology of the cadmium electrode.

Recently, Vasueva-Rao *et al.* [1] have found that the discharge efficiency of the sintered-plate cadmium electrode is improved when quaternary ammonium compounds such as acetyltrimethylammonium halides are incorporated into the active material at the time of impregnation.

In earlier studies, Gossenberger [2] made an evaluation of the behaviour of various cellulose and starch derivatives on the capacity of the cadmium electrode. It was tentatively suggested that growth of cadmium metal was inhibited by the additives. Fleischer [3] subsequently patented the use of cellulose ethers and derivatives such as CMC for reducing the fall in capacity of the cadmium electrode on cycling. Unfortunately, however, there appears to be no clear consensus as to the mode of action of expander materials. More recent studies indicate that expanders such as polyvinyl alcohol (PVA) have a marked effect on the double layer capacity of the electrode and decrease R_{sol} [4].

The electrochemical oxidation of cadmium in potassium hydroxide is thus a complicated process. The mechanism is of considerable interest in relation to the operation of the commercial nickel–cadmium battery. Most mechanistic studies have been performed using either flat cadmium electrodes or amalgams.

An earlier investigation [5] of anodic film formation on cadmium amalgam in alkaline solutions showed that the film was one-degree-oriented β-$Cd(OH)_2$ with the basal plane parallel to the electrode surface. Examination of potentiostatic i–t transients led to the conclusion that the $Cd(OH)_2$ was formed by the successive deposition of monomolecular layers. The concentration of the cadmium species [6] in equilibrium

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with $Cd(OH)_2$ indicate that it should be possible to measure the kinetics of dissolution of cadmium at potentials which include the potentials of stability of the anodic film.

The thickness of the passivating $Cd(OH)_2$ film which is formed on the electrode surface is of considerable interest, for this dimension determines the extent of the cadmium oxidation reaction (the capacity). The aim of the present work was to evaluate such effects using PVA as the expander. The variation of $Cd(OH)_2$ film thickness with potential is particularly considered because of its implications to battery performance.

1.1. *Theories of nucleation*

The theoretical expression for electrochemical nucleation is based principally on two models, namely the thermodynamic and atomistic models. The thermodynamic model uses the macroscopic surface energy to calculate the free energy for defining the critical nucleus, whereas the atomistic model considers the interactions among the atoms of the clusters. Although these quantities have clear physical meaning, their values are usually unknown. At the present time neither theory has been proved to be more adequate. Nevertheless, the thermodynamic theory for nucleation and growth has been studied in great detail by Harrison and Thirsk [7]. These researchers have studied the deposition of a new phase onto a surface under potentiostatic conditions. Hence the theoretical interpretation of potentiostatic transient for electrocrystallization has been well established.

For a two-dimensional cylindrical nucleus, growing on a flat electrode of the same material, the free energy of formation of the nucleus is [7]:

$$G_n = -\pi r^2 \imath \varrho z F \eta / M + 2\pi r \imath \sigma \qquad (1)$$

where $\imath$ is the height of the nucleus, σ is the surface energy of the nucleus–solution interface, ϱ is the density of the nucleus, M is the molecular weight and $zF\eta$ is the bulk energy per mole involved in forming the nucleus at an overpotential, η.

Fleischmann and Thirsk [8] have derived a complete equation for charge transfer-controlled nucleation under potentiostatic current–time transients for processes in which the growth of a new phase, i.e. lattice incorporation, is slow. By taking the growth of discrete centres into account [9–13] they arrived at the total growth rate for two-dimensional instantaneous and progressive nucleation at short times. However, in the later stages of crystal growth the nucleation centres overlap and the area available for electrodeposition becomes restricted. The form of the expression describing the complete growth process can be obtained by allowing for the effects of this overlap. This is done by making use of Avrami's theorem [14].

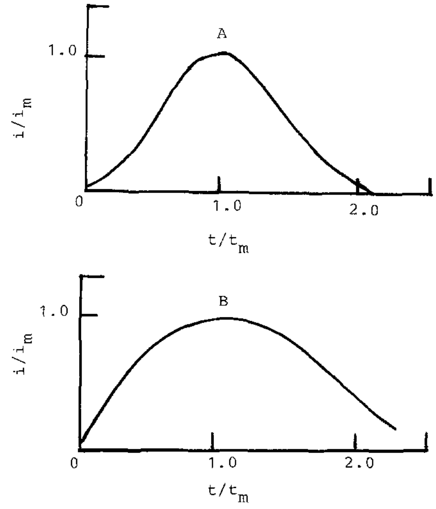

Fig. 1. Theoretical current–time curves. (A) Equation 3, progressive; (B) Equation 2, instantaneous.

For cylindrical centres growing in two dimensions with instantaneous and progressive nucleation laws respectively, the complete growth expressions are:

$$i = (2zFMN_0 k_E^2 \imath t/\varrho) \exp(-M^2 N_0 k_E^2 t^2/\varrho^2) \qquad (2)$$

and

$$i = (zFMN_0 A k_E^2 \imath t^2/\varrho) \exp(-M^2 N_0 A k_E^2 t^3/3\varrho^2) \qquad (3)$$

where N_0 is the total number of available nucleation sites and k_E is the growth rate constant. These describe peaked transients with $i = 0$ at $t = 0$ and $t = \infty$.

Fig. 1A and 1B are reduced variable plots of Equations 2 and 3, respectively, using i/i_m and t/t_m where i_m and t_m are the parameters of the maximum which are readily found by differentiation. Experimental transients can be compared with such plots to show which growth law is being followed.

For instantaneous nucleation

$$t_{\mathrm{m}} = \varrho/(2\pi N_0)^{\frac{1}{2}} M k_{\mathrm{E}} \qquad (4)$$

$$i_{\mathrm{m}} = (2\pi N_0)^{\frac{1}{2}} z F k_{\mathrm{E}} \iota e^{-\frac{1}{2}} \qquad (5)$$

and for progressive nucleation

$$t_{\mathrm{m}} = (2\varrho^2/\pi M^2 N_0 A k_{\mathrm{E}}^2)^{\frac{1}{3}} \qquad (6)$$

$$i_{\mathrm{m}} = zF(4\pi N_0 A k_{\mathrm{E}}^2 \varrho/M)^{\frac{1}{3}} 2e^{-\frac{2}{3}} \qquad (7)$$

In both cases the time at which the maximum occurs decreases with increasing growth rate constant, k_{E}, the dependence being greatest for instantaneous nucleation. Also, the size of the maximum increases with k_{E} and the dependence is again greater for instantaneous nucleation. The theoretical value of $i_{\mathrm{m}} t_{\mathrm{m}}/Q_{\mathrm{m}}$ is independent of the potential dependence of k_{E} and is 1.0 for progressive and 0.6 for instantaneous nucleation. The constancy of $i_{\mathrm{m}} t_{\mathrm{m}}/Q_{\mathrm{m}}$ with potential is a useful experimental test. (Q_{m} is the charge consumed in the rising transient.)

Armstrong *et al.* [15] have described the instantaneous nucleation of growth of a three-dimensional deposit leading to the passivation of an electrode. In order to simplify the mathematics, the nuclei are considered to be right circular cones. The final equation describing the current as a function of time after the application of a potential step is given as

$$i = ZFk_2[1 - \exp(-\pi N_0 k_1^2 M^2 t^2/\varrho^2)] \qquad (8)$$

where k_1 is the rate constant describing crystal growth parallel to the plane surface of the electrode and k_2 is the rate constant perpendicular to the surface. At long times the current attains a constant maximum rather than approaching zero as predicted for the two-dimensional case. Only in very few instances (e.g. deposition on amalgams) is true monolayer formation apparently found. In the great majority of cases the formation of successive layers of deposit is observed. This gives rise to transients significantly different from those given by Equations 2 and 3, especially at times greater than t_{m} [16, 17].

2. Experimental details

The cadmium used in this investigation was a disc electrode, area 0.283 cm^2, cut from a rod supplied by BDH (99.9% pure). The electrode was set in an Araldite holder. Measurements were made in a conventional three-electrode cell using a Hg/HgO reference electrode and a large nickel counter electrode. The solution used throughout was 5 M KOH prepared from Aristar potassium hydroxide pellets and distilled, deionized water. All solutions were deoxygenated with N_2 before use and the experiment was conducted at room temperature (25 ± 2° C).

Prior to an experiment the electrode was polished mechanically with 4/0 emery paper wetted with methanol, then cleaned with methanol and water and polished with diamond paste. Subsequent polishing was carried out on a buff (particle size, 1–3 μm) and then by rinsing with methanol and deionized water before final immersion in the working solution.

The potentiostat was a Chemical Electronics, type 40V–3A, used in conjunction with a waveform generator (also Chemical Electronics, type O1) and a PL4 JJ x–y–t recorder.

The electrode was allowed to equilibriate in the alkaline solution for about 30 min at -1.100 V until the current drain was negligible. The cathode voltage was set at this value potentiostatically and voltage pulses of varying magnitudes and long duration were applied to the electrode.

PVA is only sparingly soluble in KOH solution and once the experiment using the straight KOH solution had terminated, a 5 ml portion of a saturated solution of PVA was added to 600 ml of 5 M KOH to study the effect of the organic expander on the cadmium electrode (5 ml of a saturated solution in 600 ml of 1.67×10^{-6} M KOH).

3. Results and discussion

Potentiostatic oxidation steps were carried out from -1.100 V to potentials ranging from -0.950 to -0.700 V, and four quite distinct forms of the i–t transients were obtained as shown in Figs 2 and 3.

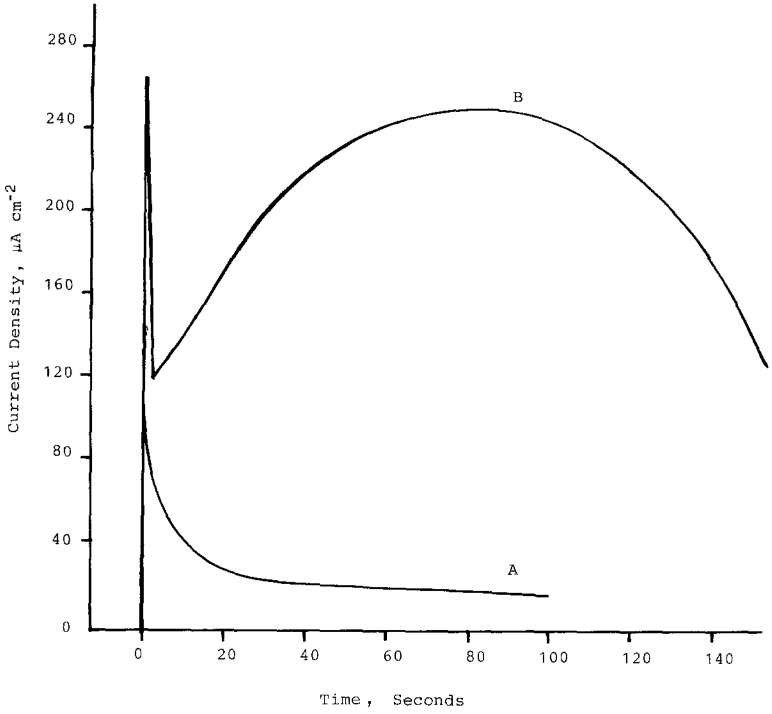

Fig. 2. Transients obtained on solid cadmium electrodes in 5 M KOH after stepping from (A) −1.100 V to −0.930 V; (B) −1.100 V to −0.892 V.

Integration of the area under the curves provides the charge, which in turn gives the number of $Cd(OH)_2$ monolayers on the assumption that the calculated charge for the basal plane of β-$Cd(OH)_2$ is 302.5 C cm^{-2}. The data are shown in Table 1 together with the dimensionless quantity, $i_m t_m/Q_m$, where i_m and t_m are the co-ordinates of the current maximum. A

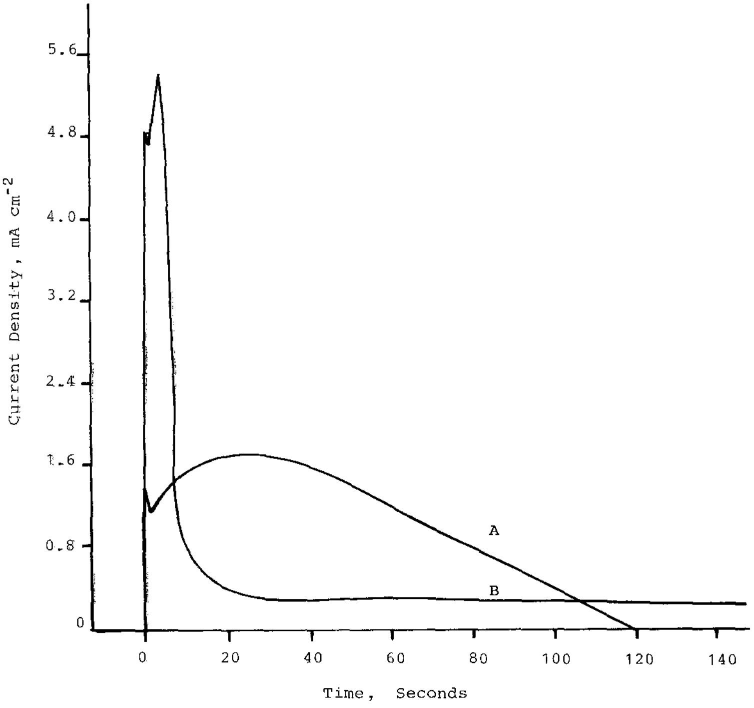

Fig. 3. Transients obtained on solid cadmium electrodes in 5 M KOH after stepping from (A) −1.100 V to −0.882 V; (B) −1.100 V to −0.861 V.

Table 1. The variation of $i_m t_m/Q_m$ *and deposit thickness (P, monolayer equivalent) with potential*

E *(mV)*	$i_m t_m/Q_m$	P *(no. of monolayers)*
−892	0.383	714
−882	0.138	555
−861	0.111	213
−798	0.109	452

Table 2. The variation of $i_m t_m/Q_m$ *and deposit thickness (P, monolayer equivalent) with potential in the presence of PVA*

E *(mV)*	$i_m t_m/Q_m$	P *(no. of monolayers)*
−894	0.627	763
−879	0.788	441
−858	0.821	438
−787	0.483	537

change in the value of this quotient indicates a transformation in the mechanism for nucleation and growth. It is clear from the data that the thickness of the deposit varies with the formation potential, the more positive potential giving rise to a thinner layer. This confirms the suggestion of Fleischmann and Thirsk [12] that the deposit thickness decreases with overpotential. The values of $i_m t_m/Q_m$ are interesting in that they decrease with increasing overpotential. This indicates that with increasing overpotential changes occur in the current controlled by the crystallization process.

The shapes of the transient response are similar to those predicted for two-dimensional nucleation and growth. Two models for nucleation and growth possibly describe this relationship [7]. However, the first possibility for progressive nucleation and two-dimensional growth appears unlikely in view of the thickness of the deposit (200 to 750 monolayers). Furthermore, this would require $\log(i/t^2)$ to be proportional to t^3 at long times, but this is not observed. The other possibility is instantaneous nucleation with two-dimensional growth from cylindrical nuclei. Equation 2 describes the current due to the growth of a two-dimensional layer from instantaneously formed cylindrical centres.

The postmortem diagnosis for two-dimensional nucleation and growth is to check that the transient, when plotted in the non-dimensional form i/i_m versus t/t_m, conforms to a theoretical plot derived from Equation 2 (Fig. 1A). This is demonstrated in Fig. 4A where the transient of Fig. 2B is plotted in dimensionless form against a derivative from Equation 2. The correlation is quite good, especially when it is remembered that this is quite near the potential region for cadmium dissolution.

The form of the transient does not change drastically with the addition of PVA (Figs 5, 6). The data for the monolayer equivalent derived from the charges under the curve together with $i_m t_m/Q_m$ are shown in Table 2.

Fig. 4B shows a typical transient plotted in the non-dimensional form, the solid line giving the theoretical curve. It can be seen that although the experimental curve has the same overall shape, the quantitative fit is not very good. Although the monolayer equivalent indicates

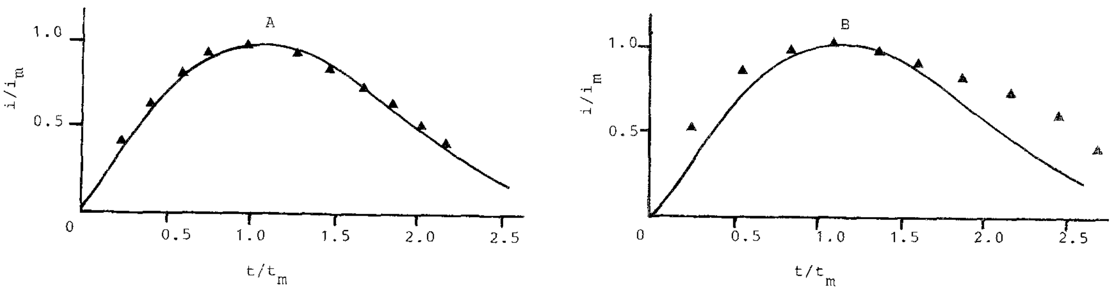

Fig. 4. (A) Transient of Fig. 2B plotted in dimensionless form and compared with the curve of Equation 2 derivative. (B) Transient of Fig. 5B plotted in dimensionless form and compared with the curve of Equation 3 derivative. ▲, Experimental; ——, theoretical.

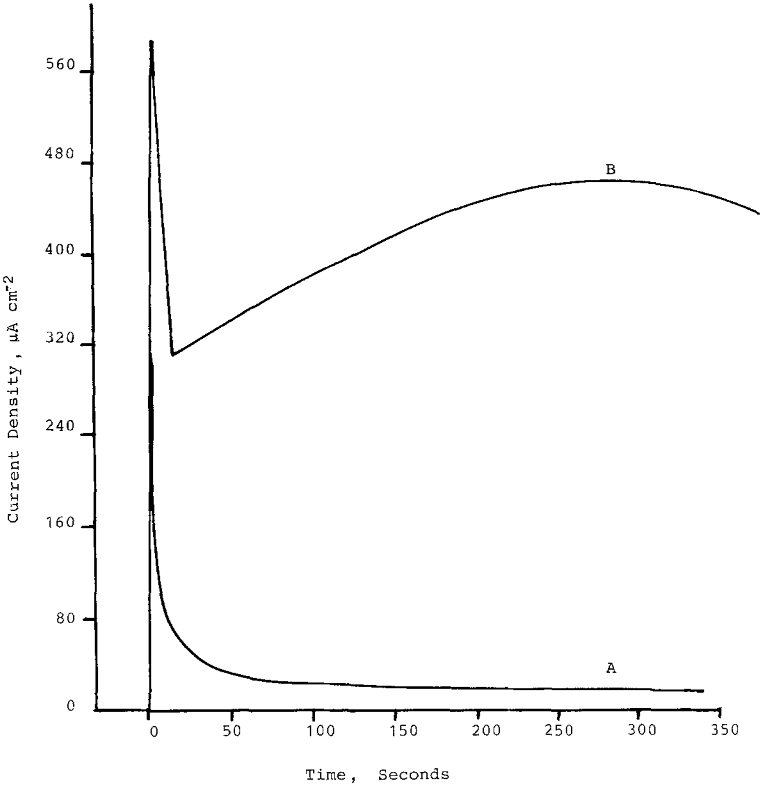

Fig. 5. Transients obtained on solid cadmium electrodes in 5 M KOH saturated with PVA after stepping from (A) −1.100 V to −0.930 V; (B) −1.100 V to −0.894 V.

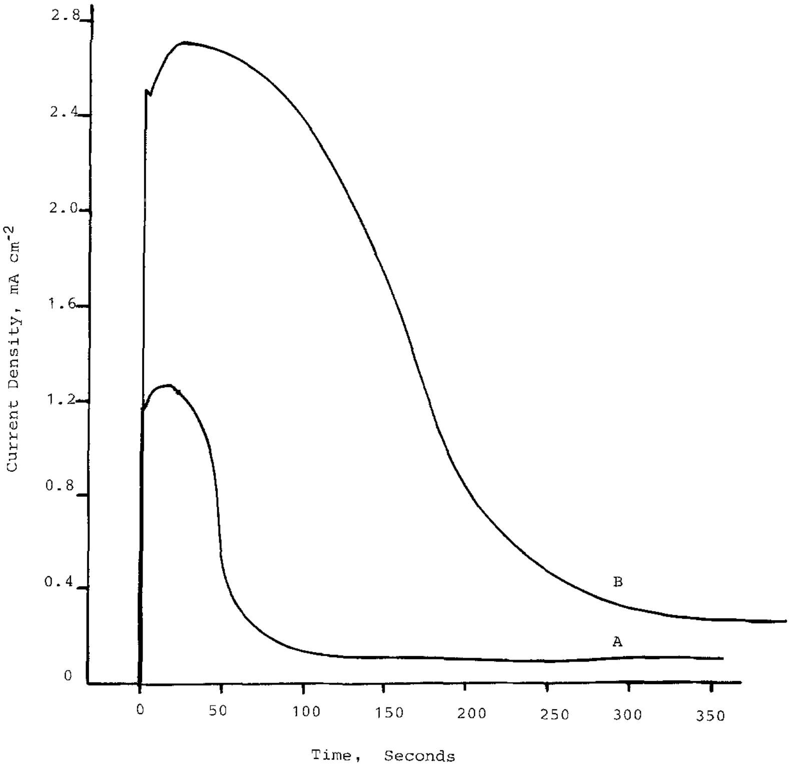

Fig. 6. Transients obtained on solid cadmium electrodes in 5 M KOH saturated with PVA after stepping from (A) −1.100 V to −0.879 V; (B) −1.100 V to −0.858 V.

instantaneous nucleation and two-dimensional growth, the fact that the value of $i_m t_m / Q_m$ suggests a progressive mechanism is further shown by the rather poor fit of the experimental curve with the theoretical curve for instantaneous nucleation.

The effect of PVA expander material on the formation of thick layers of cadmium hydroxide thus appears to modify the two-dimensional nucleation process. The general effect of adding PVA is to lower i_m and increase t_m. Perhaps the adsorption effect which has been shown in the previous paper [4] distorts the general procedure for two-dimensional instantaneous nucleation. If progressive nucleation does occur then this explains the uniform crystallite size of cadmium hydroxide crystals on discharge [18].

The experimental data do not show which parameter in the growth equation is affected by the expander. However, the overall process appears to be inhibited. It is likely that the growth rate constant, k_E, is unchanged by the PVA, and since the total number of available nucleation sites, N_0, is reduced by the adsorption of PVA on latent nuclei, it would be very important to take this fact into consideration. This has been experimentally observed [4]. Lowering of the dissolution rate by the adsorbed species results in a retardation of cadmium ion movement to the growing nuclei and thus a lowering in k_E. This may explain the deviation from a two-dimensional instantaneous nucleation process on adding PVA.

Acknowledgements

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