

Short Communication

Cathodic processes on zinc in alkaline zincate solutions

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Abstract

The charging process of alkaline zinc secondary batteries is accompanied by the formation of hydrogen. Both the current and the coulombic efficiency, and in part the energy efficiency, are dictated by the production of hydrogen. Gasometric methods are used to determine the rates of hydrogen evolution and a potentiodynamic polarization method is employed to study the behaviour of zinc in alkaline solutions. It is found that an increase in ZnO concentration and a decrease in KOH concentration lower the rate of hydrogen evolution.

Keywords: Secondary batteries; Alkaline zinc batteries; Hydrogen evolution

1. Introduction

The electrochemical behaviour of zinc in alkaline solution, with special emphasis on the electrochemical kinetics, was reviewed in 1974 [1]. When zinc is deposited from alkaline solutions, three types of deposits are encountered [2,3]:

(i) smooth deposits at low overpotentials in vigorously stirred electrolytes;

(ii) dark-grey, porous deposits (mossy or bulbous) in quiescent, concentrated, hydroxide-zincate electrolytes at low overpotentials (< 75 mV); these deposits are also formed in cells with paste-type zinc electrodes, and

(iii) dendritic deposits in zincate electrolyte at high overpotentials (75 to 85 mV).

In concentrated alkaline solutions, the hydrogen-evolution reaction is found to have a Tafel slope of 124 mV/decade for 6 M and 10 M KOH solutions [4,5]; the respective exchange-current densities are 0.85×10^{-9} and 1.5×10^{-9} A/cm².

Synder and Lander [6] investigated the self-discharge of zinc battery electrodes and found a decrease in hydrogen production with either increasing KOH concentration or increasing mercury content of the electrode. In zincate-saturated alkaline media, Dirkse and Hampson [7] observed the corrosion of the zinc electrode to decrease significantly. In the presence of zincate

ions, increased corrosion eventuated with increasing KOH concentration [8]. For various alkaline zincate electrolytes, hydrogen production increased with decreased zincate and KOH concentrations [9].

The work reported here describes a gasometric method for measuring the rate of hydrogen evolution, and a potentiodynamic (E -log i) method to study the behaviour of zinc in alkaline zincate solutions.

2. Experimental

2.1. Gasometric method

The gasometric instrument has a thermostatic bath assembly that comprises a metal trough (60 cm \times 30 cm \times 30 cm) a relay, an electrical heater and a contact thermometer. The bath is used as a reservoir for water that is maintained at constant temperature with an accuracy of ± 1 K. The water is circulated continuously through the two major parts of the instrument, namely, the experimental cell and the vertical tubes of the gas collector. Both of the latter are provided with glass jackets for the circulation of the water maintained at constant temperature.

The double-walled, H-type, glass cell had a 200 ml capacity, three ground-joint openings, and one stopcock for gas release at the top. One part of the H-cell had

two openings: a broad one for the working electrode (a rectangular strip of pure (99.9999% wt.% zinc), and a gas-release stopper to expel the excess gas pressure that builds up when the working electrode is introduced.

The gas collector consists of vertical tubes of different capacities that are made from standard graduated burettes. The tubes are surrounded by glass jackets for the circulation of constant-temperature water. The reactions are carried out at a particular specified temperature, and the gases are collected at the same temperature with an accuracy of ± 1 K.

The gas is collected over a solution of 20-25 wt.% sodium chloride acidified with HCl or H₂SO₄ and coloured with methyl orange or methyl red. The colour facilitates observations of the meniscus of the liquid for measurement of the gas volume. Further, the solubility of the gases such as CO₂, H₂, etc., is very much reduced in such liquids, and this improves the accuracy of measurement. The gas volume is always measured at atmospheric pressure, using a pressure reservoir bulb. The reservoir is fitted with a tube of narrow bore (3 mm) at right angles to avoid parallax error during the

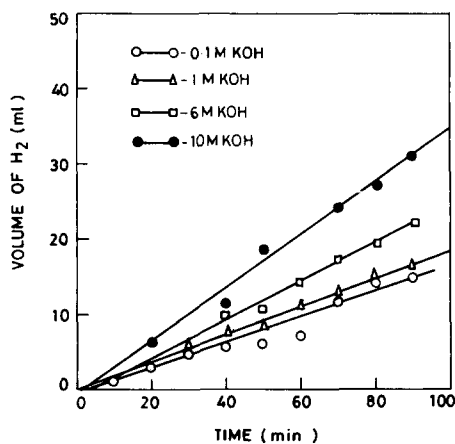


Fig. 1. Hydrogen evolution in KOH solutions.

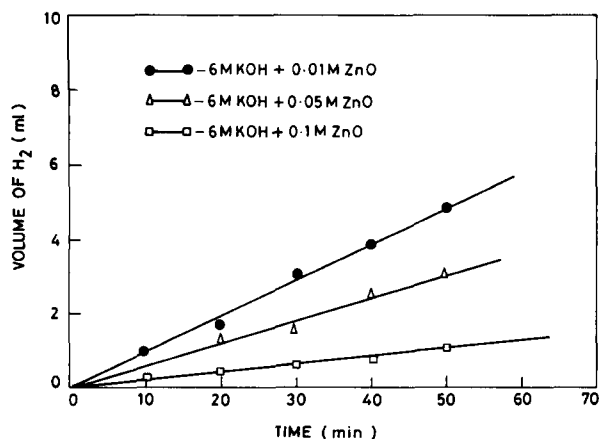


Fig. 2. Hydrogen evolution in 6 M KOH with different ZnO concentrations.

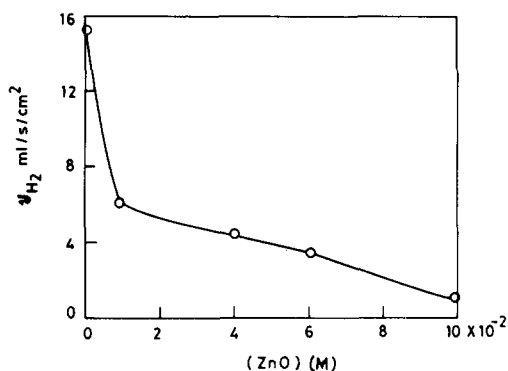


Fig. 3. Variation in rate of hydrogen evolution with ZnO concentration in 6 M KOH.

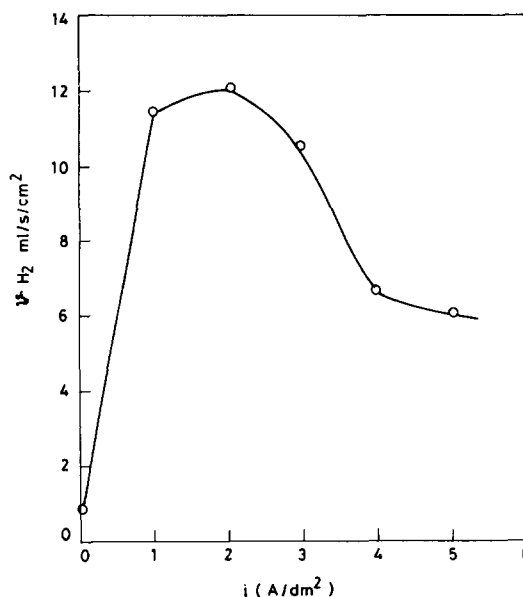


Fig. 4. Rate of hydrogen evolution in 6 M KOH + 10^{-2} M ZnO solution at different current densities.

adjustment of the levels inside the burette and the reservoir bulb that ensures the pressure of the gas inside the tube is at atmospheric pressure. As the liquid levels inside and outside the burette are kept the same from the beginning of the experiment, the necessity of any correction to the pressure due to aqueous surface tension does not arise.

Potentiostatic polarization studies (E -log i) were conducted with a BAS 100 Electrochemical Analyser, USA. The electrode potential was scanned away from the corrosion potential on either side, and the linear segments of the E -log i curves were extrapolated to the corrosion potential, to obtain the corrosion-current density, i_{corr} . The anodic and cathodic linear segments of E -log i curves gave the respective Tafel slopes.

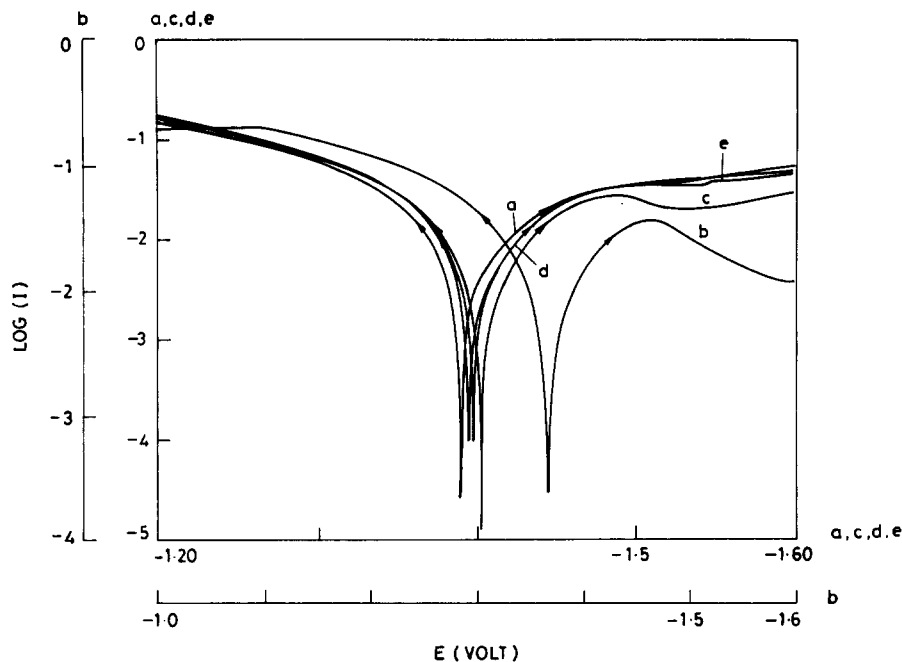


Fig. 5. Potentiodynamic polarization curves for zinc in 6 M KOH containing various amounts of ZnO: (a) 0.01 M; (b) 0.02 M; (c) 0.03 M; (d) 0.05 M, and (e) 0.08 M. Scan rate=100 mV/s.

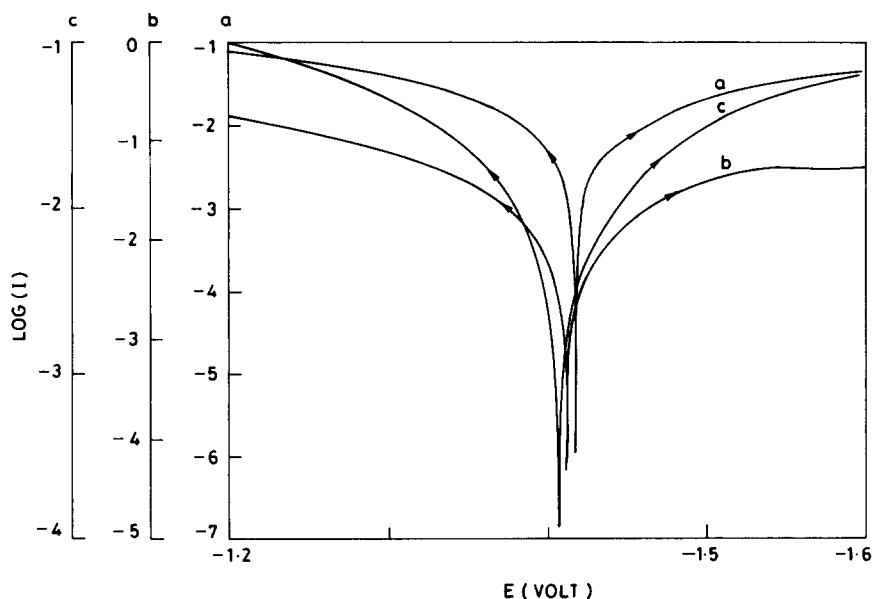


Fig. 6. Potentiodynamic polarization curves for zinc in 10 M KOH containing various amounts of ZnO: (a) 0.01 M; (b) 0.02 M, and (c) 0.03 M. Scan rate=100 mV/s.

3. Results

Fig. 1 presents the volume of hydrogen collected, with time, for the corrosion of zinc in KOH solutions. Increase in the KOH concentration accelerates the rate of hydrogen evolution ($\text{ml}/(\text{s m}^2)$). In presence of ZnO, the rate decreases in 6 M KOH solution (Fig. 2). The rate exhibits a sharp decline at 2×10^{-2} M ZnO and then gradually decreases (Fig. 3). When zinc is polarized cathodically at different current densities, the volume

of hydrogen increases linearly with time and the rate of evolution is found to be a maximum at $2 \text{ A}/\text{dm}^2$ in 6 M KOH containing 10^{-2} M ZnO. This suggests that at high current densities, either the freshly formed zinc hinders the evolution of hydrogen, or the availability of water at the interface is restricted (Fig. 4).

Typical E - $\log i$ curves for zinc in 6 M and 10 M KOH solutions with various amounts of ZnO are presented in Figs. 5 and 6, respectively. The current obtained by extrapolating the cathodic Tafel line to

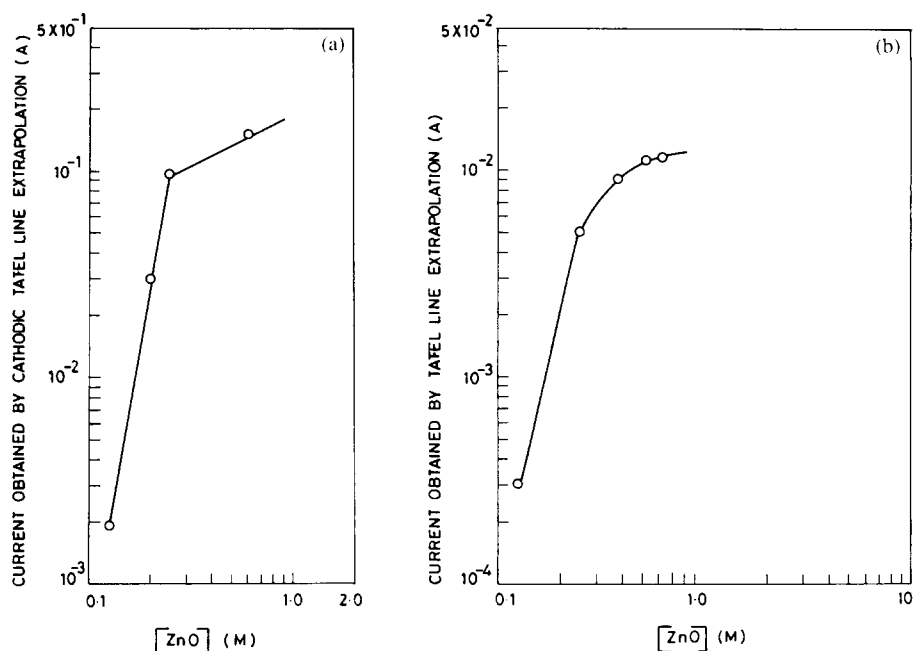
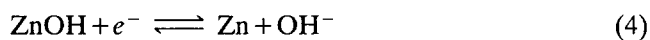
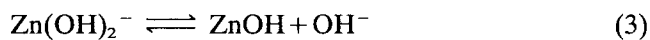
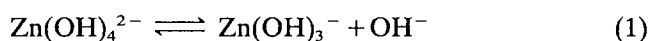


Fig. 7. Effect of ZnO concentration on current density obtained by extrapolation of cathodic Tafel line: (a) 6 M KOH, and (b) 10 M KOH.

the open-circuit potential is found to increase with ZnO concentration (Fig. 7).

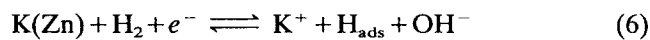
4. Discussion

The predominant soluble species of zinc in alkaline solutions is the tetrahedral $\text{Zn}(\text{OH})_4^{2-}$ ion. Potentiometric experiments [10], infrared and Raman spectral studies [11], and nuclear magnetic resonance investigations [12] confirm the soluble species to be $\text{Zn}(\text{OH})_4^{2-}$. Therefore, the mechanism of zinc deposition [13] is:



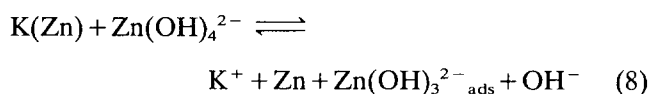
Epelboin and co-workers [14–16] have postulated that coupling between the discharge reactions and surface diffusion of the adsorbed Zn(I) ions can lead to variations in the current density over the surface of the electrode and, thereby, to the formation of mossy zinc.

Under cathodic polarisation in KOH solution, the proposed mechanism for hydrogen evolution, as suggested by Muralidharan and Rajagopalan [8], is:



If the discharge of K^+ ions is slow, then the rate of hydrogen evolution depends on both the potential and the K^+ -ion concentration. This indicates that hydrogen production should increase with KOH concentration.

In presence of zincate ions, the above reaction scheme is altered and can give rise to an alternate route along which the $\text{K}(\text{Zn})$ species is discharged, i.e.:



If this reaction occurs, then the presence of ZnO slows down the rate of hydrogen evolution. With increasing KOH concentration, the formation of the $\text{K}(\text{Zn})$ species increases, whereas the discharge of this species via reduction of water is decreased. Hence, the above reaction is more significant at higher KOH concentrations, and lowers hydrogen production with increasing KOH concentration. At higher current densities, the following may occur:

(i) discharge of K^+ ions leading to $\text{K}(\text{Zn})$, and this intermetallic compound then reacts with $\text{Zn}(\text{OH})_4^{2-}$ to produce $\text{Zn}(\text{OH})_3^{2-}$;

(ii) reduction of $\text{Zn}(\text{OH})_4^{2-}$ to zinc, and

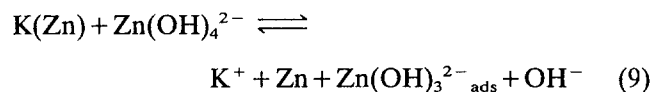
(iii) decrease in water activity at the interface.

All of these three effects would hinder hydrogen evolution. At low zincate concentrations (10^{-2} M) in 6 M KOH, hydrogen evolution is found to occur slowly, while above 10^{-2} M, hydrogen evolution is not observed visually. Therefore, the currents obtained by extrapolation of Tafel plots to the open-circuit potential in 6 M and 10 M KOH solution containing ZnO are only

the exchange-current densities of the zinc/zincate reaction.

5. Conclusions

Either an increase in ZnO concentration or a decrease in KOH concentration decreases the rate of hydrogen evolution. This may be due to the following reaction:



At cathodic-current densities above 2 A/dm², the hydrogen evolution became less due to a decrease in the water activity at the interface.

References

- [1] R.D. Armstrong and M.F. Bell, *Specialist Periodical Reports, Electrochemistry*, Vol. 4, The Chemical Society, London, 1974, p. 1.
- [2] S. Arouete, K.F. Slurton and H.G. Osum, *J. Electrochem. Soc.*, **116** (1969) 166.
- [3] R.D. Naybour, *J. Electrochem. Soc.*, **116** (1969) 520.
- [4] Z.A. Iofa, L.V. Komlev and V.S. Bagotskii, *Zh. Fiz. Khim.*, **35** (1961) 1571.
- [5] T.S. Lee, *J. Electrochem. Soc.*, **122** (1975) 171.
- [6] R.N. Synder and J.J. Lander, *J. Electrochem. Technol.*, **3** (1965) 161.
- [7] T.P. Dirkse and N.A. Hampson, *Electrochim. Acta*, **16** (1971) 2049.
- [8] V.S. Muralidharan and K.S. Rajagopalan, *J. Electroanal. Chem.*, **94** (1978) 21.
- [9] R.E.F. Einerhand, W.H.N. Vissche and E. Barendrecht, *J. Appl. Electrochem.*, **18** (1988) 799.
- [10] T.P. Dirkse, *J. Electrochem. Soc.*, **101** (1954) 328.
- [11] J.S. Fordyce and R.L. Baum, *J. Chem. Phys.*, **43** (1965) 843.
- [12] G.H. Newman and G.E. Blomgren, *J. Chem. Phys.*, **43** (1965) 2744.
- [13] J.O'M. Bockris, Z. Nagy and A. Damjanovic, *J. Electrochem. Soc.*, **119** (1972) 285.
- [14] I. Epelboin, M. Kasouri, E. Lejay and R. Wiart, *Electrochim. Acta*, **20** (1975) 603.
- [15] I. Epelboin, M. Kasouri and R. Wiart, *J. Electroanal. Chem.*, **55** (1975) 488.
- [16] I. Epelboin, M. Kasouri and R. Wiart, *J. Electroanal. Chem.*, **65** (1975) 373.