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Corrosion of zinc in NH_4Cl solution

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Zinc corrosion in NH_4Cl solution is of importance in Leclanche's cells. The dependences of E_{corr} and i_{corr} with the concentration of NH_4Cl are discussed in this paper.

Key words: Zinc corrosion, ammonium chloride solution, Tafel slope

INTRODUCTION

In Leclanche's cells, zinc dissolves forming $Zn(NH_3)_2Cl_2$

EXPERIMENTAL

A three electrode cell assembly with zinc (99.5%) with platinum foil and SCE was used. Potentiodynamic polarisation was carried out using the BAS electrochemical Analyser 100 A at 100 mV/sec.

RESULTS AND DISCUSSION

Figure 1 presents typical polarisation curves obtained in 0.5M NH_4Cl solution. The dependence of E_{corr} and i_{corr} in NH_4Cl solution was studied in detail. Zinc dissolves in solutions containing anions and forms tetrahedral complexes [1]. The charge transfer may proceed via monovalent zinc ions which is stabilised by the presence of ligands.

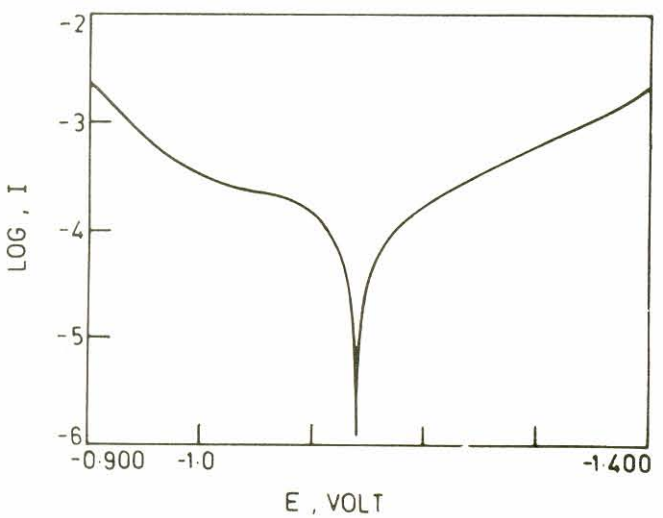

Fig. 1: Polarisation of zinc in 0.5M NH_4Cl

Dissolution of zinc

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^- \quad \cdots(1)$$

$$Zn + Cl^- \rightleftharpoons \underset{ads}{ZnCl} + e \quad \cdots(2)$$

$$\underset{ads}{ZnCl} + NH_4^+ \longrightarrow Zn\begin{matrix}NH_3\\Cl\end{matrix} + H^+ \quad \cdots(3)$$

$$Zn\begin{matrix}NH_3\\Cl\end{matrix} + Cl^- \rightleftharpoons Zn\begin{matrix}NH_3\\Cl\end{matrix} + e \quad \cdots(4)$$

$$Zn\begin{matrix}NH_3\\Cl\\Cl\end{matrix} + NH_4^+ \rightleftharpoons Zn(NH_3)_2Cl_2 + H^+ \quad \cdots(5)$$

If step 3 is rate determining,

$$i_a = \vec{K}_a(Zn)(NH_4^+)(Cl^-)\exp - F\Delta\emptyset/RT$$

Broadly, both theoretical and experimental values agree, except in the case of the anodic reaction with respect to NH_4^+ ions (Table I).

TABLE–I: Mechanistic parameters derived for the dissolution of zinc

S. No.	Parameter	Theoretical value	Experimental value
1.	Anodic Tafel slope (mV/decade)	60	70 + 10
2.	Anodic reaction order w.r.t (NH_4^+)	1.0	0.9
3.	Anodic reaction order w.r.t (Cl^-)	2.0	1.5 ± 0.1
4.	Anodic reaction w.r.t pH	−1.0	—

Corrosion of zinc

If the cathodic reaction is the reduction of oxygen, a cathodic Tafel slope of 70 ± 10 mV suggests as follows:

$$O_2 + 2M \rightleftharpoons 2MO \quad \cdots(1)$$

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$$MO + H_2O \rightleftharpoons MO - H - OH \quad \cdots (2)$$

$$MO + H - OH + e \rightleftharpoons MO - H - OH^- \quad \cdots (3)$$

$$MO - H - OH^- + H^+ \longrightarrow MOH + H_2O \quad \cdots (4)$$

$$MOH + H^+ + e \rightleftharpoons M + H_2O \quad \cdots (5)$$

If step 4 is rate determining,

$$i_c = \vec{K}_c\,[O_2][H^+]\exp F\Delta\emptyset/RT$$

At E_{corr}, $i_{corr} = i_a = i_c$

$$\vec{K}_a(Zn)(NH_4^+)(Cl^-)\exp - F\Delta\emptyset_{corr}/RT$$

$$= \overleftarrow{K}_c\,[O_2](H^+)\exp F\Delta\emptyset_{corr}/RT$$

$$\Delta\emptyset_{corr} = \Delta\emptyset^0_{corr} + \frac{RT}{2F}\log\left\{\frac{(NH_4^+)(Cl^-)}{(O_2)(H^+)}\right\}$$

The experimental and theoretical values agree very well except in the case of Cl^- (Table II).

CONCLUSION

The mechanism of corrosion of zinc in NH_4Cl solution reveals the dissolution involving $Zn^{ZnCl}_{ads} + NH_4^+ \longrightarrow Zn\lessdot^{NH_3}_{Cl} + H^+$ as the rate determining step, with the reduction of oxygen as the cathodic reaction.

TABLE–II: Parameters derived for the mechanism of zinc corrosion in NH_4Cl solutions

S.No.	Parameter	Theoretical value	Experimental value
1.	Anodic Tafel slope	60 ± 10	70 ± 10
2.	Cathodic Tafel slope	60	70 ± 10
3.	$\left[\frac{d\,E_{corr}}{d\,C_{NH_4Cl}}\right]$	30	37.2 mV
4.	$\left[\frac{d\log i_{corr}}{d\log(NH_4Cl)}\right]$	—	0.71
5.	$\left[\frac{d\log i_{corr}}{d\log C_{Cl}}\right]$	3.2	2.9
6.	$\left[\frac{d\log i_{corr}}{d\log C_{NH_4^+}}\right]$	1.6	0.3

REFERENCE

1. *Encyclopedia of Electrochemistry of Elements*, Vol V, Allen J Bard.