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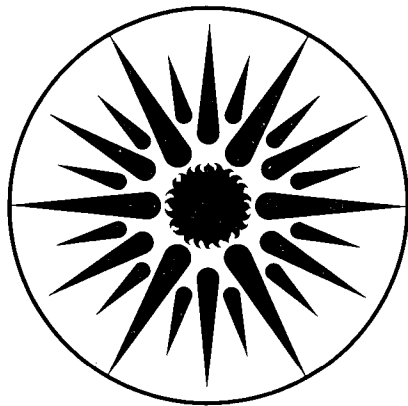1990-05-01

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE
DIVISION

Zinc Air Battery Development
for Electric Vehicles: Final Report

R.A. Putt

May 1990

**APPLIED SCIENCE
DIVISION**

DISCLAIMER

ZINC AIR BATTERY DEVELOPMENT

FOR ELECTRIC VEHICLES

Final Report

May 1990

by

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for

ACKNOWLEDGEMENT

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EXECUTIVE SUMMARY

This document reports the progress and accomplishments of a 16 month program to develop a rechargeable zinc-air battery for electric vehicle propulsion, from October 1988 through January 1990.

The program was the first stage in the transition of alkaline zinc electrode technology, invented at Lawrence Berkeley Laboratory, to private industry. The LBL invention teaches the use of a copper metal foam substrate for the zinc electrode, in combination with forced convection of electrolyte through the foam during battery operation. Research at LBL showed promise that this approach would avoid shape change (densification and dendrite growth), the primary failure mode of this electrode.

The program comprised five tasks; (1) cell design, (2) capacity maximization, (3) cycle testing, (4) materials qualification, and (5) a cost/design study. The cell design contemplates a plate and frame stack, with alternating zinc and oxygen electrode frame assemblies between rigid end plates. A 200 Ah cell, as may be required for the EV application, would comprise a stack of five zinc and six oxygen electrode frame/assemblies.

The experimental program was very successful, achieving both key objectives. The first was to increase the loading, or specific capacity, of the zinc electrode from 50 mAh/cm^2, the LBL target, to 100 mAh/cm^2, absent densification and dendrite growth. Charge capacities as high as 120 mAh/cm^2 were routinely achieved.

The second objective, 600 charge/discharge cycles on the zinc electrode, was substantially achieved. By the end of the program one cell had accrued 510 cycles, another 152, and both continued to cycle trouble-free.[1] Cycling was conducted in an unattended, automatic manner 24 hours per day. The zinc corrosion rate, determined as a byproduct of this testing, was 0.1 mA/cm^2, and was judged to be satisfactorily small, since at that rate it would require 40 days for complete self-discharge of a fully charged battery.

The cost/design study indicated that, in large volume production, the complete zinc-air battery system cost would lie in the range $50-100/kWh.

Based on the extremely positive results of the experimental program it was concluded that the LBL zinc electrode design solves

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[1]As of 4/30/90 Cell #1 had achieved 648 cycles.

the fundamental problem of shape change for the alkaline zinc electrode, and thus represents a major breakthrough in advanced battery technology for electric vehicles.

INTRODUCTION

The zinc-air battery is an excellent candidate for electric vehicle propulsion because (i) zinc is the most electropositive metal which is kinetically stable in aqueous electrolytes, (ii) oxygen is one of the most powerful oxidizing agents, and (iii) aqueous potassium hydroxide is surpassed only by sulfuric acid in conductivity at ambient temperature. These factors combine to give this system the attractive combination of high energy density and benign chemistry.

The overall cell reaction is the electrochemical oxidation of zinc to zinc hydroxide, as follows:

		E^o (25°C)
Anode	$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2e$	-1.245 V
Cathode	$\frac{1}{2}O_2 + H_2O + 2e \longrightarrow 2OH^-$	+0.401
Overall	$Zn + \frac{1}{2}O_2 + H_2O \longrightarrow Zn(OH)_2$	1.646 V
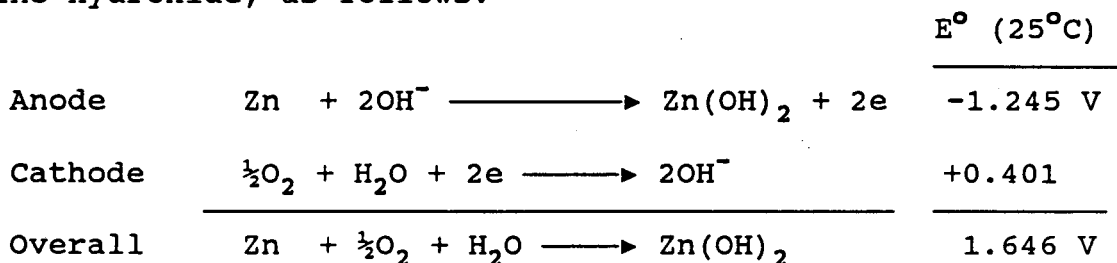
Development of the zinc-air battery for the EV application has taken several design paths over the last 20 years towards overcoming the two key problems, namely (i) zinc electrode shape change, specifically dendrite growth and densification, and (ii) the irreversibility of the oxygen electrode.

Lawrence Berkeley Laboratory, in its efforts to overcome the zinc electrode problems, invented the use of a copper metal foam substrate for the zinc electrode in a flowing electrolyte cell.[2] This high porosity foam (Figure 1) is characterized by:

- a density of 3 to 6%;

- 4 to 6 cells/cm;

- a cell dimension of 0.2 cm;

- filament diameters of 0.04 cm; and

- an effective surface area of 10 to 100 cm^2/cm^3

The foam substrate provides enhanced surface area for zinc deposition and allows electrolyte flow through the very large pores in the structure (Figure 2) vertically upward, parallel to

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[2]U.S. Patent #4,842,963; Philip N. Ross, Jr., inventor; U.S. Department of Energy, assignee.
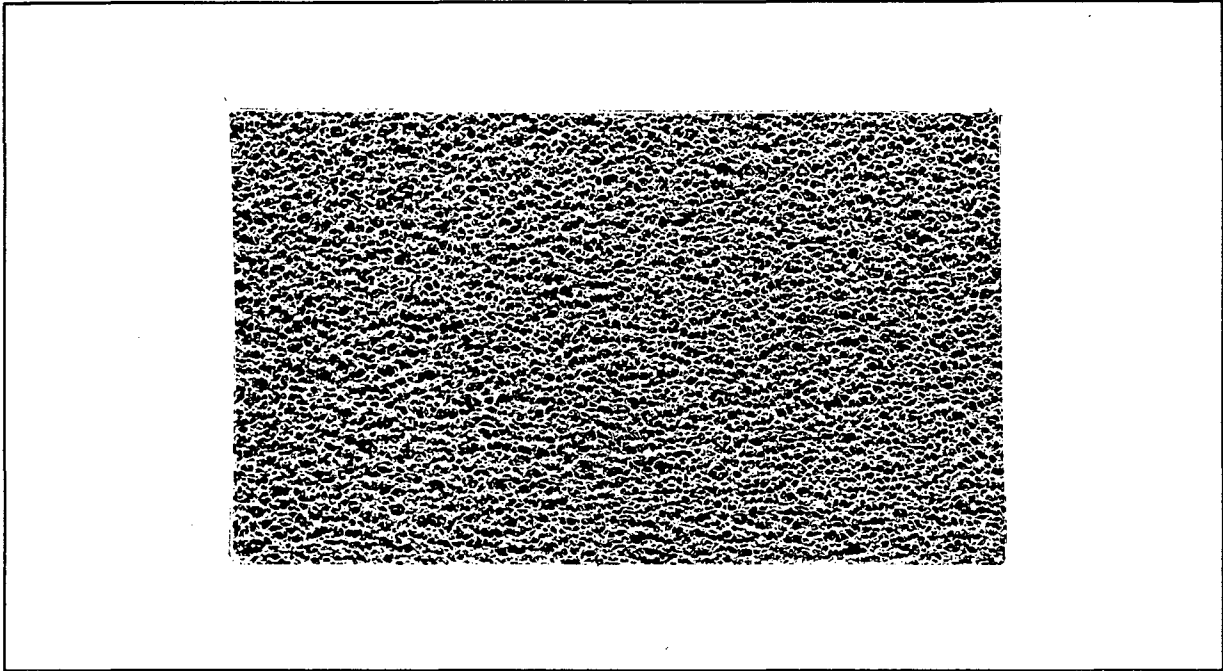
Figure 1: Photograph of 10 Pore
Copper Foam Metal (actual size)

Zinc
Electrode

Air
Electrode

Air
Flow

Separator
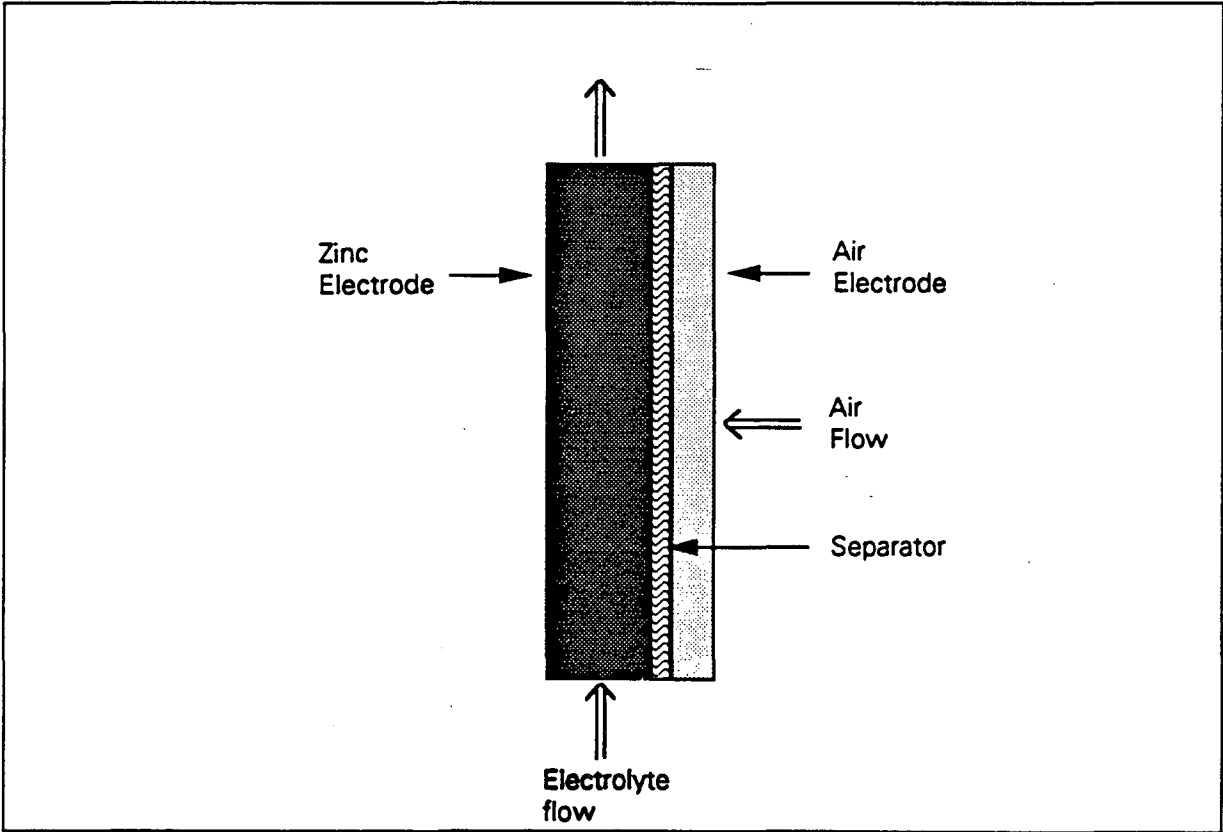
Electrolyte
flow

Figure 2: Cell Design Concept

its face. By increasing the surface area the effective loading (in terms of mAh/cm^2) is correspondingly reduced, minimizing the potential for dendrite growth.

The flowing electrolyte supplies and removes zincate ions uniformly to and from the filaments of the substrate during charge and discharge, respectively. This ensures uniform zinc deposits and thus avoids shape change and densification.

The initial development and cycle testing at LBL was very successful; over 100 charge/discharge cycles in cells using this zinc electrode concept were achieved. Therefore LBL elected to complement the program with a more applied development effort by an industrial contractor, and the present program ensued.

This program had the overall objective of technology transfer to the industrial community. More specific objectives were to...

- Maximize the achievable loading of the zinc electrode.

- Demonstrate the extended cycle life of the zinc electrode.

A loading target of 100 mAh/cm^2 was set to achieve both the cost and energy density objectives for the electric vehicle application. A cycle life of at least 500 cycles is likely to be the minimum necessary to achieve life cycle cost goals for the EV application.

The program was organized into five tasks, as follows:

- Task 1: Cell Design Concept

- Task 2: Zinc Electrode Capacity Maximization

- Task 3: Cycle Life Testing

- Task 4: Materials Qualification

- Task 5: Design/Cost Study

This report is also organized in this fashion. **SECTION 1** discusses the cell design concept, upon which the laboratory cell designs for performance and cycle life testing were based. **SECTION 2** describes the sequence of experiments conducted to achieve the loading target. **SECTION 3** reviews the results of cycle life testing. **SECTION 4** discusses materials qualification for this battery, and **SECTION 5** contains the results of a preliminary cost study on the cell stack components and the balance of system.

SECTION 1: CELL DESIGN CONCEPT

The goal of the cell design effort was to design a 200 Ah (minimum) cell which would meet performance, energy density, and cost objectives for the electric vehicle application. The design which was developed achieves the capacity target via a multi-plate cell design which is based on limited experimental experience with the system. This design will evolve during the course of a subsequent development program.

Design Basis

The elementary cell design (see **INTRODUCTION**) comprises (i) a metal-foam substrate zinc electrode, through which electrolyte flows parallel to the electrode face, (ii) a bifunctional oxygen electrode with air access to the backside (the side away from the zinc electrode), and (iii) a separator which provides electrical insulation between the electrodes and constrains the electrolyte flow within the zinc electrode. To accomplish this in a practical cell design required that several key design elements be addressed. Together these elements form the design basis discussed below.

Electrode Dimensions

Cost and energy density considerations suggest the use of electrodes having facial dimensions as large as possible. However, operational and performance considerations place limitations on these dimensions. From test experience to date it is believed that the limiting dimension is the zinc electrode height because of depletion of zinc in the electrolyte. For the present design a negative electrode height of 15 cm was selected, although as scale-up progresses this could likely increase to 30 cm or more. A square electrode design was chosen arbitrarily, thereby making the zinc electrode width 15 cm as well.

The thickness of the zinc electrode substrate depends on the selection of a monopolar versus bipolar design, as discussed below. Specifically, the monopolar zinc electrode is twice the thickness of the bipolar one. For the monopolar electrode, sufficient thickness for the penetration depth of 1-2 mm (see **SECTION 2**) on each face, plus a central region of 1-2 mm for flow when the faces are closed off by zinc at end of charge, are required. Therefore, a zinc electrode thickness of 0.6 cm was selected.

The oxygen electrode should be somewhat smaller in facial dimensions than the zinc electrode, to taper the zinc deposit along the periphery to minimize edge growth. Presently a 0.3 cm

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border on each edge is specified, making the facial dimension of the oxygen electrode 14.4 cm in each direction. The electrode thickness is assumed to be 0.5 mm. There are two oxygen electrodes, one facing a zinc electrode on each side of the electrode frame. The oxygen electrodes are separated by a spacer which allows air flow between the electrodes. In this design the flow gap is 0.5 cm, which results in a total thickness of the positive electrode assembly (i.e. two oxygen electrodes, flow spacer, and frame) of 0.6 cm.

Separator Dimensions

The separator for this battery has not been fully defined as yet. It is likely to be a multi-layer structure, and in the present design a total separator thickness of 0.25 mm is assumed.

Monopolar versus Bipolar

Deciding between the monopolar and bipolar design options requires a number of tradeoffs. The bipolar approach is favored from energy density, and particularly power density, standpoints because of the reduced materials requirements for current collection and because of the reduced conduction path lengths for electrical current. Further, electrolyte leakage is reduced owing to the elimination of current collectors in the electrode frames.

However, despite these advantages, the bipolar design meets with serious operational and materials problems in this battery, as follows:

Bipolar Plate Materials Selection. The bipolar plate must serve as an electronically conductive, but ionically insulating, separator between back to back zinc and oxygen electrodes. Further, it must be electrochemically stable to the oxygen electrode while having a high overpotential for hydrogen evolution. No single material comes to mind which meets these requirements, and one is forced to devise a composite structure, which is generally problematic in battery development.

Leakage Currents. A bipolar battery stack generates a high voltage, end-to-end, over a relatively short distance. For a flowing electrolyte battery this gives rise to leakage (shunt) currents in the flow passages within the stack. One must employ flow channels, which connect the flow ports to the electrode compartments, with a high length-to-cross section ratio to minimize the impact of leakage currents on battery efficiency and electrode-to-electrode capacity distribution. Unfortunately, the tortuous path provided by these channels poses a high risk of plugging by the zinc hydroxide suspended in the electrolyte.

Metal Foam Cost. In the bipolar design there are twice as many zinc electrodes as there are in the monopolar design, since in the monopolar design both sides of the electrode are used for zinc deposition. Even though, in principle, the zinc electrode for the bipolar design can be half the thickness (and thus perhaps half the weight of copper) of that for the monopolar design, the metal foam cost would be higher by almost a factor of two for the bipolar design. That is because the processing cost, which is proportional to area, for the metal foam dwarfs the materials cost, which is proportional to thickness as well as area.

The monopolar design was selected because of these perceived problems. This selection has relatively little impact on the program at present, since most of the development work performed to date or anticipated is applicable to both designs. Further, as has been shown in other advanced battery programs, a switch from monopolar to bipolar design, if warranted, can be made in stride with minimal delay.

Cell Design

The multi-plate cell design (Figure 3) comprises a plate-and-frame stack of zinc electrode assemblies, oxygen electrode assemblies, separators, and end plates. Each of these is discussed below.

Zinc Electrode Assembly

The zinc electrode assembly (Figure 4) consists of a zinc electrode, a frame, and a feedthrough. The zinc electrode has a substrate of copper foam, to provide the sparse, macroporous structure sought in this technology. The frame, molded from a mechanically strong and chemically compatible plastic such as nylon or glass-filled polypropylene, (i) holds the zinc electrode in position, (ii) provides electrolyte flow uniformly within the zinc electrode, (iii) allows passage of the electrical feedthrough from the electrode to an external connection, and (iv) provides a flat peripheral face for a leak-tight seal against the separator (or a gasket, if used) and the positive electrode frame in the plate-and-frame stack.

The electrolyte flows from the inlet port at the bottom, through the channels, into and through the electrode, and through the outlet channels at the top to the outlet port. The inlet and outlet ports are diagonally positioned to improve electrolyte flow uniformity across the electrode by balancing pressure drops.

The electrical feedthrough, a cylindrical copper rod, passes through an O-ring seal in the frame and connects to the external
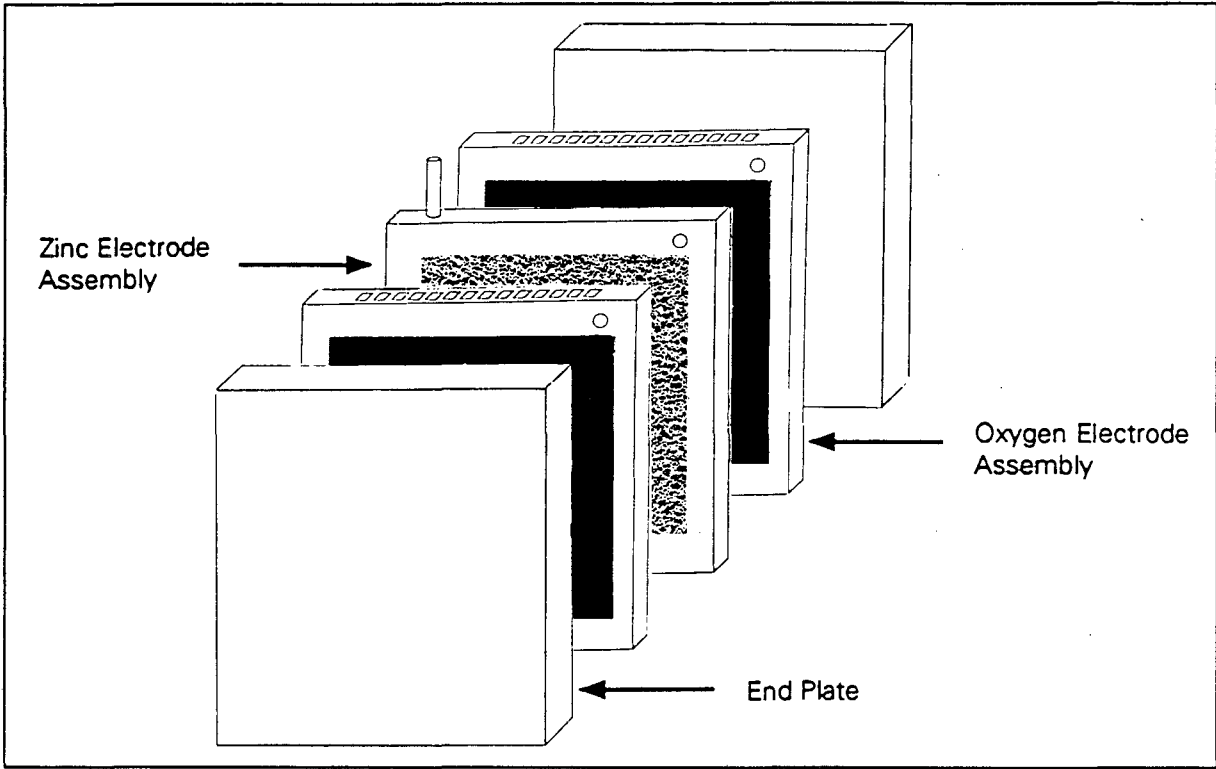
Figure 3: Multi-plate Cell Design
(separators not shown, for clarity)
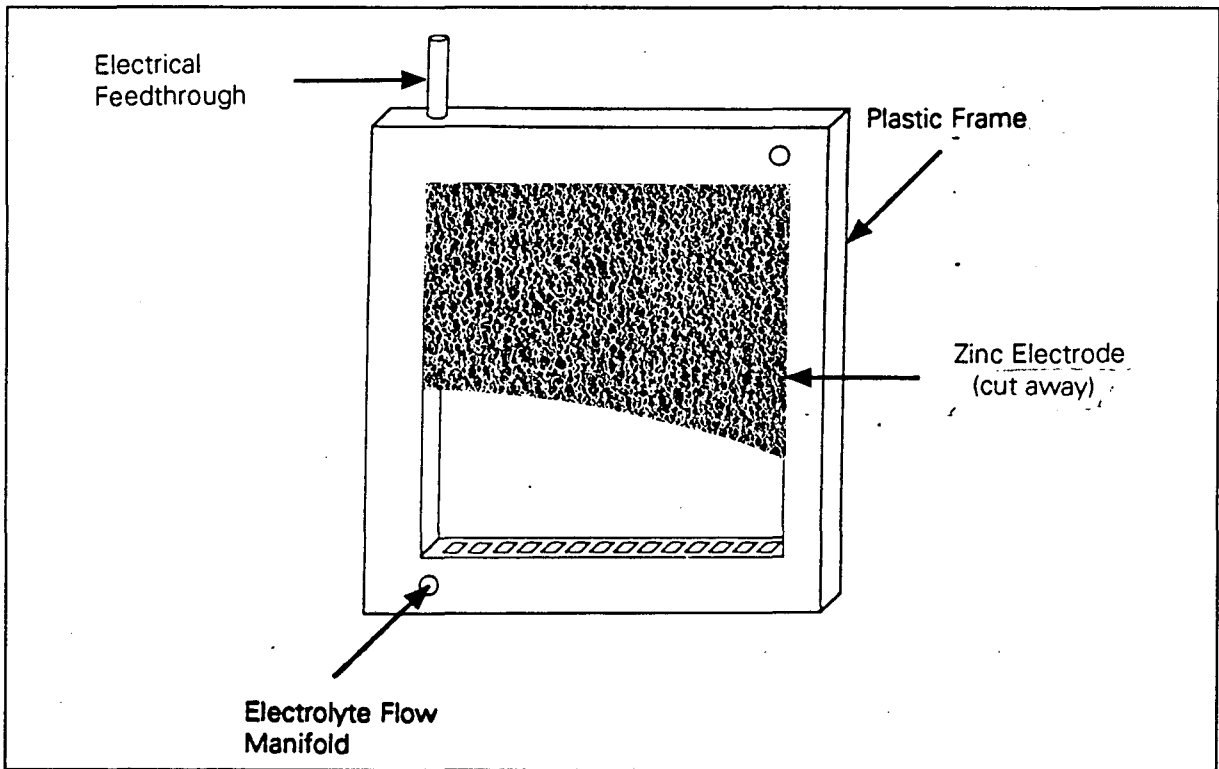
Figure 4: Zinc Electrode Assembly

bus bar. The cylindrical design was chosen because of the ease and reliability of O-ring seals. A square or rectangular cross-section for the feedthrough would be difficult to seal in a leak-tight manner.

Oxygen Electrode Assembly

The oxygen electrode assembly (Figure 5), comprises two back-to-back oxygen electrodes separated by a frame and a spacer. The bifunctional oxygen electrode, which is being developed elsewhere, is a thin (0.5 mm), Teflon®-bonded porous carbon structure pressed onto an expanded metal grid for support and current collection.

The frame, molded out of a suitable plastic such as nylon or glass-filled polypropylene, spaces the electrodes apart and provides passages for air flow behind the electrodes. There are holes in the bottom and top of the frame to allow air passage from and to inlet and outlet air manifolds bolted to the bottom and top of the cell stack, respectively. The spacer is a rigid, highly open (>90%), plastic structure which contacts the oxygen electrodes to maintain them snug against the separator while offering minimal resistance to air flow.

Separator

The separator is a multi-layer structure which is sandwiched between zinc and oxygen electrode assemblies. The materials evaluated for the separator are discussed in **SECTION 2**.

End Plate

The end plate (one at each end of the stack) (i) serves as a rigid strongback which distributes the clamping forces evenly over the face of the stack, and (ii) provides connections for electrolyte flow into and out of the stack. These connections line up with the flow ports molded into the electrode frames.

The end plates, molded out of a strong, rigid plastic, must be thick enough (1.25 cm) and properly designed so that they do not deform significantly under the peripheral clamping forces. They may be used in conjunction with a steel plate for added rigidity. A detailed end plate design was not conducted in this program.

Cell Stack

Multiple zinc electrode assemblies, oxygen electrode assemblies, and separators would be placed in alternating fashion
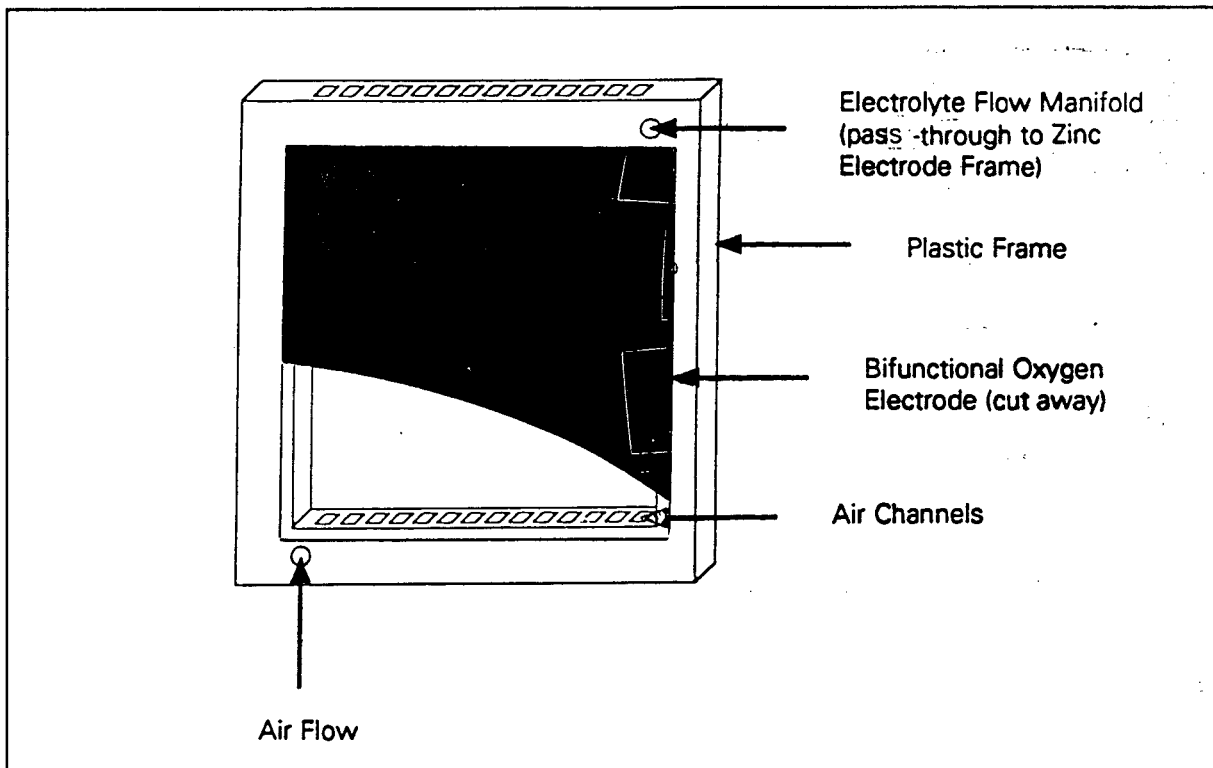
Figure 5: Oxygen Electrode Assembly

between the end plates to form the cell stack. The capacity of the stack is limited, for a given number of zinc and oxygen electrode assemblies, by the amount of zinc that can be reliably plated onto the foam substrates without incurring dendrite shorting or non-uniform densification. Based on experimental results (see **SECTION 2**) a reasonable goal is 100 mAh/cm^2 discharge capacity. For 15 cm x 15 cm zinc electrode dimensions the capacity is 22.5 Ah per face, or 45 Ah per zinc electrode assembly.

For the present design a stack consisting of five zinc electrode assemblies and six oxygen electrode assemblies was selected. The oxygen electrode assemblies on the ends would only have one oxygen electrode, since one side of each assembly would face against an end plate. The capacity of this stack would be 225 Ah, which is a 12% over-design margin above the 200 Ah target.

SECTION 2: CAPACITY MAXIMIZATION

This section discusses the experimental investigations with alkaline zinc electrodes having copper metal foam substrates. The experimental work conducted was preliminary screening of the factors likely to effect zinc electrode morphology.

Experimental Objective

The primary objective of the experimental work was to demonstrate a reproducible 100 mAh/cm^2 capacity density with a morphology characterized by (1) uniformity of deposit across the face and within the pores of the foam substrate and (2) the absence of dendrites which penetrate the separator. This objective targets the two major failure modes of the alkaline zinc electrode, i.e. densification and dendrite shorting.

Zinc Electrode Substrate

The copper metal foam (purchased from Foametals, Inc; Willoughby, Ohio) is available in a wide range of pore sizes and densities. Both 10 and 20 pores per inch material, with densities ranging from 3 to 6%, were evaluated. These offered the best combination of pore size and openness for this application. The cell design discussed in SECTION 1 suggested a thicknesses of 0.3 cm (in the bipolar cell design) and 0.6 cm (in the monopolar cell design).

The metal foam is unsuitable as received owing to surface oxidation; zinc deposition is patchy and poorly adherent. However, it etches readily in approximately 1M nitric acid, yielding a dull, matte sheen on the filaments. The degree of etching must be controlled carefully to prevent weakening the structure.

Zinc deposition on a properly etched substrate is uniform across the face and the deposit adheres well. However, the deposit does not plate uniformly throughout the depth of the substrate (as discussed later in this section), and the presence of bare copper filaments causes two problems, ie. (i) copper has a lower overvoltage for hydrogen evolution than zinc, which lowers current efficiency substantially, and (ii) bare copper discolors to a dull brown during electrode cycling and becomes inactive for zinc deposition. If the electrode is discharged of all zinc the whole electrode becomes progressively inactive, and electrode polarization increases from cycle to cycle (Figure 6), becoming unacceptably high within 10 cycles. These problems require pre-plating the copper foam substrate.
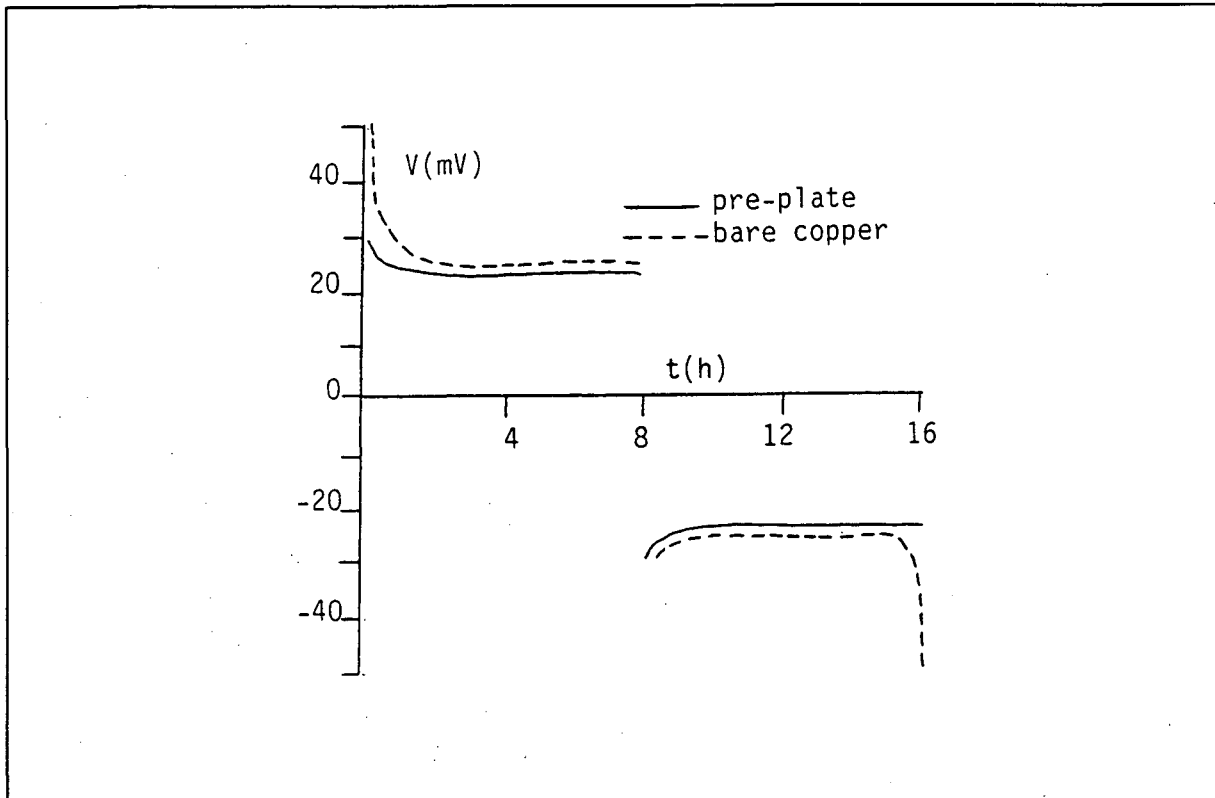
Figure 6: Charge-Discharge Curve, Zinc-Zinc Cell

The pre-plate metal must protect the copper foam during normal battery operation, withstand anode-limited cell reversal, and allow at least a minimal current density of oxygen evolution so that all cells in a series string can fully discharge.
Dense zinc was selected for convenience, and it performed well during this program.

The pre-plating process for zinc evolved into two steps, as follows:

High Current Density Strike

This is used to cover quickly the entire substrate while it is still freshly etched. The etched substrate is rinsed thoroughly with water and placed into a plating bath of 3M KOH with 10 g/l zinc. The anode is a strip of nickel-plated steel evolving oxygen. The substrate is plated at a current density of 50 or 100 mA/cm^2 (for 3 and 6% dense metal foam, respectively) for approximately 2 minutes, with vigorous stirring, at room temperature.

Low Current Density Plate

This step builds a thickness of dense zinc on all filaments

of the substrate. The bath is the same as above with the addition of a brightener. The current density is reduced to 8 mA/cm^2 or 10 mA/cm^2 (for 3 and 6% dense metal foam, respectively), and plating is conducted with vigorous stirring at room temperature for 8 to 10 hours.

Experimental Cell and Flow System Design

The experiments were generally half-cycle in nature. That is, zinc was plated onto the metal foam substrate, with oxygen evolution at the positive, to a given loading. The cell was then taken apart for visual observation and physical characterization.

The experimental cell (Figure 7) comprised two acrylic cell halves to hold the zinc and oxygen electrodes. The electrode compartments were 2.5 cm wide by 5 cm high. Channels in the cell halves allowed flow between the tubing fittings on the back side of the cell halves and the electrode compartments. Electrolyte flowed vertically through the metal foam zinc substrate and across the planar nickel-plated steel oxygen electrode substrate. The cell was held together by metal clamps which compressed a PTFE gasket placed on the mating surfaces of the cell halves to prevent leakage.
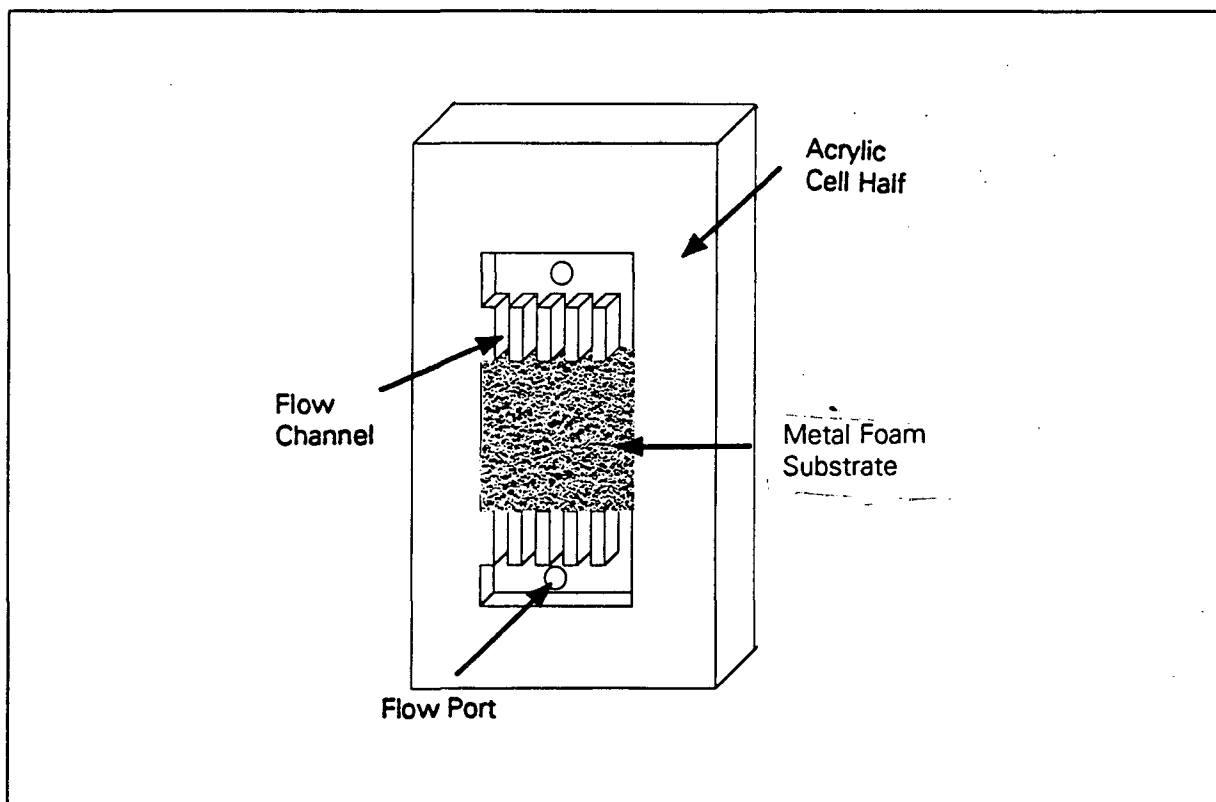

Figure 7: Test Cell Fixture, Zinc Electrode Half

The electrolyte was pumped from a reservoir by a Masterflex®
peristaltic pump through the cell. For simplicity the electrolyte
was passed in series from the zinc electrode compartment to the
oxygen electrode compartment prior to its return to the reservoir.
This eliminated the need for two pumps. C-flex® tubing was used,
which demonstrated excellent chemical stability and very good wear
resistance in the pump heads.

Several candidate separators were evaluated. Non-woven
synthetic papers and ion exchange membranes were prone to dendrite
penetration. Celgard® 3401, on the other hand, owing to its small
(0.04 micron) pore size, did not allow dendrite penetration, and
one to three layers were used for most of the experiments.

Experimental Results

Nearly all experiments were directed towards achieving the
100 mAh/cm^2 loading target with uniform, non-dendritic zinc. A
preliminary study was devoted to materials selection and
operational procedures. Once a satisfactory system was developed
which yielded reproducible results, specific experiments were
conducted to achieve the stated objective.

Nature of the Deposit

In general the deposit morphology was mossy and dull gray in
color. The distribution of the deposit across the electrode face
was generally uniform, but there was considerable non-uniformity
in the normal direction. That is, the deposit was generally
heaviest at the face nearest the separator, and tapered off with
distance into the foam. This was expected, given the excellent
kinetics of the zinc electrode as compared with solution phase
conductivity.

The deposit was generally closed off at loadings of 100
mAh/cm^2 or more. That is, the mossy zinc covered the entire front
face of the electrode, thereby obscuring the filaments of the foam
substrate. The penetration of the mossy zinc into the foam varied
between 1 and 2 mm. Visually the density of the mossy zinc
appeared to be high enough to restrict severely electrolyte flow
through it. In this case, the electrolyte flow path would be
behind the deposit, within the central portion of the foam where
little zinc had been deposited.

This closing-off effect must be taken into account in the
design of the cell (see **SECTION 1**). That is, there must be
sufficient foam substrate thickness to provide for a region of
closed-off deposit (on one face for the bipolar design, both faces
for the monopolar design) as well as a central region for

electrolyte flow.   Ideally the deposit should be uniform throughout the substrate, but this has not been achieved in practice.

Attempts to Make the Deposit More Nearly Uniform

The primary motive for obtaining a uniform deposit throughout the substrate is to maximize the loading without dendrite growth. A uniform deposit would have a substantially lower local current density and, in turn, capacity density, than would a deposit concentrated on the front face of the substrate. Since it is generally believed that dendritic growth is favored as the current density and capacity density increase, a uniform deposit would minimize or eliminate dendritic morphology.

Several parameters were varied in a preliminary attempt to increase deposit uniformity, namely (i) zinc concentration, ranging from 10 to 100 g/l, (ii) electrolyte flow field; the electrolyte flow was varied from the front to the back face of the substrate, (iii) current density, ranging from 5 to 10 mA/cm^2, (iv) pulse plating, at a duty cycle ranging from 10 to 20%, and (v) plating additives, lead (at 100 ppm) and a fluorosurfactant.

In general there was little, if any, significant effect of the variables studied. There was a degree of irreproducibility in deposit appearance from run to run which made it difficult to discern real differences ascribable to the controlled variables. However, the two areas which need further study, based on promising but inconsistent results, are current density and pulse plating. There were indications that lower current densities favor more uniform deposition, and that pulse plating, given the proper duty cycle and frequency, may alter the deposit distribution.

Lower current densities (5 mA/cm^2 or less) may be of little practical significance in the EV application since it would take nearly a day (20 h) to achieve full capacity of 100 mAh/cm^2. Pulse plating, on the other hand, can be performed on full scale batteries, given the advances in solid state power switching technology, and it deserves a careful study.

Separator Evaluation

Four candidate separators were evaluated during this program, as follows:

• PVA: Polyvinyl alcohol synthetic papers are employed with good success in alkaline zinc-manganese dioxide batteries and they are low cost. However, they

are unsuitable in this system because they are easily penetrated by dendrites in one or two cycles.

• Ion Exchange Membranes: Samples of radiation-grafted membranes (e.g. R1030, manufactured by RAI) were tried, but, like PVA, they suffered dendrite penetration in one or two cycles.

• Celgard® 3401: Considerably more success was achieved with this material. It is a microporous polypropylene with a very small pore diameter (0.04 micron), and is impregnated with an insoluble surfactant to render it hydrophilic.

Cells with 3401 separators were capable of over 200 cycles in the absence of dendrite penetration. Furthermore, the experimental results suggest that the likelihood of dendrite penetration is directly proportional to current density, and perhaps more importantly, capacity density (loading). By restricting the loading to some reasonable upper limit, e.g. 120 mAh/cm^2, dendrite penetration can be avoided.

• Celgard® K703: This is a laminate of 3401 with two layers of cellophane. Cellophane was selected owing to its well-known resistance to dendrites, and K703 proved to be an excellent dendrite barrier. Dendrite penetration was experienced only at loadings well above 200 mAh/cm^2. The shortcoming of this material is that the cellophane layers become prone to ripping during handling after exposure to the electrolyte for several months. Whether this is a problem in a battery that is not disassembled on a regular basis has not been determined.

Edge Growth

As the zinc loading increases beyond 100 mAh/cm^2 (where the deposit becomes closed off) zinc growth begins laterally away from the electrode edges, along the face of the separator. This edge growth is undesirable because the zinc there becomes isolated from the electrode during discharge and thus represents a capacity loss. The extent of edge growth is related not only to deposit loading but also to the thickness of the electrolyte film between the separator and the electrode frame. Edge growth can be reduced or eliminated by providing a tight gasket seal which displaces the electrolyte film in this region.

SECTION 3: CYCLE LIFE TESTING

The LBL zinc electrode design was developed to increase cycle life. The demonstration of over 500 cycles in this test program, discussed below, validated the LBL concept.

Test Bed

It was critical to develop, early on, a highly reliable cycle testing system which could operate continuously and automatically, to allow for round-the-clock cycle testing. The test bed comprised the test cell, flow loop, and electrical test and measurement system.

The test cell design required innovation because an efficient, long-lived, bifunctional oxygen electrode was not available. The cycle testing at LBL employed alkaline nickel positive electrodes similar to those used in nickel-zinc and nickel-cadmium cells. However, LBL reported problems with these as well, related to overcharge requirements and limited cycle life. Consequently a zinc-zinc cell design was conceived (Figure 8), in which both the working and counter are metal-foam zinc electrodes. Since both electrodes require the same flow, the electrolyte can be pumped in series from the working electrode to the counter, which simplifies the flow system considerably.

The advantages of this design are (i) both electrodes are zinc, thereby increasing the information generated and experience gained as compared with a cell having a nickel counter electrode, (ii) the chance of contamination by a foreign counter electrode, e.g. nickel, is eliminated, (iii) data collection is more accurate, since the open circuit voltage of the cell is zero, which permits use of a millivolt scale on the recorder, (iv) a load resistor is not required, as the cell is driven by the power supply for both charge and discharge, and (v) the potential for damage in cell reversal is reduced substantially because the cell cannot go, on its own, into cell reversal. The voltage limit on the power supply can be set low enough that damaging reverse potentials are not reached in over-discharge.

The cell halves used in cycle testing were identical to those used in the capacity maximization studies, which allowed complete interchange of hardware.

The flow loops employed the same components as well, including the Masterflex® pump with C-flex® tubing and the polyethylene reservoir. As mentioned earlier, the discharge from the working electrode cell half was directed to the inlet of the counter electrode cell half for series flow.
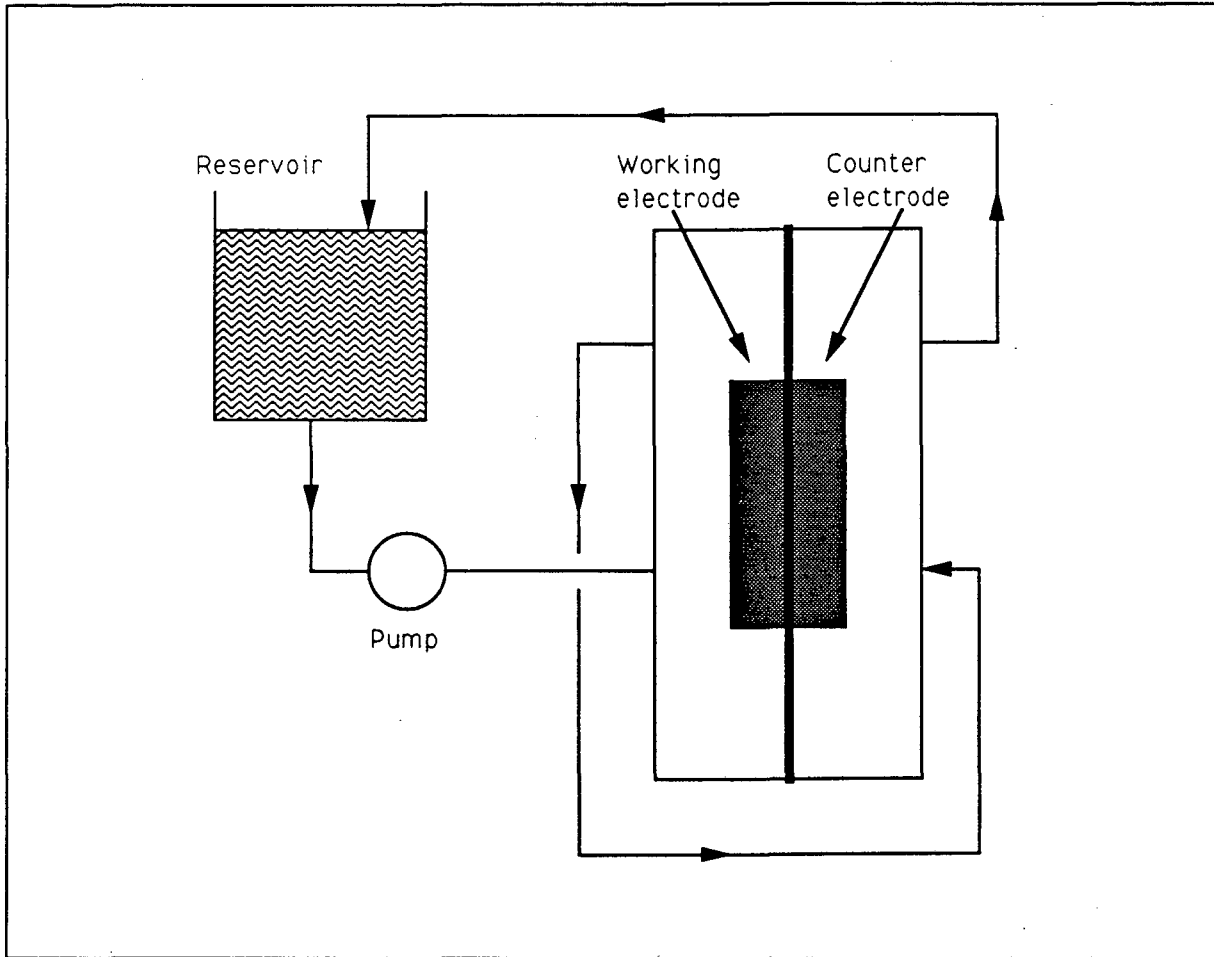
Figure 8: Zinc-Zinc Cell Test System Diagram

The test and measurement system comprised two independent subsystems. The cell current was provided by a constant current, voltage limiting power supply. There were a set of reversing contacts, to switch between charge and discharge, which were controlled by a recycle timer. The measurement system consisted of a strip chart recorder to record the voltages of the cells.

Cycle Test Procedures

Two zinc-zinc cell systems were dedicated to the cycle test program. Cycle testing of cell #1 began in month 4 of the program, and testing of cell #2 began in month 6.

The tests began by initially forming a deposit on one of the electrodes (working or counter) in a zinc-oxygen cell, in which the anode was a nickel-plated steel sheet evolving oxygen. The initial charge loading ranged from 100 to 150 mAh/cm^2. At the end of charge the cell was taken apart and the oxygen anode was replaced by the other zinc electrode, and cycling was commenced.

The depth of discharge was as high as 100% in the early days of the cycle test program, but was subsequently reduced to approximately 50% or less.

There was a need for periodic recharging of one or both electrodes during cycle testing, since a small but significant corrosion by the electrolyte caused a steady decrease in the electrode capacities. Recharging was performed on an electrode when its capacity had declined, through corrosion, such that 100% depth of discharge was reached. This was accomplished by disassembling the cell, placing the electrode to be recharged opposite the oxygen anode, and charging to the desired loading. Then the zinc-zinc cell was reassembled and cycle testing was resumed. This procedure would be achieved in a zinc-air cell or battery by overcharging it periodically, since it represents a completely reversible loss of capacity.

Cycle Test Results

Two zinc-zinc cycle test systems were employed during the course of this program. The results of cycle testing on each one are presented below.

Cycle test system #1

Table 1 presents a synopsis of the cycle testing conducted on cell #1. This table contains two sets of cycle data. The first is for the number of cycles on the electrodes, which were the same throughout the cycle testing program, which spanned 13 months. The second set counts the number of cycles achieved for a given separator.

The most noteworthy result is the achievement of 510 cycles on the two zinc electrodes, with cycling continuing thereafter. These electrodes demonstrated steady performance cycle to cycle, with no indication of shape change, densification, or any other mode of degradation or failure. This result is a major breakthrough for the alkaline zinc electrode, and validates the LBL concept.

Separator failure from dendrite penetration was common over the first eight months of cycle testing (month 11 of the program). The cycle life for the separators varied, ranging from 26 to 84 cycles. In month 12 it was deduced that the electrodes were being recharged to excess; charge capacities as high as 150 mAh/cm^2 were reached on a regular basis. Thereafter charge capacities were limited on recharge to a range of from 100 to 120 mAh/cm^2 in an effort to avoid dendrite-related failures.

TABLE 1: CYCLE TEST CELL #1 OPERATING LOG
(01/25/89 to 01/29/90)

MCN	ECN	SCN	RECHARGE	CHANGES/COMMENTS
0	0	0		START OF CYCLING: 2 LAYERS 5401
26	26	26	C: 100	
26	26	0		REPLACED SEPARATOR: 2 LAYERS 5401
110	110	84	W: 100	
110	110	0		REPLACED SEPARATOR: 2 LAYERS 5401
135	135	25	C: 100	
135	135	0		REPLACED SEPARATOR: K-703
160	160	25	W: 100	
179	179	44	C: 100	
179	179	0		REPLACED SEPARATOR: K-703
209	209	30	C: 100	
231	231	52	C: 150	
			W: 150	
231	231	0		REPLACED CELLOPHANE LAYERS
233	233	0		REPLACED SEPARATOR: K-703
307	307	74	W: 80	
307	307	0		REMOVED CELLOPHANE LAYERS, ADDED VOLARA FRAME
309	309	0		REPLACED SEPARATOR: 2 LAYERS 3401
344	344	35	C: 110	
356	356	47	C: 110	
397	397	88	W: 110	
418	418	109	W: 120	
440	440	131	C: 60	LIMITED MAXIMUM ELECTRODE CAPACITY TO 120 mAh/cm^2
			W: 50	
465	465	156	W: 90	
489	489	180	W: 120	
510	510	201		END OF TEST PROGRAM: CELL STILL CYCLING

Key:

MCN   = Master Cycle Number (sequential from start of cycle test program)

ECN   = Electrode Cycle Number (number of cycles on the current electrodes)

SCN   = Separator Cycle Number (number of cycles on the current separator)

RECHARGE = Recharged capacity in mAh/cm^2

Corrosion Rate Calculations:

W = 920 mAh/cm^2 / 369 days / 24 hours per day = 0.10 mA/cm^2
C = 830 mAh/cm^2 / 369 days / 24 hours per day = 0.09 mA/cm^2

The data show that limiting charge capacity in this manner has a marked effect; there was no further incidence of separator failure by dendrite penetration subsequent to this (cycle 309). An additional 201 cycles accrued during the four remaining months of the program without further dendrite problems.

An estimate of the corrosion rate of the zinc electrodes by the electrolyte was made from the cumulative ampere-hours of charge required during recharge evolutions on both electrodes. The data and calculations yield a result of 0.1 mA/cm^2. For the design discharge capacity of 100 mAh/cm^2, this corresponds to a C/1000 self-discharge rate. Stated another way, it would take approximately 40 days for the battery to self-discharge completely, which is judged presently to be satisfactorily slow.

During the course of the cycle test program a number of separators were tried for their dendrite penetration resistance. All failed eventually when the charge capacities exceeded 120 mAh/cm^2, however two layers of Celgard® 3401 succeeded when the charge capacities were properly limited.

Cycle test system #2

A second cycle test system was placed into service in month six of the program. Table 2 presents the test results. In this cell a number of separator combinations were tried with poor success in the absence of proper charge capacity limitations. No more than 84 cycles were achieved prior to dendrite shorting. However, Celgard® K-703 successfully resisted dendrite penetration for 131 cycles without penetration under proper charge capacity limitations, and continued to cycle dendrite-free through the end of this program.

Electrode failure was observed after 248 cycles. The failure was related to the cumulative oxidation of the metal foam substrate after the cell was allowed to reach over-discharge for several cycles prior to recharge. It appeared that the repeated over-discharge dissolved the protective dense zinc electroplate, leaving behind a zinc-bare copper surface which oxidized irreversibly, preventing recharge of the electrode. This failure once again points to the importance of protecting the copper foam with a pre-plate, zinc or otherwise, for over-discharge tolerance.

This failure provided an opportunity to test a 10 pore, 6% dense electrode for cycle testing. Other than replacement of the one layer of Celgard® 3401 at the beginning of month 14, cycling since then proceeded successfully.

TABLE 2: CYCLE TEST CELL #2 OPERATING LOG
(03/12/89 to 01/29/90)

MCN	ECN	SCN	RECHARGE	CHANGES/COMMENTS
56	0	0		START CYCLING: 3 LAYERS 5401
78	22	22	W: 80	
86	30	30	W: 120	
137	74	74	C: 100	W FAILED BECAUSE OF EXCESS OVER-DISCHARGE
137	0	74		REPLACED BOTH ELECTRODES
148	11	85	W: 100	
151	0	0		REPLACED SEPARATOR: K-703; REPLACED C
172	21	21	C: 85	
211	60	60	C: 120	
212	61	61	W: 130	
233	82	82	C: 150	
233	82	0	W: 150	REPLACED SEPARATOR: K-703
234	83	0		REPLACED SEPARATOR: K-703
274	123	40	C: 120	
274	123	0		REPLACED SEPARATOR: K-703, ADDED VOLARA FRAME
288	137	54	C: 60	
288	137	0	W: 100	REPLACED SEPARATOR: K-703
289	138	0		REPLACED SEPARATOR: 3 LAYERS 3401
356	205	67		C FAILED FROM OVER-DISCHARGE
358	0	69		REPLACED C
358	0	0		REPLACED SEPARATOR: ONE LAYER 3401
375	17	0		REPLACED SEPARATOR: K-703, PLUS ONE LAYER 3401
408	50	33	C: 120	
440	82	65	C: 60 W: 50	LIMITED MAXIMUM ELECTRODE CAPACITY TO 120 mAh/cm^2
510	152	135	W: 100 C: 55	END OF TEST PROGRAM: CELL STILL CYCLING

Key:

MCN = Master Cycle Number (sequential from start of cycle test program)

ECN = Electrode Cycle Number (number of cycles on the current electrodes)

SCN = Separator Cycle Number (number of cycles on the current separator)

RECHARGE = Recharged capacity in mAh/cm^2.

Corrosion Rate Calculation:

W = 830 mAh/cm^2 / 323 days / 24 hours per day = 0.11 mA/cm^2

C = 870 mAh/cm^2 / 323 days / 24 hours per day = 0.11 mA/cm^2

SECTION 4: MATERIALS QUALIFICATION

The objective of the materials qualification program was to identify and evaluate candidate materials and components for service in a rechargeable zinc-air battery system. The approach was to screen available materials, then to conduct cycle or performance testing on the more promising ones. This section discusses the results of those efforts.

Zinc Electrode Substrate

Based on the work conducted in the capacity maximization and cycle testing tasks, as well as the design considerations from **SECTION 1**, 10 pore copper metal foam, as produced by Foametal Inc., is recommended. Its density should be in the range of from 3 to 6%, but more likely in the higher end of that range, because foams with lower densities are very fragile. Its thickness should be 0.6 cm, based on the selection of the monopolar cell design (see **SECTION 1**).

This material will require a pre-plate with a suitable metal, perhaps zinc, to protect it during over-discharge. Depending on the success in developing a protective pre-plate, there may have to be an operational restriction to limit or prevent the over-discharge of the zinc electrode to avoid the irreversible oxidation experienced in the test program.

Separator

The separator of choice presently is Celgard® K-703, a laminate of Celgard® 3401 (micro-porous polypropylene) and two layers of cellophane, owing to the demonstrated dendrite barrier properties of the cellophane layers. Alternately, two or more layers of Celgard 3401® have shown satisfactory dendrite barrier properties as well. More extensive cycle life testing will be required to elucidate differences in performance between the two.

All other candidate separators, including polyvinyl alcohol papers, ion-exchange membranes, and radiation-grafted micro-porous polypropylenes, were readily penetrated by dendrites in one or two cycles. It appears that the very small pore size of the Celgard® materials is required for a dendrite barrier.

Electrode Frames

The preferred materials for the electrode frames are nylon and glass-filled polypropylene, owing to their chemical stability to the electrolyte, good mechanical strength, and ease of injection molding.

Plumbing and Reservoirs

Polypropylene reservoirs and fittings were used in the experimental program with good success. Further, polypropylene containers, pipe, and fittings are readily available commercially, and polypropylene has fewer additives (potential sources of electrolyte contamination) than does polyvinyl chloride. Therefore, polypropylene is the material of choice for the plumbing and reservoirs.

C-flex® tubing was used in the peristaltic pumps with excellent success. It is a very 'clean' material (it is used in medical applications), is stable in concentrated potassium hydroxide, and has demonstrated excellent wear resistance. It would be the preferred choice for any flexible tubing in the battery system.

SECTION 5: COST STUDY

A cost study was included in this program to constrain the cell design and choice of materials to those which are, or can be, cost effective for electric vehicle application. The primary focus was on the cell stack components, specifically the zinc electrode substrate, separator, electrode frames, and end plates, as well as the electrolyte. The cost of the oxygen electrode was not addressed, since that is still under development and will require substantial improvements in performance and life. Furthermore, a cost study of the balance of system (pump, compressor, plumbing, reservoir, etc.) was not conducted, but an estimate of this from the literature was used instead. The estimated cost for each component addressed is discussed below.

Zinc Electrode Substrate

For this study the manufacturer was requested to provide a cost estimate for a 10 pore (per inch), 6% dense copper metal foam in large volume production. Their estimate was a range of from $0.10 to $0.15 per cubic inch. This converts, for a discharge capacity of 100 mAh/cm^2, an average discharge voltage of 1.1 volts, and a thickness of 0.6 cm, to a cost of from $17 to $26/kWh for the monopolar design.

Separator

The preferred separator, Celgard® K-703, is estimated to cost $1.15 per square foot in large volume production. Using the parameters from above, and realizing that the separator would extend across the entire face of the electrode frame, this converts to a cost of $22/kWh.

This cost could be reduced by up to one-half if the separator only extended across the electrode face. This would, however, require sealing the edges of the separator to the electrode frame, and providing an alternative gasket material between the zinc and oxygen electrode frames, neither of which is considered to be overly difficult.

Electrode Frames

The electrode frames would be injection molded using either nylon or glass-filled polypropylene. The more cost effective choice is glass-filled polypropylene, for which the zinc and oxygen electrode frames are estimated to be $0.32 each, or $6.40/kWh each.

End Plates and Cell Stack Hardware

The end plates would also be molded from either nylon or glass-filled polypropylene, and would have to be thicker (approximately 1.25 cm) for strength and for threaded or welded plumbing sockets. Cell stack hardware would comprise stiffener plates for the plastic end plates, tie rods, nuts, and washers, all these to clamp the stack together tightly. The total cost for these items is estimated to be $4/kWh.

Electrolyte

It is reasonable to expect a zinc ion concentration increase from 20 g/l (at the start of discharge) to 220 g/l (at the end of discharge), a net change of 200 g/l. This sets the electrolyte volume required for the battery. Bulk KOH, sold as a 45% solution in drums or tank cars, sells for approximately $19.50/100 pounds, representing a cost of $3.33/kWh.

Zinc Oxide

Zinc oxide is available commercially in bulk for $1.15/pound. Once again using a concentration change of from 20 to 220 g/l, which represents a 91% utilization of the zinc ions present, the cost is estimated at $3.86/kWh.

Summary

The costs for the above elements are tabulated below:

Item	Low	High
Zinc Electrode Substrate	$17/kWh	$26/kWh
Separator	11	22
Electrode Frames:		
Negative	6	6
Positive	6	6
End Plates and Hardware	4	4
Electrolyte	3	3
Zinc Oxide	4	4
Subtotals	$51/kWh	$71/kWh

Depending upon the cost of the oxygen electrode, the total battery cost, including pumps, plumbing, wiring, and controls, is not expected to exceed $100/kWh. The major opportunity for cost reduction is in the cost of the copper foam zinc electrode substrate. The $0.15 per cubic inch price represents an almost tenfold increase over the materials cost for processing. All other cost components above are, or are derived from, present-day items of commerce at market price.

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