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Zinc/Air Technology December 1993 Meeting Report

Nancy Clark, Kim Kinoshita

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Zinc/Air Technology
December 1993 Meeting Report

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Abstract

A Zinc/Air Battery Review and Strategic Planning Meeting was held in 1993. One outcome of the meeting was recognition of the need for a report on the current status of the technology. This report contains contributions from many of the attendees at the above meeting and expresses their views on where the technology is today and what could/should be done to improve its performance.

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1. INTRODUCTION

A Zinc/Air Battery Review and Strategic Planning Meeting sponsored by Sandia National Laboratories, Lawrence Berkeley Laboratory, and the U.S. Department of Energy (DOE) Office of Propulsion Systems was held on December 1-2, 1993, in Albuquerque, NM. The meeting reviewed the status of the technology, identified major issues, and recommended methods to resolve these issues.

The meeting was attended by representatives from government, industry, and research organizations (see Table 1 for attendance list). On the first day of the meeting, representatives from these groups presented overviews on the status of the different types of zinc/air technologies. On the second day, the whole group met to discuss the status of the technology and to make recommendations for future work.

The major conclusions on the zinc/air technology status can be summarized as follows:

- Zinc/air battery technology research has made significant progress in the last several years; however, substantial progress is needed for zinc/air to become a leading battery technology for the EV market.
- Two zinc/air technologies now exist – mechanically fueled/recharged and electrically recharged.
- Both technologies are in prototype fleet tests as shown in Figures 1 and 2.
- Compared with some similar battery technologies, both zinc/air technologies share the advantages of low cost, environmentally friendly materials, and room-temperature operation.
- The mechanically fueled zinc/air technology has an apparent additional advantage of relatively high specific energy at high power levels. The major disadvantage of this system is that a substantial infrastructure is required to reprocess the spent zinc anode material.
- The mechanically fueled technology could initially penetrate the fleet and specialty vehicle markets where infrastructure limitations would be minimized.
- The electrically recharged zinc/air battery has an advantage compared to the mechanically fueled battery in that it can be recharged the same way as other battery systems. The disadvantage of this system is that it presently has low specific energy at high power levels. However, it can provide medium power bursts

Table 1. Attendee List: Zinc/Air Battery Review and Strategic Planning Meeting

Name	Company	Address	City, State, ZIP	Phone Number
Bayles, Gary	Westinghouse Electric Corporation	1310 Beulah Road	Pittsburgh, PA 15235	412/256-1694
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Figure 1. Electrically Rechargeable Fleet Test at San Diego Gas & Electric with DEMI Battery.

Figure 2. Mechanically Rechargeable Fleet Test by Postdlenst of Germany with Electric Fuel Battery.

(80 to 100 W/kg) and constant power levels (15 to 20 W/kg) at high specific energy (135 Wh/kg).

- Both mechanical and electrical systems have adequate private funding at this time, which suggests to some that the U.S. government should limit funding for this technology to concept testing and progress monitoring. Others feel some government seed money could provide rapid advances in technology.

The summary that follows is divided into three sections:

- Section 2 summarizes the status of the technology as gleaned from the presentations and other available sources.
- Section 3 reports on the results of attendees' comments at the meeting.
- Section 4 presents an analysis of the suitability of zinc/air batteries for use in EVs.

2. STATUS OF ZINC/AIR BATTERY SYSTEMS

This section presents a brief overview of the electrochemical reactions occurring in alkaline zinc/air batteries, the different design concepts for zinc/air cells, and the development of prototypes and demonstration of zinc/air systems.

Principles of Operation

The electrochemical reactions that occur in zinc/air cells with alkaline electrolyte are as follows:

Discharge

Negative electrode: $Zn + 4OH^- \rightarrow Zn(OH)_4{}^{2-} + 2e^-$ (1)

Positive electrode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (2)

The overall cell discharge reaction is represented by the following:

$2Zn + O_2 + 4OH^- + 2H_2O \rightarrow 2Zn(OH)_4{}^{2-}$ (3)

During electrical recharge, the reverse of reaction 3 occurs. The zinc/oxygen cell has a standard potential of 1.651 V, while the nominal open-circuit voltage of alkaline zinc/air cells is about 1.45 V. In principle, the zinc/air cell is negative-electrode-limited because the oxygen consumed at the positive electrode is obtained from air, which is available in unlimited supply for most applications. The practical performance (i.e., specific energy, specific power, cycle life) depends strongly on the structure and design of both the zinc and O_2 electrodes.

Types of Zinc/Air Batteries

Various design concepts for zinc/air batteries have been proposed, with the major differences between the various designs being the cell configuration and the zinc electrode structure. These designs include zinc electrodes with the following structures: 1) planar electrode, 2) unconsolidated powder electrode, and 3) consolidated porous electrode. The electrolyte in these designs may be stagnant but subject to natural convection (generally the case in primary cells), or pumped, as in some designs of rechargeable cells. The planar zinc electrode may be a porous structure such as a compact bed of polymer-bonded Zn/ZnO powder (i.e., a form of paste electrode traditionally used in alkaline Zn/NiOOH cells). The structures of the zinc electrodes in the other two battery designs—2 and 3—are radically different. In one concept for design 2, unconsolidated zinc particles may be deposited during charge onto an inert substrate of small polymeric beads (or on small zinc particles) and circulated as a slurry through the cell. In another concept for design 2, the unconsolidated particles rely on natural convection during discharge to circulate the electrolyte in the cell. Currently, this cell is operated as a primary zinc/air cell that is mechanically recharged by periodic replacement of the spent zinc electrode. In design concept 3, zinc is electrodeposited during charge onto a porous, flow-through reticulated structure (copper foam or carbon), which provides an open, porous structure with high surface area; zinc is subsequently dissolved anodically during discharge. In each of these cell designs, the electrode for O_2 reduction is a porous structure in which an extended interface between the electrolyte and gas phases is established.

There are three main configurations for zinc/air cells, which can be classified as (1) conventional primary cells, (2) mechanically rechargeable cells, and (3) electrically rechargeable cells. Each of these designs is briefly described below.

Conventional Primary Cells

Conventional primary zinc/air cells are available in prismatic and cylindrical (button) designs; both types are available commercially. In a typical design of an alkaline zinc/air button cell, the caustic solution is immobilized by the addition of a thickening agent (e.g., carboxymethyl cellulose) to prevent electrolyte creep and is retained between a polymer-bonded porous carbon for the air electrode and a porous zinc electrode. A fine zinc powder, which may contain mercury to suppress hydrogen evolution, is commonly used in button cells of the type used in hearing aids. Small primary zinc/air button cells, with a capacity of about 6,500 mAh, have a high specific energy of 300 Wh/kg.

Mechanically Rechargeable Cells

In mechanically rechargeable cells, the zinc electrode is physically replaced after its useful life has been exhausted by electrochemical discharge in the cell. This may involve mechanical removal of the used zinc electrode structure and replacement with a fresh zinc electrode. At the same time, the electrolyte may be replaced, if needed. The advantages of this cell design are that (1) recharge of the zinc electrode is decoupled from the cell and (2) a bifunctional air electrode (which is needed in electrically rechargeable cells) is not required. In other words, the zinc can be rejuvenated chemically or electrochemically in other facilities removed from the zinc/air cell.

The structure of the zinc electrode is a key technical issue because various designs are available. For example, the zinc electrode could have a flat-plate planar structure, a polymer-bonded porous structure, or an unconsolidated particulate structure. The use of a particulate zinc powder offers the opportunity of a high surface area for the electrochemical reaction and hence the possibility of high-rate discharge, if the air electrode is capable of sustaining high current densities. Depending on the physical structure of the zinc electrode, different techniques can be used to replace the electrode material.

One approach uses forced convection to retain reaction products within a storage tank within the battery as a pumpable fluid. This fluid is removed from the battery by pumping, and fresh particles of zinc are returned to the battery by entrainment within a high-velocity stream of regenerated electrolyte. The high-velocity stream does not actually contact the cell, but fills a series of hoppers positioned above each cell with zinc particles. During discharge, the hoppers slowly feed into the galvanic cell.

Another approach is to package the zinc electrode as a removable cassette. Refueling is done by removing the spent cassette and replacing it with a fresh one. The mechanically rechargeable cell has the disadvantage that the spent zinc electrode must be physically removed and replaced with a fresh electrode together with lost electrolyte. If rapid replacement were feasible (and the infrastructure for doing this were available), the mechanically rechargeable battery would have an advantage over the electrically rechargeable battery, which will likely require overnight charging. This maintenance could be done rapidly, in principle, if provisions for quick replacement are designed in the battery stack. Cassette replacement has been demonstrated in prototype systems in Europe. In the U.S., the hopper system has been demonstrated on the cell level. Another issue is how other battery components will survive the wear and tear of recharging.

Electrically Rechargeable Cells

The electrically rechargeable zinc/air cell avoids some of the complications associated with zinc handling in mechanically rechargeable cells. In this concept, zinc is redeposited on the negative electrode during charge to restore the zinc electrode. Depending on the cell design, O_2 reduction (discharge) and O_2 evolution (charge) can occur at the positive (air) electrode, the so-called bifunctional air electrode. An alternate design is to incorporate two positive electrodes to separate the reactions of O_2 reduction during discharge and O_2 generation during charge (this electrode is commonly referred to as the third electrode), which are electrically isolated from each other. This design requires a more complex arrangement of electrical circuitry to connect the electrodes for O_2 reduction and generation, as well as additional cost, weight, and volume.

Various designs of electrically rechargeable zinc/air systems have been conceived. One design is similar to the conventional primary cell; that is, a bifunctional air electrode would be used instead of the monofunctional electrode to permit recharge. The negative electrode could be a porous zinc structure that undergoes dissolution and deposition during discharge and charge, respectively. In one version, the electrolyte is retained within the cell container and remains stagnant. Another design considers a circulating electrolyte that flows through the porous zinc structure. By utilizing a forced-convection system and deposition of zinc in a porous structure, the problems associated with "shape change" and zinc dendrites that are commonly encountered with electrochemical deposition/dissolution of zinc in rechargeable alkaline zinc systems are minimized, and improved cycle life is obtained.

Electrically rechargeable batteries could be easily adapted to the existing electrical network without modification, which is a major advantage over mechanical recharge. Unfortunately, the positive (air) electrode has a very limited life when used as a bifunctional electrode. The third-electrode concept for electrically rechargeable zinc/air systems may be a possibility, but the added complexity, increased battery size, and additional cost are issues that have to be considered.

Status of Zinc/Air Technology

Historical Perspective

Mechanically rechargeable zinc/air cells were assembled by Lessons Moos Laboratories into batteries consisting of 22 series-connected cells (25-Ah capacity), which produced 24 V and a specific energy of 172 Wh/kg (to a 22-V cutoff at a discharge current of 2 A). Large batteries of 200-Ah capacity that utilized a nickel catalyst in the air electrodes were successfully tested by Sanyo Electric Company in Japan. General Motors Corporation (GM) built and tested a 1-kWh battery (noncirculating electrolyte) that was mechanically rechargeable and consisted of 20 bicells (two 465-cm^2 air cathodes connected in parallel and a central zinc anode in each cell). A specific power of 31-57 W/kg and a specific energy of 66 Wh/kg were achieved with 35% KOH at ambient temperature.

The experiments at GM were followed by a test of a 35-kWh zinc/air battery that was also mechanically rechargeable. The battery design was similar to that of the earlier version except the electrodes were smaller (315 cm^2). The 35-kWh battery consisted of six 49-cell modules, with two series-connected strings of three modules that were connected in parallel. Battery tests at 70-80°C indicated that the performance ranged from about 121 Wh/kg at 22 W/kg to 73 Wh/kg at 73 W/kg. It was concluded from these tests that a mechanically rechargeable system was impractical for high-power vehicle applications because of the excessive time required for changing monolithic anodes and electrolyte.

Sony Corporation investigated the concept of a mechanically rechargeable zinc/air battery with circulating electrolyte containing a zinc slurry. In their system design, regeneration of the zinc slurry is performed outside the battery in a separate electrolysis cell. A 3-kW battery (100 V at 30 A) was tested in a vehicle. The complexity of this zinc/air battery system and its low power density resulted in the termination of the project.

Compagnie Generale d'Electricité (CGE) in France also pursued development of a rechargeable zinc/air battery system that employed separate electrodes for charge and discharge, thereby avoiding the stability problems of the air electrodes. Their design employed a cylindrical geometry with the air electrode on the outside of a tubular cell and a zinc slurry/KOH solution circulated through the inside of the cell. The air electrodes PTFE-bonded active carbon on a mild steel screen, with no additional electrocatalyst present for O_2 reduction. The discharge products from the cell were fed into a separate electrolysis unit where zinc dendrites were deposited and formed a slurry for use in the discharge cell. In this system, the O_2-evolution electrode consisted of different materials and different construction from the air-reduction electrodes utilized in zinc/air batteries. The zinc/air battery system developed by CGE was projected to be capable of 110 Wh/kg and 80 W/kg. The energy efficiency of the system was comparatively low (about 40%), which is a major drawback of this type of secondary zinc/air battery system.

Zinc/air cells that incorporate a third electrode for use during charge were tested by the Yuasa Battery Company, Japan. In their cell design, the zinc electrode was positioned between the air electrode for O_2 reduction and the electrode for O_2 evolution (0.1-mm nickel plate), the so-called third electrode. During charge, when the third electrode was used to evolve O_2, the air-reduction electrode remained electrically isolated. The electrolyte containing zincate ions was circulated in the 10-mm gap between the air electrode and the porous substrate (silver or nickel) for zinc deposition, and a zincate-free electrolyte was circulated in the 10-mm gap between the third electrode and the zinc electrode. When the cell was charged, zinc deposition occurred preferentially on the side of the porous substrate facing the air-reduction electrode. During discharge, the third electrode was electrically disconnected from the cell, and normal electrochemical reactions occurred at the zinc and air-reduction electrodes. This design configuration avoided subjecting the air-reduction electrode to high anodic potentials that could be detrimental during charge. Zinc-electrode discharge capacities of 300 to 400 mAh/cm^2 were obtained upon repeated charge/discharge cycling with this cell.

Recent Research and Development Activities on Zinc/Air Systems

A summary of more recent activities, starting in the 1980s, is presented, and the status of the technology and demonstration activities is summarized in Tables 2 and 3, respectively. The information was obtained from the patents and published literature.

Table 2. Summary of Zinc/Air Technology Status as of December 1993

Organization	Zinc/Air Concept	Status of Technology
AER	Electrically recharged	• 130 Wh/kg at C/20 rate, 20 cycles (400-hr total operating life).
DEMI	Electrically recharged	• MOD 9 battery: 150 Wh/kg at C/10 rate, 227 cycles at 10 W/kg.
Electric Fuel	Mechanically refueled	• Laboratory-scale battery (85 kg) yielded 178 Wh/kg at 71 W/kg. Prototype 110-kWh battery demonstrated in 3.5-ton van.
LBL/UCB	Mechanically refueled	• Tested 77-cm^2 single cells, 100 Wh/kg (limited by test discharge cycle) at 290 W/kg; projected 174 Wh/kg at 57 W/kg. • Demonstrated hydraulic refueling of zinc particles.
LBL/UCB	Electrically recharged	• Demonstrated electrical recharge in spouted bed zinc/air cell; charge and discharge at 83 mA/cm^2 with 45 wt% KOH electrolyte containing 64.3 g/ℓ dissolved zinc.
LLNL	Mechanically refueled	• Tested 600-cm^2 cells; 0.9 V at 116 mA/cm^2, 70°C.
MATSI	Recyclable primary and electrically recharged	• Fabricated and tested 70-cm^2 primary cells; achieved 50 mA/cm^2 at 1.16 V, 25°C. • Demonstrated over 600 charge/discharge cycles for zinc electrode in flowing electrolyte cell.
Westinghouse	Electrically recharged	• Demonstrated over 180 charge/discharge cycles on bifunctional air electrode in full EV-size cells. • Achieved 70 W/(kg system) at 30% depth of discharge (DOD) and cell cutoff voltage of 0.65 V. • Obtained about 70 Wh/(kg system) with pulse power (40 W/kg) to cell cutoff voltage of about 0.8 V/cell.

Table 3. Summary of Zinc/Air Battery Demonstrations as of December 1993

Organization	Technology Demonstrations
AER	• Developed batteries for portable applications (operating life 400 hr): - 2.7 kg, 88 Wh/kg, 11-14 V operating voltage, - 0.8 kg, 130 Wh/kg, 4.75-6 V operating voltage.
DEMI	• Demonstrated zinc/air-lead/acid (or Cd/NiOOH) hybrid system in compact car (Honda) and van (Chrysler); 135 Wh/kg zinc/air battery.
Electric Fuel	• Demonstrated cold-start operation after storage at -20°C. • Developed patented monofunctional air electrode and high utilization zinc electrode of compacted porous zinc. • Tested mini Jeep (630 kg without 85-kg batteries): - 165 Wh/kg with peak of 140 W/kg (controller limited), - SFUDS-type cycle yielded 191 Wh/kg (nominal) and 165 Wh/kg (high-power test cycle). • Demonstrated in van a 310-V battery (650-kg); 420-km range at constant 60 km/h, 300 km with postal cycle. • Demonstrated in a Mercedes postal van (3500 kg) for 1-1/2 years.
LBL/UCB/SRI	• Developed design concept for hybrid battery system for Chrysler TEVan utilizing mechanically refueled zinc/air battery. • Projection - 50-kWh battery with 178 Wh/kg (156 Wh/ℓ) and 107 W/kg (94 W/ℓ).
LLNL	• Designed 12-cell bipolar stack (12 V at 100 A, 440 Ah) for demonstration in hybrid battery system (lead/acid, 120 V at 50-75 A, <200 Ah) that is on-board electric bus.
MATSI	• Fabricated and tested 5-cell batteries; demonstrated 360 Wh/kg at C/29 rate (70-cm^2 cell) and 464 Wh/kg at C/100 rate (300-cm^2 cell) in flat, prismatic design, 25°C. • Obtained more than 350 electrical charge/discharge cycles in laboratory-scale cell with flowing electrolyte in porous zinc electrode.
Westinghouse	• Developed technology to fabricate 400-cm^2 air electrodes by machine. • Developed low-cost pasted zinc electrode.

AER Energy Resources, Inc. (AER)

The main focus of the AER effort is to develop electrically rechargeable zinc/air batteries for portable electronic products such as computers, printers, and cellular telephones. Technology for the air electrodes was originally obtained under a licensing agreement with DEMI (see below) and more recently with Westinghouse Electric Corp. Small batteries (<0.8 kg, 5 cells, 5 V) will soon be available for portable computers. Based on a total operating life of about 400 hr, the present cycle life is about 50 cycles for an 8-hr discharge in portable computers. A 12-V battery for extended operation to 20 hr for portable electronics is being evaluated. This technology does not utilize forced convection (i.e., pumps) of the electrolyte through the battery stack. For the proposed application for this zinc/air battery, electrolyte management involving the addition of water is not needed.

Dreisbach ElectroMotive, Inc. (DEMI)

The electrically rechargeable zinc/air cells contain a bifunctional air electrode, gelled electrolyte, and an anode of zinc metal powder. The negative electrode consists of zinc powder and a current-collector screen, with the complete structure wrapped with one or more layers of an absorbent paper to allow wicking of electrolyte from the bottom of the anode to the region between the anode and the separator. The bottom of the cell case is compliant and concave upwards to allow for expansion of the anode during discharge. An increase of 20-25% in the anode volume occurs because of an increase in the amount of solid material when zinc is converted to ZnO and the lower density of the discharged product (i.e., 5.6 g/cm^3 for ZnO, 7.2 g/cm^3 for zinc). The cell case contains holes to permit O_2 ingress during discharge. The composition of the air electrode has not been disclosed by DEMI, but it is likely to be a PTFE-bonded, porous carbon structure. The Model 5A cell has the following parameters and performance:

Cell dimensions	30.5 cm × 55.9 cm × 1.5 cm
Cell weight	2.5 kg
Cell volume	2.6 ℓ
Electrode area (est.)	1500 cm^2
Rated capacity	400 Ah @ 1 A
Pulse current	80 A
Maximum charge current	20 A

Analysis of the performance of DEMI's mature zinc/air system indicates that the rated specific energy ranges from 100-216 Wh/kg, the rated capacity from 290-400 Ah, the average cell voltage from 0.86-1.4 V, and the charge and discharge times from 2.9-400 hr. A hybrid system consisting of the Model 5 (135 Wh/kg) and 4-kWh Cd/NiOOH battery in a van had a range of 251 miles. The life of the air electrodes was about 60 charge/discharge cycles.

A more recent version of DEMI's zinc/air cell, Model 9, was tested in an EV. The following results were reported: 150 cycles at low rate (C/10-C/20), 150 W/kg peak power, and 150 Wh/kg at low-rate discharge. More recently, the following results were obtained: 115 cycles at 20 W/kg with 100 Wh/kg delivered, and 227 cycles at 10 W/kg. The goal is to achieve 400 cycles and 150 Wh/kg to yield a vehicle range of 250+ miles.

The DEMI technology does not utilize forced convection of the electrolyte through the battery stack. Achieving longer cycle life will require some provision to replenish water in the electrolyte periodically, which is lost by net evaporation (net loss from evaporation and absorption of water from the air environment), electrochemical reaction, or leakage.

Electric Fuel Limited

This program evolved from the technology originally considered by Luz International (Los Angeles, CA) in the late 1980s to develop a low-cost battery. A slurry zinc electrode is used in a battery that is mechanically rechargeable. In this concept, the spent zinc electrode, which is inside a cassette in the battery, is replaced with a fresh cassette after it is discharged. The spent cassettes are electrochemically regenerated at a centralized facility. Battery performance of approximately 225 Wh/kg at a continuous discharge (40 W/kg) has been obtained. Two 32-cell modules with nominal capacity of 216 Ah and 75 V was discharged for 5 hr with 80% zinc utilization. Other tests of the battery technology (64 cells, 16 kWh) have been conducted in a mini Jeep. Currently, their technology has been scaled up (440 cells, 110 kWh) and demonstrated in a Mercedes postal van in Germany from June 1993 to January 1994. Mechanical recharge was done by a semi-automated prototype facility.

Lawrence Livermore National Laboratory (LLNL)

LLNL has been conducting research and development (R&D) on refuelable zinc/air batteries since 1992 and is currently conducting tests on a 12-cell engineering module under the auspices of the Department of Transportation through CALSTART. Four generations of cells have been built and tested, representing anode areas of 80, 250, 600, and 1000 cm^2. All are configured for use with zinc particles of sizes greater than 0.5 mm—

e.g., possessing a specific surface area that is sufficiently small to minimize corrosion losses. Using a proprietary current collection technique, peak power densities of 5.5 kW/m^2 have been obtained (50% DOD); coulomb efficiencies of ~99% have been demonstrated in runs lasting 16 hr in 600-cm^2 cells.

The basis of the battery is a thin-gap, wedge-shaped cell that maintains an artificially expanded bed of ~40% solid volume by particle bridging and void formation. The particle bridges and voids persist even under vibrations that normally compact powders. Measured hydraulic power dissipation of the bed is negligible: <0.1% of the gross power output. The bed is continuously replenished with particles by gravity feed from the overlying hopper. Shunt power losses total less than 0.6% of the power output.

Currently, LLNL is testing fourth-generation bipolar cells with 250-cm^2 anodes. These were developed for stacking into a 6.1-kWh 12-cell module. After laboratory tests, LLNL is under contract to test the module on a moving bus (Santa Barbara Municipal Transit Authority) in September. The stack occupies a volume of 28 liters and weighs (filled) 43 kg.

Lawrence Berkeley Laboratory (LBL)/University of California at Berkeley (UCB)

The DOE-sponsored program was initiated at LBL/UCB in the 1980s and involved research and development on various designs of zinc/air technologies, both electrically and mechanically recharged. An electrically rechargeable zinc/air cell that incorporates a porous, flow-through reticulated electrode (for zinc deposition and zinc dissolution) and a bifunctional air electrode was developed which, in principle, eliminates many of the complexities associated with rechargeable cells that require a third electrode or those systems with a separate electrolysis unit for zinc recovery. The reticulated electrode consists of a copper foam as the substrate for the zinc deposits. The copper foam has the following typical properties: 3-6% of theoretical density, 4-6 pores/cm, 0.2-cm average pore diameter, 0.4-cm filament diameter, and 10-100 cm^2/cm^3.

An alternative zinc/air cell design has been developed that utilizes zinc particles in the negative electrode. The most recent concept for a zinc/air cell consists of a stationary bed of zinc particles (600-mm particles, bed thickness of 5 to 6 mm) separated from an air electrode (77 cm^2) by a microporous diaphragm. Channels permit natural convective flow of the electrolyte, which arises from density gradients produced during anodic dissolution of the zinc particles. The feasibility of mechanical (hydraulic) recharge of the zinc particles was demonstrated. Another variation of zinc/air cell with natural convection of the electrolyte was demonstrated that consists of a porous foam structure and a bifunctional air electrode. A cell design (spouted-bed cell), which contains zinc particles circulated in the negative electrode compartment by forced convection of electrolyte, is also being evaluated. This cell can be electrically recharged.

MATSI

The LBL technology that utilizes the flow-through porous structure for the zinc electrode was further evaluated by MATSI. They verified that zinc can be cathodically deposited (charge) and anodically dissolved (discharge) from a reticulated substrate for over 800 cycles in a laboratory cell containing dissolved zinc in an alkaline electrolyte that is mechanically pumped. The current efficiencies for charge/discharge are essentially 100%.

More recently, MATSI has concentrated on developing primary zinc/air cells with high specific energy for application in portable electronic components (33 Ah, 0.9 kg) and EVs. An effort is under way with GNB to demonstrate a hybrid vehicle (Mercury Gran Marquis) using a lead/acid battery (830 W/kg) and primary zinc/air battery (440 Wh/kg, 80 kWh). The objective of the demonstration is to show performance of 0-60 mph in 10 sec, 300-mi range at 55 mph in a vehicle with a curb weight of 4000 lb. It is proposed that the discharged battery be replaced with a fresh battery at a facility that can handle the removal and replacement of zinc/air batteries. The used battery will be transported to a reprocessing plant where the zinc is electrochemically regenerated and returned to the zinc/air battery.

Westinghouse Electric Corporation (WEC)

A program was initiated at WEC in 1992 to advance the technology necessary to develop an electrically rechargeable zinc/air battery for EV applications. The pilot-scale production of EV-size bifunctional air electrodes was demonstrated. Preliminary Design, Prototype Engineering, and Initial Battery Cost Analysis reports were issued. It was concluded that the specific energy of the electrically rechargeable zinc/air system was too low (<100 Wh/kg) for consideration as a viable long-term USABC battery. Other problems remaining to be solved are zinc electrode shape change and carbon corrosion of the air electrode.

Status of Zinc/Air Component R&D

The DOE has supported R&D to develop improved cell components for zinc/air battery technologies. A brief summary of the organizations, cell components and status of this effort is included in Table 4. Much of the R&D on cell components, particularly the R&D

Table 4. Zinc/Air Battery Component R&D

Organization	Component	R&D Status/Objective
Alupower, Inc.	Air electrode	• Developing continuous process for low-cost manufacturing of air electrodes.
Case Western Reserve University	Air electrode	• Completed an extensive R&D program on oxygen electrocatalysis for monofunctional and bifunctional air electrodes.
Eltech Research Corp.	Air electrode	• Developing improved electrocatalysts and supports for bifunctional air electrodes.
E-TEK, Inc.	Air electrode	• Developed gas-diffusion electrodes for monofunctional air electrodes.
Giner, Inc.	Air electrode	• Identified high-performance, high-cost electrocatalyst ($Na_xPt_3O_4$) for bifunctional air electrodes. • Identified promising electrocatalyst support ($LiNiO_x$ and ZrN) for bifunctional air electrodes.
LBL	Air electrode	• Identified electrocatalyst and carbon support for bifunctional air electrodes.
LBL/UCB	Zinc electrode	• Demonstrated reticulated foam structures for electrically rechargeable zinc electrodes. • Demonstrated particulate zinc for zinc/air cells and hydraulic refueling of zinc particles in laboratory cell.
MATSI	Air electrode	• Develop novel oxygen electrodes. • Demonstrate low-cost manufacturing processing.
	Zinc electrode	• Demonstrated recharge of reticulated foam structures for zinc electrodes.
SNL	Air electrode	• Evaluated cobalt-based macrocycles for oxygen electrocatalysts.
Westinghouse	Air electrode	• Developing electrode structures for long-life bifunctional air electrodes.

at industrial organizations, is proprietary; consequently, Table 4 only summarizes published information.

A major emphasis of the R&D programs has been to identify practical electrocatalysts for oxygen reduction and evolution. Replacement of the costly noble metals by metallorganic macrocycles and transition metal oxides for oxygen electrocatalysis has received the most attention. Case Western Reserve University (CWRU) has completed an extensive study of various electrocatalysts for monofunctional and bifunctional air electrodes. Heat-treated transition metal macrocycles such as cobalt tetramethoxyphenyl porphyrin (CoTMPP) dispersed on high-surface-area carbon have high activity for O_2 reduction in alkaline and acid electrolytes, as well as good stability in concentrated alkaline solutions. The stoichiometric lead ruthenate pyrochlore, $Pb_2Ru_2O_{7-y}$, showed good activity at CWRU for O_2 reduction and generation in concentrated alkaline solutions. The pyrochlore metal oxide showed a higher activity for O_2 reduction than the perovskite metal oxide, $SrFe_xRu_{1-x}O_{3-y}$, which also contains ruthenium.

Eltech Research Corp. investigated the viability of graphitized carbon blacks and metal oxides as electrocatalyst supports in bifunctional air electrodes for electrically rechargeable zinc/air cells. In their studies, graphitized carbon blacks of both Monarch 120 and Shawinigan acetylene black appeared to be suitable electrocatalyst supports. Electrochemical tests of $NiCo_2O_4$/Monarch 120 in small cells achieved over 350 cycles (discharge 4 hr at 10 mA/cm^2, charge 8 hr at 5 mA/cm^2) at MATSI. In other tests, Eltech has observed that the addition of Nafion to the electrode structure is beneficial for O_2; discharge at 450 mA/cm^2 in 5 M KOH at 60°C was sustained for about 6,000 cycles (3-hr discharge, 3-hr open circuit).

Alupower, E-TEK, and MATSI are developing technologies to fabricate air electrodes. Alupower has developed a continuous-web process to form air electrodes consisting of a four-ply laminate of two reactive layers, a current collector, and a microporous hydrophobic film. This process is reported to be well suited for mass production of air electrodes. E-TEK has developed gas-diffusion electrodes that are useful in monofunctional air electrodes. The goal of the MATSI program is to demonstrate a low-cost manufacturing process.

Giner, Inc., is developing bifunctional air electrodes for rechargeable alkaline fuel cells in a National Aeronautics and Space Administration (NASA) program. This technology is relevant to electrically rechargeable zinc/air cells. Tests indicate that $Na_xPt_3O_4$ is a highly promising electrocatalyst, and $LiNiO_2$ and ZrN appear to be attractive electrocatalyst supports for bifunctional air electrodes. A major drawback of the electrocatalyst is the projected high cost for transportation applications.

Research at LBL indicates that $Bi_2Ru_2O_7$ is a promising electrocatalyst for bifunctional air electrodes. The attractive features of this material are that it (1) can be made in high-area form, (2) has metallic conductivity, and (3) has reasonable stability in acid and alkaline electrolytes. On the other hand, its cost may be problematic.

SNL is evaluating cobalt macrocylic complexes in air electrodes. Corrosion of the electrocatalyst support is a major problem, particularly with carbon supports such as Black Pearls 2000, which has a high surface area of about 2000 m^2/g.

3. DISCUSSION OF STATUS BY MEETING ATTENDEES

This chapter is a compilation of comments that were made during the group discussions at the planning meeting concerning the status of zinc/air battery technology. The discussion began with summary comments regarding reported energy densities. The mechanical systems were reported to be in the range of 133-200 Wh/kg, and the electrical systems were reported in the range of 60-150 Wh/kg. Realizing that energy density is only one significant factor in analyzing the technology, the group proceeded to discuss a comparison of the electrical and mechanical systems.

One of the key tradeoffs is specific power vs. specific energy vs. life. Some considerations are:

- Electrically rechargeable systems have a limited amount of zinc, which limits both power and energy.
- Mechanical systems are not zinc limited, which allows power and energy to be decoupled.
- Best reported power-to-energy (P/E) ratio for both systems is one that is not high enough for most EV applications. This suggests that if an efficient power "supply" like a double-layer capacitor (DLC) or flywheel existed, a hybrid system would be desirable.
- The lower the current densities, the longer the life of the air electrode in both systems.
- Energy efficiency may be limited in both systems to 50-70%.

The major technical issues with zinc/air batteries were summarized.

Mechanical system:

- Stability of components because of mechanical replacement of zinc on a regular basis,
- Potential shunt currents that can limit the system life, and
- Need to reprocess the electrolyte and zinc in an energy- and cost-effective way.

Electrical system:

- Limited life of bifunctional air electrode and
- Lack of catalysts that are equally good in charge and discharge.

The cost of energy for recharge or reprocessing was discussed. The mechanical system can reprocess zinc when electricity is cheap but requires an infrastructure unique to a single electrochemical system. Electrical systems are likely to be more expensive to recharge, but utilities may, as has Southern California Edison, institute a dual rate structure and meters to consumers that own EVs, which gives electrical systems the same recharge rate.

The attendees of the meeting provided the following observations and recommendations addressing the above issues:

1. A key to success of zinc/air batteries is the air electrode.
    - Monofunctional air electrodes cannot take energy from regenerative braking. (Is there a way this could be done such as by using a third electrode?)
    - Bifunctional electrodes are subject to carbon corrosion (the products of this react with OH- to lower its concentration). Possible solutions are lower oxygen overvoltage on charge, use of a noncarbon system, use of a composite electrode and/or development of more corrosion-resistant carbon, and use of a third electrode for oxygen generation, thereby requiring a monofunctional air electrode.
2. Expanded research on an electrically rechargeable zinc system is also needed.
    - R&D to identify limiting features in zinc performance (DOD limits, capacity limits, and cycle life).
    - Collaboration with zinc industry to identify best alloys for use.
3. System improvements are needed.
    - Consider zinc/oxygen.
    - Consider a flowing electrolyte, especially in applications in which high current densities are required.
    - Use electronic control to provide charge balance to prevent zinc electrode reversal, etc.
    - Use failure modes and effects analysis to drive potential improvements.
4. Components issues should be considered.
    - Lower-cost separators.
    - Lower-cost/better air electrode catalyst.
    - CO_2 removal and watering system.

5. Quantitative understanding of *real* infrastructure costs for both mechanically and electrically recharged systems should be provided (to be realistic, perhaps life-cycle costs should be calculated).

6. A team effort, one involving industry, the government, academia, and the national laboratories, would be the best approach to solving technical problems.

7. If speed to marketplace is a real issue, private funding may provide more flexibility (e.g., DEMI and Electric Fuel, Ltd., have ~$40 million in private funding each).

8. It appears that industry is *not* communicating well the benefits/costs of technology — without this information there will be no real consumer interest (examples of benefits include low potential cost and inherent safety).

9. Recycling issues need to be worked out with the zinc industry as that user-friendly, low-cost technologies can be developed.

10. Fleet applications appear to be the *best* first application, especially for mechanically rechargeable systems.

11. Test system in *real* use conditions:
    - This would require prototyping several types of systems.
    - Government could buy zinc/air batteries as part of the Energy Implementation Act.
    - If government did buy parts, all could be evaluated to some test regime so that comparisons are made between options under the same conditions.
    - Another possible test is in real vehicles by real users.

12. Zinc/air is an old technology that, without major breakthroughs, may not have the credibility to continue receiving government funding. However, investor interest suggests that progress has been significant towards commercialization.

13. Most feel that the U.S. should have a zinc/air program, given the potential of the zinc/air system.

Summary of Most Important Activities to be Pursued

1. Development of an improved air electrode to meet a battery goal of 200 Wh/kg with long (~1000 cycles) life. The peak power requirement of 400 W/kg should be sacrificed for cycle life, if necessary.

2. For electrically rechargeable systems, develop improved zinc electrodes with high utilization and long life. For mechanical systems, demonstrate that regeneration of zinc and electrolyte and electrode replacement can be done cost-effectively. (This would include a study to determine electrolyte life and limits.)
3. Develop total cost models for mechanically and electrically rechargeable systems as well as hybrid systems.
4. Develop a realistic and reliable funding stream to take current concepts to reality, and/or, for more mature systems, demonstrate their feasibility.
5. Develop cost-effective separators.

Other Summary Comments

1. Mechanically rechargeable systems are really fuel cells and compare well with the current proposals for fuel cells.
2. An assessment of the state of art needs to be compiled and compared to USABC requirements.
3. The two leading developers (DEMI and Electric Fuel) have received financial commitments from private sources.
4. A hybrid system (zinc/air plus power source) may be the best approach where high power is needed.

4. ZINC/AIR TECHNOLOGY ASSESSMENT

USABC has established mid-term and long-term criteria to provide a basis for evaluating various advanced battery technologies for EV applications. The mid-term criteria are applied to the more mature advanced battery technologies where process capability can be demonstrated to validate high-volume manufacturing capability. The long-term criteria are more aggressive and intended to apply to less mature battery technologies having potential to significantly improve EV performance and range at a lower cost.

Every electrochemical couple when compared to these criteria has its strengths and weaknesses. Zinc/air is no exception. Generally speaking, zinc/air's potential strengths are its high specific energy and low cost. It offers ambient operating temperature, it can be safe and environmentally benign, and it is rechargeable.

Potential weaknesses include the following: low specific power, medium energy density, low to medium power density, low cycle life, low energy efficiency, high maintenance, and fragile packaging.

The inability to meet all the USABC criteria does not necessarily mean that the technology is unsuitable for EVs. Numerous trade-offs may compensate for weaknesses *or* the technology may be suitable for certain niche applications. The intent of USABC criteria is to provide a *balanced* set of criteria that can be used to evaluate the *overall* capabilities of any EV battery technology under consideration. With this in mind, the following is an analysis of demonstrated zinc/air capabilities relative to the USABC long-term criteria. The analysis is based on data in this report with some necessary assumptions to approximate the general capabilities of zinc/air technology as related to EVs.

Performance Analysis

A strong relationship exists between specific energy and specific power (continuous-rate) for zinc/air, as illustrated by the Ragone plots in Figure 3. These plots are primarily based on data for the Electric Fuel and DEMI zinc/air vehicle battery systems, which most likely represent the state of the art for mechanically and electrically recharged zinc/air EV batteries, respectively. Data from other zinc/air programs scaled to EV battery levels are also included and generally agree with the data for vehicle battery systems.

The advantage of high specific energy offered by zinc/air batteries is quickly eroded when power is required from the battery because of electrode polarization during discharge and the decrease in cell voltage. The decrease in cell voltage is attributed to (1) polarization

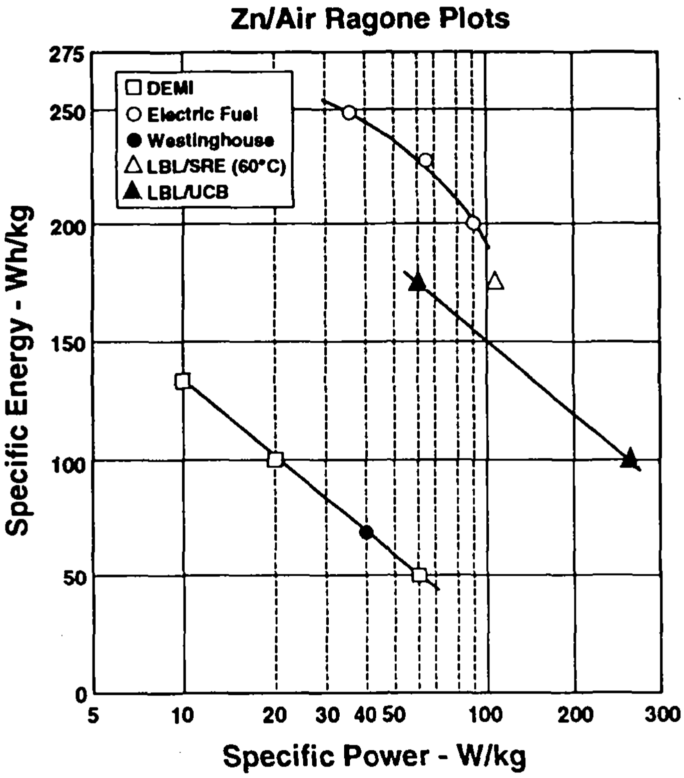

Figure 3. Zinc/Air Ragone Plots Generated from Data Presented at Zinc/Air Meeting.

of the zinc electrode, from reduction of the conductivity of the electrolyte and (2) polarization of the air electrode. The amount of voltage reduction increases as current density and depth of discharge (DOD) increase.

Very little information is available on the specific power capabilities of zinc/air battery systems. USABC defines peak power as the power available at 80% DOD for a period of 30 seconds at a voltage of two-thirds of the open circuit voltage. This differs from the Ragone information in that it is a measure of pulse power rather than of the continuous power capability of the battery. It establishes the power available from the battery system for vehicle acceleration. DEMI reported a specific peak power capability for its most recent cell as 150 W/kg. The conditions that DEMI used to measure specific power are not known. This cell was also reported to have a specific energy of 150 Wh/kg at a low rate of discharge (C/10-C/20).

The Ragone plots in Figure 3 also suggest that the mechanically rechargeable systems have significantly higher specific energy capability than the electrically rechargeable systems. For a given power level, the mechanically recharged system's specific energy is on the order of 3 to 4 times higher than that for the electrically recharged systems. Possible reasons for this difference include the less efficient bifunctional air electrode as well as zinc utilization.

The available weight and volume data also suggest that the density of the zinc/air battery is on the order of 1 kg/ℓ. These and other available data compare the performance of the zinc/air technology and benchmark it against the USABC long-term criteria, as illustrated in Table 5.

Table 5. Zinc/Air vs. Performance Selected USABC Long-Term Primary Goals

Parameter	USABC Long-Term		Zinc/Air Technology Mechanical	Zinc/Air Technology Electrical
Specific Energy	200 Wh/kg	(C/3)	200 Wh/kg	87 Wh/kg
Specific Power	400 W/kg	(pulse)	90 Wh/kg	150 W/kg*
Energy Density	300 Wh/ℓ	(C/3)	225 Wh/ℓ	87 Wh/ℓ
Power Density	600 W/ℓ	(pulse)	124 W/ℓ	150 W/ℓ *
P/E Ratio	2:1		0.55	1.7

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* DEMI data assuming defined conditions for specific power were used.

It was suggested that the rationale for using the USABC goal of the C/3 rate for specific energy may not be appropriate for those zinc/air batteries with an energy density greater than 150 Wh/kg. This situation results because of the sizable reduction in the zinc/air specific energy values as a function of power. The C/3 value was selected as a baseline to provide a standard by which to compare various battery technologies on an equal basis. For most battery technologies, this would be adequate because a specific energy is not very sensitive to lower discharge rates. As illustrated in Figure 4, in the case of zinc/air, this is not true and, therefore, other C/x rates should be considered in its evaluation.

Table 6 was presented as an example of the use of a lower discharge rate for the specific energy determination.

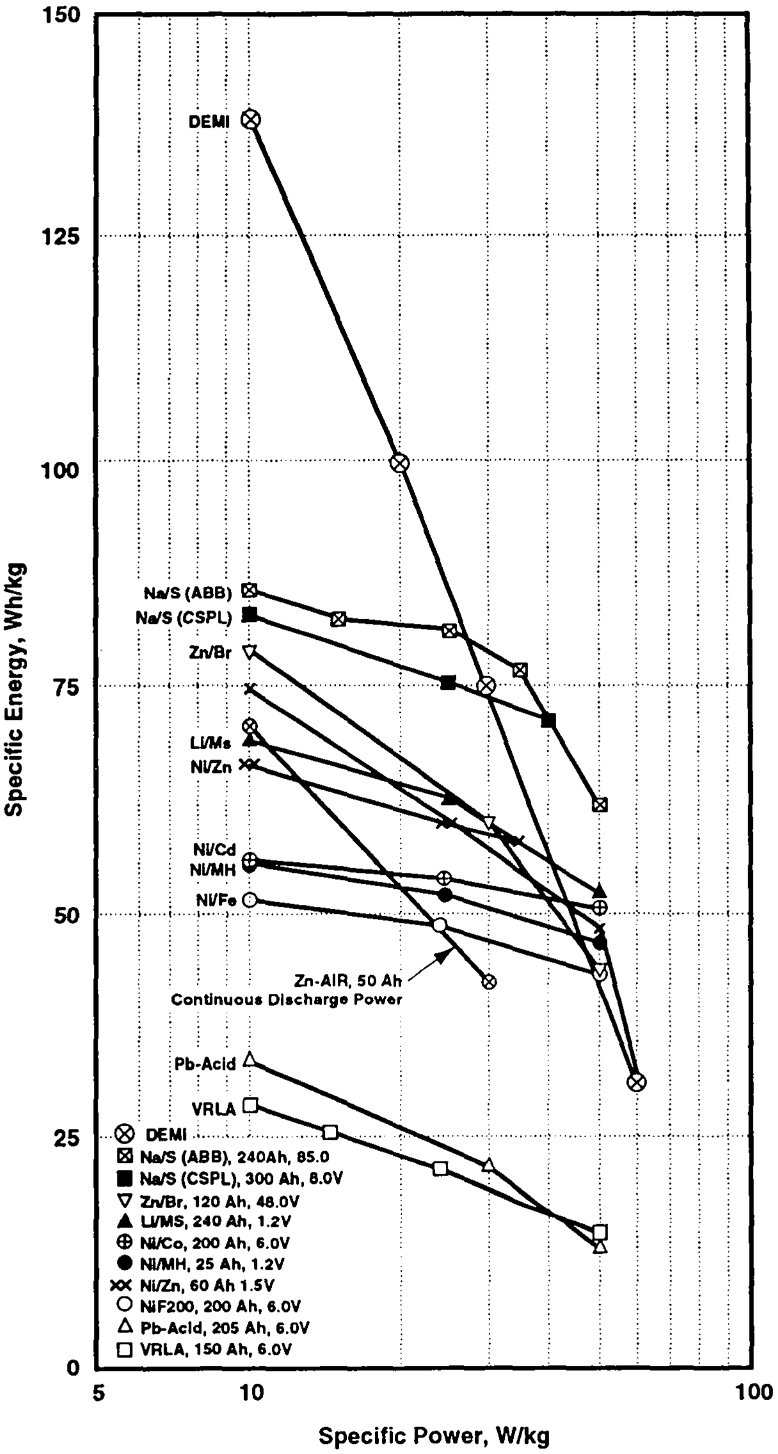

Figure 4. EV Battery Ragone Plots from Argonne and INEL Data.

Table 6. Example for Lower Discharge Rate

Mini Van Example

Vehicle Weight - 1727 kg
Battery Weight - 425 kg (included in vehicle weight)
Battery Rating - 34 kWh (80 Wh/kg)

Performance Power Requirements

Parameter	Power	W/kg
0-60 mph in 12 sec	82.0 kW	193
55 mph on 7% grade	43.5 kW	102
Maximum Power on FUDS	46.7 kW	109
Average Power on FUDS	5.6 kW	13
Power for 65 mph Continuous power	21.1 kW	50

Summary

Continuous Power	50-100 W/kg
Peak Power	193 W/kg
Average Power on FUDS	13 W/kg
C/3 rate for 80 Wh/kg	26.7 W/kg

Although the continuous and peak power demands are significantly higher than the C/3 rate, except in the case of continuous running at high speed, these demands are more the exception than the rule. As an example, the maximum power for FUDS is 46.7 kW, while the average power is only 5.6 kW. At low speeds and FUDS-type driving, lower average rates of discharge occur when a zinc/air battery can potentially provide more energy than some other technologies. In the case of a hybrid battery system, the discharge rate would be C/6 for the FUDS cycle (peak/average power ratio). At this rate, the specific energy of zinc/air would be on the order of 230 Wh/kg for the mechanically recharged system and 110 Wh/kg for the electrically recharged system (roughly a 25% increase in energy and range for both configurations). On the other hand, for missions having frequent high-power demands and/or significant high-speed interstate highway driving, the zinc/air battery system would be at a distinct disadvantage.

This suggests that certain niche applications may be ideal for zinc/air technology and might be explored to determine whether it can offer capabilities competitive with other technologies under consideration. As an example, a zinc/air battery optimized for specific energy in conjunction with a flywheel or an ultracapacitor system could result in a high-energy, high-performance system. Another example could be a large, slow-moving cargo- or people-moving van with space available to accommodate a large battery, such as a 120-kWh battery pack. With power-to-energy ratios of 0.5 to 1 available, peak power would be about 60 to 120 kW. The Electric Fuel postal application is a good example of this type of vehicle.

Calendar and Cycle-Life Analysis

In the case of the electrically charged zinc/air battery, a significant number of issues are currently limiting cycle life to fewer than 100-150 cycles. The most significant is the corrosion of the air electrode substrate from the high voltage required during charging because of cell polarization. This issue has been worked on for many years, with some advances occurring in the past year. However, there is still no clear long-term resolution in sight.

In the case of the mechanically recharged system, the wear and tear from disassembly and/or hydraulically refueling is an area of concern that needs to be addressed. The air electrode is not subject to the corrosion problem previously described. The mechanically charged zinc/air battery appears to be capable of meeting long-term calendar and cycle-life goals; however, more test data are required before this can be assured.

In both cases, the need to control input air humidity and remove carbon dioxide to ensure sustained cycle life is a critical step.

Cost Analysis

An in-depth analysis of the zinc/air battery cost in production volumes has not been performed. The battery consists of mainly zinc, KOH electrolyte, separator, air electrode, air humidifier/filter system, and injection-molded plastic parts to contain the system. The system has been promoted as a low-cost technology because the zinc/air battery material costs appear to be low. Preliminary material cost estimates to date vary widely from as low as \$30/kWh to over \$100/kWh. Much of the variation is caused by the lack of a firm design, specific production volumes, and uncertainty in the cost of the air electrode and separator, which are likely to be the most expensive items in the system.

Operational Considerations

Operating Environment

The USABC long-term criteria require battery operation at temperatures from -40 to 65°C. Zinc/air batteries, like most batteries, perform better at higher temperatures because of more rapid electrode kinetics and significantly lower cell polarization. Operation at lower temperatures is expected to lead to reduced power capability and less efficient operation. However, operation at low temperatures is possible, although at reduced power levels, as demonstrated in tests at -20°C by Electric Fuel.

Recharge Time

High charging voltages are required because of cell polarization for the electrically charged systems. The voltage is a function of the rate of charge. At higher charge rates, low efficiency and corrosion of the air electrode are significant issues for which there are no practical solutions. Thus, fast charge capability and high regeneration rates are unlikely in the near to mid term.

The mechanically charged system avoids some of these issues but, in turn, introduces new issues to be addressed. Its most significant advantage is fast charge capability. The most significant disadvantage is the requirement of a unique infrastructure required to recharge the battery systems. Fleet vehicles appear to be the most likely application if zinc/air can offer significant advantages over other technologies and thereby justify the unique infrastructure investment. Another disadvantage is the inability to accept regenerated power from the EV drive system, which can be resolved with a hybrid battery system as previously described.

USABC Long-Term Secondary Goals

Efficiency

The development of an efficient, high-rate bifunctional air electrode remains a challenge for R&D personnel. The coulombic efficiency for secondary zinc/air batteries is currently in the range of 55-60%. Westinghouse cells were measured at 55% coulombic efficiency. Overall battery energy efficiency, when considering auxiliary pumps and humidity controls, may be limited to 60%.

A departure from the bifunctional electrode may provide some improvement in efficiency. Having an additional oxygen-evolving electrode or bipolar electrode for recharging zinc/air batteries should increase the coulombic efficiency to 70%. MATSI and Phil Ross at LBL have proposed such a "three" electrode system. Others have suggested using two air electrodes — one for discharge and the other for charge, with the zinc electrode in the middle.

Mechanically rechargeable systems currently have an overall energy efficiency of 40%. (Discharge voltage of 1.23 V, 85% coulombic efficiency and recharge coulombic efficiency of 90% at 2.4 V for the CGE system). More recent studies indicate that overall efficiency of 50% may be possible.

Self-Discharge

The rate of self-discharge is low for primary zinc/air batteries. For button cells the self-discharge is 3% per year at 20°C. For large cells, it is 5-15%/yr under open circuit conditions, which exceeds the long-term criteria.

Maintenance

The zinc/air battery is not a maintenance-free system. The need to filter carbon dioxide and maintain humidity control will require periodic replacement of filters and replenishing of water reserves.

Thermal Loss

Heat will most likely be needed to maintain performance at low temperatures. If so, a thermal management system with heaters will be required. Thermal loss and the energy required will have to be considered when designing the system. In view of the low operating efficiency of the system, heat rejection at high operating temperatures must also be considered. The thermal management system and related power required will increase cost and reduce the overall system performance capabilities.

Abuse Resistance

Abuse resistance should not be a problem with proper system design accompanied by a robust packaging design of the zinc/air system.

Recyclability

Zinc/air batteries should be recyclable.

Packaging Constraints

None apparent at this time, other than the size of the battery, which may present a vehicle packaging problem in terms of available space.

Environmental Compliance

Should not be a problem with proper procedures.

Reliability

More testing is required to identify potential failure modes in the electrochemical system. Electrochemical problems such as anode passivation at high discharge rates, zinc dendrite formation on charge, and polarization and stability of the air electrode will have to be addressed.

Good packaging design will be required to provide a robust zinc/air battery system capable of surviving vehicle environments.

The need for carbon dioxide filters and humidity control systems increases the overall system complexity and adds to system weight and cost, although these are projected to be minimized by DEMI. Failure of these systems will also lead to cell replacement costs.

Safety

Hydrogen evolution on overcharge and the possibility of electrolyte leakage are the only significant chemical hazards of this system. Overcharge can be managed by controlling the cutoff voltage. Mechanisms would be needed to neutralize the potassium hydroxide electrolyte in the event of a spill.

Vibration Tolerance

Good packaging design will be required to provide a robust zinc/air battery system capable of surviving vehicle environments. Related weight increases may reduce present specific energy and power predictions.

Overcharge/Overdischarge

Overcharging is not a major problem for a secondary zinc/air battery. The air electrode can accept overcharge. The zinc electrode will evolve hydrogen on overcharge. If needed, a hydrogen and oxygen recombination device could be used to convert the gases to water. For primary systems, overcharge is not an issue.

In the case of overdischarge, the main problem is with the zinc electrode. If all the zinc is removed, then the lead and copper substrate will be stripped from the zinc electrode surface. The lead and copper ions will be transported to the air electrode where poisoning of the catalyst will occur, causing failure of the cell. If adequate cell balance can be achieved, this problem can be solved by having a discharge cutoff voltage. However, if cell balance cannot be controlled over the life of the battery, individual cells may be overdischarged unless the voltage of each cell is monitored. This in turn would add additional cost and weight to the system and thereby further reduce these attractive features of zinc/air technology.

Summary

The mechanically recharged zinc/air system is more advanced than the electrically charged system. This is primarily because many of the problems and issues associated with the electrical system are avoided by the mechanical system. However, some of the inherent characteristics of zinc/air technology remain and are addressed below along with issues uniquely associated with mechanically recharged systems.

1. The specific power and power density for the proposed zinc/air systems have been relatively low. As an example, the Electric Fuel system P/E ratio is 0.55. The P/E ratio can be increased; however, this approach will most likely result in a significant decrease in specific energy.

   An alternative approach would be to optimize the zinc/air battery design for energy storage and use a power battery, flywheel, or ultracapacitor to provide the system power. The addition of a power section, however, increases complexity and cost, adds weight and volume, and thereby leads to reduced specific energy and energy density.

   Another alternative is the use of a very large capacity battery sized to provide the required power at the available P/E ratio (e.g., 120 kWh = 66 kW). To be effective, this approach would require a very low cost ($/kWh) system and would apply only to vehicles capable of containing the large battery volume and carrying the battery weight.

2. The overall dc/dc efficiency of the zinc/air system is a major concern. Although estimates vary between 40-70%, the more likely scenario is less than 60%. Low overall efficiency increases the cost per mile. What is more important, it also increases the smoke-stack emissions per mile, which is counterproductive in view of the intent of the zero emission vehicles.

3. Although the zinc/air battery system is viewed as an ambient temperature system, its performance varies significantly over the required operating range of -40 to 65°C.

   For a general-purpose vehicle, the driver expectation of vehicle performance must be consistent and representative of current internal combustion engine (ICE) vehicles. Inconsistent performance will reduce EV acceptability and may lead to potential safe driving issues.

To provide consistent performance, a thermal management system will be required to maintain battery temperature at ambient temperatures. The thermal management system also needs to provide cooling at high temperatures to reject heat generated by polarization and battery impedances.

The added weight of the thermal management system and the power for heating the battery pack need to be accounted for in the zinc/air system performance calculations. It will have a negative effect on the present zinc/air performance predictions.

4. Niche applications are possible; however, they will not very likely drive the battery volumes to the levels required to realize the economy of scale needed to reduce battery costs significantly, nor will they be sufficient to meet mandated volumes.

5. Numerous preliminary zinc/air battery cost analyses have been performed with widely varying results; however, the cost of materials is lower than for many other technologies. A substantial cost advantage over other available technologies will be difficult to sell without a credible in-depth cost analysis to identify the real cost potential of this technology.

6. The need for an infrastructure to charge the battery mechanically is a significant issue that could seriously affect the viability of this approach. Although a case can be made for fleet applications, it is questionable whether this technology can be used for the general public. (LLNL's refueling approach may answer some of these questions after being demonstrated in a fleet application this fall.) Overnight charging at home and opportunity charging in parking garages are very convenient and not too difficult to provide for electrically charged vehicles. On the other hand, conveniently located neighborhood service stations would be required for the mechanically charged zinc/air battery to be competitive in the personal vehicle market. The capital investment required for these stations would be difficult to justify without large numbers of mechanically charged zinc/air vehicles in the area. Unless the mechanically charged zinc/air system offers significant advantages over prevailing technologies, it is highly unlikely that the investment could be justified.

7. The inability to accept regenerated power while braking is a distinct disadvantage of the mechanically recharged zinc/air battery. While improving the overall vehicle efficiency, regeneration also reduces braking system wear and tear, which

is a significant factor considering that EVs generally weigh more than their ICE counterparts.

The electrically recharged zinc/air system would be the preferred battery configuration if it could acquire the desirable attributes of the mechanically recharged system. Unfortunately, formidable challenges remain that seriously limit its performance, life, and cost. For a variety of reasons, its specific energy and energy density are significantly less than those of the mechanical system. The cycle life is limited but improving every year.

An in-depth review of many of the above issues was made at a symposium/workshop held at CWRU in December 1993. The following brief summary of issues addressed was presented with regard to zinc/air technology:

> Despite years of intense research and development, the use of zinc electrodes for rechargeable battery applications continues to be hampered by problems associated with morphological changes and losses in capacity upon repeated charge-discharge cycling. Some of these limitations can be overcome by using electrolytes with low zinc solubility or by employing ionically conducting polymers as part of the electrode structure to restrict zincate ion mobility. Mechanically rechargeable zinc-based systems and zinc/bromine batteries were also discussed, citing as their major disadvantages the need for a large infrastructure, and safety issues, respectively.
>
> In the case of monofunctional air electrodes, the high fabrication cost is a problem, as well as the performance limitations attributed to water management and carbon dioxide tolerance. In the case of the bifunctional oxygen electrodes, these problems are further compounded by the lack of carbon or other materials exhibiting low corrosion rates at high potentials. One possible approach towards improving water transport and possibly corrosion is to use composite electrodes involving ionically conducting polymers either intimately mixed with the electrode material or as films adhered to the electrode surface. Perhaps the most challenging problem facing oxygen electrodes is to identify low-cost catalysts both for the reduction and evolution of oxygen.

This analysis suggest that a number of fundamental development issues remain to be resolved before the electrically rechargeable zinc/air system can be considered a viable candidate for EVs. Cycle life, cost, and specific power and power density need to be addressed or zinc/air will have at best limited use in electric vehicles.

Conclusions

In summary, the mechanically recharged zinc/air system may be a possible candidate for niche applications, particularly for large fleet vehicles, if it can offer significant competitive advantages over other competing technologies. Its use will depend upon the application, demonstrated capabilities of the system, investment and operating costs, and the ability of the application to accommodate the mechanical recharge stations.

When viewed as a fuel cell, the mechanically rechargeable zinc/air system is clearly as good a range extender as are other fuel cells. The advantages are that a reformer is not needed, and the problem with hydrogen fuel storage is avoided. Other potential advantages of zinc/air systems over fuel cells are the lower cost, higher power, and longer life. The mechanically recharging infrastructure required is a disadvantage.

At this point, the electrically recharged zinc/air battery system may be able to achieve the mid-term level of performance established by USABC if it can improve its cycle life, specific power, and power density and demonstrate its cost-competitiveness. It will, however, have to compete with other battery technologies that may already be in production when zinc/air's performance and cost issues are resolved.

In either case, it will be difficult to assess the true potential of zinc/air battery technology for EVs without *credible* investment and operating cost projections. In addition, these projections must be based on complete zinc/air battery system configurations, including all the necessary support systems required for a useful and reliable EV battery.

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