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SHORT COMMUNICATION

Evaluation of calcium-containing zinc electrodes in zinc/silver oxide cells

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1. Introduction

The redistribution of zinc-active materials (shape change), growth of zinc dendrites and migration of silver throughout the cell are important factors limiting the life and performance of Zn/AgO cells. These phenomena can be partly overcome by improvements in separator materials and by additives to the zinc electrode. Many investigations have shown that the addition of $Ca(OH)_2$ to the zinc electrode can improve the performance of Zn/AgO cells [1] and Zn/NiOOH cells [2, 3]. Cairns *et al.* [1] found 25 mol % $Ca(OH)_2$ addition to the zinc electrode in the Zn/AgO cell exhibited somewhat higher capacities and longer cycle life. Thus, $Ca(OH)_2$ is a beneficial additive to the zinc electrode in Zn/AgO cells and the object of this work is to further study the effect of $Ca(OH)_2$ concentrations on the behaviour of Zn/AgO cells.

2. Experimental detail

2.1. *Cell construction*

Four kinds of cells containing 0, 10, 25 and 40 mol % $Ca(OH)_2$ in the zinc electrodes were fabricated and tested. All cells were designed to be silver-limiting in capacity and to have 3.4 Ah of rated capacity. Each cell contained four AgO electrodes, three full-capacity zinc electrodes, and two half-capacity zinc electrodes which were used as the outermost electrodes in the cell pack. Cell design calculations are shown in Table 1. All positive electrodes used in this work were provided by BST Inc. and the negative electrodes were made by a vacuum-table process [4], which is outlined in [1]. The zinc electrode compositions were: 93 wt % ZnO (Merck ZA, ACS), 2 wt % PbO (Aldrich), 4 wt % polytetrafluoroethylene (PTFE) (Du Pont, TFE-30), and 1 wt % newsprint (The Morilla Company). The Zn–Ca electrodes containing 10, 25, and 40 mol % $Ca(OH)_2$ (based on the mole percent of Zn and Ca in the uncycled electrode, not including inert materials) were fabricated. Since the density of $Ca(OH)_2$ ($2.24\,g\,cm^{-3}$) is smaller than that of ZnO ($5.61\,g\,cm^{-3}$), the Zn–Ca electrodes occupied a greater volume and thus required more binder, which led to a thicker negative electrode. Four percent PTFE was added in the 0 mol % and 10 mol % $Ca(OH)_2$ electrodes, but five percent PTFE was used for the 25 mol % $Ca(OH)_2$ electrode and 6% for the 40 mol % $Ca(OH)_2$ electrode; e.g., the 40 mol % $Ca(OH)_2$ electrode was ~0.226 cm thick and contained 91 wt % ZnO + $Ca(OH)_2$, 2 wt % PbO, 6 wt % PTFE and 1 wt % newsprint. The procedure for cell fabrication was similar to that in [1].

2.2. *Cell assembly and cycling tests*

Each silver electrode was wrapped with a layer of nonwoven polyamide wicking material (Japan Vilene Company, Ltd, FT-218), and five layers of cellophane (Hoechst Japan Limited) as the outer separator layers.

Table 1. Zn/AgO cell design (silver-limiting capacity design)

	Zn/AgO	*Zn–Ca/AgO*
Rated capacity	3.4 Ah	3.4 Ah
Electrode size (each plate)	4.45 cm × 3.56 cm	4.45 cm × 3.56 cm
Weight of ZnO or Ag/cell	ZnO: 14.78 g Ag: 10.32 g	ZnO: 13.4, 11.33, 9.19 g $Ca(OH)_2$: 1.36, 3.44, 5.58 g Ag: 10.32 g
Ratio of active materials (mass ratio)	$M_{Zn}/M_{Ag} = 1.15$	$M_{Zn-Ca}/M_{Ag} = 1.04, 0.88, 0.71$
Porosity (as metal based)	ZnO: 60–70% Ag: 55–60%	Zn–Ca: 60–70% Ag: 55–60%
Cell pack	5:ZnO, 4:AgO, 8:Sep.	5:Zn–Ca, 4:AgO, 8:Sep.
Separator system	$-\vert 2\,cg^{*}\Vert 5\,cp^{\dagger}\vert Pellon\vert +$	$-\vert 2\,cg^{*}\Vert 5\,cp^{\dagger}\vert Pellon\vert +$
Thickness for each plate	ZnO: 0.112 cm Ag: 0.038 cm	Zn–Ca = 0.140, 0.180, 0.226 cm Ag = 0.038 cm
Total thickness of cell	1.113 cm	1.204, 1.366, 1.549 cm

* 2 layers of Celgard.
† 5 layers of Cellophane.

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Two layers of Celgard 3401 (Hoechst Celanse, Corporation) microporous polypropylene sheet were heat-sealed around the zinc electrode. The cell pack (separator/electrode) assembly was designed for split-wrap configuration [5]. The cell cases (provided by BST, Inc.) were made from 0.18 thick polysulfone. Spacers were used to place the cell stack so that the whole cell pack was located in a tightly fitting cell case. Each cell was filled with 22 ml of ZnO-saturated KOH (Fisher) electrolyte and allowed to stand for about one week to ensure that electrolyte would wick thoroughly into the electrodes. The cell was then vented through an Ascarite (Thomas Scientific, 8–20 mesh) column to prevent CO_2 from entering cell and a Hg/HgO reference electrode was placed in a separate reference compartment to analyse the behaviour of individual electrodes. Cells were cycled using a computerized battery life cycle test system. All cells were tested at constant current. To render the cell active, two formation cycles were performed before regular cycle testing. The formation condition was similar to that in [1]. After formation cycles, the cells were cycled using the following procedure: 0.3 A charge current to a 2.01 V cell cutoff voltage, and then stand in open-circuit for 30 min, followed by a 0.6 A discharge to 1.1 V cell cutoff voltage. Cycling continued until cell capacity dropped and remained below 80% of the rated capacity.

3. Results and discussion

A total of six cells were subjected to cycle-life testing to evaluate the addition of $Ca(OH)_2$ to the zinc electrode in zinc/silver oxide cells. The cell capacity data shown in the work are based on the cell rated capacities, i.e. 3.4 Ah ≡ 100% capacity, regardless of the initial or maximum capacity of the cell. Cells E0 and E0(2) had 100% zinc electrodes (without adding $Ca(OH)_2$ in zinc electrodes) were used as control cells in this work. Figure 1 shows a plot of capacity versus cycle number for all the cells. All cells had a similar capacity before 15 cycles. However, cells E10 and E40, respectively, with 10 and 40 mol % $Ca(OH)_2$ in the zinc electrode, exhibited a lower capacity than the control cell, E0. Cell E25 with 25 mol % $Ca(OH)_2$ showed a slightly higher capacity and longer cycle-life than the control cell, E0. Cells E0(2) and E25(2) were intended to replicate the cells E0 and E25, respectively. The replicated cells had similar cell performance to the original cells. Recently, Cairns *et al.* [1, 3] reported that the addition of $Ca(OH)_2$ to the zinc electrode forms an insoluble Ca-zincate complex ($Ca(OH)_2 : 2Zn(OH)_2{\cdot}2H_2O$) near the reaction site in the porous zinc electrode, even at 45 wt % KOH electrolyte, and large amounts of their complex crystals in the cycled Zn–Ca electrodes were found by SEM. The reactions of the Zn and Zn–Ca electrodes [6] can be described as:

Zn electrode

$$ZnO + 2OH^- + H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Zn(OH)_4^{2-} \quad (1a)$$

$$Zn(OH)_4^{2-} + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Zn + 4OH^- \quad (1b)$$

Zn–Ca electrode

$$Ca(OH)_2.2Zn(OH)_2.2H_2O + 4OH^-$$

$$\underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} 2Zn(OH)_4^{2-} + Ca(OH)_2 + 2H_2O \quad (2a)$$

$$Zn(OH)_4^{2-} + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Zn + 4OH^- \quad (2b)$$

During charge, zinc is deposited in the zinc electrode from zincate in solution, where the zincate is continually consumed by dissolving ZnO in the zinc electrode. However, in the ZnCa electrode, the Ca-zincate complex decomposes to form zincate. Cell E10 contained only 10 mol % $Ca(OH)_2$ which was

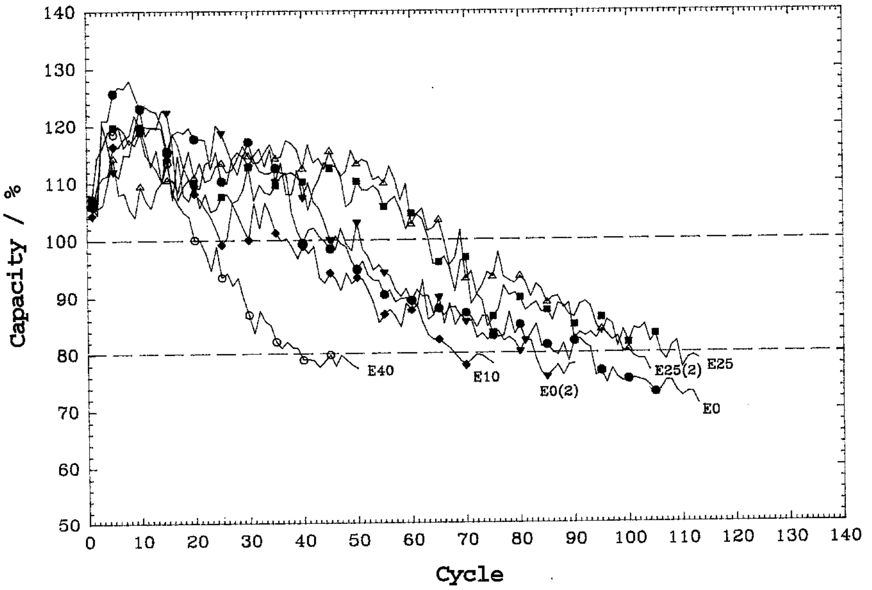

Fig. 1. Capacity against cycle number for all of the testing cells. E0 (●), E0 (2) (▼), E10 (◆), E25 (■), E25 (2) (△), E40 (○). Other details: rated capacity: 3.4 Ah; E0 and E0(2): 0% $Ca(OH)_2$; E10: 10% $Ca(OH)_2$; E25 and E25(2): 25% $Ca(OH)_2$; E40: 40% $Ca(OH)_2$.

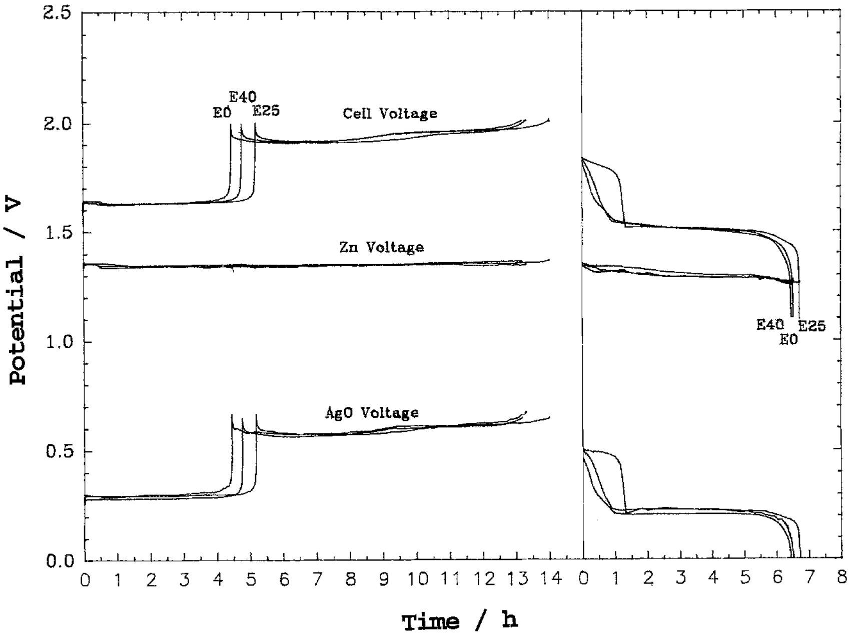

Fig. 2. Cell voltage and electrode potentials at different cycles for cell E0. The uppermost curves represent the cell voltage, the middle curves represent the negative of the Zn electrode potential (against Hg/HgO), and the lowermost curves represent the positive of the AgO electrode potential (against Hg/HgO). Cell charge is shown on the left-hand side, and cell discharge is shown on the right-hand side.

not enough for maintaining cycling capacity because of too small an amount of calcium to bond with the amount of zinc required for full capacity. In contrast, cell E40 with 40 mol % $Ca(OH)_2$ did not have enough zinc in the zinc electrode to react with all the calcium and thus, the excess $Ca(OH)_2$ lowered the zincate concentration to a value below saturation [3]. Cell E25 with 25 mol % $Ca(OH)_2$ was found to maintain the required capacity and performed well in cycling as shown in Fig. 1.

Figure 2 shows cell voltage and electrode potentials at cycle 15 for cells E0, E25 and E40. The calcium-containing cells (E25 and E40) were found to have the longer first charge plateau. The longer first charge plateau can be attributed to the fast Ca-zincate complex decomposition which causes the higher OH^- concentration near the silver electrode. A possible mechanism including a two-step process for Ag oxidation is illustrated in Fig. 3 [7]. In the first-step process, the silver lattice was distorted and expanded while the oxidation of Ag and the O^{2-} ions from the splitting of the OH^- ions were able to diffuse in the lattice and thicken the Ag_2O layer. When this layer reached a critical thickness, the resistance or the charge voltage increased sharply (passivation). The second step occurred when the charge voltage increased until the second electron was removed from the Ag^+ in the Ag_2O layer, and more O^{2-} ions diffused in to form an AgO film. Owing to the silver lattice being further expanded, the O^{2-} ions penetrated more deeply and thus the formation of AgO was greater than that of Ag_2O on the same electrode. At moderate current densities, both step reactions are approximately 100% efficient [8]. Therefore, the length of the plateau is a function of the relative thickness of the oxide films and the second charge plateau (the formation of AgO) is longer than the first one (the formation of Ag_2O). Generally, the thickness of the film depends on the

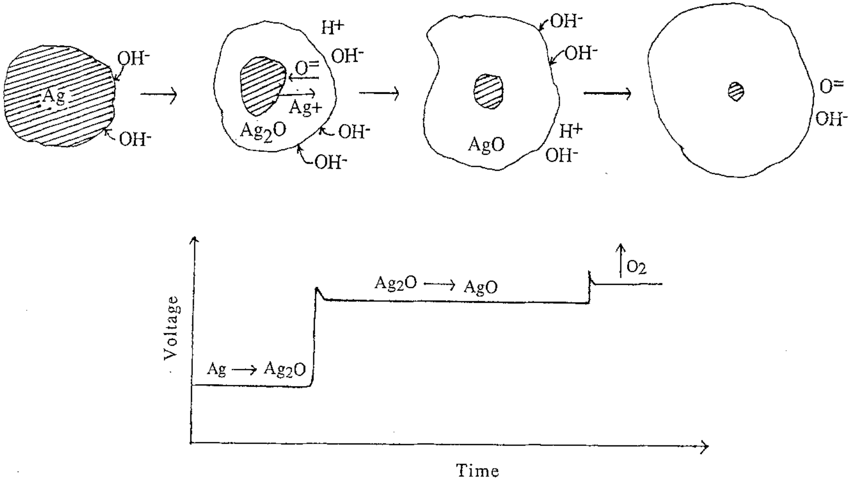

Fig. 3. Possible mechanism for Ag oxidation.

Table 2: Cycle-life performance data for 3.4 Ah Zn/AgO cells

Cell	*Total cycles completed*	*Final capacity /% (capacity)*	*Cycles*	*Capacity loss**† /Ah (cycle)$^{-1}$	*Average* /Ah (cycle)$^{-1}$
E0	113	70.88	93	0.292	3.41
E0(2)	90	78.10	83	0.354	3.47
E10	75	78.32	67	0.380	3.42
E25	113	78.9	105	0.240	3.43
E25(2)	104	76.8	100	0.274	3.50
E40	50	77.4	39	0.720	3.44

* Calculated based on the cell capacity at first cycle.
† Capacity loss before cells reach 80% of rated capacity.

current density, electrolyte concentration, and physical state of the electrode [8]. During charge, because of the faster Ca-zincate decomposition rate (compared to the dissolution of ZnO) in higher KOH concentration electrolytes, OH^- transport from the Zn electrode to the Ag electrode is facilitated, which results in the longer first charge plateau (or thicker Ag_2O film) in the ZnCa electrodes. However, after a few cycles, the deposition of silver on the separator hinders OH^- ion transport from the zinc to the silver electrode. Active material loss in the electrodes also causes a shorter charge plateau and lower capacity.

Table 2 lists cycle-life performance data for the various cells that were cycled. The table indicates the values of the capacity loss rate and the average delivered capacity per cycle, both based on the cell performance before its capacity dropped to 2.72 Ah (80% of rated capacity) [1]. The capacity loss rate, expressed as %/cycle, is based on the initial cell capacity and can be estimated by

$$Y = (1 - C_+^{1/n}) \times 100$$

where n is the total cycle number, C_+ is the terminal fractional capacity (based on the initial cell capacity), and Y is the average fractional capacity loss for each cycle. The data shown in Table 2 show that the 25 mol % calcium-containing Zn/AgO cell has the superior cycle-life performance.

4. Conclusions

The addition of 25 mol % $Ca(OH)_2$ to the zinc electrode in Zn/AgO cells exhibited the best performance among the cells with different $Ca(OH)_2$ contents in the Zn electrode. Zn–Ca/AgO cells with 25 mol % $Ca(OH)_2$ can maintain the required capacity and perform well. During charge, the calcium-containing cells have the longer first charge plateau because the rate of Ca-zincate complex decomposition is very fast in higher KOH concentration electrolytes. This particular behaviour may be attributed to the formation of an insoluble Ca-zincate complex reaction site in the porous zinc electrode.

Acknowledgement

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