

## Short Communication

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### Effect of carbonate ions on the behaviour of zinc in 30% KOH

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#### Abstract

The effect of carbonate ions on the electrochemical oxidation and redeposition of zinc in alkaline medium is investigated using cyclic voltammetry. Peak current values increase in the presence of carbonate. Carbonate as an additive to the electrolyte is found to be beneficial.

#### Introduction

Absorption of carbon dioxide is a common phenomenon in vented alkaline cells. This has initiated studies into the effect of absorbed CO<sub>2</sub> on the performance of zinc electrodes. For example, Jost [1] patented an alkaline carbonate electrolyte for Ni–Zn cells. Later, Conway and Kannangara [2, 3] showed that carbonate ions favour the retention of zinc in NaOH solutions. Alder *et al.* [4] have recommended the use of alkaline carbonate electrolyte for improving the cycle life of Ni–Zn cells.

The present study arose from a report by Sato *et al.* [5] that advocated the avoidance of exposure to atmospheric carbon dioxide during the production of zinc alkaline cells. These authors showed a decrease of the passivation time in the presence of carbonate. On account of this contrary behaviour, we have conducted a study of the effect of carbonate on zinc electrode characteristics in practical battery electrolyte, viz., 30% (5.3 M) KOH.

#### Experimental

Solutions were prepared from GR grade KOH (Fisher), GR grade K<sub>2</sub>CO<sub>3</sub> (Sarabhai M), and triple-distilled water. The working electrode was a pure zinc (99.99%) rod (0.20 cm<sup>2</sup> dia.) embedded horizontally in a Teflon mount. This electrode was polished with emery paper (4 0s grade), degreased with

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acetone, and finally washed with triple-distilled water. A platinum foil of large area was used as the counter electrode. The electrochemical measurements were conducted at  $25 \pm 2$  °C using a BAS 100A Electrochemical Analyser. The reference electrode was Hg/HgO (1 M KOH); all potentials are reported against this electrode.

## Results and discussion

A typical cyclic voltammogram for zinc in 5.3 M KOH is shown in Fig. 1. On starting from  $-1800$  mV, an anodic peak, A, appears in the potential range  $-950$  to  $-1025$  mV. There is a sharp fall in current following attainment of the peak. During the negative-going sweep, an anodic current peak (designated  $A_1$ ) appears at a potential slightly negative to peak A, and a cathodic peak, C, appears between  $-1450$  and  $-1540$  mV.

The beginning of the positive-going scan corresponds to the dissolution of zinc to form transiently soluble  $Zn^{2+}$  species [6–10]. Subsequent hindrance to zinc oxidation results through the formation of a film of  $Zn(OH)_2/ZnO$ . Formation of this film depends on the extent to which zinc hydroxide dissolves in KOH to form zincate. When a critical concentration of zincate is reached at the electrode/electrolyte interface, the formation of a primary passivating film of ZnO is initiated and a dissolution–passivation mechanism is instigated.  $i_p A$  varies linearly with the square root of the sweep rate, which indicates that the zinc oxidation reaction mainly involves a diffusion controlled process.

The anodic peak  $A_1$ , appearing in the reverse scan, is due to the re-established oxidation of zinc after the occurrence of some of the previously deposited oxide. The peak C is attributable to the reduction of the electrode reaction product.

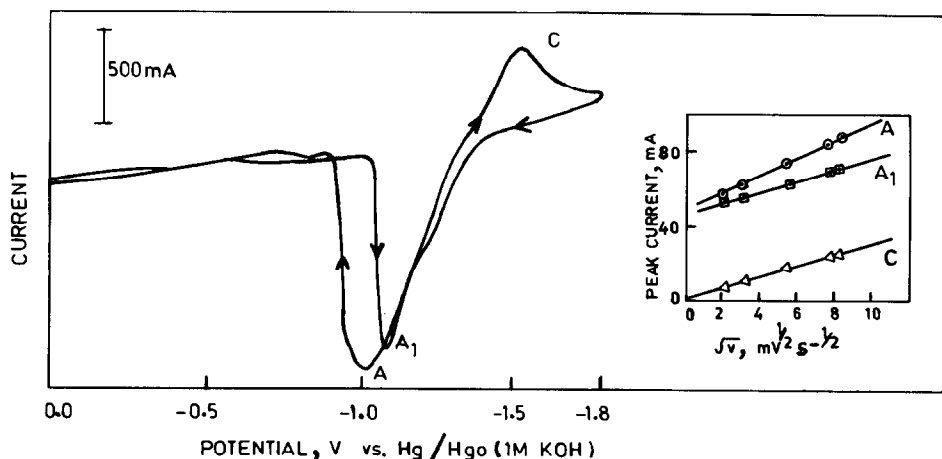


Fig. 1. Cyclic voltammogram for zinc in 5.3 M KOH; sweep rate  $70 \text{ mV s}^{-1}$ . Inset shows effect of sweep rate on peak current.

The cyclic voltammogram of zinc in 5.3 M KOH in the presence of potassium carbonate is shown in Fig. 2. In general, the peak current values are higher in the presence of carbonate than they are in KOH alone (Table 1). An interesting feature of the cyclic voltammogram in  $K_2CO_3$ , that is absent in KOH is that the anodic peak A exhibits, at lower sweep rates (Fig. 3), a flat potential region over 100–150 mV. This is possible if a diffuse precipitation occurs at a rate equaling the dissolution rate.

The variation of  $i_p$  with  $[K_2CO_3]$  is shown in Fig. 4. The two maxima observed may be attributed to the formation of two different carbonate complexes of zinc in alkaline medium.

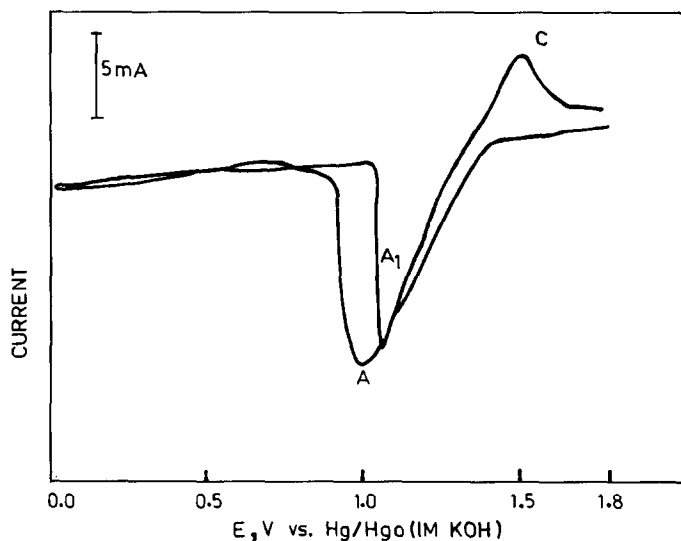


Fig. 2. Cyclic voltammogram of zinc in 5.3 M KOH in the presence of 0.015 M  $K_2CO_3$  at a sweep rate of  $70 \text{ mV s}^{-1}$ .

TABLE 1

Cyclic voltammetric data for the anodic dissolution and redeposition of zinc in 5.3 M KOH in the presence of various concentrations of  $K_2CO_3$

$K_2CO_3$ (M)	$i_{pA}$ (mA)	$i_{pA_1}$ (mA)	$i_{pC}$ (mA)	$E_{pA}$ (mV)	$E_{pA_1}$ (mV)	$E_{pC}$ (mV)	$\Delta E = E_{pA} - E_{pC}$ (mV)
0	73.0	67.0	17.0	-950.0	-1062.5	-1500.0	550.0
0.015	95.0	110.4	28.0	-1062.5	-1062.5	-1487.5	425.0
0.031	102.0	120.8	32.0	-1075.0	-1075.0	-1475.0	400.0
0.062	85.1	100.0	20.0	-1050.0	-1050.0	-1475.0	425.0
0.125	93.8	120.8	40.0	-1087.5	-1050.0	-1475.0	388.0
0.250	87.5	110.4	33.5	-1075.0	-1050.0	-1487.5	412.5
0.500	84.0	104.3	33.0	-1112.5	-1087.5	-1475.0	363.0
0.100	75.0	93.8	29.2	-1100.0	-1075.0	-1500.0	400.0
0.200	66.5	80.0	32.6	-1112.5	-1100.0	-1525.0	413.0

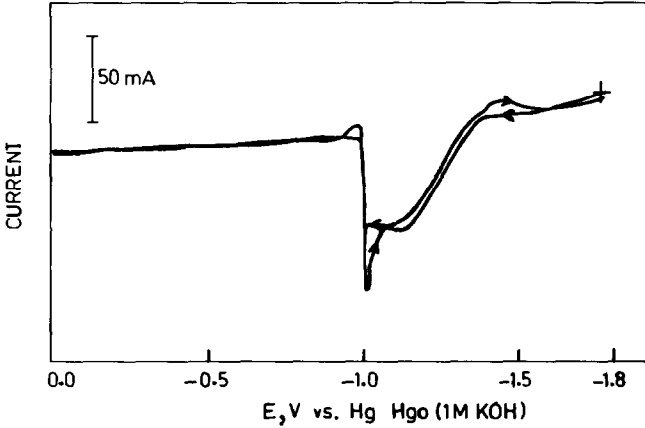


Fig. 3. Cyclic voltammogram of zinc in 5.3 M KOH in the presence of 0.015 M  $K_2CO_3$  at a sweep rate of  $5 \text{ mV s}^{-1}$ .

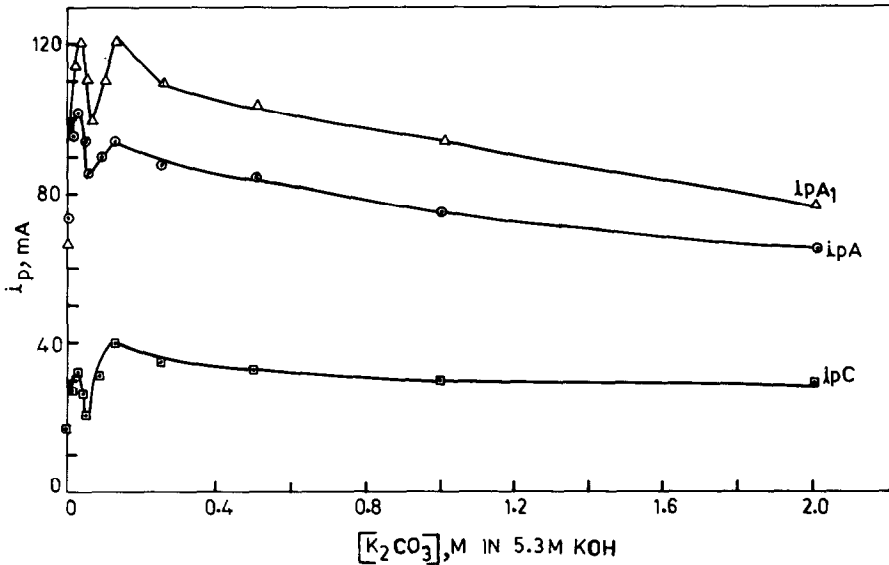


Fig. 4. Variation of peak current with the concentration of potassium carbonate in 5.3 M KOH at a sweep rate of  $30 \text{ mV s}^{-1}$ .

The greater magnitude of peak current observed in the presence of  $K_2CO_3$  can be explained as follows: the anodic film in carbonate solutions is less coherent and more porous than the film formed in KOH alone [2]. Thus  $CO_3$  seems to help  $ZnO/Zn(OH)_2$  to remain in solution in preference to a colloidal form [2, 3]. This is supported by the fact that the solubility of zinc carbonate is greater than that of  $ZnO/Zn(OH)_2$  [11, 12].

An improved cycle-life performance of Ni-Zn cells has been achieved in alkaline carbonate electrolytes, reaching 334 cycles in contrast to 106

cycles obtained for the standard cell in the absence of carbonate. This finding, reported by Alder *et al.* [4], shows that after 100 cycles the cell containing carbonate retains a quantity of zinc equivalent to more than 90% of its original capacity, whereas the standard cell retained only 60% of its original capacity. They also demonstrated a greatly reduced zinc electrode shape-change by *in situ* X-ray analysis. Thus, it is evident that carbonate ions hold zinc in solution.

Table 1 reveals that  $\Delta E$ , the difference between  $E_pA$  and  $E_pC$ , is at a minimum at a concentration of 0.5 M  $K_2CO_3$ , which indicates that the system tends toward reversibility at this concentration. Further, at 0.5 M  $K_2CO_3$ ,  $i_pC$  is also considerably higher than it is in KOH alone. From these observations it is obvious that an optimum concentration of 0.5 M  $K_2CO_3$  is a suitable battery electrolyte additive in zinc alkaline cells.

## Conclusions

The present study demonstrates the beneficial role played by absorbed  $CO_2$  in vented zinc cells. An optimum concentration of 0.5 M  $K_2CO_3$  is a suitable additive to the battery electrolyte.

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