Lawrence Berkeley National Laboratory

Recent Work

Title

TECHNOLOGY BASE RESEARCH ON ZINC/AIR BATTERY SYSTEMS: FINAL REPORT

Permalink

<https://escholarship.org/uc/item/0kj5h4bv>

Authors

Alcazar, H.B.S.

Nguyen, P.D.

Pinoli, A.A.

Publication Date

1987-09-01

c.2

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE DIVISION

Technology Base Research on Zinc/Air Battery Systems: Final Report

H.B. Sierra Alcázar, P.D. Nguyen,
and A.A. Pinoli

September 1987

RECEIVED
APPLIED SCIENCE
DIVISION
OCT 27 1987

NOV 10 1987

LIBRARY AND
DOCUMENTS SECTION

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks*

**APPLIED SCIENCE
DIVISION**

LBL-23960
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

**TECHNOLOGY BASE RESEARCH
ON
ZINC/AIR BATTERY SYSTEMS**

Final Report

September 1987

by

H.B. Sierra Alcázar, P.D. Nguyen and A.A. Pinoli

Pinnacle Research Institute
10342 Tantau Avenue
Cupertino, California 95014

for

Technology Base Research Project
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, Subcontract No. 4534410 with the Lawrence Berkeley Laboratory.

Abstract

The capacity extension of additives was tested in a 200 cm² bi-cell and a Zn powder moving-bed slurry. It was found that for the Type A additives in 12 M KOH, 25 g/l of silicate provided higher capacity than stannate, titanate and aluminate additives. The optimum concentration of sorbitol (a Type B additive that stabilizes polymeric chains involving ZnO) was found to be 15 g/l in 12 M KOH. A silicate and sorbitol combination added to Zn powder slurry in 12 M KOH provided a 20% increase in discharge capacity (195 Ah/l at 200 A/cm²) compared to the maximum capacity obtained with silicate alone. A much lower capacity (74 Ah/l) was realized with silicate as Type C additive (precipitation of ZnO away from the Zn surface, for low KOH concentrations). The mechanisms of passivation and capacity extension were discussed and a model presented.

The cell voltage and power densities were determined for the discharge process as a function of (a) current densities, (b) cathode depolarizer (air or oxygen), and (c) type of slurry (Zn powder or Zn coated polymeric bead). Air depolarization was observed to decrease the maximum power densities of both slurry types. The power densities obtained with Zn powder slurries were higher at all current densities investigated than those obtained with Zn coated polymeric beads (Zn-powder peak power densities more than doubled peak power densities obtained with Zn coated polymeric beads).

The recharge process was studied with a planar electrode and with a rotating cylinder electrode. The current efficiency and cathode potentials were determined for glassy carbon and Mg cathodes. The dendritic Zn deposits were mechanically removed from the rotating cylinder electrode with fixed blades. Mechanical removal proved to be unsatisfactory in the embodiment investigated due to preferential dendritic growth on the blades. Further investigations of discharge cell designs are underway.

Contents

Abstract	iii
1. INTRODUCTION AND EXECUTIVE SUMMARY	1
1.1 Additives to Extend Capacity	1
1.2 Discharge at 3 M KOH Concentrations	2
1.3 Comparison of Bead and Zn Particle Slurries	2
1.4 Scraped Rotating Cylinder Recharge Cell	4
2. DISCHARGE STUDIES	5
2.1 DISCHARGE CELL EXPERIMENTAL	5
2.1.1 Bi-cell Components	7
2.1.2 Fluidization System	8
2.1.3 Discharge Control	9
2.1.4 Electrolyte and Slurry Preparation	10
2.2 ROTATING DISK EXPERIMENTAL	10
2.2.1 RDE Cell	10
2.3 DISCHARGE RESULTS	12
2.3.1 Additives to Extend Capacity	12
2.3.2 Discharge of Low KOH Concentration	16
2.3.3 Discharge with Zn Powder Slurries and with Coated Polymeric Bead Slurries	17
2.3.4 Scale Up Model	18
2.4 DISCUSSION OF DISCHARGE STUDIES	20
2.4.1 Discharge Model	20
2.4.2 Reactions with Type A Additives	23
2.4.3 Mechanism of Type C Additive	23
2.4.4 Additive Combination	24
2.4.5 Slurry Types and Cell Performance	24
2.4.6 Effect of Air and Pure Oxygen Depolarizers	25
3. RECHARGE STUDIES	26
3.1 EXPERIMENTAL	26
3.1.1 Coated Polymeric Bead Recharge System	26
3.1.2 Planar Electrode Recharge Cell	29
3.1.3 The Scraped Rotating Cylinder System	31

3.2 PLANAR CATHODE RECHARGE RESULTS	— — — — 32
3.2.1 Cathode Potential and Current Efficiency vs Current Density	— — — — — 33
3.2.2 Effect of Zincate Concentration	— — — — — 36
3.2.3 Comparison of Mg and GC Cathodes	— — — — — 36
3.3 SCRAPED ROTATING CYLINDER RESULTS	— — — — 39
3.3.1 Recharge with the Scraped Rotating Cylinder	— — — — 39
3.3.2 Morphology of Scraped Zn	— — — — — 42
3.4 POLYMERIC BEAD SLURRY RECHARGE	— — — — — 44
4. CONCLUSIONS	— — — — — 45
5. REFERENCES	— — — — — 46

1. INTRODUCTION AND EXECUTIVE SUMMARY

The slurry Zn/air battery is a good candidate to power electric vehicles¹. Unlike many other batteries, the energy and power specifications can be designed independently of each other, and in situ or centralized recharging are possible, allowing great versatility in the design of range, power and weight distribution of electric vehicles.

The research effort described here in addresses developments in the discharge^{2,3} and the recharge⁴ processes performed in separate cells. The objective of the discharge studies is to find ways to increase the capacity and specific power of the battery. To achieve this objective the following parameters were investigated in a 200 cm² bi-cell:

- (a) capacity extension additives
- (b) KOH concentration
- (c) temperature
- (d) coated-polymeric bead slurries
- (e) Zn powder slurries
- (f) air and oxygen depolarizers.

Fundamental studies on the effect of additives on Zn passivation were started by determining the potentiodynamic critical currents and transition times from galvanostatic transients at a rotating disk electrode.

The objective of the recharge studies is to find a practical way to recharge either the polymeric bead or Zn particle slurries. A fluidized-bed cell was designed to recharge the beads. Engineering improvements are required to solve buoyancy of the polymeric beads and other problems for this cell. A scraped rotating cylinder cell was built to produce dendritic Zn slurries from discharged Zn particle slurries. Magnesium and glassy carbon cathodes were evaluated in both a rotating cylinder cell and a static disk cell. Some of the important experimental findings for the discharge and recharge studies are described in the summary section. The report is divided in two parts: discharge and recharge studies. The discussion of the experimental material will be complemented with three papers to be presented at the 22nd IECEC meeting (August 10-14, 1987)², the 172nd Electrochemical Society Meeting (Oct 19-23)³, and the 3rd Battery Materials Symposium, IBA (Oct 13-16)⁴. A recent review on the effect of additives, that includes unpublished results performed at Continental Corporation has been submitted for publication⁵.

1.1 Additives to Extend Capacity

A summary of the additive study is found in Fig. 1.1 that shows the capacity (Ah/l of Zn powder slurry) achieved when the indicated additives were added to a 12 M KOH at 55 °C. The hatched bar indicates the % utilization of Zn powder (starting concentration of 300 g/l) until passivation is reached. Sorbitol is an additive believed to increase the discharge capacity by stabilizing the polymer chains involving $\{OZnO\}_n \dots \{Zn(OH)_4\}_m \dots \{OZnO\}_n$ by means of hydrogen bonds. Sorbitol by itself extends the capacity just below that obtained by silicate. Titanate, aluminate, stannate, and silicate additives are believed to act by stabilizing micelles of ZnO and zincate ions. However when sorbitol is combined with silicate, a 20% increase in capacity is

obtained with respect to silicate alone, which indicates complementary mechanisms. This finding is considered to be very significant to the advancement of the state of the art.

Fig. 1.1 Zinc utilization and capacity extension by selected additives. Discharge of 300 g/l simulated dendritic Zn powder in 12 M KOH, at 55°C, using 4.5 x ratio of stoichiometric air and 200 mA/cm² current density at the 200 cm² bi-cell.

1.2 Discharge at 3 M KOH Concentrations. Experiments were undertaken to find the optimum combination of silicate concentration and current density. The “electropolishing like” conditions where an “infinite capacity” could be achieved by precipitation of ZnO away from the anode, were sought but not found. Some discharge capacity values are presented in Fig. 1.2. The best combination was obtained with 15 g/l silicate and Zn powder slurry discharged at 200 mA/cm² and 25 °C. Interestingly capacity decreases with increasing temperature in this system (see discussion section 2.4.3, page 23).

1.3 Comparison of Bead and Zn Particle Slurries. Slurries made with a mixture of zinc powders outperformed Zn coated beads (from SORAPEC) in discharge with silicate additive in 12 M KOH, as shown in Fig. 1.3.. The beads presented buoyancy problems that were more unmanageable in the fluidized bed used for recharge than in the moving slurry bed used for discharge. The effect of pure oxygen versus air as depolarizers was assessed. Enhanced cell potential and power at higher current densities were possible with oxygen, as shown in Fig 1.3.

Fig. 1.2. Capacity and utilization values obtained at 100 and 200 mA/cm². Discharge performed with 300 g/l Zn powder slurry in 3 M KOH with silicate additive as indicated. A cooling heat transfer unit was used to keep the temperature constant at 25 °C in the 200 cm² bi-cell.

Fig. 1.3 Power performance of bead and Zn powder slurries at 55 °C, with respect to current density in a 200 cm² bi-cell with 12 M KOH + 300 g Zn/l. Air or oxygen were used as indicated in label.

1.4 Scraped Rotating Cylinder Recharge Cell. The concept of mechanical removal of Zn dendrites grown and removed to form a slurry was demonstrated. Complete scraping was possible both from Mg and glassy carbon cylindrical electrodes. A powdery deposit was produced at lower current densities on glassy carbon than Mg. However, with both substrates, agglomeration at the fixed scrapers favored preferential growth at the blades that short-circuited the cell. Preliminary measurements at the rotating cylinder using 12 M KOH, chemically saturated with ZnO (~ 90 g/l), indicated 83% current efficiency with glassy carbon, compared with near 100 % measured with Mg. These preliminary current efficiencies were obtained by comparison of the charge passed with zinc scraped which was deposited at various current densities. The current efficiency from recharge experiments at the static disk electrode, are shown in Fig. 1.4. These efficiency results are considered more reliable since they were derived from measurements of evolved hydrogen and were subject to less experimental error than those derived from weight measurements of scraped zinc because of oxidation under air exposure.

Fig. 1.4 Zn Deposition at the static disk electrode at room temperature. Efficiency calculated from accumulated evolved hydrogen corresponding to 300 C/cm² charge passed on a clean substrate at each current density. Electrolyte is 12 M KOH (chemically saturated with ZnO). The zinc concentration is 90 g/l in experiment with Mg, and 96 g/l with the glassy carbon disk run.

2. DISCHARGE STUDIES

This section describes the progress in improving the energy density of the Zn slurry battery. The energy density is limited by the amount of Zn that can be electrochemically oxidized per unit volume of electrolyte. The capacity extension additives improve the energy density by extending the discharge process by various mechanisms. Those additives that produce suspensions of charged micelles of solids are classified as Type A. Type B additives are those which stabilize dissolved polymeric zincate ions (by hydrogen bonding). Type C additives are those that form an "electropolishing type" layer that causes precipitation of ZnO away from the Zn surface. Type C additives can be the same as Type A additives, but they act with a different mechanism when added to low-molarity KOH electrolyte. The Type D classification is reserved for additives that act as LiOH does, for which a clear understanding of the mechanism is not available at present.⁵

The capacity of slurries in 12 M KOH with silicate (Type A additive) has been tested in tubular cells with a reported capacity of 220 Ah/l, and at 80 mA/cm² discharge¹. Similarly^{5,6}, the capacity extension of several Type A additives has been determined with 3-cm² and 100-cm² planar electrodes, discharging at up to 150 mA/cm². In those studies, 190 Ah/l was the best capacity found, with 28 g/l of silicate (as SiO₂) added to 12 M KOH. Several Type B additives enhanced the capacity of a Zn/AgO battery⁷ using 10 M KOH. As for Type C additives, K₂SiO₃ (2% v/v) in 3 M KOH was found⁸ to give continuous ZnO precipitation at 40 mA/cm², in a planar Zn electrode. However, similar conditions in a moving Zn slurry electrode⁹ did not produce continuous precipitation, and passivation occurred at a capacity of 1.45 Kc/cm², roughly three times larger than that obtained in a slurry with 3 M KOH with no silicate addition.

Data on the KOH concentrations and additives that have been found to extend the capacity of KOH slurries containing Zn powder or Zn-coated polymeric beads (from SORAPEC) are described in this section. The discharge experiments were performed in a single planar bi-cell at higher current densities than previously tested, and with air or oxygen to depolarize the air cathode. Results of the discharge process will be published shortly² as well as a performance comparison of Zn Powder and bead slurries.³

2.1 DISCHARGE CELL EXPERIMENTAL

The discharge system, shown in Figs. 2.1 and 2.2, is designed to handle high current density discharge, moderate temperature, moderate back pressure, and both dendritic powders and bead substrate materials. It consists of three major sub-systems: 1) the submersed bi-cell, 2) the fluidization system, and 3) the constant current control and monitoring system.

XBB 879-7757

Fig 2.1 Discharge System

XBL 879-3925

Fig. 2.2 Diagram of Discharge System

2.1.1 Bi-cell Components. Discharge experiments were performed on a bi-cell of 100 cm² area each side, as shown in Fig. 2.3. On the average, a new bi-cell was made for every two discharge runs. An exploded view of the 200 cm² bi-cell is shown in Fig 2.4 . A brief description of the individual components follows, listed in order from the air side to the electrolyte/particulate side:

Frame. A Noryl backing with internal polypropylene ribs is used to withstand the air back pressure and to produce a flat cell sandwich.

Air Cathode. The air cathodes are Diffusion Electrodes (Eltech Systems Corporation), AE-20, which have a multilayered structure that allows them to operate as a semipermeable barrier. Gas and electrolyte diffuse into the three dimensional structure and react at the three phase interface. The cathode is catalysed with a modified macro-cyclic. The AE-20 is capable of higher current densities than other similar electrodes from the same company, but its life may be shorter. A conductive hydrophobic layer is used which allows the silver plated nickel grid to be used as current collector on the gas side of the electrode.

XBB 879-7758

Fig. 2.3 200 cm² bi-cell

Fig. 2.4 . Exploded view of 200 cm² bi-cell.

Separator. Heavy duty Nitex monofilament nylon separators, which have an open area of 39 %, thickness of 180 microns, and mesh opening of 175 microns, are used to isolate the anodic current collector and particulates from the air cathode.

Anodic Current Collector. Copper exmets with a thickness of 0.005 in., width strand of 0.007 in., and mesh opening of .125 in., were used as anodic current collectors.

Supporting Plates. Stainless steel plates coated with PTFA were used to provide external support and make a tight air-cathode/separator/anode-current-collector cell sandwich.

The bi-cell was assembled using RTV silicone and the current collectors were soft soldered to 1/8 in copper rods for electrical connection and support.

2.1.2. Fluidization System for the Discharge Cell. The fluidization system shown in Figs. 2.1 and 2.2, consists of the following components: (a) centrifugal pump, (b) temperature control (c) bi-cell container, (d) reference electrode, (e) back pressure control column, (f) flow meter. The system is designed to operate with a small volume of slurry electrolyte(1.4 l), so that a complete discharge experiment can be finished during a normal work day. A brief description of individual components follows.

Centrifugal pump. A centrifugal pump (Gorman Rupp Industries) was used to move and fluidize both Zn particle and bead slurries. Some particulars of this pump are (a) polyethylene body and impeller, (b) 303 stainless steel shaft, and (c) Buna N lip-type seal and o-rings. A 1/12 hp motor at 3000 rpm was used to operate the pump. This pump is rated by the manufacturer for continuous 5.5 feet of head at 20 gallons per minute.

Temperature Control. A temperature controller (Dyna Sense /model 2156) was used to hold the system to a constant operating temperature by means of flexible heating tapes wound around a 5/8 in diameter x 9 in length

glass tube in line, and a thermocouple temperature sensor was placed in the bi-cell container.

Bi-cell Container. A 8 x 12 x 1 in. parallelepiped tank with an internal 4 in. radius semicircle bottom served as the bi-cell container where the fluidized slurry acted as an anode. It was made out of methylmetacrylate to hold a slurry volume of 1400 ml. The slurry inlet is tangential to the curvature of the bottom of the tank, and a baffle in the path of the mainstream redirects the flow to the center of the cell to achieve a reasonable particle distribution of particles. The top of the tank is removable and can be sealed with a rubber gasket and bolts fastened to the tank walls. The temperature sensors, current collectors, and gas lines are fed through the top of the cell. During operation, the container was filled with slurry up to the outlet port (above the bi-cell on a side wall) so that gas bubbles could be released to the upper portion of the container, and presumably leak through the top, since we did not observe pressure build-ups.

Reference Electrode. A Hg/HgO reference electrode (gold wire amalgamated with Hg and anodically oxidized) in the slurry space of the container tank was used to monitor the anode and cathode potentials so that a drop in cell voltage not attributed to passivation of the anode, such as a premature air cathode failure could be detected.

Flow and Back-pressure Control. The pressure of the feed air in the air cathode was controlled by means of a variable head of water, using a hose submerged into a 30 in. cylinder filled with water. Only a few inches of water head were necessary to keep the electrolyte from flooding the air cathode.

Air Cylinder and Scrubber. Research-grade compressed air or compressed oxygen from "Air Products" were used at the cathode. A scrubber containing NaOH and CaSO₄ grains was used to remove CO₂ and moisture from the feed air or oxygen. A flowmeter with a needle valve was used to measure the flow of air or oxygen and to control the flow rate to 4.5 the stoichiometric ratio of oxygen at the AE-20 air cathode.

2.1.3 Discharge Control. A constant current discharge was maintained by a power supply connected to the variable load and measurement instruments as shown in Fig. 2.5. A brief description of individual components follows.

Fig 2.5 Diagram of Power Supply Wiring

Power Supply. A Hewlett Packard 6261B regulated DC power supply was used to control the rate of discharge in the constant current mode. Initially, the battery voltage is high and the power supply voltage is low, but as the battery voltage decreases during discharge, the voltage of the power supply increases.

Variable Load. For low current densities, a homemade variable resistor was used as a discharging load. The wire-wound power resistors could be added in the range of 0.1 to 20 ohms. At higher than 700 mA/cm², a Jagabi compression carbon pile rheostat was used to dissipate the load. This rheostat consists of graphite blocks stacked horizontally between copper plates compressed manually by a screw. Typically loads close to one ohm were used.

Measurement and Recording. Two Keithly 179 TRMS digital multimeters and a Houston Instrument Superscribe recorder were used to measure and record the cell voltage, anode and cathode potentials vs Hg/HgO, and voltage drop across a shunt to determine current. An ESC Model 640 digital coulometer was used to measure charge passed.

2.1.4 Electrolyte and Slurry Preparation. KOH solutions were prepared by dissolving reagent grade dry potassium hydroxide (VWR) in deionized (DI) and distilled water. The concentration of the solution was determined by titration with HCl and phenolphthalein indicator.

An excess of ZnO was added to freshly made KOH solution to prepare ZnO saturated KOH solutions. The mixture is stirred for several days and then the excess ZnO is decanted and filtered out. The Zn⁺⁺ concentration in the chemically saturated solution was determined by EDTA titration.

To prepare the Zn powder slurries, a mixture of 75 w/o powder of 100 mesh and 25 w/o powder of 30 mesh size were added to obtain 300 g Zn (99.999 % pure) per liter of 12 M KOH (plus additive), or 3 M KOH (plus additive). To prepare the bead slurries, 315 g of coated beads (85% Zn) were added to each liter of 12 M KOH electrolyte (plus additive).

2.2 ROTATING DISK EXPERIMENTAL.

Potentiodynamic and chronopotentiometric studies of the passivation of Zn in KOH with selected additives were conducted at a rotating disk electrode (RDE).

A rotator manufactured by Pine Instrument Company, was used to rotate the Zn RDE 200 to 10 000 rpm, with an electronic controller and a 1/15 hp DC shunt-wound motor.

The potentiostat/galvanostat used was a PAR model 173, and the potential waveform was generated by a PAR Universal Programmer Model 176. This instrument was also used as a trigger device to jump the Model 173 from the current controls A and B, while in galvanostatic mode, and to synchronize the oscilloscope time base to capture the transition time transients. A 7047A X-Y Hewlett Packard recorder was used to register slow transients as well as polarization curves.

2.2.1 RDE Cell. A "Teflon" cell (3.5 in. dia. x 5.5 in) capable of holding 400 ml of electrolyte and equipped with a reference electrode and concentric cathode was used in this study (see Fig. 2.6). Brief description of the RDE cell components follow.

Fig. 2.6 RDE Cell

Zn RDE. A rod embedded in a “Teflon” cylinder, showing 0.1307 cm^2 effective surface area was used as the zinc rotating disk electrode (Zn RDE). The polishing stages prior to each measurement started with a thorough rinse in deionized water, wet sanding with 600 grit paper, followed by 0.3μ alumina micropolish, and a thorough rinse in deionized and distilled water.

Cathode. A circle of 62 cm^2 of nickel exmet, mesh No 2, positioned at the bottom of the cell served as cathode (counter-electrode).

Reference Electrode. The N-shape Hg/HgO reference electrode used in the RDE cell had a gas relief valve and a syringe for the expulsion of gas bubbles lodged in the Luggin capillary. The HgO was freshly made by chemically reacting mercuric sulfate with sodium hydroxide, to insure a large surface area. The mercury was triply distilled by the commercial supplier.

2.3 DISCHARGE RESULTS

2.3.1 ADDITIVES TO EXTEND CAPACITY. The capacity and zinc utilization obtained with additives Types A and B is summarized in Fig. 2.7, which shows the capacity(Ah per liter of Zn powder slurry) achieved when the indicated compounds are added to 12 M KOH at 55 °C. The hatched bar indicates the % utilization of Zn powder from the starting capacity of 300 g/l to full discharge. Sorbitol is a type of additive believed to increase the discharge capacity by stabilizing the polymer chains involving $\{OZnO\}_n \dots \{Zn(OH)_4\}_m \dots \{OZnO\}_n$, by means of hydrogen bonds (more on this in the discussion section). Sorbitol by itself extends the capacity just below that obtained by silicate. Titanate, stannate and silicate additives are believed to act by stabilizing micelles of ZnO or zincate ions. However when sorbitol was combined with silicate, a 20% increase in capacity was obtained with respect to silicate alone.

Fig. 2.7. Discharge of 300 g/l simulated dendritic Zn powder in 12 M KOH, at 55°C, using 4.5x stoichiometric air. Current density was 200 mA/cm², in the 200 cm² bi-cell.

Sorbitol Additive. Discharge experiments at four concentrations of sorbitol were performed (see Fig. 2.8) which showed that 15 g/l was the optimum concentration. However, the combination of 25 g/l silicate and 15 g/l sorbitol provided a greater capacity enhancement (see Fig 2.7) than sorbitol alone. Further testing is required to find the optimum concentrations of the combined additives.

Fig. 2.8. Discharge of 12 M KOH with sorbitol in the 200 cm² bi-cell, same conditions as Fig. 2.7

Silicate Additive. The dissolved Zn concentration obtained during discharge of simulated dendritic slurry in 12 M KOH with 25 g/l silicate was determined by titration with EDTA. Total dissolved zinc concentration increases linearly with time (see Fig 2.9) as expected. The highest concentration point shown corresponds to complete passivation. A calculation was made to relate the measured concentration in terms of depth of discharge, expressed as specific capacity (A/l), see Fig. 2.10. The coulombs of charge passed at each concentration were determined, and corrections to the specific capacity were made for volume removed and accumulated charge removed in each sample. The theoretical amount of zinc discharged, determined from accumulated charge measurements assuming 100 % current efficiency, was compared to the actual amount of zinc titrated to calculate the current efficiency profile with depth of discharge shown in Fig 2.10. Concentration profiles of centrifuged samples (see Fig 2.10) showed virtually the same profiles as the non centrifuged samples, except near passivation, where a difference was observed. The difference is attributed to ZnO precipitation in the electrolyte bulk.

Fig. 2.9 Total Zn vs t during Zn powder discharge

Fig. 2.10. Current efficiencies derived from Zn concentration measurements. The open triangles show the theoretical concentration of Zn dissolved, calculated from the measured accumulated charge, assuming 100 % current efficiency. The open diamonds are the current efficiencies calculated from the concentration of total zinc dissolved (open squares). The small full squares show the dissolved zinc concentration determined from centrifuged samples.

Fig. 2.11. Discharge of Zn powder slurry in 12 M KOH with 25 g/l silicate as SiO_2 and 25 g/l sorbitol. Current density was 200 mA/cm^2 in the 200 cm^2 bi-cell using air depolarizer. (Note: the reference electrode was remote to cathode and anode, and potentials were not corrected for IR drop).

Best Performance: Sorbitol and Silicate Combination. The maximum extension in capacity was found for the discharge experiment shown in Fig 2.11, using a Zn powder slurry (300 g Zn/l) in 12 M KOH at 55 °C . However, when no electrochemical discharge occurred, the same additive combination performed the worst in chemical dissolution, as shown in Fig. 2.12; silicate additive by itself also proved to have negative effect on capacity when compared with the 12 M KOH in the case of chemical dissolution.

Fig. 2.12. Concentration of dissolved zinc in ZnO saturated 12 M KOH solution plus (a) 15 g/l silicate (as SiO_2) and 15 g/l sorbitol, (b) 25 g/l silicate (as SiO_2), (c) no additive.

2.3.2. DISCHARGE IN LOW KOH CONCENTRATIONS Experiments were conducted to find a combination of optimum silicate concentration, temperature and current density in which a Zn powder slurry (300 g/l) in 3 M KOH would produce an "infinite capacity" by precipitation of ZnO away from the anode. The best combination was obtained with solution containing 15 g/l silicate discharged at 200 mA/cm², see Figs. 2.13 and 2.14. The capacity decrease with temperature shown in Fig 2.13 indicates a very different mechanism than that obtained during discharge in 12 M KOH.

Fig. 2.13 Discharge Capacity versus temperature for the discharge of 300 g Zn powder/l in 3 M KOH + 25 g silicate/l (as SiO₂). In a 200 cm² bi-cell. 4.5 x stoichiometric air.

Fig. 2.14 Effect of current density and silicate concentration on the discharge of 3 M KOH in the 200 cm² bi-cell at 25 °C.

2.3.3. DISCHARGE WITH Zn POWDER SLURRIES AND WITH COATED POLYMERIC BEAD SLURRIES The objectives of the discharge experiments with Zn powder slurries are to (a) determine the relationship of current density and power, (b) compare the results with those obtained with coated polymeric bead slurries, and (c) predict the performance of a battery of bi-cell arrangement for electric vehicles. The power density improvement alternatives reported in this section include: (a) usage of Zn powder or Zn coated polymeric bead slurries, and (b) usage of oxygen or air depolarizers

The performance of Zn powder slurries (mixture of powder sizes 75% of 100 mesh and 25% of 30 mesh), and the performance of Zn coated polymeric bead slurries were determined in the bi-cell with air or with pure oxygen depolarizers. Potassium silicate additive (25 g/l as SiO₂) in 12 M KOH, and 4.5 x stoichiometric ratio of oxygen needed to depolarize the cell at a particular current density were used in the experiments. The temperature was kept constant at 55 °C. The cell voltage results are summarized in Fig. 2.15. An almost linear relationship is observed between the cell voltages and current densities both with air and with oxygen. The power vs current density curves are shown in Fig 2.16. The higher cell voltages and specific powers were obtained with Zn powder slurries. Also oxygen increased cell voltages and specific power at all current densities tested, both in the case of Zn powder or Zn coated bead slurries.

Fig. 2.15 Current density vs cell voltage for the discharge of Zn powder slurries and Zn coated beads in 12 M KOH + 25 g/l silicate (as SiO₂). The squares show the voltage data corresponding to air depolarization and the triangles show the data for pure oxygen depolarization. Two consecutive sweeps of current densities in opposing directions are shown for the bead slurry data (filled symbols).

Fig. 2.16. Specific power with respect to unit area of the bi-cell for the discharge of slurries of Zn particles or beads (abbreviated B in label) in 12 M KOH + 25 g/l silicate (as SiO₂). T = 55 °C. Pure oxygen or air, (as indicated in label) was used as depolarizer at 4.5 x stoichiometric ratio.

2.3.4 Scale Up Model. A compact battery can be formed using the planar configuration of the bi-cell by stacking up a sufficient number of bi-cells to obtain the necessary power. The results of a scale up calculation for a 11 Kw battery (a power estimated to give a 100-120 Km/h cruising speed to a 1000 Kg-EV) are presented in Fig. 2.17. These results are based on the cell voltages and power curves of Figs. 2.15 and 2.16, as well as on the specific capacity of 195 Ah/l obtained with 12 M KOH with 25 g/l silicate and 15 g/l sorbitol (see Fig 2.7). Assumptions for weight of the electrolyte system and miscellaneous controls, mountings, etc. follow the weights reported by CGE for a tubular system¹ and are shown in Table 2.1. The weight of an individual cell in Table 2.2 is based on the 200 cm² bi-cell weight with the stainless steel components replaced by graphite. The number of cells in the battery for the case of Zn powder or bead slurries was determined by dividing the required 11 Kw of total power by the corresponding peak powers of the individual bi-cell when discharged with air depolarizer. A summary of assumptions and projected performance of the bead slurry and powder slurry models, compared with the CGE results¹ is presented in Table 2.2.

Fig. 2.17 Specific energy, power density, and weights as a function of capacity of a 11 Kw battery system as specified in Tables 2.1 and 2.2

Table 2.1
Weights of Battery Components

Component	Weight (kg)
Discharge cells (planar geometry)	
1 cell	.3
129 cells (powder system)	38.7
314 cells (bead system)	94.2
Air System	
Intake funnel	0.2
Filter and housing	1.0
Humidifier/Scrubber	1.0
Shroud	2.1
Water tank	0.38
Valves	1.5
Air pump	2.5
Electrolyte System	
100 dm ³ tank	7.2
4 electrolyte pumps	8.2
Inter-modular plumbing	1.2
Valves	2.2
Miscellaneous	
Control, sensors, mountings	10.0
Oxygen gained	0-6.3 (ave. 3.1)

Table 2.2

Projected Performance Comparison for Different Battery Models

	Assumption						Projected Performance *		
	Weight of Battery Components (kg)	Zn Density g/l	Capacity (AH/l)	Cell Potential (V)	Density of Slurry (kg/l)	Peak Power mW/cm^2	Capacity KWh	Energy Density W.h/kg	Power Density W/kg
CGE model (4)	102.50	350	220	1.18	1.648	550	29	99	124
Bead Slurry Model	134.78	300	195	1.10	1.546	174.5	25	90	32
Powder Slurry Model	79.28	300	195	1.10	1.611	425	32	105	40

* Projected Performance for 300 kg system (i.e. 30% the weight of a 1000 kg vehicle)

2.4 Discussion of Discharge Studies

2.4.1 Discharge Model. The electrochemical, chemical and physical processes that occur, coupled with mass transport of species to and from the the electrode interface, make the discharge process a difficult one to model even under controlled potential and hydrodynamic conditions. In the case of a moving slurry electrode, the potential and current density of individual particles are constantly changing¹⁰. However, a qualitative understanding of our results can be achieved by (a) mechanistic interpretations from previous work performed on non-slurry electrodes and KOH concentrations similar to those used in this work, but without the additives, and (b) the abundant literature on physicochemical properties of alkaline zincate electrolytes. A model of the chemical and electrochemical reactions of slurry Zn/air cells using 12 M KOH electrolyte with additives to extend the capacity is summarized in Table 2.3

The reactions (2) to (6) are based on kinetic studies by Armstrong and Bell¹¹, Epelboin et al.¹², and McKubre¹³ using AC impedance on a rotating disk Zn electrode in concentrated alkaline solution. Essentially, a two-step dissolution takes place with reaction (2) being rate determining. In the absence of OH^- at the metal/electrolyte interface, as for the case of additive Type C, reaction (3) takes place to produce Zn^{++} that will diffuse away from the surface, otherwise OH^- will react with $\text{Zn}^+_{(\text{ads})}$ to form a loosely adherent and porous $\text{Zn}(\text{OH})_2$ film, as observed by Powers et al.¹⁴. Further transport of OH^- to the interface will tend to dissolve this film to form zincate ions according to the chemical equilibrium (5). Some of the zincate ions will diffuse into the bulk solution where it can be polymerized with the help of additive Type B, or form micelles with the help of additive Type A. However, some of the zincate ions diffuse back to the metal interface where Zn reverts it to free OH^- , according to reaction (6), and the OH^- produced enhances reactions (4) and (5).

Reaction (6) is an alternative to reaction (2); in the presence of zincate ions both proceed in parallel. Accordingly, the reaction rate should accelerate with an increase in product (zincate) concentration. The current efficiency should increase with depth of discharge, based on this tenet alone. The slight decrease in efficiency with depth of discharge shown on Fig. 2.10, however, does not necessarily disprove the model, since in the case of a slurry, a decrease in the effective anode area (increasingly poorer electronic conductivity among particles caused by film build up) can account for the diminishing current efficiency.

Table 2.3
A Model for Discharge Processes at the Moving Slurry Zn/Air Cell with
Extension Additives

Passivation Reactions:

Effect of silicate or compounds of a similar structure (stannate, titanate), adsorbed to ZnO:

Polymerization stabilized by Type B additive:

Type C additive (i.e. silicate in low concentration KOH) will cause:

Precipitation without passivation at electrolyte bulk to “silicate-rich-layer” interface:

Self discharge:

As for the structure of the zincate solution, the chemical equilibrium (7) proposed by Cain et al. ¹⁵, and supported by work of Dirkse ¹⁶ and Briggs ¹⁷, accounts for a Zn^{++} complex with an invariant core, having a central Zn^{++} ion structure surrounded by four tetrahedrally arranged oxygen atoms as nearest neighbors. Each atom is associated with at least one and in some cases two protons among species in equilibrium (7). A gradual transition from isolated Zn(OH)_4^{2-} complex anions in dilute $\text{Zn}^{++}/\text{KOH(aq)}$ to an increasingly more aggregated solution structure at high Zn^{++} concentrations was consistent with the Raman and ⁶⁷Zn NMR studies reported by Cain et al.¹⁵. In equilibrium (7) Zn^{++} cations begin to share protons (through hydrogen bonding) or perhaps even oxygen atoms (through Zn-O- Zn bridges), as suggested by extant spectroscopic, physicochemical and emf measurements. For example Dmitrenko et al.⁷ suggested the polymeric state described in reaction (12), and were the first to suggest an additive Type B to increase the hydrogen bonds and stabilize the hydrogen bonds of zincate ions to ZnO nuclei, enlarging the lace-like polymeric structure, and therefore the solubility and capacity of the electrolyte.

The modest capacity extension of aluminate, in Fig. 2.7, could probably be explained by the polymeric stabilization mechanism just described. Sorbitol is definitely a Type B additive because it has multiple proton donating groups. It was selected because it is stable in concentrated alkali. Dmitrenko et al.⁷, used molasses and xylitol as Type B additives to achieve 170 and 160 g ZnO/l in 10 M KOH. Another argument for the selection of sugars as stabilizing additives is the hypothesis that the spatial structure of the saccharides will prevent a close packing of the zincate molecules, and thus reduce the probability of formation of microcrystals in the solution.

Passivation Reaction

A prepassive Zn(OH)_2 film of porous nature forms on the surface of the electrode according to reaction (4). This film can dissolve to form Zn(OH)_4^{2-} according to reaction (5). As discharge proceeds, oversaturation of OH^-

occurs, and Zn(OH)_2 reprecipitates. The prepassive film thickens and slows the transport of hydroxyl ions to the base of the pores. Passivation by formation of a dense ZnO film will then proceed as by reaction (8) taking place instead of reaction (4), because a lower pH develops at the base of the prepassive film pores. The dense ZnO then blocks reactions (2) and (6), effectively stopping the electrochemical discharge. From this model it can be deduced that even if the zincate ion has not attained its maximum concentration in the electrolyte bulk, a local low pH can develop by slow transport processes. If the bulk electrolyte exhibits a low Zn(OH)_4^{2-} concentration, the ZnO film dissolves according to reaction (9) and reactivates the electrode. It is likely that this situation exists in individual particles in the slurry, even at a low depth of discharge. The fluctuations in particle current density in the slurry helps to re-establish uniform pH along the pores. Higher flow rates and lower particle current density should also help to extend capacity. However, for a given current density (based on cell geometry), the total area of particles has a practical maximum.

2.4.2 Reactions with Type A Additives

Silicate or compounds of a similar structure (stannate, titanate) will adsorb on Zn (or ZnO) by loss of a water molecule per reaction (10). If the ZnO particles are sufficiently small, a colloid forms with a hydration sheath and adsorbed silicate forms a micelle around a small ZnO nucleus. Such small nuclei have been produced only by electrochemical discharge, although the precipitation reaction, (9), is purely chemical. It is the location and rate at which reaction (9) occurs that determine whether micelle formation, or passivation by ZnO nuclei growth and consolidation into a dense film occur.

2.4.3 Mechanism of Type C Additive

Silicate and similar compounds compete with hydroxyl ions for adsorption sites on the Zn electrode surface. As the concentration of OH^- at the electrode surface decreases in relation to silicate concentration, a silicate-rich layer forms by reaction (10). The viscosity of the diffusion layer is higher than the solution bulk and therefore the thickness of the diffusion layer increases because transport of ions is more difficult through a more viscous layer. Discharge proceeds predominantly by the charge transfer reactions (2) and (3). The formation of a porous film of Zn(OH)_2 , reaction (4), or the disproportionation reaction (6) are not expected to proceed at a significant rate because the transport of OH^- and Zn(OH)_4^{2-} ions will be impeded by the negative charge of the adsorbed silicate layer and also by the increased viscosity and thickness of the diffusion layer. The model proposed for the action of additive C is the transport of Zn^{++} through the silicate-rich diffusion layer, eq (13), until it combines with hydroxyl ions to form zincate ions according to (14), or, for a lower pH, Zn^{++} precipitates as ZnO, according to reaction (15). A continuous precipitation of ZnO is then possible, and has been found for planar⁸ and slurry electrodes⁹ discharged at very low current densities. Support for the above mechanistic model can be construed from the rather unusual dependence of capacity on temperature shown in Fig. 2.13. We hypothesize that a decrease in temperature will (a) increase the viscosity of the silicate-rich layer, (b) thicken the diffuse layer and (c) lower the diffusion coefficient of hydroxide species in this layer. Therefore, at the lower temperature, transport of reactants to the metal surface will be slower

and so will be the passivation reactions (8) and (9). Passivation will be delayed until concentration gradients of hydroxide species between the electrolyte bulk and the electrode increase to overcome the increased diffusion barriers, forming the dense ZnO film that passivates the electrode

2.4.4. Additive Combination.

The most significant observation in this project concerns the ability to extend the Zn discharge capacity with additives Type A and B combined, as shown in Fig. 2.7. This result suggests that the micelle-forming and polymer-stabilization processes that are characteristic of Type A and Type B additives can take place simultaneously, hence providing a promising direction for improving the specific energy.

It is conceivable that Type A and Type B additives in combination with mechanism C could increase the capability of the electrolyte to carry more polymeric or suspended ZnO. It is, however, difficult to increase the "infinite capacity" that might be attained with additive Type C. The problem is that, at the practical current densities necessary for an electric vehicle power source, no infinite capacity window was found, as shown in Figs. 2.13 and 2.14. The current densities were too high for mechanism C to prevail. We hypothesize the current fluctuation of the individual slurry particles allowed enough time for hydroxide species to diffuse into the silicate-rich layer, so that passivation occurred as for Type A additives (or no additives).

It is interesting to note that a Type C mechanism might still be operative at high KOH concentrations. A white precipitate was observed in the electrolyte bulk near to the passivation point. Precipitated ZnO was also detected as the difference in concentration profiles of centrifuged and non-centrifuged aliquotes, near passivation, as shown in Fig. 2.10.

2.4.5 Slurry Types and Cell Performance.

An advantage of the moving bed Zn/air battery (MSZAB) is its capacity to sustain peak power capability, however its power characteristics need improvement in order to fulfill the requirements of cruising speeds of 100 to 120 Km/Hr for EV's.

Mechanical rechargeability at central locations (equivalent to gas stations) is a convenient possibility to simplify design of the MSZAB. However, marketing considerations dictate that a recharging capability should be designed on-board the EV. The recharge processes for powder and bead slurries are opposite, in so far as a dendritic, non-adherent Zn deposit is desired to produce Zn powder slurries, whereas a smooth, adherent Zn deposit is required to recharge coated bead slurries.

Cell voltages and power versus current density curves were affected by the type of particle that composed the moving slurry. The curves in Figs. 2.15 and 2.16 show the results of discharge experiments in the bi-cell with the same slurry pumping conditions. It can be seen that cell voltages are lower for the case of polymeric bead slurries than for powder Zn slurries with approximately the same weight of Zn. Consequently the power density curves for bead slurries are considerably lower than those for Zn powder slurries. By monitoring air cathode potentials, and by using newly made bi-cells, air cathode polarization was ruled out as the cause for the lower cell potentials. A

possible explanation is that less collisions take place in the bead slurry. Huh and Evans¹⁹ reported slower collision kinetics in slurries with coated polymeric beads than in slurries with Zn coated copper beads. If there are indeed less frequent collisions of coated polymeric bead slurries than in Zn powder slurries, we can expect more chains of Zn powder in contact with the current collector than chains of Zn coated beads contacting the current collector at any given time. The diminished time-averaged effective area will then force higher local current densities in the bead slurry, leading to higher concentration polarization than in the Zn powder slurries. If this is so, more beads in the slurry and more vigorous flow might still allow the coated beads to compete as candidates for the slurry Zn/air battery.

2.4.6 Effect of Air and Pure Oxygen Depolarizers in Cell Performance.

Reduction of pure oxygen flowing through the cathode at the same 4.5x stoichiometric ratio, produced higher cell voltages and specific power at all current densities and in both types of slurries (Figs. 2.15 and 2.16) than air. In the case of Zn powder slurries, a peak power greater than 530 mW/cm² (experiment stopped at current limit of hardware) was measured for discharge with pure oxygen. Higher oxygen partial pressure provides the driving force for oxygen transport through the liquid phase for reaction at the air cathode pores. The lower partial pressure of oxygen in air, and relatively lower oxygen concentration gradients will effectively reduce the electrode area in which reaction (1) takes place. Concentration polarization is therefore the reason for the lower cell performance with air. It is plausible that increasing the oxygen partial pressure by increasing total pressure, should have a better effect than increasing the stoichiometric flowrate of air. A possible explanation for the lower power curves obtained with air with respect to those obtained with oxygen, is a cooling effect due to the relatively larger flowrates of air. The electrolyte temperature was controlled, but it is not known whether a significant temperature reduction took place at the cathode, since the air and oxygen were not preheated to the 55° C operating temperature.

3. RECHARGE STUDIES

For the slurry Zn/air battery to succeed as a power source for electric vehicles, a practical recharge method must be developed that is for use on board or at central recharge stations. The mechanical removal of Zn dendrites deposited on Mg or glassy carbon cathodes for the recharge of the slurry Zn/air battery was demonstrated in this work. The manually scraped planar electrode and the scraped rotating cylinder electrode were designed for that purpose. The recharge of Sorapec Zn-coated beads was investigated in a fluidized-bed cell.

3.1 EXPERIMENTAL

Three systems were used to investigate the recharge of Zn: (a) polymeric bead recharge, (b) static disk for Zn dendrites and (c) scraped rotating disk for Zn dendrites.

3.1.1 Coated Polymeric Bead Recharge System.

The purpose of this system is to deposit smooth and adherent zinc coatings on discharged (passivated) beads. * The deposition of zinc on the beads takes place in a fluidized bed that serves as the cathode, and a membrane separates a nickel exmet that serves as the anode. Detail of the cell is presented in Fig. 3.1 and Fig. 3.2. The bead recharge system comprises the fluidized cell, an electrolyte reservoir, a centrifugal pump and the charge control system. The gas and electrolyte flow rates are measured by appropriate by-pass connections to the scraped rotating cylinder (SRC) system.

Fluidized-Bed Cell. The fluidized-bed cell is designed so that different types of cathode current collectors and membranes to separates the catholyte and anolyte can be used interchangeably. The beads are confined in the cathode chamber by a membrane that restricts their passage to the anode chamber or to the pump and electrolyte reservoir tank. The two chambers and separator are sandwiched together by bolts and sealed with a silicon rubber gasket.

Cathode Chamber. The cathode chamber of the fluidized cell is made of methylmetacrylate plate with dimensions of 2 x 13 x 1 in.. The design allows for easy replacement of the cathode current collector in order to rapidly assess the best material and geometry for this component. The electrolyte inlet at the bottom of the chamber and the outlet at the top are covered with nylon screens to confine the beads to the cathode chamber. There are openings at the top of the chamber where beads can be fed in and collected at the beginning and end of an experiment to estimate current efficiencies and to observe the microstructure of deposits. A Hg/HgO reference electrode is installed at the bottom of the chamber, to monitor the cathode potential.

* A description of the beads will be given under the subtitle "Sorapec Beads".

CBB 879-7755

Fig 3.1. Fluidized cell to recharge bead slurries.

Flow Distributors. Several minor modifications were made to the bead recharging cell to obtain a better suspension of beads. The distribution of suspended beads was with early experiments poor because the beads tended to float or to aggregate in certain sites. To overcome these problems the flow was distributed through holes covered by a nylon mesh separator at the bottom of the cell (see Fig 3.2). A methylmetacrylate plate with holes below the outlet of the cathode chamber served to support another nylon mesh separator. Both nylon mesh membranes ensured containment of the beads inside the cathode chamber to prevent cracking by the centrifugal pump. A major cell modification is envisioned for phase II to improve bead bed expansion and distribution of the beads in the fluidized bed or else a modification to operated the cell with a moving slurry.

Fig. 3.2 Major Components of Fluidized-Bed Cell.

Current Collector. Two current collectors made of nickel and magnesium plate respectively were used in the experiments. The preliminary observations indicate that less zinc plated on the magnesium collector, some of which was mechanically eroded by the fluidized bed.

Chamber Separation Membrane. The anode and cathode compartments are separated by a membrane. In initial experiments, short circuits developed with both a single layer of nylon and a double layer of nylon mesh. Nafion separators with various pretreatments were tried next, but showed extremely short active lives before developing a very high impedance. Finally, a microporous polypropylene film (Celgard #2400, from Celanese Fibers Company) successfully prevented short circuits for long time, but with a voltage penalty due to IR drop.

Anode Chamber. The anode chamber in the fluidized cell, has the same dimensions as the cathode chamber. It contains an anode made out of nickel exmet. There is an opening with a hose at the top of the chamber to exhaust oxygen formed during the recharge.

Electrolyte Pump and Reservoir. A corrosion resistant centrifugal pump (Microtrol model 10-41-316) was used to circulate the electrolyte and to control the bed expansion in the bead recharge cell. The pump has a ceramic (barium ferrite) body and impeller and 316 stainless steel shaft coated with "Teflon". An AC motor with solid state speed control that drives the pump is capable of delivering up to 6 G.P.M. at 5 psi. A tank with 3 liters

capacity (4.5 in. diameter methylmetacrylate tube) was installed in line (see Figs. 3.1 and 3.2.) to prime the pump and to hold the electrolyte.

SORAPEC Beads. The coated polymeric beads (Sorapec) have a spherical shape with O.D. between 0.4 and 0.5 mm. The beads consists of polystyrene spheres that are coated with an electroless nickel layer thickness between 1 and 2 microns. A layer of cadmium of approximately 1 micron thickness was deposited on the nickel layer. Finally, a layer of Zn approximately 20 to 100 microns thick is electrodeposited on the cadmium layer. The cadmium substrate ensures electrical conductivity even when the zinc is completely discharged from the bead, because it is difficult to remove cadmium during discharge. For this reason the recharge process can be easily initiated on discharged beads. However a serious difficulty is the buoyancy of the beads due to loss of specific weight, both at the end of the discharge process and at the beginning of the charge process,. This buoyancy causes the beads to agglomerate near the surface of the electrolyte, and thus they are not available for electrochemical reaction.

3.1.2 Planar Electrode Recharge Cell

Recharge experiments in the planar electrode cell provided information on the behavior of various substrates for the rotating cylinder cathode. The three electrode cell shown in Fig. 3.3 was designed to measure evolved hydrogen, from which the current efficiency was calculated for various current densities, total charge and substrate combinations. The cathode potentials were measured with respect to a Hg/HgO electrode with a Luggin capillary close to the disk cathode.

Mg Planar Electrode. The Mg electrode (99.99 % pure Mg plate 1/4 in. thick) has a square geometry with an active area of 3.3 cm², encased in an epoxy mold (Dexter Hysol, room temperature cure, two part epoxy, resin EE 4183 and hardener HD 3404). A 1/4 " wide, 5" long extension of the Mg plate that is insulated with a heat shrink PVC tube sleeve encased with epoxy mold, served as an electrical connection and as a mechanical positioner for the electrode. The surface finishing for each experiment consisted of two polishing steps: wet 600 grit followed by 0.05 micron Buehler Alumina Micropolish. However, the data point at each current density was obtained by removing with a plastic blade the Zn dendrite on the electrode between measurements.

Glassy Carbon Planar Electrode. A glassy carbon disk (exposed area of 6.937 cm²) made in-house and cured at 1000 °C served as the working electrode. The electrical contact to the glassy carbon electrode was made by gluing the back of the glassy carbon disk to a 3/4" diameter copper disk with conductive silver epoxy (TRA-DUCT BA-2902). The copper disk was soldered to a copper wire. The electrode was encased in the same type of epoxy compound as the Mg electrode. The copper wire connector was protected with heat-shrink PVC tubing encased in the epoxy mould and in an acrylic tube that helped to provide mechanical support. Surface finishing of this electrode was limited to a 0.05-micron alumina polishing (Buehler). However, the data point at each current density was obtained by removing with a plastic blade the Zn dendrite on the electrode between measurements.

Counter Electrode (Anode). The anode consisted of a 3/4" x 1-1/4" piece of nickel exmet that was spot

Fig. 3.3 Major Components of the Planar Electrode System

welded to a 3" long nickel wire covered with heat shrink "Teflon" for electrical insulation. This anode was surrounded by a perforated 1" O.D. acrylic tube serving as support to a "Nitex" monofilament nylon separator. The purpose of the separator was to prevent oxygen from reaching the cathode.

Reference Electrode. A H-shaped Hg/HgO reference electrode with a Luggin capillary positioned at approximately 3 mm from the working static electrode was used to monitor cathode potentials. The DVM used in the measurements had an input impedance of 10 Mohms.

Hydrogen Collector. Hydrogen evolved from the cathode was collected with an inverted funnel connected to the end of a buret with two-part five minute epoxy. A pipette bulb and stopcock were attached to the top of the buret to regulate the level of electrolyte in the column. Hydrogen volume was measured by displacement of electrolyte in the buret. The moles of evolved hydrogen were calculated and compared with the charge passed, after correcting for temperature, pressure and electrolyte vapor pressure. The current efficiency in the recharge process was calculated from the volume of evolved hydrogen.

3.1.3 The Scraped Rotating Cylinder System. The scraped rotating cylinder (SRC) system (see Fig 3.4) is designed to regenerate the zinc powder slurry discharged in the 200 cm² bi-cell. Zinc is electrodeposited on a magnesium or glassy carbon substrate, which is rotated and scraped by two fixed blades to remove Zn dendrites. These dendrites fall to the bottom of the cell to be fluidized later by an auxiliary centrifugal pump that transfers the resulting slurry to the discharge cell.

The SRC Cell. A methylmetacrylate tank 7-in. dia. x 12-in. height (4 liter capacity) contained two removable polypropylene blades that protruded from the tank walls and pressed tangentially against the rotating cylinder cathode in the center of the tank. The edges of the blades scrape the surface of the rotating cylinder and remove the dendrites deposited on the surface. A methylmetacrylate stud with a PTFE socket serves as bearing to center and support the rotating cylinder at the bottom of the tank. The inlet and outlet for the electrolyte and slurry are located at the top and bottom of the tank, respectively, for optional recirculation with the external centrifugal pump.

The SRC cathode. A glassy carbon or magnesium metal cylinder (1-in. O.D.) was used as the cathode which was mounted in the shaft of a Pine Instrument Company Analytical Rotator. The magnesium electrode was made from a solid rod that screwed directly in the stainless steel shaft. A PTFE sleeve covered the shaft and bottom of the cylinder electrode to expose only the outside diameter of the rotating Mg cylinder to the electrolyte. The glassy carbon (tube) was similarly mounted. Electrical contact to the glassy carbon was achieved with mercury tightly sealed by PTFE inserts into the annular space between a copper shaft extension and the glassy carbon I.D.

The SRC was hermetically sealed in the cell with a Buna N o-ring covered with silicone grease. The Pine Analytical Rotator is capable of rotation speeds up to 10 000 rpm. The number of graphite brushes in the current collector was increased to improve the total current handling capability of the instrument.

A timer connected to the rotator was used to program the various regimes of rest and rotation sequences for the SRC so that enough time elapsed for a given dendritic growth at a particular current density.

Anode for the SRC cell. A nickel exmet (0.005-in. thick with width strand of 0.007 in. and mesh designation number 2) was used as the anode. The exmet was pressed against the inside wall of the tank walls into a 7-in. diameter 10 in. high concentric cylinder electrode. The active area was determined by the amount of electrolyte in the cell.

Control and Measurement System. Most of the control and measurement instruments for the recharge process were located remote from the recharge cell itself, as a precaution for hydrogen explosions. The mass flow control subsystem comprised instruments to measure and control the flow of gas and electrolyte slurry. The current control subsystem comprised the power supply, voltmeters and analog recorders. There were provisions for switching gas flows from the bead recharge cell to the SRC cell and most of the instrumentation and sensors could then be shared in alternating runs.

Electrolyte Flow Rate Control. The flow of slurry was measured by a rotating paddle sensor (MK 525 Metalex Flow Sensor) connected to a MK 514 Signal Conditioner and a MK 584 Powered Flow Indicator (Signet Scientific). A magnetically coupled centrifugal pump with remote-variable speed control was used to circulate the slurry.

Gas Flow. Air was forced into the cell by an air pump ("Penn PlaxSilencer" aquarium air pump) with

Fig. 3.4 Schematic Diagram of the Scraped Rotating Cylinder.

variable speed and no oil contamination to dilute the evolved hydrogen . Two mass flow transducers and a 822/22 mass flow controller (made by Datametrics Dresser Industries, Inc.) were installed to monitor the inlet and outlet gas flows to the SRC cell or the bead recharge cell. The inlet transducer had a 1 liter/s range while the outlet transducer had a 10 liter/second range.

Current Control and Potential Measurement. A Hewlett Packard regulated DC power supply (Mod. 6261 B was used in the constant current mode to control the rate of recharge. Two Keithly 179 TRMS digital multimeters and a Houston Instrument Superscribe two pen recorder were used to measure and record cell voltage and anode and cathode potentials (with respect to a Hg/HgO reference electrode close to the SRC). Note that the reference electrode used was not covered by a protection membrane. The cathode potential measurements should be used for qualitative trend information rather than for absolute thermodynamic value.

3.2 PLANAR CATHODE RECHARGE RESULT

The current efficiency and cathode voltage were measured as a function of charge passed, electrode substrate, dissolved Zn concentration and current density at room temperature in an unstirred vessel. The electrolyte concentrations did not vary significantly because of the short duration of the experiments.

Typical profiles of the current efficiency as a function of charge passed are shown in Fig. 3.5, for constant current recharge at 200 mA/cm². It can be seen that the current efficiency increases with time (proportional to charge passed) because of the nucleation and growth process. The current efficiency for Mg is higher than that for glassy carbon because hydrogen evolves at a lower overpotential on Mg. Further studies were performed with charges of 30 and 300 c/cm². The surfaces on which a charge of 30 c/cm² was passed represent an initial dendritic growth state. The surfaces on which a charge of 300 c/cm² was passed represent a steady state growth, in which either no further effective area increases occur or, if the effective area increases, the effective current density is below a threshold where hydrogen evolution is significant. The results in Fig. 3.6 show the current efficiency versus current density curves for early growth (30 c/cm²) and mature growth (300 c/cm²) of electrodeposited Zn. A linear relationship between the current density and efficiency is observed at current densities >100 mA/cm². In this discussion we refer to the cathode area that includes surface roughness as effective area, to differentiate it from the geometric, or projected area. All current densities in the results below are referred to the geometric area of the cathode.

Fig. 3.5 Recharge of 12 M KOH containing 90 g Zn/l (from chemical saturation with ZnO). 200 mA/cm² constant current density experiments using a planar glassy carbon or a magnesium electrode. Efficiency calculated from charge passed and volume of H₂ evolved.

3.2.1. Cathode Potential and Current Efficiency vs Current Density

Figs. 3.7 and 3.8 present the cathode potential and current efficiency versus current density curves taken at 30 and 300 c/cm², respectively. In Fig 3.7 the potential curve was time averaged, in other words, the potential shown has a value between the more negative initial potential V_{in} and the less negative potential, V_f , read when 30 coulombs of charge per square centimeter had passed. In Fig 3. the final potential at each current density is plotted,

Please continue on page 36

Fig. 3.6 Current efficiency determined after specific charge (30 or 300 c/cm²) passed at each constant current density. A planar Mg electrode was used to recharge from a 12 M KOH solution saturated with ZnO (90 g Zn/l determined by EDTA titration).

Fig. 3.7. Current density and cathode potential (average) versus current density curves taken at 30.3 c/cm². Recharge of 12 M KOH with 90 g/l ZnO. Mg planar electrode.

Fig. 3.8. Charging performance of 12 M KOH chemically saturated with ZnO (90 g zinc/l) on a planar Mg disk at room temperature. Measurements taken at 300 coulombs/ cm^2 of charge.

Fig. 3.9. Current efficiency versus current density curves for the electrodeposition of Zn on a vertical, planar Mg electrode. 12 M KOH solutions chemically saturated with ZnO at 50 and 90 g Zn/l, and electrochemically discharged from a Zn powder slurry to a concentration of dissolved Zn of 169 g/l. This last electrolyte had 25 g/l silicate (as SiO_2) capacity extension additive. All measurements were made after 300 c/cm^2 had passed at a manually scraped electrode.

this cathode potential is called steady state potential because very small variation is observed when depositing beyond the 300 c/cm^2 at which it was determined. The cathode potential decreases in an approximately linear fashion with increased current densities, with a steeper slope for the smaller effective area experiments.

3.2.2 Effect of Zincate Concentration in Current Efficiency.

The current efficiency versus current density curves obtained at three zincate concentrations in 12 M KOH are shown in Fig. 3.8. The results show that zincate ions transport is rate limiting in the electrodeposition process because the current efficiency decreases as the electrolyte is depleted of zincate ions at high current densities, unless the time before scraping (charge passed) and the current were programmed in an optimized fashion to keep dendritic growth without excessive hydrogen evolution.

3.2.3. Comparison of Mg and GC Cathodes .

The cathode substrate material has very little influence on the current efficiency obtained at various current densities after the electrodeposited zinc has achieved a steady effective area where further deposition takes place. Fig 3.5 shows that a nearly constant current efficiency is achieved when a porous Zn deposit forms after passing 300 c/cm^2 at 200 mA/cm^2 . When other current densities were used (see Fig. 3.2.7) the current efficiencies when 300 c/cm^2 charge passes are very similar on Mg and glassy carbon substrate. Perhaps the slightly higher current efficiency observed for Mg results from lower hydrogen evolution during the nucleation and early growth period. The Mg substrate has a higher hydrogen overpotential. In addition, Mg substrates will generate a higher effective area than GC, so for a given charge passed Mg will show a lower effective current density, hence a higher efficiency versus current density (based on projected area).

Cathodic Polarization Curves on Mg and Glassy Carbon Substrates. The cathodic potentials for Zn electrodeposition from zincate-saturated 12 M KOH electrolytes were determined as a function of current densities. The initial potential (V_{in}) was obtained after switching on the constant current, and the final potential V_f , sometimes referred to as V_{ss} , was similarly determined after the passage of 300 c/cm^2 . The results are presented in Figs 3.10 to 3.12.

Fig. 3.10 Current efficiency versus current density curves determined at 300 c/cm² on planar vertical electrodes of glassy carbon and Mg. 12 M KOH, chemically saturated with ZnO (96 g Zn/l for the glassy carbon experiment and 90 g Zn/l for the Mg electrode experiment).

Fig. 3.11. Initial, V_{in} , and final, V_{ss} , cathode potential versus current density curves for the deposition of Zn on a planar Mg electrode in 12 M KOH + 25 g/l silicate (as SiO_2) + 169.5 g/l Zn (electrolyte discharged until passivation from Zn powder slurry). Steady state potentials determined after 300 c/cm² of charge passed.

Fig. 3.12. Initial and steady state potentials during Zn deposition on Mg cathode, in 12 M KOH with zincate concentration of 90 and 50 g Zn/l . Steady-state potential measured at 300 coulombs/cm².

Fig. 3.13. Steady state potentials of Mg and glassy carbon cathodes during Zn deposition from 12 M KOH chemically saturated with zincate (90 g Zn/l). Steady state potential measured at 300 coulombs/cm².

3.3. SCRAPED ROTATING CYLINDER RESULTS

3.3.1 Recharge with the Scraped Rotating Cylinder.

The mechanical removal of dendrites of electrodeposited Zn to form a slurry was demonstrated with the scraped rotating cylinder (SRC) electrode. Complete removal of Zn from Mg and glassy carbon SRC's was achieved. Glassy carbon substrate favors a powdery deposit at lower current densities than Mg, (see tables 3.1 and 3.2). However, with both substrates, agglomeration of Zn at the fixed scrapers short circuited the cell. Preliminary measurements with the rotating cylinder in 12 M KOH, chemically saturated with ZnO (approx. 90 g/l), showed a current efficiency of 83 % for a glassy carbon substrate, and near 100 % for Mg at the current densities indicated in Fig. 3.14. The current efficiencies were obtained by comparing charge passed with mass of zinc scraped at current densities based on projected area. The current efficiency results differ from those obtained with the planar electrodes (see Figs 3.9 and 3.10). The current efficiency results measured from rotating cylinder experiments should be taken to indicate relative performance of the substrates, instead of absolute values, because some experimental error is suspected in the weight of Zn. Although precautions were taken to rinse as well as possible the electrodeposited Zn with DI water and alcohol, and dry under nitrogen atmosphere at 50 °C, some unknown amount of ZnO was formed. The current efficiencies reported in Fig 3.14 are therefore shifted up by an approximately equal amount for Mg and glassy carbon SRC electrode.

Initial recharge experiments were performed with the SRC enclosed in a cylindrical anode (2 in. diameter). Premature short circuits due to zinc accumulated in the scrapers were observed. The Zn accumulated at the blades that eventually short circuited the cell resulted not only from Zn scraped off the rotating cylinder, but predominantly from Zn preferentially grown on the scraped Zn that initially got stuck at the scraping blades and remained in electrical contact with the rotating cathode. The diameter of the anode cylinder was increased to ~6 in. and the scrapers repositioned but the problem of preferential growth of zinc in the blades remained. Higher current densities produced a powdery deposit that fell to the bottom of the tank and therefore prolonged the time before short circuits occurred. Glassy carbon substrate, with a lower current efficiency (see Fig. 3.14) also featured a slower preferential growth at the scrapers than magnesium substrate, and a more powdery deposit. However short circuits due to preferential growth at the blades eventually aborted all recharge attempts with the SRC.

The cathode potentials, see Fig 3.15, showed values similar to the initial potentials determined in the static electrodes, see Figs. 3.11 to 3.13. Eventually the reference electrode was short circuited with spongy Zn. No Luggin capillary was used for the SRC cell.

Table 3.1**RECHARGE ON GLASSY CARBON SCRAPED ROTATING CYLINDER**

Current Density (mA/cm ²)	Scraping Structure	Microscopic Structure
250	A layer of scrapped zinc accumulates at the blade and grows preferentially.	Not available.
500	Powder zinc deposits on cathode and falls as fine particles when scraped. Some accumulation and preferential growth occurs at blade, forming big agglomerates.	Combination of spongy agglomerations and round flakes. The round flakes have dendrite and porous spongy structure.
1000	Powder zinc forms at the cylinder and some larger chunks grow at the scraper blade.	Dendrites and porous spongy agglomerates in an approximate ratio of 1:4 form.

Table 3.2**RECHARGE ON THE MAGNESIUM SCRAPED ROTATING CYLINDER**

Current Density (mA/cm ²)	Scraping Structure	Microscopic Structure
422	Dense deposits smeared by the scraping blades.	A small amount of dendrites and powder initially form.
1267	Large spongy chunks grow at the scraping blades and remain in contact with the rotating cylinder electrode.	Distinct dendrites and a small amount of powder fall off the scrapers and the growth at the blades is a porous spongy mass.

Fig. 3.14. Preliminary current-efficiency measurements during charge experiments using a Mg or glassy carbon rotating cylinder cathode. The electrolyte is 12 M KOH solution, chemically saturated with ZnO. The range of current densities (on the basis of projected area) at which measurements are made is indicated on the bars.

Fig. 3.15. Potential (mV vs Hg/HgO) of the rotating cylinder cathode versus current density, during recharge experiments from 12 M KOH chemically saturated with ZnO (90 g Zn/l).

3.3.2. Morphology of Scraped Zn

The morphology of electrodeposited Zn in the SRC is documented in Figs 3.16 to 3.19. At low current densities, 422 A/cm² and lower, dense Zn deposited on the Mg SRC, which was scraped as long strips, see Fig. 3.16. The spongy agglomerations resulted from electrodeposits accumulated at the blades due to relatively higher local current density. In contrast, glassy carbon substrate did not form dense deposits at low current densities, see Fig 3.17, but showed the same preferential growth of spongy Zn at the blades.

At high current densities a powdery dendritic Zn was obtained with both substrates at the cylinder cathode while spongy deposits grew preferentially at the blades in chunks that floated while maintaining electric contact with the SRC. A relatively larger amount of powdery was scraped off the cylinder body with GC than with Mg substrate.

XBB 879-7759

Fig 3.16 Aspect of deposited Zn at the Mg rotating cylinder. The long strips were scraped from the length of the cylinder, and have a flat side corresponding to the Zn-Mg interface, and a rough side corresponding to the Zn-electrolyte interface. The strips are quite dense, in contrast with the spongy agglomerations, formed mainly at the electrolyte surface-blade-rotating cylinder interface.

XBB 879-7760

Fig. 3.17. Aspect of deposited Zn at the GC rotating cylinder, at current densities in the range 250 to 500 mA/cm². A spongy growth took place preferentially at the scraper blade, limiting further growth at the body of the cylinder.

Fig. 3.18. Spongy and dendritic growth was observed during recharge at 1267 mA/cm² at the Mg SRC, rotating at 300 rpm continuous. The bigger spongy agglomerations in the figure were grown preferentially at the scraper blades, a lesser amount of powdery Zn was scraped off the cylinder body.

XBB 879-7761

XBB 879-7762

Fig. 3.19. At 1000 mA/cm², a powdery (dendritic) Zn was formed and scraped off the glassy carbon SRC, using continuous rotation at 300 rpm. The bigger spongy agglomerations in the figure were grown preferentially at the scraper blades. A relatively bigger amount of powdery Zn was scraped off the cylinder body with GC than with Mg substrate.

3.4 POLYMERIC BEAD SLURRY RECHARGE. Several attempts were made to recharge bead slurries, but were aborted because of short-circuits, separator problems and fluidization problems. The separator and short-circuiting problems were solved, but not the fluidization problems. Beads agglomerated both at the bottom and at the top of the anode chamber where they were confined by separator membranes and woven nylon mesh. Buoyancy caused the beads to accumulate at the top and bad flow distribution caused agglomeration of denser beads. New designs will attempt to solve these problems in Phase II of this research effort.

4 CONCLUSIONS

1. The maximum capacity found for Zn powder slurry discharge was achieved with a combination of Type A and B additives. This discharge capacity was 191 Ah/l at 200 mA/cm² (12 M KOH plus 25 g/l SiO₂ and 15 g/l sorbitol).
2. The optimum concentration for sorbitol (Type B additive) was found to be 15 g/l in 12 M KOH Zn powder slurry at 55 °C. The capacity obtained was 141 Ah/l at 200 mA/cm².
3. The additives were ranked in descending order of capacity extension capability as follows: silicate plus sorbitol > silicate > sorbitol > stannate > aluminate > silicate (Type C mechanism in low KOH concentration).
4. Cell voltage and power performance curves of Zn powder slurries were found superior to those of Sorapec Zn coated polymeric bead slurries under similar test conditions.
5. Oxygen depolarization of the cathode increased the cell voltage and power performance, compared to that attained with air depolarization.
6. Mg showed higher current efficiencies than glassy carbon as substrate for Zn deposition in the recharge process.
7. Lower zincate concentrations and shorter times between electrode scraping diminished the current efficiency during recharge at the SRC.
8. The glassy carbon cathode required higher charging voltages at all current densities, but produced dendritic deposits at lower current densities than the Mg cathode.
9. The higher generation of hydrogen associated with the glassy carbon cathodes produced powdery dendritic zinc that is easier to remove than that produced in Mg cathodes.

5 REFERENCES

1. A. Appleby, J. Pompon and M. Jaquier, "Economic and Technical Aspects of the CGE Zn-Air Vehicle Battery", I.E.C.E.C Record, August 1975.
2. Héctor B. Sierra Alcázar and Phu D. Nguyen. "Additives to Increase the Discharge Capacity of the Moving Bed Zinc/Air Battery", to be presented at the 22nd IECEC, August 10-14, 1987, Philadelphia PA.
3. H. B. Sierra Alcázar and Phu D. Nguyen. "Technology Base Research on the Slurry Zn/Air Battery" to be presented at the 172nd Meeting of the Electrochemical Society, Honolulu, HI, October, 18-23, 1987.
4. Phu D. Nguyen and H. B. Sierra Alcázar. "Performances of Zn Coated Polymeric Bead and Zn Powder in a Moving Slurry Zinc/Air Battery: A Comparison". to be presented at the 3rd Battery Material Symposium, Honolulu HI, Oct 13-16, 1987 .
5. Peter C. Foller. "The Effect of Additives on the Suspension of the Products of the Discharge of Zinc in Alkaline Solution" submitted for publication to J. Applied Electrochem.
6. Peter C. Foller, "Improved Slurry Zinc/Air Systems as Batteries for Urban Vehicle Propulsion". J. Applied Electrochem. **16**, 527, (1986)
7. V.E. Dmitrenko, V. I. Baulov, M. S. Zubov, N. N. Balyakina, and A. V. Cotov. "Structure of Supersaturated Zincate Solutions". Translated from Elektrokhimiya, **21**, 3, 349,(1985).
8. J.S. Drury, N.A. Hampson and A Marshall. "The Anodic Behaviour of Zinc In Silicate-containing Alkaline Solutions" J. Electroanal. Chem. and Interfacial Electrochem., **50**, 292, (1974).
9. A. Marshall, N. A. Hampson and J.S. Drury. "The Discharge Behaviour of the Zinc/Air Slurry Cell". Electroanal. Chem. and Interfacial Electrochem., **59**, 33-40, (1975).
10. T. Huh and J. W. Evans. "Electrical and Electrochemical Behavior of Fluidized Bed Electrodes". J. Electrochem. Soc. **134**, 308 (1986)
11. R.D. Armstrong and M. F. Bell, J. Electroanal. Chem. **55**, 201 (1974)
12. I. Epelboin, M. Ksouri, and R. Wiart, J. Electroanal. Chem., **75**, 113, (1977)
13. M.C.H. McKubre, "Temperature Limitation of Primary and Secondary Alkaline Battery Electrodes. Part III", Annual Report, August 1981. Department of Energy contract No. 450561. SRI Project PYD 1535.
14. R.W. Powers and M.W Breiter, J. Electrochem. Soc., **116**, 719 (1969).
15. K.J. Kain , C. A. Melendres, V. A. Maroni. J. Electrochem. Soc., **134**, 519 (1987).
16. Dirkse T.P., Abstract 77, p. 124. The Electrochemical Society Extended Abstracts, Vol **85-2**. Las Vegas, NV, Oct 13-18, 1985.
17. Briggs A.G., Hampson N.A., Marshall A., J. Chem. Soc., Faraday Trans. **2**, 1978 (1974)
18. Dirkse T.P., J. Electrochem. Soc., **102**, 497 (1955).
19. J. I. Cooper, "Weight and Volume Estimate for Al/Air Batteries designed for EV Applications", Proceedings 1st International Workshop on Reactive Metal/Air Batteries; Bonn , W. Germany (1979).

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720