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STUDY OF MODEL ZINC ELECTRODE
PORES IN ALKALINE ELECTROLYTE

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May 1983

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INTRODUCTION

The objective of this research is to obtain information on the behavior of zinc-electrode pores and evaluate potential failure modes of the rechargeable alkaline zinc electrode. The failure modes include zinc redistribution, densification, passivation and dendrite shorting. This communication will focus on the development of a model zinc electrode pore and a discussion of results from preliminary experimentation.

An understanding of the porous structure in operating Zn electrodes is required to set appropriate dimensions for experimentally-accessible model pores. Polymer-bonded porous zinc electrodes manufactured by dough, paste or slurry methods consist of interparticle macropores 1-40µ in diameter, of varying lengths statistically distributed, up to values greater than the electrode thickness. SEM studies of electrodes that have undergone different cycle-life tests show that the porous structure gradually changes with increasing time, showing a loss of porous structure as a result of zinc redistribution/densification.

CELL DESIGN

The model zinc electrode pore used in this study is based on a design used by T. Katan.(1) Modifications have been made to better simulate actual pore dimensions and to simultaneously observe visual and electrochemical behavior in the cell. The model pore simulates a straight pore of uniform diameter running through the cross-section of the zinc electrode starting from a point nearest to the separator (the mouth) and extending to a point furthest from the counter electrode (the root). The pore under study is shown in Figure 2 and is 1.5 mm long.
It consists of a polished zinc surface immersed in alkaline electrolyte. At the root of the pore is an insulating teflon spacer which defines the separation ("pore radius") between the electrode and quartz coverslide. At the pore centerline is a quartz slide on which are deposited cadmium microreference electrodes, placed such that potential information can be obtained throughout the length of the pore. Current flows throughout the length of the pore parallel to the surface of the working electrode, and away from the counter electrode. The counter and working zinc electrodes are encased in lucite and polished to give a uniform and reproducible zinc surface. The quartz slide permits visual observation of the pore through a microscope and camera. The distance between the working and counter electrodes is 0.25 mm. The teflon spacer allows one to build pores of radii from 5 to 40 microns. Figure 3 shows an assembled pore. Visible are the working and counter zinc electrodes, teflon spacer, quartz slide and reference microelectrodes. The reference microelectrodes extend to a printed-circuit board connection to obtain potential measurements. Above the cell is a microscope objective lens.

A microcomputer and custom-built circuit were necessary to obtain, store and process potential and optical information. Figure 4 shows a block diagram of the system configuration. A galvanostat is employed to pass a constant current through the cell and measure working and counter electrode potentials. A custom-built potentiostat interface measures the reference microelectrode potentials, and the rest potentials of the cadmium reference electrode and zinc working electrode are filtered out. The resulting difference in potential, reflecting the load overpotential on the zinc surface, is then amplified and sent to the computer. Amplification is necessary to improve the signal-to-noise ratio in this
system because typical overpotentials range from 0 to 30 millivolts. The computer controls the course of the experiment and all data acquisition. This allows for very accurate and precise readings of potential over time.

Shown in Figure 5 is the complete experimental arrangement. Visible are the assembled cell, microscope, camera, custom-built potentiostat interface, and galvanostat/potentiostat.

The cadmium reference microelectrode (Figure 6) consists of thin films of titanium, copper and cadmium deposited onto quartz. Quartz, titanium and copper were chosen for their abilities to meet microelectrode design requirements and withstand strong alkaline and organic solutions used in photolithographic processing. The vapor-deposited titanium and copper were cut into the desired pattern by microelectronic photolithographic techniques and the resulting configuration is shown in Figure 7. Cadmium was chosen for the reference electrode because of its stability in strong KOH electrolyte. After the photolithographic process is complete, most of the copper metal is insulated by sputtered quartz. Afterwards, the remaining copper is plated with cadmium. These procedures produce a cadmium reference microelectrode of dimensions 0.1 mm x 1 mm. The larger distance is in the direction perpendicular to current flow, over which we expect little change in potential. The seven microelectrodes are spaced equidistant 0.19 mm apart throughout the pore length. Thus, we are able to obtain accurate potential readings as a function of time and distance into the pore without seriously altering transport processes in the pore.
Figure 8 shows the cadmium reference electrode. The lighter area is quartz-insulated copper.

EXPERIMENTAL

Screening experiments were performed with the model single-pore cell to determine the effects of different alkaline electrolytes and the rate of discharge on zinc behavior in pores. A goal of these experiments is to evaluate zinc electrode behavior in pores of realistic dimensions close to typical discharge operating conditions. Experiments were initially performed on relatively large pores (18-20 microns) to determine the difference in behavior of electrodes in different electrolyte compositions and at different rates of discharge. Initially, two electrolytes were studied, one 31 wt% KOH solution and the other an electrolyte of composition 15 wt% KOH and 15 wt% KF. It is expected that the reduced solubility of zinc species in the fluoride electrolyte will reduce the extent and rate of zinc redistribution.

Rate-of-discharge effects were also studied by discharging the zinc electrodes at different constant currents to 20 mAh. Experiments were done at current densities of 1250, 30 and 7 mA/cm². Current density is based on the frontal pore electrolyte and electrode area, as shown in Figure 9. "I" is the total current, "w" is the width of the pore and "d" is the electrode/glass separation. It is assumed that the electrode porosity is 50% \((A_p/A_e = 0.5)\).

An average rate of discharge of 7 mA/cm² corresponds to the c/3 rate. The experiment at the very high rate of 1250 mA/cm² was performed to reproduce previous experiments.¹
RESULTS AND DISCUSSION

Figure 10 shows typical zinc-electrode potential behavior in 31% KOH at 30 mA/cm² discharge current density. Overall, one sees a slow rise in the cell potential, reflecting the difference between working and counter electrode potentials. This behavior is associated with changes in overall electrolyte composition and electrode surface-layer changes caused by the formation of ZnO/Zn(OH)₂ species. At the mouth of the pore nearest the counter electrode, (X/L = 0.03) one sees a 10 mV rise in potential followed by a moderate drop. At the middle of the pore (X/L = 0.60) the same behavior is observed, only later in time, which may indicate the passage of a precipitate "front" (1) on the surface of the electrode into the pore. The lack of change in potential at the rear of the pore indicates little electrochemical activity.

One way to infer differences in behavior at different rates of discharge is to look at the initial potential distributions throughout the pore at different rates of discharge. Figure 11 shows both a change in the magnitude of measured potentials and in the shape of the potential curves at various locations. At moderate rates of discharge, we see only a slight rise of several mV in potential as we go from the root of the pore to the mouth of the pore. At 30 mA/cm², this behavior is accentuated, and at the mouth of the pore we see larger changes in potential. The overpotential levels off in the middle of the pore (at X/2 = 0.60). However, at very high current densities, we see an exponential decay of the overpotential from the mouth to the root of the pore. The initial current distribution can be estimated from the initial potential distribution by assuming linear kinetic polarization and
no mass-transfer limitations. The results of this analysis are shown in Figure 12. It shows roughly a four-fold difference between the local current density at the mouth of the pore and the local current density at the root of the pore.

It is informative to compare the electrode behavior as observed visually with electrode potential measurement. Figures 13-15 detail electrode behavior as a function of time and distance into the pore as seen in-situ through the microscope at low magnification and seen post-mortem through the SEM at high magnification. Figure 13 shows the results confirm observations\(^{(1)}\) at these current densities in pores of greater length. The upper three photographs were taken in-situ over time at 100x and show the movement of well-defined "fronts" corresponding to precipitation of zinc-bearing oxides and/or hydroxides. It is believed that the electrode discharge proceeds via a dissolution-precipitation mechanism, in which zinc dissolves primarily as a zincate ion and then precipitates as ZnO. It was found\(^{(1)}\) that, at very high rates of discharge, a zinc etch pattern formed initially, followed by the formation of a floculent film, and then followed by the formation of a darker and denser passivating film. This behavior was seen in the movement of surface fronts from the higher-current-density areas at the mouth of the pore to the lower-current-density areas at the root of the pore. In Figure 13, the left-hand upper photograph shows the zinc electrode immediately after current initiation. The smooth black area is the polished zinc surface. At the mouth of the pore, one can see the beginnings of an etch pattern, indicated by the whitish grain. The center-top picture shows the extension of the etch front into the pore. Finally, further into the discharge, the etch front has moved well into
the pore, and a gray film has covered the etched zinc nearest to the mouth of the pore. SEM photographs taken of the end of the discharge show the deposit morphology at different positions in the pore. The lower-left photograph provides evidence of a non-porous film nearest to the mouth of the pore. A floculent white film exists at the middle of the pore (lower-center photograph). Finally, little activity is seen at the root of the pore (lower-right photograph) as the electrode is similar in appearance to photos of an undischarged, polished electrode. The behavior is different at lower current densities: no etch or ZnO film fronts can be observed in-situ during the discharge. However, the potential information indicates that a front may exist, and SEM photographs (after completion of discharge) indicate changes in morphology as one proceeds to the pore. The deposit at the mouth of the pore is raised above the surface and is porous, whereas the deposit is filamentary and porous at the middle of the pore. There is no optical or electrical evidence of a passivating-type film seen at higher current densities. Nor does this occur at low current densities in the fluoride electrolyte (see Figure 15). However, both the in-situ and SEM photographs indicate differences between behavior in 31% KOH and 15% KOH, 15% KF electrolytes. An etch pattern becomes more visible with increasing time. Etching is followed by the formation of a thin, milky white film on the electrode surface. However, the film formation occurs much more rapidly in the caustic-fluoride electrolyte than in 31% KOH electrolyte. This is consistent with the expectation that the ZnO film will precipitate at an earlier time because of the reduced solubility of zinc in 15% KOH, 15% KF. The SEM photographs indicate that the deposit is porous but different in morphology than the deposit in 31% KOH. Note that the
photographs (Figure 15) are at lower magnification than the previous photographs (Figure 13-14). Higher magnification better shows the porous structure.

CONCLUSIONS

There are four major observations that were made:

1) Surface morphology of zinc electrodes varies with position, rate of discharge, and electrolyte composition.

2) Passivation is an unlikely failure mechanism for the rechargeable alkaline zinc electrode at rates of discharge typical for electric vehicle applications.

3) Current penetration depth extends well into pore length, up to 0.6 – 0.7 X/L.

4) A fluoride electrolyte of composition 15% KOH, 15% KF could reduce zinc redistribution rates by earlier Zn/Zn(OH)\(_2\) film formation.

REFERENCES


OPTICAL AND ELECTROCHEMICAL

STUDY OF

MODEL ZINC ELECTRODE PORES

IN ALKALINE ELECTROLYTES

Figure 1. Introduction - Title Slide
SINGLE PORE CELL

Microscope and camera

Electrolyte

Cover slide

Counter electrode

Electrical leads

Side view

Reference microelectrode

Spacer

Zinc working electrode

Figure 2. Side View of Model Single Pore Cell
Figure 3. Assembled Model Single Pore Cell
SYSTEM CONFIGURATION

Figure 4.
Figure 5. Experimental Apparatus Arrangement
CROSS SECTION VIEW OF A CADMIUM REFERENCE MICROELECTRODE

Figure 6. Cross-Sectional View of Thin-Film Cadmium Reference Microelectrode
Figure 7. Close-up View of Cadmium Reference Microelectrode
Figure 8. Cadmium Reference Microelectrodes
## MODEL SINGLE PORE
### SCREENING EXPERIMENTS

<table>
<thead>
<tr>
<th>Aqueous Electrolyte</th>
<th>Pore Radius (um)</th>
<th>Current Density (mA/cm²)</th>
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<tbody>
<tr>
<td>31% KOH, 1% LiOH</td>
<td>18</td>
<td>30</td>
</tr>
<tr>
<td>15% KOH, 15% KF</td>
<td>18</td>
<td>30</td>
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**Electrolyte Effects**

<table>
<thead>
<tr>
<th>Rate of Discharge Effects</th>
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<tbody>
<tr>
<td>31% KOH, 1% LiOH</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>18</td>
</tr>
<tr>
<td>19</td>
</tr>
</tbody>
</table>

1Current Density Determination

\[
C.D. = \frac{I}{w d A_t} \frac{A_p}{A_t}
\]

\[
\frac{A_p}{A_t} = 0.5
\]

Figure 9. Single Pore Cell Experiment Summary
Figure 10. Transient Potential Distribution Behavior at 30 mA/cm$^2$ Discharge Current Density in 31% KOH
Figure 11. Effect of Discharge Current Densities on Initial Potential Distribution, in 31% KOH
Figure 12. Experimentally-Determined Initial Current Density Distribution at 30 mA/cm² Average Density in 31% KOH
Figure 13. Optical Microscope and SEM photographs of a Zinc Electrode Discharged at 1250 mA/cm² in 31% KOH

OPTICAL MICROSCOPE and SEM PHOTOGRAPHS
of A ZINC ELECTRODE DISCHARGED AT 1250 mA/cm² in 31% KOH
Figure 14. Optical Microscope and SEM Photographs of a Zinc Electrode Discharged at 30 mA/cm\(^2\) in 31% KOH.
OPTICAL MICROSCOPE and SEM PHOTOGRAPHS

of A ZINC ELECTRODE DISCHARGED AT 30 mA/cm² in 15% KOH , 15% KF

Figure 15. Optical Microscope and SEM Photographs of a Zinc Electrode Discharged at 30 mA/cm² in 15% KOH, 15% KF.
CONCLUSIONS

1) SURFACE MORPHOLOGY OF ZINC ELECTRODES VARIES WITH POSITION, RATE OF DISCHARGE, AND ELECTROLYTE COMPOSITION.

2) PASSIVATION IS AN UNLIKELY FAILURE MECHANISM FOR Zn/NiOOH BATTERIES AT RATES OF DISCHARGE TYPICAL FOR ELECTRIC VEHICLE APPLICATIONS.

3) CURRENT PENETRATION DEPTH EXTENDS WELL INTO PORE LENGTH, UP TO 0.6 – 0.7 X/L.

4) A FLUORIDE ELECTROLYTE OF COMPOSITION 15% KOH, 15% KF COULD REDUCE ZINC REDISTRIBUTION RATES BY EARLIER Zn/Zn(OH)₂ FILM FORMATION.

Figure 16.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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