THE ELECTRODEPOSITION OF ZINC ONTO GRAPHITIC CARBON SUBSTRATES FROM ALKALINE ELECTROLYTES

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Summary

The electrodeposition and dissolution reactions of zinc on both solid and pasted graphitic substrates, in a series of KOH electrolytes containing zincate, have been studied using cyclic voltammetry. The data acquired have been used to aid the interpretation of the effects of graphitic additions on the charge and discharge reactions of conductor-modified secondary cells with zinc anodes.

Introduction

The efficiency of secondary cells with zinc anodes is reduced by the metal's high degree of dissolution during the discharge reaction. This leads, after repeated cycling, to the phenomena of shape change and dendritic growth, the latter eventually resulting in premature short-circuiting of the cell. The suppression of dendrites and, hence, the promotion of an extended cycle life has been the aim of many investigators.

Enhanced performance has been obtained by the incorporation of certain additives into electrode formulations. The majority of these are metal oxides (*e.g.*, PbO, Bi_2O_3, Tl_2O_3) [1 - 3] and heavy metals (*e.g.*, Hg, Pb, Cd) [4, 5]. The electrodeposition of zinc, and the effect these additives have on it, has been widely reported [6 - 10]. In particular McBreen *et al.* [9, 10] found evidence of underpotential deposition (to a monolayer thickness) prior to bulk deposition. This was only applicable, however, to metals whose work function was higher than that of zinc.

Polymeric additives are another alternative and have been examined extensively by McNeil and Hampson [11 - 13]. The most promising of these

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are polycarbonate and PTFE which promote a porous and, hence, a more retentive structure.

More recent investigations by Duffield *et al.* [14, 15] have shown that the addition of graphite (along with PTFE) can further enhance cell cycle life. It is proposed that this is achieved by retaining oxidised zinc species within the vicinity of the electrode during discharge. On subsequent recharge, the reduction of any zinc oxide formed is more easily facilitated by its close proximity to the conductive graphite. The electrodeposition of zinc onto graphite substrates is not widely reported. Despić [16] has, however, carried out such investigations but from a buffered, acidic zinc sulphate solution. Viswanathan *et al.* [17] have examined a zinc–potassium hydroxide (KOH) system but were interested primarily in the commercial production of electrodeposited zinc powder.

Although the inclusion of graphite in zinc anode formulations promotes enhanced cycle life, it could also create some unwanted effects. In particular its relatively low hydrogen overpotential (lower than that of zinc) may lead to an increased level of gassing during charging. It was therefore considered pertinent to study the electrodeposition and dissolution of zinc on planar and pasted graphitic substrates in a series of KOH electrolytes containing zincate.

Experimental

Experimental investigations were carried out in a 7 M KOH (AnalaR grade) electrolyte containing varying amounts of dissolved zinc oxide (ZnO, AnalaR grade). The electrolyte was purged with oxygen-free nitrogen for fifteen minutes prior to and during electrochemical investigations. A standard three-limbed electrolytic cell was employed for all experiments. The reference electrode limb contained an Hg/HgO electrode (to which all potential measurements refer). This limb terminated in a Luggin capillary which was sited directly below the working electrode. The counter electrode limb contained a high surface area nickel gauze.

Three types of working electrode were employed: solid zinc, solid graphite, and porous, pasted graphite. The zinc electrodes were made from rods (99.999%, Koch-Light Ltd.) set in Teflon shrouds, giving a circular electrode area of 0.071 cm^2. Preparation consisted of polishing on 600 and 1200 grade silicon carbide (SiC) paper before etching in 10% v/v (S.G. 1.42) HNO$_3$. Thorough washing with triple-distilled water followed before subsequent smoothing on roughened glass and a final rinse.

The solid graphite electrode (RWO grade, Ringsdorff-Werke) were also in rod form and set in Teflon (giving an identical cross-sectional area to that of the zinc). Pre-treatment consisted of polishing on 600 and 1200 grade SiC paper. Vigorous rubbing on tissue paper followed to remove any SiC from the surface. Immersion in 10% v/v (S.G. 1.42) HNO$_3$ was then performed before a final rinse in triple-distilled water.

The porous graphite electrodes were fabricated from paste mixes containing 95% graphite powder (KS 2.5, Lonza) and 5% PTFE suspension in isopropanol. The paste was mixed and then rolled to give a resultant sheet which was tough and fibrous in nature. It was then pressed into a recessed, Teflon-mounted, solid graphite electrode to a depth of 2 mm and carefully trimmed with a glass blade until it was flush with the holder surface.

Cyclic voltammograms were obtained for the various electrode and electrolyte compositions. The sweep limits for the two forms of graphite were 0 and -2000 mV (a less negative cathodic limit was utilised when only the initial zinc deposition reaction was of interest). A sweep rate of 20 mV s^{-1} was applied using a ramp generator in conjunction with a potentiostat. Current and potentials were recorded with an X–Y chart recorder.

Results and discussion

Figure 1 illustrates the cyclic voltammogram obtained for a solid graphite electrode in a 7 M KOH / 5 g dm^{-3} ZnO electrolyte, with a potential
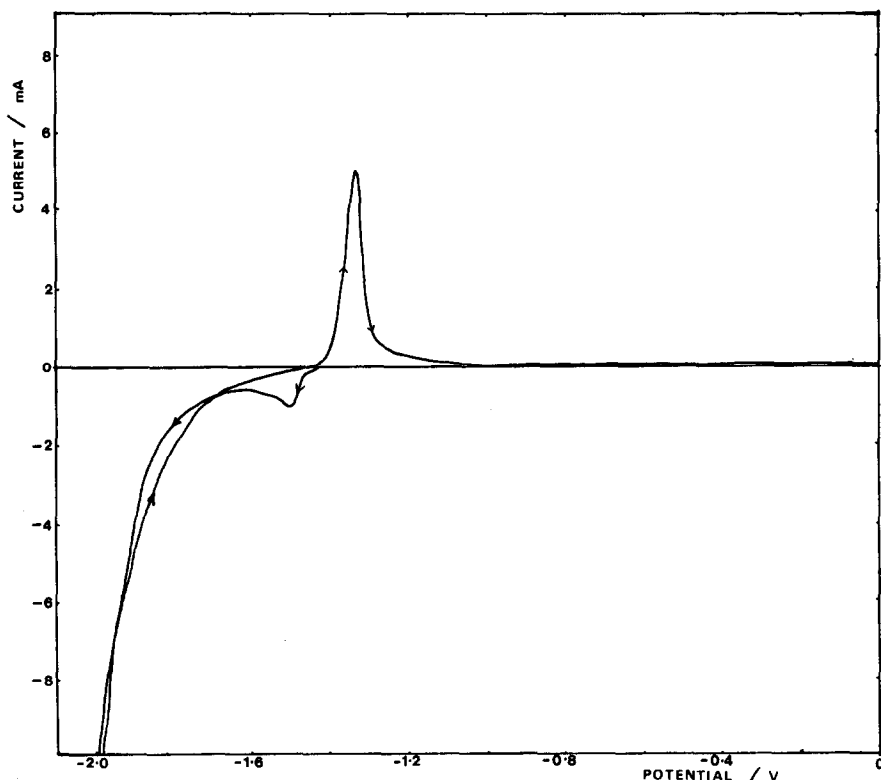

Fig. 1. Cyclic voltammogram on planar graphite disc (0.071 cm^2) in 7 M KOH + 5 g dm^{-3} ZnO.

window set between 0 and −2000 mV. Initially, on sweeping in the cathodic direction, zinc deposition commences at −1430 mV with a current maximum at −1500 mV. The current then diminishes, due to the mass transport limitation of zincate species, until the ultimate onset of hydrogen evolution. No evidence was found for underpotential deposition on this substrate but this cannot be used to support or refute the empirical relationship between work function and the occurrence of underpotential deposition proposed by McBreen *et al.* [9, 10]. This is because the reported values for the work functions of graphite and zinc overlap, falling within the ranges 4.34 - 5.0 eV [18, 19] and 4.28 - 4.9 eV [18, 20], respectively. On sweep reversal, zinc stripping commences at −1440 mV with a 100% coulombic efficiency with respect to deposition.

This behaviour can be compared with that shown in Fig. 2 for a solid graphite electrode in 7 M KOH without the addition of ZnO. Hydrogen evolution is seen to commence at about −1400 mV and the resulting current continues to rise until sweep reversal at −2000 mV. The superposition of the two responses (*i.e.*, Figs. 1 and 2) indicates that in the presence of zincate
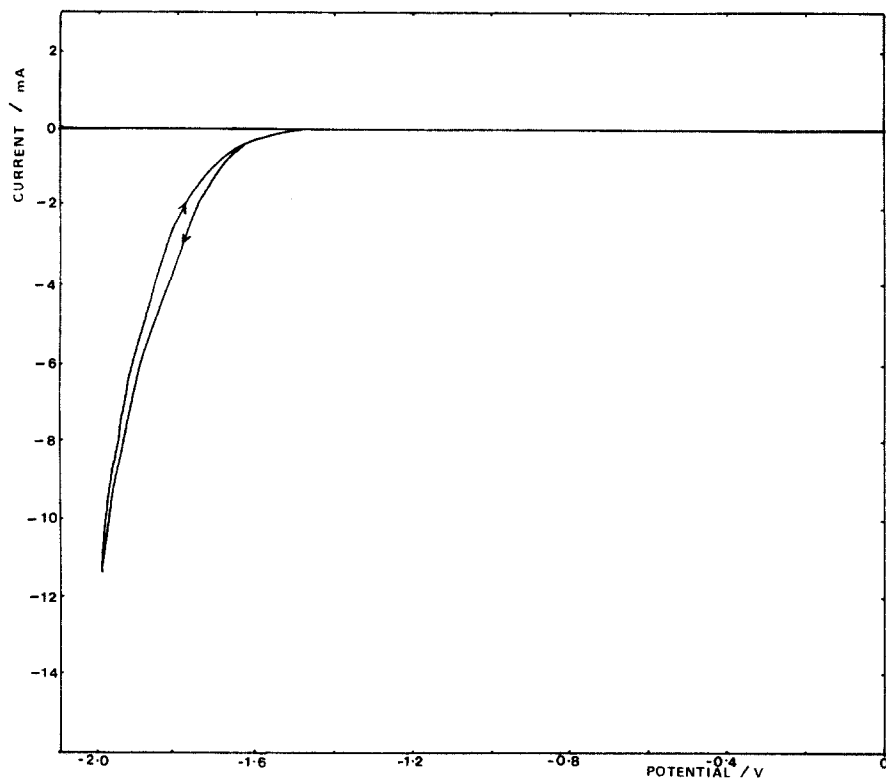

Fig. 2. Cyclic voltammogram on planar graphite electrode in 7 M KOH with no addition of ZnO.

species, at potentials more cathodic than −1430 mV, both zinc metal deposition and hydrogen evolution from the graphite surface are thermodynamically feasible. The low residual current observed at potentials around −1400 mV in Fig. 2 suggests that both processes occur concurrently. The subsequent rapid rise in current due to zinc deposition (Fig. 1) shows its kinetic favourability at these potentials. It is evident that the subsequent hydrogen evolution current profile in Fig. 1, *i.e.*, off electrodeposited zinc, exhibits marked differences from that of the uncovered graphite, the latter exhibiting behaviour indicative of a lower hydrogen overvoltage than that of zinc. This is illustrated by comparison with Fig. 3 where the hydrogen evolution current from planar zinc is recorded in the absence of zincate species. It can be seen that hydrogen evolution from zinc occurs at a potential some 250 mV more cathodic than from graphite. This is an important observation with regard to secondary cells with zinc anodes which contain graphite as a conductor-modifier. When the cell is charged its acceptance efficiency will be determined by the hydrogen evolution potential. Thus it will be beneficial if the graphite in the electrode is overplated with zinc before such potentials are reached.
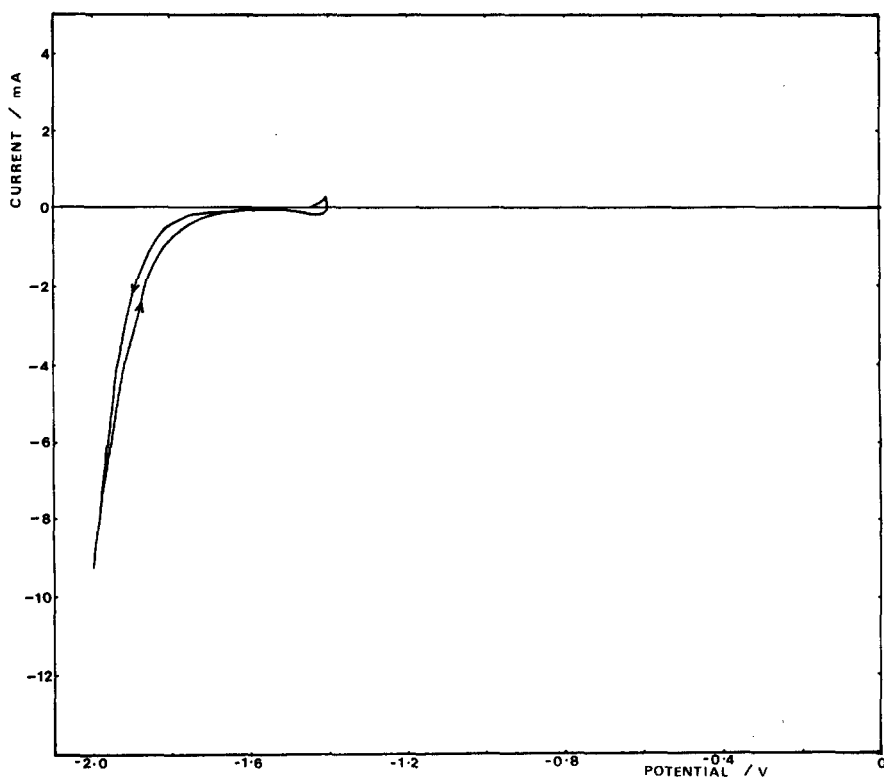

Fig. 3. Cyclic voltammogram on planar zinc disc (area 0.071 cm^2) in 7 M KOH with no addition of ZnO.

The ease with which zinc deposits on graphite is dependent on the concentration of the electroactive zincate species in solution. A series of voltammetric experiments was conducted with varying concentrations (5, 10, 20 and 40 g dm^{-3}) of ZnO dissolved in 7 M KOH. With increasing ZnO concentration the peak sizes and overall charges increase (due to the relationship between exchange current and zincate concentration). More importantly, with increasing ZnO concentration the potential for metallic deposition becomes less negative. Since the substrate surface is consistent, this process is likely to be a Nernstian phenomenon. A direct comparison of the voltammetric behaviour of the graphite/7 M KOH system containing 5 g dm^{-3} and 40 g dm^{-3} of ZnO is shown in Fig. 4. The salient results of the series of experiments are summarised in Table 1.

Similar behaviour was observed for electrodes in which graphite was dispersed with, and bound by, PTFE (*i.e.*, pasted electrodes), as used in conductor-modified systems [14, 15, 21]. In general, both the deposition and dissolution peaks on the pasted electrodes are much broader than their planar equivalents (Fig. 5). This is due to surface roughness or "porosity" causing an uneven potential distribution (with respect to the electrolyte) over
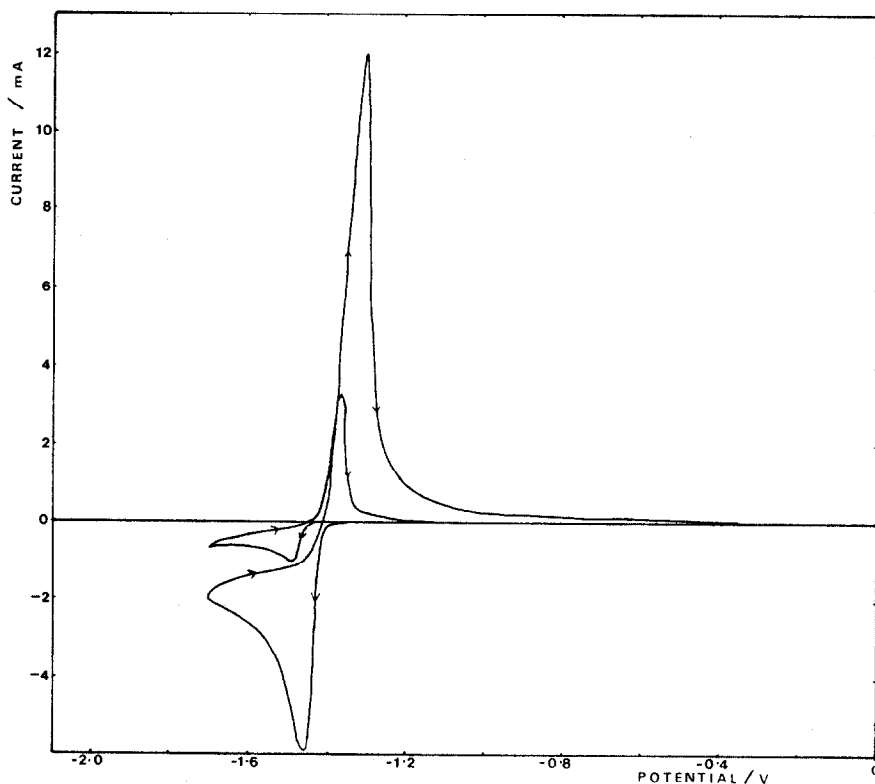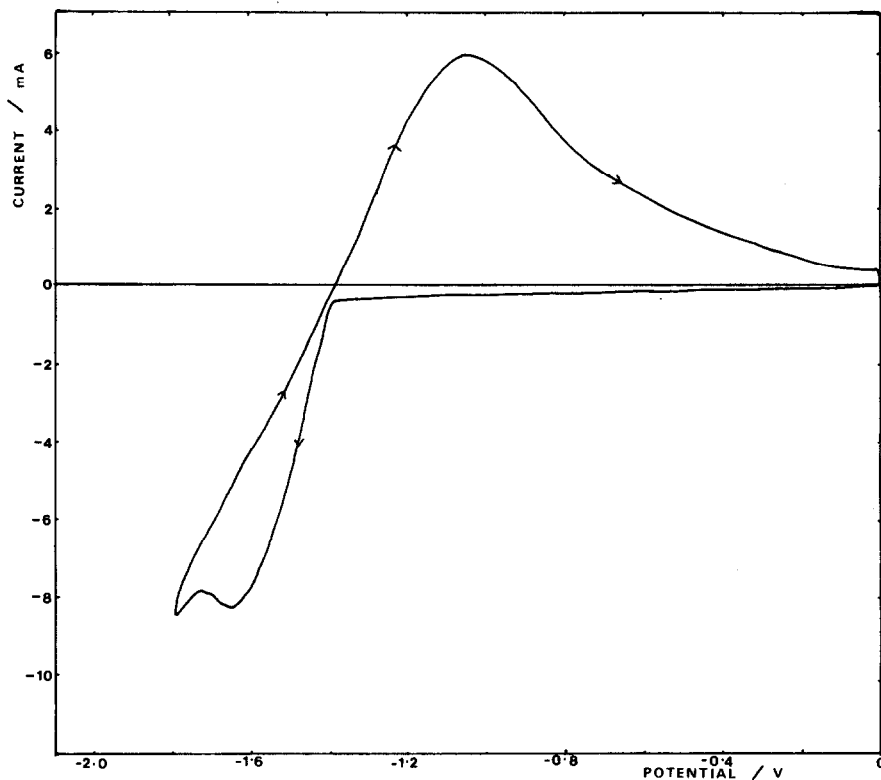

Fig. 4. Cyclic voltammogram on planar graphite in 7 M KOH with additions of (i) 5 g dm^{-3} ZnO and (ii) 40 g dm^{-3} ZnO.

TABLE 1

Results obtained from various concentrations of ZnO with a planar graphite electrode

Concentration of ZnO (g dm^{-3})	Onset of deposition (mV)	Potential at current maximum (mV)	Charge in deposition peak (mC)	Onset of dissolution (mV)
5	−1430	−1500	11.3	−1440
10	−1415	−1490	21.4	−1420
20	−1405	−1470	37.3	−1415
40	−1395	−1460	64.1	−1410

Fig. 5. Cyclic voltammogram on pasted graphite electrode in 7 M KOH + 40 g dm^{-3} ZnO.

the active area of the electrode. The important trend of a positive shift in deposition potential with increasing ZnO concentration, however, was again evident.

The major consequences of this behaviour with regard to cell/battery performance can be summarised as follows. In a graphite modified, zinc anode system, which undergoes some degree of dissolution on discharge, the maximum concentration of zincate in the electrolyte, and consequently the largest area of uncovered graphite, will occur when the system is fully discharged. Upon re-charge zinc deposition on the graphite will occur with a

resultant decrease in dissolved zincate. This reduction increases the probability of concurrent hydrogen evolution from the graphite. As the zincate discharges onto the graphite, however, the available area for hydrogen evolution is also reduced. Hence, the relationship between zincate concentration and deposition potential is a favourable one with regard to the successful operation of a cell with a graphite modified zinc anode.

The results obtained in these experiments also help to explain more fully the initial cycling behaviour (formation) of graphite modified electrodes as reported by Duffield et al. [14, 21]. The initial increase in capacity can be attributed to progressive coverage of the graphite surface by electrodeposited zinc, this area diminishing with successive cycles until all the available graphite is covered. The cell capacity then begins to fall with increasing cycle number as the efficiency of the zinc anode diminishes.

Conclusions

(i) Zinc electrodeposits onto solid graphite with no apparent underpotential deposition.

(ii) At potentials more cathodic than -1430 mV both hydrogen evolution and zinc deposition are thermodynamically viable, although the latter is more pronounced at the less negative potentials in this range.

(iii) Increasing the zinc oxide concentration in the electrolyte moves the onset of zinc deposition to a less cathodic potential.

(iv) In terms of cell charging it is apparent that zinc will deposit on graphite in preference to hydrogen evolution off that surface.

(v) Pasted PTFE electrodes produced similar results, although the voltammetric deposition peaks were much broader.

(vi) The results reported in these investigations suggest the cell cycling anomalies noted by Duffield et al. can be explained in terms of initial deposition of zinc onto uncoated graphite.

Acknowledgements

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