Fig. 3 Oxidizability of trimethylenediamine (T.D.) and N-acetyltrimethylenediamine (Ac-T.D.)

Fig. 4 Oxidizability of hexamethylenediamine mixed with acetic acid (Hx.D+Ac) and N-acetyl (Ac-Hx.D.), N,N'-diacetylhexamethylenediamine (Ac-Hx-Ac),

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Studies on the Negative Plate of Nickel Cadmium Alkaline Batteries.

III. The Overpotential in Solid Phase of the Cadmium Electrode in Alkaline Electrolyte

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Our study^{1), 2)} on the mechanism of the discharge of cadmium electrode in alkaline electrolyte has shown that the reaction process may be considered as occurring in the slow and quick ones. The former was reasonably explained on the basis of that the primary product (CdO or $\text{Cd}(\text{OH})_2$) reacts with the electrolyte and redeposits as $\text{Cd}(\text{OH})_2$. In this paper consideration is given of the electrochemical aspects of the quick process.

Experimental methods The method for preparing the electrode and measuring the overpotential was similar to that in the previous work¹⁾. Rapid potential changes were measured by a cathode-ray oscillograph with an accuracy of 1 mV, (vertical axis) and 8 μ sec. (horizontal axis) and a mechanical oscillograph. The electrolyte employed in this work was saturated with purified nitrogen and soluble cadmium salt.

Results It has been observed that the potential changes caused by the slow process occur between 10 or 20 seconds and 5 minutes after interrupting current. The values of the overpotentials in this process are hardly varied by the different current densities, and are small as compared with the total.

Representative shapes of potential changes caused by the quick process are shown in Figs. 1a, and 1b.

Fig. 1a Potentials vs. time after interrupting currents (4.79N-KOH 25°C)

Fig. 1b Potentials vs. time after interrupting currents (4.79N-KOH 25°C)

It is observed that in the sweeping velocity of 1/1000 seconds (Fig. 1a) a greater part of overpotential was recovered more quickly as the discharge currents and amounts increased, while in sweeping velocity of 1/1600 seconds (Fig. 1b) potential changed for the first 8μ seconds and the subsequent rise remained much smaller.

Changes in concentration and temperature of electrolyte affected all the overpotential. From the further detailed measurement of overpotential within the first 8μ seconds in various conditions, it became evident that its magnitude was the iR drop of electrolyte, and therefore was not due to the resistance overpotential.

The relation between the overpotentials and logarithm of the current densities (mA/cm^2) at various discharge amounts lay on straight lines which had a short arrest at a higher current density. The respective line was in parallel and slope was about $18 \text{ mV}/\log i$. These results indicate that the overpotential does not depend on the electrochemical process of $\text{Cd} \rightarrow \text{Cd}^{2+} + 2e$ and the diffusion process in electrolyte.

Discussion

According to the results above and previously described¹⁾, we suggest that the overpotential in the quick process is responsible for the primary reaction product accumulated on the electrode surface, and for the electrical resistance of the solid phase. Thus, the postulate applied is as follows:—The electrode reduced to metal is oxidized anodically according to the equation $\text{Cd} \rightarrow \text{Cd}^{2+} + 2e$ and the primary product with OH^- in electrolyte is formed. As illustrated schematically in Fig. 2, Cd^{2+} is transported through the solid layer having lattice defects of “Frenkel type”²⁾ and reached to the outer surface of the electrode.

Fig. 2 Schematic diagram of the electrode surface during discharge

We may account for the experimental facts on the basis of the above postulate. The quantitative explanation¹⁾ is described below.

(a) **Relation between the overpotentials and the current densities** Now considering that concentration gradient for Cd^{2+} in inside and outside of the solid layer deposited on cadmium (respectively A and B in Fig. 2) is linear, then the following equation is given

$$\frac{i}{2F} = \frac{k(m-m_0)}{\delta} \dots \dots \dots (1)$$

in which k is transport velocity and m and m_0 are the activities of Cd^{2+} in A and B sides in Fig. 3, respectively. Let m_s and i_s be m and i at saturation respectively.

$$\frac{i_s}{nF} = \frac{k(m_s - m_o)}{\delta} \dots \dots \dots (2)$$

Simplification of Eq. 1 using Eq 2. leads to

$$i = i_s \left(1 - \frac{m_s - m}{m_s - m_o}\right) \dots \dots \dots (3)$$

The electrode potential E at equilibrium in the solid layer before discharge is given by the following equation

$$E = E_{eq} + \frac{RT}{2F} \ln m_o$$

in which E_{eq} is potential in the solid layer involving no lattice defect.

Thus, overpotential ΔE is

$$\Delta E = \frac{RT}{nF} \ln \frac{m}{m_o} \dots \dots \dots (4)$$

combining Eqs. 3 and 4

$$\Delta E = \frac{RT}{nF} \ln \left(\frac{s}{i_s} i + 1\right) \dots \dots \dots (5)$$

in which

$$S = \frac{m_s}{m_o} - 1, i \leq i_s$$

Values of $\ln \left(\frac{s}{i_s} i + 1\right)$ of 5.5 N KOH electrolyte at various temperatures are plotted against ΔE and shown in Figs. 3a, 3b and 3c. Application of different concentrations of electrolyte is shown in Fig. 4

In Fig. 4, the calculated values in various conditions lie on the theoretical line of Eq. 5. However, a short arrest is found at a certain high current density, indicating that the value of the current against the critical overpotential for theoretical line is i_s . The deviation from the straight line would be attributed to the other mechanism of electrical conductance. We may assume that the changes of

Fig. 3a Application of $\Delta E = (RT/2F)$

$$\ln \left\{ \left(\frac{S}{i_s} \right) i + 1 \right\} \quad 25^\circ\text{C}, S = \frac{m_s}{m_o} - 1$$

Fig. 3b Application of $\Delta E = (RT/2F)$

$$\ln \left\{ \left(\frac{S}{i_s} \right) i + 1 \right\} \quad 10^\circ\text{C}, S = \frac{m_s}{m_o} - 1$$

Fig. 3c Application of $\Delta E = (RT/2F) \ln \left\{ \left(\frac{S}{i_s} \right) i + 1 \right\} \quad 5^\circ\text{C}, S = \frac{m_s}{m_o} - 1$

Fig. 4 Application of $\Delta E = (RT/2F)$

$$\ln \{ (S/is)i+1 \} \quad S = \frac{ms}{m_o} - 1$$

Fig. 5 Schematic representation of the decay curve

Fig. 6a Application of $t = (\delta/k) \ln(e^v - 1) - (\delta/k) \ln(e^{x-1})$

Fig. 6b Application of $t = (\delta/k) \ln(e^v - 1) - (\delta/k) \ln(e^{x-1})$

$ms/m_o, (is)$ as shown in respective figures are accompanied by the increase of overpotential caused by the decrease of electrical conductivity of layer.

(b) **The analysis of decay curves** The similar consideration to (a) leads to Eq. 13

$$\frac{dm}{dt} = - \frac{k(m - m_o)}{\delta} \dots\dots\dots (6)$$

Integration of Eq. 6

$$\ln (m - m_o) = \frac{-k}{\delta} t + c \dots\dots\dots (7)$$

$t = 0 \rightarrow m = m_p$ c: integration constant

$$\therefore \ln \frac{m_p - m_o}{m - m_o} = \frac{k}{\delta} t \dots\dots\dots (8) \quad m_p: m \text{ immediate after interrupting current}$$

In Fig. 5

$$\Delta E_p = \frac{RT}{nF} \ln \frac{m_p}{m_o} \dots\dots\dots (9)$$

$$\Delta E = \frac{RT}{nF} \ln \frac{m_p}{m} \dots\dots\dots (10)$$

(9), (10)

$$\frac{m}{m_0} = l^x \dots\dots\dots (11)$$

in which, $x = \frac{nF}{RT} (\Delta E_p - \Delta E)$

$$\frac{m_p}{m_0} = l^p \dots\dots\dots (12)$$

in which, $p = \frac{nF}{RT} \Delta E_p$

(11), (12) $\longrightarrow$ (13)

$$t = \frac{\delta}{k} \ln (l^p - 1) - \frac{\delta}{k} \ln (l^x - 1) \dots\dots\dots (13)$$

Values of $\ln (l^x - 1)$ are plotted against time as shown in Figs. 6a and 6b. The straight line are obtained within the limited time. It is satisfactory for Eq. 13 that the direction of the slope is negative, that the values of the gradients are identical in spite of difference of the current. We believe that the partial application of Eq. 13 comes from the unsuitable assumption that the activity gradient of Cd^{2+} is linear.

It may be suggested that besides the above postulate, O^{2-} or both Cd^{2+} and O^{2-} transport through the solid phase, but the equations on the basis of these assumptions were difficult to account for the facts.

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Studies on Inhibitor for Metallic Aluminum in Basic Medium. II. 8-Hydroxyquinoline Derivatives in Basic Medium as Inhibitor for Metallic Aluminum

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Hackerman¹⁾ proved that chemical absorption is one of the mechanisms of corrosion inhibition of organic substances in acidic medium, besides Mann's physical absorption²⁾. In the previous paper³⁾, the addition of o-hydroxyazo compounds cannot inhibit the corrosion of aluminum in acidic or neutral medium but can do only in alkaline medium, and this fact leads to the conclusion that o-hydroxyazo compounds combine with aluminum by reacting only in alkaline medium.

In this paper some quinoline derivatives were examined and the reason why only the substances which have OH group in their 8-position can inhibit the corrosion of aluminum in alkaline medium is concluded that the substances form metal chelates (as shown in Fig. 1) with aluminum in such condition.

Fig. 1 Neutral chelate of aluminum