

01 Jan 1967

The Anodic Dissolution Of Cadmium

James W. Johnson

Missouri University of Science and Technology

E. Deng

S. C. Lai

William Joseph James

Missouri University of Science and Technology, wjames@mst.edu

Follow this and additional works at: https://scholarsmine.mst.edu/che_bioeng_facwork

 Part of the [Biochemical and Biomolecular Engineering Commons](#), and the [Chemistry Commons](#)

Recommended Citation

J. W. Johnson et al., "The Anodic Dissolution Of Cadmium," *Journal of the Electrochemical Society*, vol. 114, no. 5, pp. 424 - 428, The Electrochemical Society, Jan 1967.

The definitive version is available at <https://doi.org/10.1149/1.2426620>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Chemical and Biochemical Engineering Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

The Anodic Dissolution of Cadmium

To cite this article: J. W. Johnson *et al* 1967 *J. Electrochem. Soc.* **114** 424

View the [article online](#) for updates and enhancements.

You may also like

- [The Alkaline Manganese Dioxide Electrode: I. The Discharge Process](#)
David Boden, C. J. Venuto, D. Wisler et al.
- [Gallium Arsenide Electrode Behavior](#)
W. W. Harvey
- [The Effects of Crystallographic Orientation and Oxygen Pressure on the Oxidation of Iron](#)
W. E. Boggs, R. H. Kachik and G. E. Pellissier

The Anodic Dissolution of Cadmium

J. W. Johnson, E. Deng, S. C. Lai, and W. J. James

Departments of Chemical Engineering and Chemistry, The University of Missouri at Rolla, Rolla, Missouri

ABSTRACT

The anodic dissolution of cadmium has been studied in aqueous solutions containing Cl^- , Br^- , I^- , Ac^- , SO_4^{2-} , and NO_3^- ions. The normal valence (+2) was found in all solutions with the exception of NO_3^- . The apparent valence (calculated) of cadmium ions in nitrate solutions varied from 1.2 to 2.0 and was found to be a function of NO_3^- concentration, current density, and temperature. An anodic dissolution mechanism has been proposed involving local corrosion and disintegration of the anode which is consistent with the experimental results.

Since early in this century, various investigators have noted and reported discrepancies in the actual and theoretical quantities of Cd dissolving anodically in certain oxidizing electrolytes (primarily nitrates) (1-3). This phenomenon has also been reported for Mg (4,5), Be (6,7), Zn (8,9), Al (10,11), and Sn (12,13), to name a few.

Several theories have been proposed to explain the behavior. They are: (a) complex ion ($\text{Cd} \cdot \text{Cd}^{+2}$) formation, (b) uncommon valence ion (Cd^+) formation, (c) film control, (d) local corrosion, and (e) disintegration. The uncommon valence ion theory has been widely accepted, but recent papers have somewhat discounted its validity, especially as pertains to Be (7), Mg (4,14,15), and Zn (9,16). Experiments carried out in this laboratory with amalgamated anodes also make it doubtful that the theory applies to Cd (17).

This investigation concerns the anodic dissolution of Cd in electrolytes (ca. neutral) containing various anions both with and without Cd ions present. The anions selected show some variation in the solubilities of their Cd salts and a considerable variation in their ability to complex with Cd ions. Also, they have been associated with studies of the anodic disintegration of other metals (18-23). It was hoped that some insight might be gained on the processes responsible for the low faradaic efficiency.

Experimental

The Cd anodes were prepared from ASARCO special high-purity (99.999+) rod. All solutions employed analytical grade chemicals and distilled water. The anodes were fabricated by press-fitting small machined Cd specimens into Teflon holders. A platinized-platinum cathode was used. The electrolyses were carried out in the usual H-cell (300 ml electrolyte capacity) under an inert atmosphere (prepurified nitrogen). When no Cd ions were initially present in the electrolyte, the Cd dissolved was determined by EDTA titration. When Cd ions were present, a direct weight loss method was used. A calomel (1N) reference electrode in conjunction with a salt bridge was used for the potential measurements. The apparatus and procedure have been described (7,9).

Apparent valence of Cd in nitrate electrolytes in the absence of Cd^{+2} .—The anodic dissolution of Cd was studied in KNO_3 - K_2SO_4 solutions at temperatures of 25°, 45°, and 65°C. The NO_3^- concentration was varied from 0 to 1N, while the total electrolyte concentration was held constant at 1N to insure good conductance. Apparent valences were calculated using the equation

$$V_i = \frac{VW}{W_i} \quad [1]$$

where V_i is the apparent valence of the dissolving Cd, V normal valence = 2, W is the calculated weight of Cd lost from the anode (determined from coulombic

data), and W_i is the actual weight of Cd lost from the anode (determined by titration or weight loss).¹ The apparent valence of the Cd ions as a function of current density is shown in Fig. 1a, b, and c for the various temperatures. It may be noted that the apparent valence is affected by current density, NO_3^- concentration, and temperature. In these solutions (with the exception of 1N K_2SO_4), a gray film, later shown to be a mixture of $\text{Cd}(\text{OH})_2$ and minute Cd particles, was formed very rapidly on the anode surface on be-

¹Note also that the apparent valence is the product of the current efficiency of the anode and the normal valence.

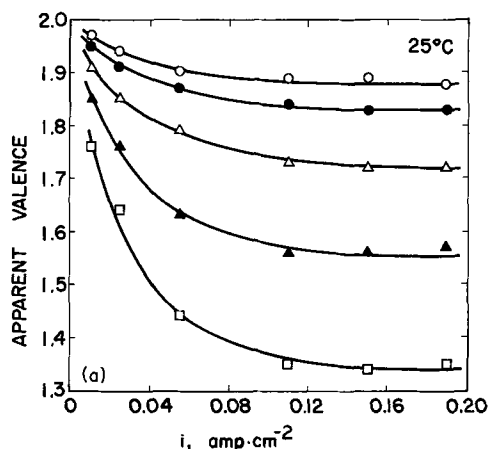


Fig. 1a. Apparent valence of cadmium dissolving anodically in KNO_3 - K_2SO_4 solutions at 25°C. \circ , 0.01N KNO_3 -0.99N K_2SO_4 ; \bullet , 0.03N KNO_3 -0.97N K_2SO_4 ; \triangle , 0.1N KNO_3 -0.9N K_2SO_4 ; \blacktriangle , 0.3N KNO_3 -0.7N K_2SO_4 ; \square , 1N KNO_3 .

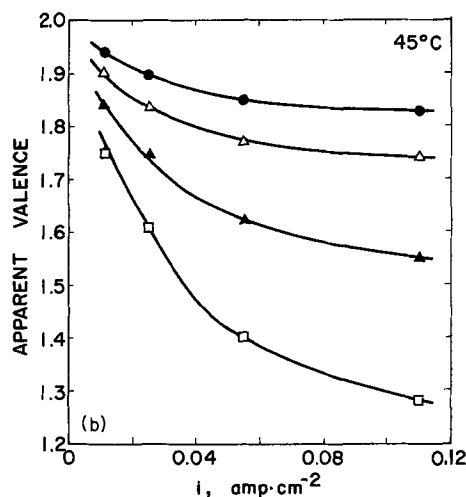


Fig. 1b. At 45°C. Symbols are the same as in Fig. 1a.

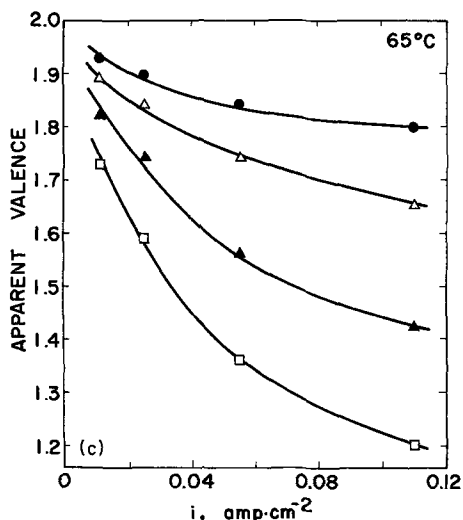


Fig. 1c. At 65°C. Symbols are the same as in Fig. 1a.

ginning the electrolysis. The film appeared to thicken with some darkening as the current density was increased. At higher current densities, $> 0.010 \text{ amp} \cdot \text{cm}^{-2}$, small portions of the film spalled off the surface. These portions turned completely white [$\text{Cd} \rightarrow \text{Cd}(\text{OH})_2$] within a few minutes if allowed to remain in contact with the electrolyte or moist air. The extreme reactivity is believed to be due to the small size of the metallic particles. Numerous attempts to determine quantitatively the amount of particles formed as a function of current density were unsuccessful. However, a small amount of the spalled gray film was collected by rapidly removing the anolyte from the cell during electrolysis, filtering with a vacuum filter, and rinsing the film thoroughly with dry acetone. Although much of the gray color faded during this operation, the remainder was stabilized by the acetone rinse. An x-ray analysis showed the film to be a mixture of Cd and $\text{Cd}(\text{OH})_2$. Microscopic studies showed a $\text{Cd}(\text{OH})_2$ matrix with metallic particles dispersed throughout.

Apparent valence of Cd in various electrolytes in the presence of Cd^{2+} .—Apparent valence measurements were made in $\text{CdCl}_2\text{-KCl}$, $\text{CdBr}_2\text{-KBr}$, $\text{CdI}_2\text{-KI}$, $\text{CdSO}_4\text{-K}_2\text{SO}_4$, $\text{Cd}(\text{Ac})_2\text{-KAc}$, and $\text{Cd}(\text{NO}_3)_2\text{-KNO}_3$ solutions at 25°C. The ionic strength was held constant at 1.5. The Cd^{2+} concentration was varied from 10^{-3} to 1N and the current density from 10^{-3} to $10^{-1} \text{ amp} \cdot \text{cm}^{-2}$.

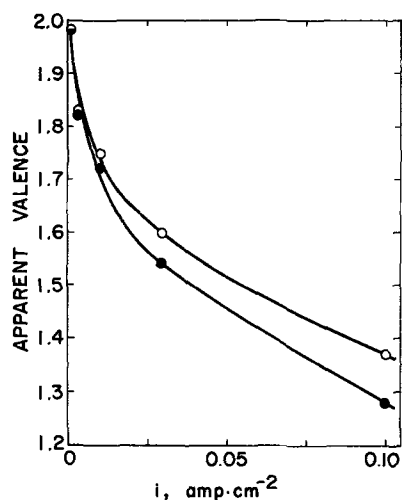


Fig. 2. Apparent valence of cadmium dissolving anodically in $\text{Cd}(\text{NO}_3)_2\text{-KNO}_3$ solutions (ionic strength = 1.5) at 25°C. O, 1N $\text{Cd}(\text{NO}_3)_2$; ●, 0.001, 0.01, and 0.1N $\text{Cd}(\text{NO}_3)_2$.

The normal valence of two was obtained for Cd in all solutions except those containing NO_3^- . Figure 2 shows a plot of the apparent valence vs. current density for these latter solutions. In all the electrolytes, except those containing NO_3^- , a very thin, tightly adherent, brownish-black film was noted. This was believed to be CdO as reported by Huber (24). In NO_3^- solutions, a gray film similar to that mentioned previously was present.

Polarization studies.—Potentials of the Cd electrode were measured at 25°C in solutions of $\text{CdCl}_2\text{-KCl}$, $\text{CdBr}_2\text{-KBr}$, $\text{CdI}_2\text{-KI}$, $\text{Cd}(\text{NO}_3)_2\text{-KNO}_3$, $\text{CdSO}_4\text{-K}_2\text{SO}_4$, and $\text{Cd}(\text{Ac})_2\text{-KAc}$. The current density was varied from 10^{-3} to $10^{-1} \text{ amp} \cdot \text{cm}^{-2}$. The overpotentials were calculated as the difference between the electrode potential at a given current density and the rest potential (potential at zero current density) in the same solution. Very stable potentials were obtained within a few minutes in all solutions except those containing NO_3^- . In NO_3^- solutions, the potentials fluctuated widely at current densities greater than $10^{-2} \text{ amp} \cdot \text{cm}^{-2}$. The fluctuations seemed to be associated with a rapid passivation and activation of the electrode, possibly caused by spalling of the gray film from the electrode. Rest potentials and Tafel slopes for the Cd electrode in the various electrolytes are shown in Table I. The linear portions of the curves existed over a current range of approximately one order of magnitude (10^{-3} to $10^{-2} \text{ amp} \cdot \text{cm}^{-2}$). Above current densities of $10^{-2} \text{ amp} \cdot \text{cm}^{-2}$, the potential rose rapidly, probably due to IR drop in the reference and/or passivation of the metal. The potentials were not noticeably affected by stirring.

Discussion

The deviation from Faraday's law of the anodic dissolution of Cd is evidently associated with the nitrate ion. Its oxidizing capability must be important as the production of nitrite ion in an amount nearly equivalent to the deviation has been reported (8, 17). In this study, it alone of the anions present possessed this capability.

Nitrate ions are most likely reduced at local cathodic sites on the Cd surface. That such sites are active during anodic dissolution is shown by the evolution of hydrogen that occurs simultaneously with such processes on certain metals. The conspicuous absence of evolved hydrogen during the anodic dissolution is probably due to the high hydrogen overpotential of Cd. The apparent valence in the various electrolytes

Table I. Rest potentials and Tafel slopes for the cadmium electrode in various electrolytes (ionic strength = 1.5) at 25°C.

Electrolyte	Rest potential, v (NHS)	Tafel slope, v
0.001N $\text{CdCl}_2\text{-1.499N KCl}$	-0.599	0.036
0.01N $\text{CdCl}_2\text{-1.485N KCl}$	-0.560	0.023
0.1N $\text{CdCl}_2\text{-1.35N KCl}$	-0.520	0.014
1N CdCl_2	-0.453	0.038
0.001N $\text{CdBr}_2\text{-1.499N KBr}$	-0.609	0.036
0.01N $\text{CdBr}_2\text{-1.485N KBr}$	-0.589	0.036
0.1N $\text{CdBr}_2\text{-1.35N KBr}$	-0.557	0.020
1.0N CdBr_2	-0.459	0.031
0.001N $\text{CdI}_2\text{-1.499N KI}$	-0.687	0.032
0.01N $\text{CdI}_2\text{-1.485N KI}$	-0.669	0.027
0.1N $\text{CdI}_2\text{-1.35N KI}$	-0.631	0.021
1N CdI_2	-0.450	0.024
0.001N $\text{CdSO}_4\text{-0.999N K}_2\text{SO}_4$	-0.539	0.028
0.01N $\text{CdSO}_4\text{-0.987N K}_2\text{SO}_4$	-0.519	0.028
0.1N $\text{CdSO}_4\text{-0.867N K}_2\text{SO}_4$	-0.484	0.024
0.001N $\text{Cd}(\text{Ac})_2\text{-1.499N KAc}$	-0.551	0.026
0.01N $\text{Cd}(\text{Ac})_2\text{-1.485N KAc}$	-0.521	0.019
0.1N $\text{Cd}(\text{Ac})_2\text{-1.35N KAc}$	-0.529	0.018
1N $\text{Cd}(\text{Ac})_2$	-0.450	0.026
0.001N $\text{Cd}(\text{NO}_3)_2\text{-1.499N KNO}_3$	-0.418	0.065
0.01N $\text{Cd}(\text{NO}_3)_2\text{-1.485N KNO}_3$	-0.399	0.076
0.1N $\text{Cd}(\text{NO}_3)_2\text{-1.35N KNO}_3$	-0.349	0.079
1N $\text{Cd}(\text{NO}_3)_2$	-0.264	0.060

can be readily explained if NO_3^- acts as a depolarizer. In solutions containing no NO_3^- , local corrosion cannot occur and the normal valence is observed. When NO_3^- is present, it removes hydrogen from the local cathodes, corrosion proceeds along with anodic dissolution, and a valence lower than normal is observed. The metallic particles appearing in the gray surface film probably result from a disintegration of the electrode caused by a combination of local corrosion and anodic dissolution. These two processes would undermine and dislodge particles whose formation is initiated by the protection of an area by the local cathodic (depolarization) reaction. Also, uneven current densities on the electrode surface caused by nonuniform or disrupted surface films would lead to a similar situation.

With this concept of the anodic dissolution, a model can be described mathematically to give the apparent valence of Cd as follows.

Consider the total rate that Cd is being removed from the electrode surface as the summation of separate rates in a manner similar to that proposed by Hoey and Cohen (15). For this case, anodic dissolution, local corrosion, and disintegration will be considered. Thus

$$r_t = r_e + r_c + r_d \quad [2]$$

but,

$$W/W_i = r_e/r_t = r_e/(r_e + r_c + r_d) \quad [3]$$

and from Eq. [1]

$$V_i = 2r_e/(r_e + r_c + r_d) \quad [4]$$

The rate of anodic dissolution is proportional to the current density in the external circuit as related by Faraday's law

$$r_e = k_e i \quad [5]$$

The local corrosion rate would be a function of several variables, among which are the electronegativity of the metal, the number of local cathodes (purity and metallic structure), hydrogen ion concentration, depolarizer (NO_3^-) concentration, corrosion potential, and the rate at which local cathodes are uncovered. Undoubtedly, the expulsion of Cd ions from the electrode during the anodic dissolution (passage of current) ruptures the protective film and exposes the metal underneath. A greater rate of rupturing the film (increasing current) will expose more metal with its associated local cathodes and allow local corrosion to occur faster, i.e., the rate at which local cathodes are uncovered is a function of current density. This is essentially the concept proposed by Robinson and King (25) in which the corrosion rate of a metal increases with increasing current. Thus, for a given metal specimen

$$r_c = k_c' i^a C_{\text{NO}_3^-}^b C_{\text{H}^+}^c C_{\text{Cd}^{+2}}^d \quad [6]$$

If the local corrosion rate is controlled by the depolarization reaction rather than by the deposition of H^0 on the local cathodes, then C_{H^+} and $C_{\text{Cd}^{+2}}$ should have little influence, and

$$r_c = k_c i^a C_{\text{NO}_3^-}^b \quad [7]$$

Disintegration was proposed as occurring as a consequence of local corrosion, so as a first approximation

$$r_d = k_d' r_c = k_d i^a C_{\text{NO}_3^-}^b \quad [8]$$

therefore

$$\begin{aligned} V_i &= 2k_e i / (k_e i + k_c i^a C_{\text{NO}_3^-}^b + k_d i^a C_{\text{NO}_3^-}^b) \\ &= 2 / (1 + k' i^{a-1} C_{\text{NO}_3^-}^b) \\ &= 2 - 2k' i^{a-1} C_{\text{NO}_3^-}^b + 2(k' i^{a-1} C_{\text{NO}_3^-}^b)^2 - \dots \end{aligned} \quad [9]$$

Neglecting terms with orders of two or higher gives

$$V_i = 2 - k i^m C_{\text{NO}_3^-}^n \quad [10]$$

which can be conveniently tested with data from Fig. 1 and 2. Log-log plots of $2 - V_i$ vs. i and $C_{\text{NO}_3^-}$ are

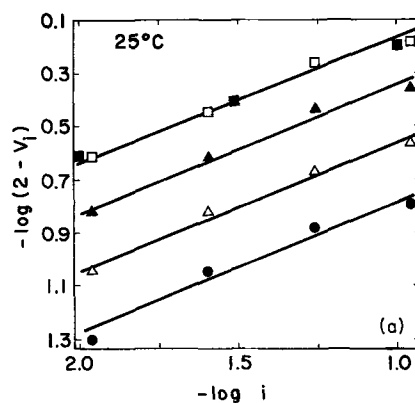


Fig. 3a. Effect of current density on the apparent valence of cadmium at 25°C. ●, 0.03N KNO_3 -0.97N K_2SO_4 ; △, 0.1N KNO_3 -0.9N K_2SO_4 ; ▲, 0.3N KNO_3 -0.7N K_2SO_4 ; □, 1N KNO_3 ; ■, 1N $\text{Cd}(\text{NO}_3)_2$.

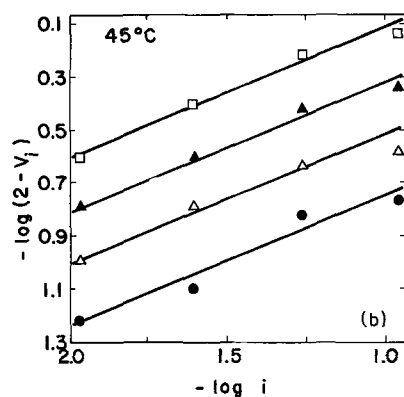


Fig. 3b. At 45°C. Symbols are the same as in Fig. 3a

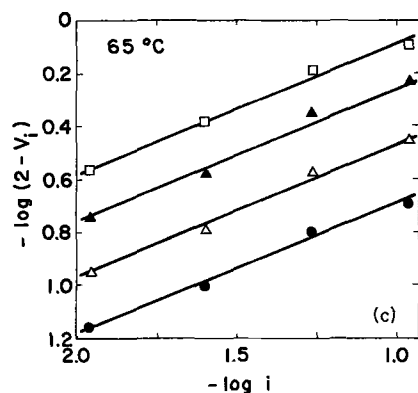


Fig. 3c. At 65°C. Symbols are the same as in Fig. 3a

shown in Fig. 3 and 4. Average values for m and n evaluated from the slopes of these plots are 0.49 and 0.41, respectively. The lines through the data points in the figures have been drawn using these slopes. This is seen to correlate the data very well.

The effect of $C_{\text{Cd}^{+2}}$ can be seen by leaving this term in Eq. [6] and reducing it in the previously described manner to

$$V_i = 2 - k i^m C_{\text{NO}_3^-}^n C_{\text{Cd}^{+2}}^p \quad [11]$$

Figure 5 shows a log-log plot of $(2 - V_i) C_{\text{NO}_3^-}^{-0.41}$ vs. $C_{\text{Cd}^{+2}}$ for various constant current densities. These plots are approximately linear, with a slope p equal to 0.005, thus showing that the effect of Cd^{+2} is slight.

The constancy of the exponents in Eq. [10] and [11] with temperature compels the proportionality constant k to account for the temperature variation of V_i . An

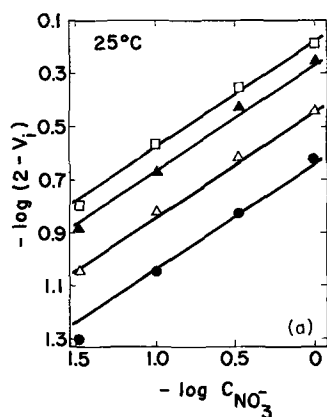


Fig. 4a. Effect of NO_3^- concentration on the apparent valence of cadmium at 25°C. ●, 0.011 $\text{amp}\cdot\text{cm}^{-2}$; △, 0.025 $\text{amp}\cdot\text{cm}^{-2}$; ▲, 0.055 $\text{amp}\cdot\text{cm}^{-2}$; □, 0.110 $\text{amp}\cdot\text{cm}^{-2}$.

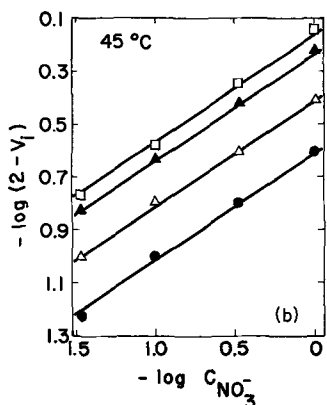


Fig. 4b. At 45°C. Symbols are the same as in Fig. 4a

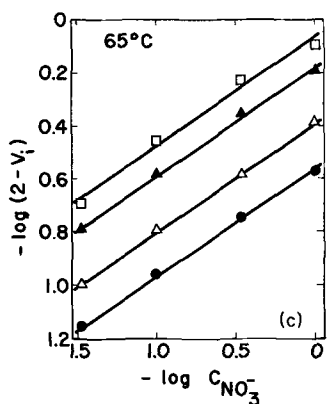


Fig. 4c. At 65°C. Symbols are the same as in Fig. 4a

Arrhenius plot was prepared as shown in Fig. 6 which gave an activation energy of 810 cal and k equal to $8.72 \exp(-810/RT)$. Inasmuch as the k -value is a ratio of rate constants (see Eq. [9]), this activation energy should be regarded more as a method of expressing a temperature variation rather than as having any mechanistic significance. Substituting numerical values in Eq. [10] gives

$$V_i = 2.00 - 8.72 i^{0.49} C_{\text{NO}_3^-}^{0.41} \exp(-406/T) \quad [12]$$

which can be used to calculate the apparent valence of Cd ions (or the current efficiency of the Cd anode).

Linear regions were observed in the overpotential vs. $\log i$ plots at current densities less than 0.01 $\text{amp}\cdot\text{cm}^{-2}$. Since the current efficiencies were approximately 100% in all the solutions except NO_3^- , the slopes can probably be associated with the electrochemical dissolution mechanism. Lake and Casey (26)

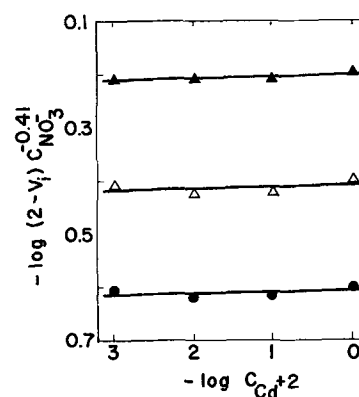


Fig. 5. Effect of Cd^{+2} concentration on the apparent valence of cadmium at 25°C. ●, 0.01 $\text{amp}\cdot\text{cm}^{-2}$; △, 0.03 $\text{amp}\cdot\text{cm}^{-2}$; ▲, 0.10 $\text{amp}\cdot\text{cm}^{-2}$.

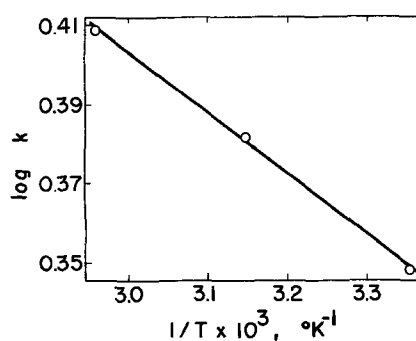
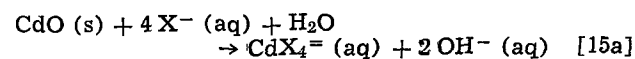
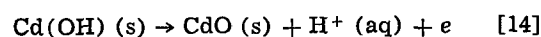
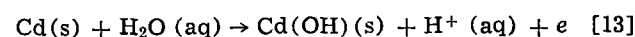
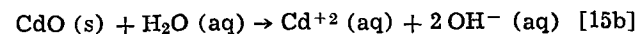


Fig. 6. Effect of temperature on the apparent valence of cadmium (k from Eq. [10]).

have suggested that Cd dissolves either as the oxide or as a complex and that $\text{Cd}(\text{OH})_2$ precipitates when solubility limits are reached. This, together with observations from these studies, suggests a mechanism as follows



or



where X^- represents halide ions which are known to complex readily with Cd^{+2} . For either [15a] or [15b] controlling, the theoretical Tafel slope would be 30 mv, approximately equal to that observed. In nitrate solutions, the anodic dissolution is accompanied by local corrosion and disintegration whose rates are varying with current density. Therefore, the measured potentials are probably mixed potentials and do not have mechanistic significance.

Conclusions

The anodic dissolution of Cd has been studied in aqueous solutions containing various cations (K^+ , Cd^{+2}) and anions (Cl^- , Br^- , I^- , Ac^- , $\text{SO}_4^{=}$, NO_3^-). The calculated valence of the Cd ions was the normal value (+2) in all solutions except those containing NO_3^- . In the latter solutions, the calculated (apparent) valence was less than two (anodic efficiency less than 100%) and was a function of NO_3^- concentration, current density, and temperature.

The low efficiency of the Cd anode in nitrate solutions is explained in terms of a mechanism in which the anodic dissolution is accompanied by local corrosion and disintegration. The role of NO_3^- is that of

a depolarizer which removes H° from local cathodic sites on the anode surface. (Cd has a relatively high hydrogen overvoltage and hence hydrogen is not evolved.) Momentary protection of portions of the anode surface (local cathodic sites, uneven film formation, or film disruption) allows anodic dissolution to undermine and ultimately detach metal particles from the surface. These particles are noted in surface films on the anode and the phenomenon by which they are formed has been termed "anodic disintegration." This mechanism leads to a mathematical model which is consistent with the experimental results.

Acknowledgment

The authors are grateful for support of this work by the Office of Naval Research.

Manuscript received Nov. 14, 1966; revised manuscript received Jan. 18, 1967. This paper was presented at the Philadelphia Meeting, Oct. 9-14, 1966. This is Paper No. 15 from the Graduate Center for Materials Research, Space Sciences Research Center at Rolla.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1967 JOURNAL.

REFERENCES

1. G. Bredig, *Z. Phys. Chem.*, **32**, 127 (1900).
2. E. F. Burton, *Phil. Mag.*, **11**, 425 (1906).
3. M. C. Del Boca, *Helv. Chim. Acta*, **16**, 565 (1933).
4. M. E. Straumanis and B. K. Bhatia, *This Journal*, **110**, 357 (1963).
5. R. L. Petty, A. W. Davidson, and J. Kleinberg, *J. Am. Chem. Soc.*, **76**, 363 (1954).
6. B. D. Laughlin, J. Kleinberg, and A. W. Davidson, *ibid.*, **78**, 559 (1956).
7. M. E. Straumanis and D. L. Mathis, *J. Less-Common Metals*, **4**, 213 (1962).
8. D. T. Sorensen, A. W. Davidson, and J. Kleinberg, *J. Inorg. Nucl. Chem.*, **13**, 64 (1960).
9. W. J. James and G. E. Stoner, *J. Am. Chem. Soc.*, **85**, 1354 (1963).
10. E. Rajjola and A. W. Davidson, *ibid.*, **78**, 556 (1956).
11. M. E. Straumanis and K. Poush, *This Journal*, **112**, 1185 (1965).
12. M. L. Rumpel, A. W. Davidson, and J. Kleinberg, *J. Inorg. Chem.*, **3**, 935 (1964).
13. M. E. Straumanis and M. Dutta, *ibid.*, **5**, 992 (1966).
14. J. H. Greenblatt, *Corrosion*, **18**, 125t (1962).
15. G. R. Hoey and M. Cohen, *This Journal*, **105**, 245 (1958).
16. M. E. Straumanis and Y. Wang, *Corrosion*, **22**, 132 (1966).
17. Y. C. Sun, M. S. Thesis, University of Missouri at Rolla, 1964.
18. J. W. Johnson, C. K. Chi, and W. J. James, *Corrosion*, in press.
19. J. S. Sanghvi, M. S. Thesis, University of Missouri at Rolla, 1965.
20. B. W. Jong, M. S. Thesis, University of Missouri at Rolla, 1966.
21. C. I. Lu, M. S. Thesis, University of Missouri at Rolla, 1966.
22. Y. C. Sun, Ph.D. Thesis, University of Missouri at Rolla, 1966.
23. C. K. Wu, M. S. Thesis, University of Missouri at Rolla, 1967.
24. K. Huber, *This Journal*, **100**, 376 (1953).
25. J. L. Robinson and P. F. King, *ibid.*, **108**, 36 (1961).
26. P. E. Lake and E. J. Casey, *ibid.*, **105**, 52 (1958).

Rate-Controlling Processes in the High-Temperature Oxidation of Tantalum

John Stringer¹

Metal Science Group, Battelle Memorial Institute, Columbus Laboratories, Columbus, Ohio

ABSTRACT

The oxidation of tantalum in the temperature range 500°-950°C is approximately linear. At atmospheric pressure, the rate constant increases with temperature in the temperature range 500°-650° and 800°-950°C, but decreases slightly as the temperature increases from 650° to 800°C. The reaction rate depends on the square root of the oxygen pressure at low pressures and high temperatures, but at lower temperatures the pressure dependence decreases as the pressure increases. On the basis of experimental evidence in the literature, it is concluded that in the temperature range 500°-800°C the rate-controlling process is a reaction at the interface between the atmosphere and a layer of tantalum pentoxide growing adherently on the metal surface. This interface reaction is preceded by an equilibrium adsorption of oxygen on the interface, the adsorption taking place with dissociation. In the temperature range 800°-950°C, the over-all linear rate is a consequence of the diffusion-controlled growth of adherent pentoxide to a critical thickness, at which the scale fails from the metal. The corollary to this conclusion is that the rate of the diffusion process must be strongly dependent on the oxygen pressure.

The oxidation of tantalum, and the not-dissimilar oxidation of niobium, has been studied extensively for both practical and theoretical reasons. The reaction kinetics are of considerable interest, since the dependence of the reaction rate on both temperature and oxygen pressure is unusual.

After an initial period (a few minutes at 950°C and a few hours at 500°C) the reaction rate becomes approximately constant (linear rate law). The linear rate constant increases with temperature from 500° to 650°C and from 800° to 950°C, but decreases slightly in the temperature range 650°-800°C. The rate constant increases with pressure, the effect decreasing as the pressure increases. Increasing the temperature in-

creases the pressure at which the pressure-dependence starts to diminish.

The principal reaction product is tantalum pentoxide, Ta_2O_5 . The oxide grows adhering to the metal surface and is formed under compressive growth stresses. Eventually these cause the scale to fail from the metal surface. Growth of adherent oxide recommences immediately on the freshly exposed metal surface, and repetition of this process produces a laminated detached scale. In addition to the pentoxide, platelets of a suboxide are formed penetrating into the metal from the scale/metal interface. Finally, oxygen also dissolves in the metal.

While the oxidation of niobium has a number of points of similarity to that of tantalum, notably in the temperature- and pressure-dependence of the rate

¹ Present address: Department of Metallurgy, University of Liverpool, Liverpool, England