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The Secondary Alkaline Zinc Electrode

F.R. McLarnon and E.J. Cairns

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THE SECONDARY ALKALINE ZINC ELECTRODE

by

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ABSTRACT

Zinc is the most commonly used battery electrode, and zinc primary batteries have found numerous applications. The zinc electrode is electrochemically reversible in alkaline electrolytes, and there is a strong incentive to develop a practical secondary battery based on this metal. However, secondary batteries that use zinc electrodes typically exhibit short lifetimes, because of problems with zinc material redistribution and undesirable zinc morphologies that form during recharge. There has been a world-wide effort to develop a long-lived secondary alkaline zinc electrode, and marked improvements in cell lifetimes have resulted. This article reviews these efforts, paying particular attention to R&D during the period 1975-1990.

Keywords: Zinc Electrode, Secondary Batteries, Alkaline Electrolytes

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INTRODUCTION

Zinc has been used by human cultures throughout recorded history, and it is a high-volume metal (1). World-wide production of zinc was about 7 million tons during 1989, including 345,000 tons of zinc produced in the U.S. (2). The U.S. now consumes about 1.34 million tons of zinc per year, half of which is used in galvanizing and electrogalvanizing for corrosion protection. Other uses of zinc include die casting, brass, zinc oxide (pigments) and battery electrodes. It is the use of zinc in battery electrodes, which represents only a small fraction of its current consumption, that is the subject of this review.

Batteries have long been recognized for their capacity to efficiently convert and store electrical energy. Batteries now find use in a myriad of devices, and the world-wide market for batteries is expected to grow along with our increasing use of electricity and electrical devices. Also, there are exciting new technologies that will use advanced batteries. For example, large-scale energy storage technologies, such as electric vehicles or electric utility load leveling, can provide needed flexibility in the choice of primary fuels for energy generation. Advanced *rechargeable* batteries are the leading candidates for such applications (3). Other new uses for rechargeable batteries include power sources for cordless power tools, video equipment, communications equipment, lap-top computers, *etc.* Much of the recent R&D on advanced rechargeable batteries has been driven by such applications, and secondary zinc electrodes have received considerable attention for the same reason.

The status of R&D on the zinc electrode has been addressed by prior reviews (4-9), and the reader should consult these references for a discussion of earlier work on primary and secondary cells, including those that use acidic or neutral electrolytes (*e.g.*, Zn/Br_2). The present work addresses the secondary alkaline zinc electrode and focuses on R&D during the period 1975-1990.

APPLICATIONS OF SECONDARY ALKALINE ZINC ELECTRODES

Zinc is the most commonly used battery electrode because of its low equilibrium potential, reversibility, compatibility with aqueous electrolytes, low equivalent weight, high specific energy and volumetric energy density, abundance, low cost, low toxicity, and ease of handling. Primary Zn-electrode batteries are preferred where moderate specific energy and low manufacturing costs are important considerations. For applications where moderate specific energy, high specific power, high energy efficiency, low toxicity and low life-cycle costs are important, rechargeable Zn-electrode batteries are attractive candidates. These applications include all kinds of electric vehicles (automobiles, vans, material-handling equipment, tanks, *etc.*) and portable electric-powered equipment. The advantages of electric vehicles, compared to internal-combustion-engine vehicles, are well documented: *a*) the use of petroleum-derived fuels can be avoided, *b*) exhaust emissions are greatly reduced, and *c*) thermal and audible signatures are minimized. Lead-acid (Pb/PbO_2) and Cd/NiOOH batteries are now the preferred energy storage devices for portable power applications. Substitution of Zn-electrode batteries will not only result in better performance, but also afford reduced toxic disposal problems.

Secondary alkaline zinc batteries have not received serious consideration for applications such as utility load leveling, which require very long battery lifetimes.

SECONDARY ALKALINE ZINC CELLS

The use of *primary* Zn-electrode batteries is widespread, but *secondary* Zn-electrode batteries have not penetrated commercial markets. The Zn electrode has been coupled with numerous electrolyte/positive-electrode combinations in an international search for a high-performance, long-lived secondary battery. An alkaline-electrolyte battery is desirable because of the inherent electrochemical reversibility (low overpotential) of the Zn electrode, the high ionic conductivity of the electrolyte, good low-temperature performance, and the availability of rugged, compact, non-toxic and long-lived positive electrodes (*e.g.*, NiOOH and MnO_2).

However, Zn electrodes have found only limited use in secondary batteries, with both alkaline and acidic electrolytes. A fundamental problem is the short and unpredictable lifetime of the Zn electrode when it is subjected to charge-discharge cycling. This problem has been traced to the redistribution of Zn active material (shape change) and the formation of unwanted Zn electrode morphologies (dendrites, filamentary growths, nodules) during recharge. These phenomena are linked to two important characteristics of Zn: (*a*) its high solubility in common battery electrolytes, and (*b*) its rapid electrochemical kinetics.

The design features of various secondary alkaline zinc cells that have been investigated during the past 15 years are summarized in the following sections.

Zinc/Nickel Oxide

The Zn/KOH/NiOOH cell is based on dissolution-precipitation reactions at the Zn electrode:

$$Zn + 4OH^- = Zn(OH)_4^{2-} + 2e^- \tag{1}$$

$$Zn(OH)_4^{2-} = ZnO + 2OH^- + H_2O \tag{2}$$

The NiOOH electrode reaction during discharge is:

$$NiOOH + H_2O + e^- = Ni(OH)_2 + OH^- \tag{3}$$

and the overall cell reaction is:

$$Zn + 2NiOOH + H_2O = ZnO + 2Ni(OH)_2 \tag{4}$$

The reverse reactions occur during cell recharge. A plot of the time dependence of Zn/NiOOH cell voltage and electrode potentials during a typical charge-discharge cycle is shown in Fig. 1. Most of the cell voltage loss is associated with the NiOOH electrode, whereas the Zn electrode exhibits a small overpotential. The average cell discharge voltage is about 1.65 V, and the theoretical cell specific energy is 326 Wh/kg.

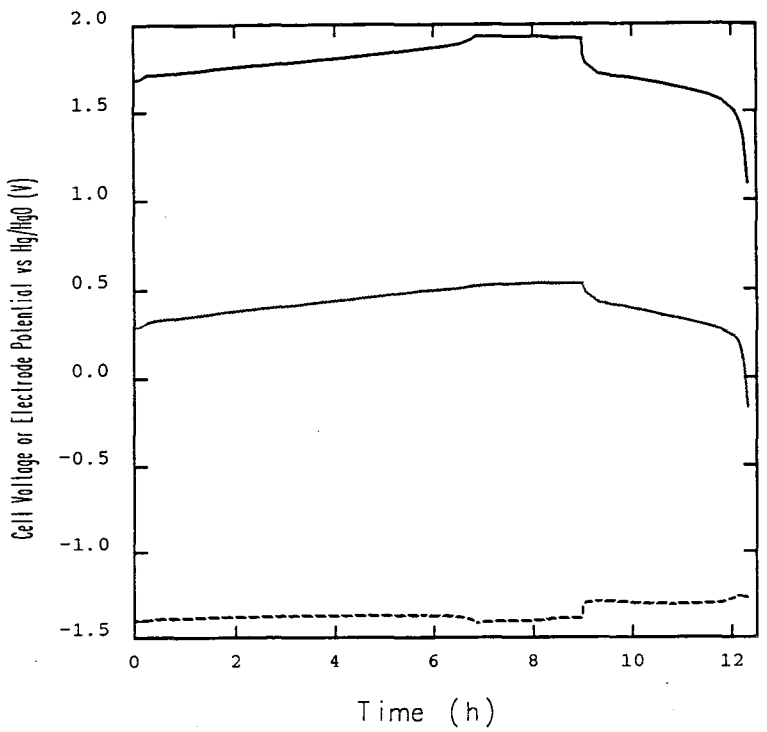

Figure 1. Zn/NiOOH cell voltage and electrode potentials during a charge-discharge cycle.
_____ Cell voltage
..... NiOOH electrode potential (*vs* Hg/HgO)
---------- Zn electrode potential (*vs* Hg/HgO)
The cell is charged at a constant current of 0.225 A for 0<t<6.8 h, followed by a constant-voltage charge at 1.93 V for 6.8<t<8.4 h, an open-circuit period for 8.4<t<8.9 h, and a constant-current discharge at 0.5 A for 8.9<t<12.2 h.

The Zn/NiOOH battery is recognized for its high specific energy of 55-80 Wh/kg (depending on cell design), excellent peak specific power of 260-170 W/kg at 0-80% DOD (10), good low-temperature performance, and moderate self-discharge rate (<0.8%/day). Figure 2 shows a plot of specific energy *vs* specific power (Ragone plot) for a 4-cell 144-Ah Zn/NiOOH module that was constructed by General Motors/Delco Remy (10). Good power-energy characteristics are maintained, even at 0°C. Many versions of this promising system were investigated during the 1970s and 1980s, and Table 1 lists the organizations and approaches that have been used. Four basic cell designs have been developed: *a*) vented static-electrolyte, *b*) sealed static-electrolyte, *c*) vibrating electrode, and *d*) flowing electrolyte. Important cell construction features for these designs are described in the following four paragraphs.

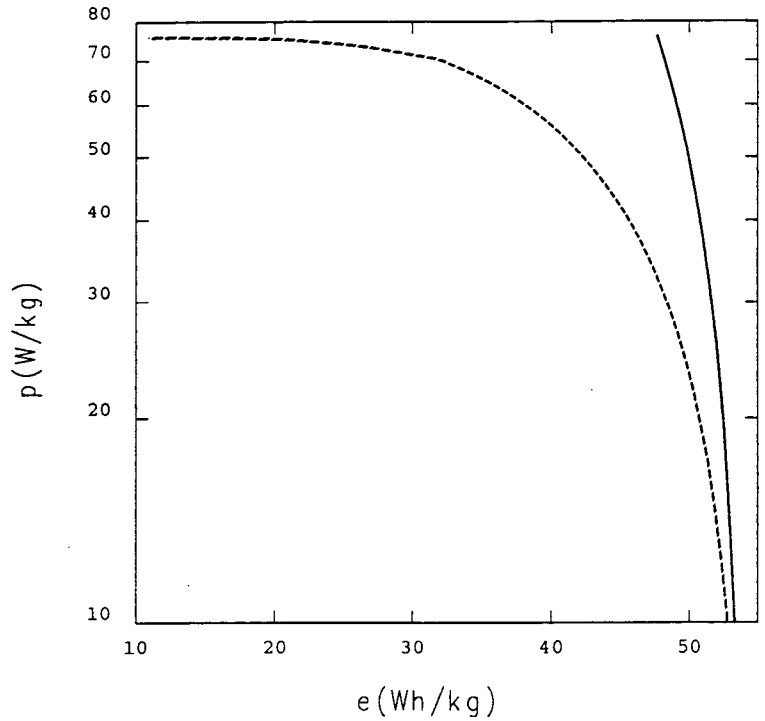

Figure 2. Plot of specific power *vs* specific energy for a 4-cell 144-Ah Zn/NiOOH module that was constructed by General Motors/Delco Remy (10).
_____ Initial module temperature 24°C
---------- Initial module temperature 0°C

Vented static-electrolyte cells: Cells of this type are designed to be capacity-limited by the NiOOH positive electrode, which is typically a porous sintered structure formed by either an electrochemical or chemical precipitation process. The porous Zn electrode is usually prepared by applying a polymer-bonded paste of ZnO to a screen or mesh current collector, using a quantity of ZnO equivalent to two-to-four times the stoichiometric amount of active NiOOH. It has been shown that the Zn/Ni mass ratio has a significant effect on cell lifetime (25,44,45), as does the Zn/electrolyte mass ratio (46). The electrolyte is usually an aqueous solution containing 20-35 wt% KOH and 1 wt% LiOH, and is saturated with ZnO (about 1 M). When an excess amount of electrolyte is used (flooded-electrolyte configuration), the height of the electrolyte meniscus can have a significant effect on the rate and extent of Zn material redistribution (33,47-49). Most cell designs call for a minimum amount of electrolyte, barely enough to wet the electrodes and provide an ionic conduction path. Microporous separator materials serve to retard Zn dendrite

Table 1. Zn/NiOOH Cell and Battery Development.

Organization	Features	Reported Cycle-Life	Cell/ Battery	References
General Motors	Ca additions low-KOH electrolyte pasted-rolled electrodes	300 600	battery cell	11-14
Gould	Zn-selective separator voltage-limited charging	200	battery	15,16
Energy Research	pasted-rolled electrodes foil current collector	100	battery	17-21
Exide	vibrating Zn electrode	1000	cell	22
Yardney	multilayer separator	100	battery	23-25
Rockwell	rotating-shutter separator	200	cell	26
Eagle Picher	cellophane separator	425	battery	27-29
DAUG*	Ca additions	400**	battery	30
LBL	modified electrolyte voltage-limited charging Ca additions	500	cell	31-33
Electrochimica	modified electrolyte modified electrode	500	cell	34-36
Labcom	pulsed charging pressure-limited charging	600	cell	37,38
Sorapec	pulsed charging Pb additive flowing electrolyte	700	cell	39
Lucas	polymer-bonded Ni electrode	300	cell	40
Yuasa	sealed cells	200	cell	41
Sanyo	sealed cells metal oxide additives	500	cell	42
Japan Storage Battery	sealed cells Zn electrode additives	200	cell	43

* Deutsche Automobilgesellschaft Forschungslaboratorium

** 25-Ah cell

growth, and wicking materials are used to help wet the electrodes. Modest overcharging is required to accommodate the inherent inefficiency of the NiOOH electrode, and this type of cell is vented to the atmosphere to allow release of the O_2 gas formed during the charging process. This O_2 loss causes an imbalance between the negative and positive electrode states of charge. A proper balance can be restored by completely discharging the cell, and then charging until an adequate Zn metal reserve is established. A cell pack is constructed by sandwiching alternate negative and positive electrodes, which are held under compression, and the packing pressure is an important design parameter (50). A diagram of a typical cell arrangement is shown in Fig. 3. Although the electrodes are usually aligned in registry to one another, the use of off-center alignment and differently sized electrodes has been touted to improve cell cycle-life performance (51,52).

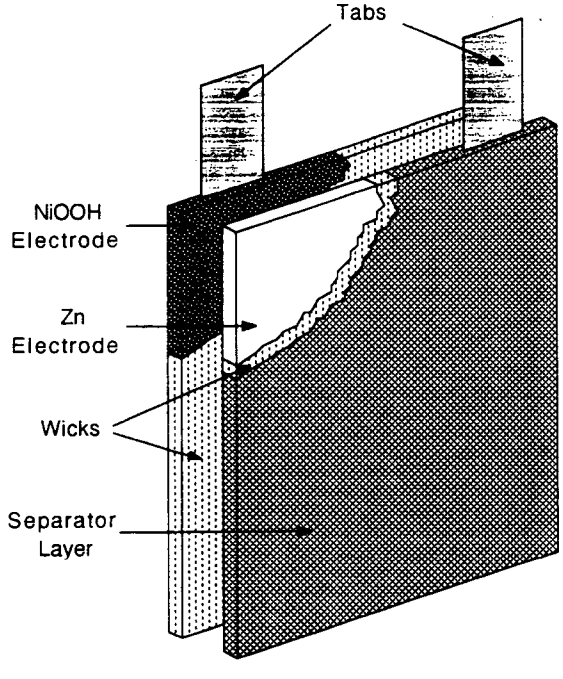

Figure 3. Typical Zn/NiOOH cell construction.

Sealed static-electrolyte cells: The development of a sealed Zn/NiOOH cell is necessary for battery applications that require low maintenance and safe operation (53-56). Most of the design features of sealed cells are similar to those described above for vented cells. Sealed cell construction requires the efficient transfer of O_2 from the NiOOH electrode (where it is evolved on overcharge) to the Zn electrode. Cell designs that include gas passageways (57) and optimized wicking/absorbing materials (58-60) have been developed for this purpose. Also, a H_2 recombination device may be needed for long-lived cells. Such devices have been incorporated as auxiliary (third) electrodes (61-67), or as catalysts contained in the NiOOH electrode (68). Auxiliary electrodes have also been used to dissolve residual Zn deposits (69-72), react with excess O_2 (73), and serve intermittently as extra positive electrodes (74-77).

Vibrating-electrode cells: Cells of this type were developed by AGA-Tudor (78-81), Soviet investigators (82,83) and Exide (22,84). A cam arrangement was used to vibrate a planar Zn electrode, typically at a frequency of 20 Hz and an amplitude of 1.5-2.5 mm. Zinc/nickel oxide batteries as large as 20 kWh were constructed. Agitation of the electrolyte resulted in uniform zincate-ion concentrations, which effectively eliminated the Zn active material redistribution problem. Lifetimes greater than 1000 cycles were obtained on single cells, however the specific energy was typically less than 50 Wh/kg, because of the heavy mechanical parts and the excess volume of electrolyte that were required. Design variations of this concept include Zn/NiOOH cells with rotating "shutter" separators (26), moving sheet and rotating electrodes (85). These cell types are no longer under development.

Flowing-electrolyte cells: Cells using flowing electrolyte have been developed by Sorapec and Renault (39,86,87). An original concept was the use of Zn-coated polymer "beads," which were circulated through the negative-electrode compartment by flowing electrolyte. Single-cell lifetimes greater than 1000 cycles were obtained, however this line of investigation was abandoned because of problems with cell complexity, parasitic Zn deposits, and cost (39). Other variations of flowing-electrolyte Zn/NiOOH cells have also been investigated (88,89).

The above descriptions of static-electrolyte Zn/NiOOH cells correspond to what might be called a baseline Zn/NiOOH technology. Cells constructed in this way can be expected to fail after about 100 deep-discharge cycles, usually by capacity loss caused by Zn active material redistribution or cell shorting by Zn dendrite penetration through the separator to the NiOOH electrode. The cell modifications that incorporate vibrating electrodes or flowing electrolyte have been successful in extending cell and battery lifetimes; however these designs increase system complexity and degrade the battery specific energy.

The Zn electrode fabrication procedures and new cell components that are described in the later sections of this manuscript can result in improved cell lifetimes, with less mechanical complexity than for the mechanical flow systems described above. These improvements can lead to Zn/NiOOH cells with improved lifetimes (>100 cycles), and suggest that numerous small-battery applications may lie ahead for Zn/NiOOH. However, the extented lifetime that is required for significant penetration into commercial electric vehicle markets has not yet been demonstrated. Some recent reviews have addressed Zn/NiOOH battery development issues (90,91).

Zinc/Air

Primary Zn/air batteries are commercially available, and they are used for applications where high specific energy is important and low discharge rates are acceptable, *e.g.*, powering hearing aids and remote signal lights. Small Zn/air cells can be designed to deliver about 300 Wh/kg (92), and they are well suited for such applications.

The secondary Zn/KOH/air cell is based on the same discharge reactions as those at the Zn electrode in the Zn/NiOOH cell [Eqs. (1) and (2)] and the following reaction at the air electrode:

$$\tfrac{1}{2}\,O_2 + H_2O + 2e^- = 2OH^- \tag{5}$$

and the overall cell reaction is:

$$Zn + \tfrac{1}{2}\,O_2 = ZnO \tag{6}$$

Because equilibrium conditions may not be reached during a typical cell discharge, the reaction product may be $Zn(OH)_2$ rather than ZnO. The reversible cell voltage is 1.65 V, whereas the average cell discharge voltage is about 1.2 V. The theoretical cell specific energy is 1200 Wh/kg. Various secondary Zn/air cell designs have been investigated during the past fifteen years. These are listed in Table 2 and described in the following sections.

Table 2. Zn/Air Cell and Battery Development.

Organization	Features	Size	Cell/ Battery	References
Leesona Moos	mechanical recharge	1 kW	battery	93
Gulf General Atomic	mechanical recharge	20 kW	battery	94
General Motors	mechanical recharge	35 kWh	battery	95
Alsthom	Zn slurry	-	-	96
Sony	Zn slurry mechanical recharge	3 kW	battery	97
CGE	Zn slurry electrical recharge	15 kW	battery	98-100
Sorapec	Zn-coated particles	-	cell	101
Pinnacle Research Institute	Zn slurry fluidized-bed recharge	-	cell	102,103
Lawrence Berkeley Laboratory	Zn particulate bed solutal natural convection mechanical recharge	120 Wh	cell	104
Yuasa	electrically rechargeable third electrode	-	-	105
Lawrence Berkeley Laboratory	reticulated Zn electrode flowing electrolyte bifunctional air electrode	2 W	cell	106-108

Mechanically rechargeable consolidated-electrode cells: Zinc/air batteries can be configured to accept replacement Zn anodes, so that the battery can be operated by adding metal plates and fresh electrolyte ("mechanical" recharging) and removing the oxidized Zn product as a highly concentrated electrolyte phase. The major advantages of this cell design are *a*) the air electrode need only reduce O_2, thereby avoiding life-limiting corrosion processes in the bifunctional air electrode, and *b*) it may be possible to develop a cell design that permits easy replacement of the Zn electrodes, suggesting rapid "refueling" of an electric vehicle battery. General Motors built and tested a 32-kWh mechanically rechargeable Zn/air battery that delivered 73-121 Wh/kg at 70-80°C, depending on the discharge rate (95). There were difficulties with the mechanical recharging process, however, and mechanically rechargeable consolidated-electrode Zn/air battery development has not continued.

Mechanically rechargeable particulate-electrode cells: The negative electrode in this type of cell can be a Zn-KOH slurry, a fluidized bed of Zn-containing particles, or a packed bed of Zn particles. Most cell designs call for the regeneration of the particles and/or slurry to be performed outside the cell in a separate electrolysis compartment.* This design thereby avoids the problem of instability of the air electrode in the bifunctional mode. The Compagnie Generale d'Electricite (CGE) design employed a cylindrical geometry, with the Zn-KOH slurry circulated inside the cell (98). The cell discharge product ($K_2Zn(OH)_4$-supersaturated KOH electrolyte) was fed into a separate electrolysis unit where Zn dendrites were deposited onto a metal substrate, and subsequently scraped off to re-form the slurry. The CGE Zn/air battery system was projected to deliver about 90 Wh/kg and 120 W/kg (based on the use of high-performance O_2-reduction electrodes), however the overall energy efficiency was low, ~40% (100).

Pinnacle Research Institute (PRI) has developed advanced components for the slurry Zn/air cell (102,103). A novel feature was the use of a separate fluidized-bed scraped rotating-cylinder

* Some Zn/air system designs include the discharge cell and the slurry-regeneration cell on-board an electric vehicle. This kind of system has been termed "electrically rechargeable."

recharge cell. Zinc was electrodeposited on an inert substrate (Mg or glassy carbon), which was rotated and scraped by fixed blades to remove Zn dendrites. PRI was able to produce dendritic Zn, which was subsequently discharged in a parallel-plate slurry Zn/air discharge cell.

A novel particulate-electrode Zn/air cell under development at the Lawrence Berkeley Laboratory (104) uses natural convection, driven by concentration gradients, to provide the necessary electrolytic mass transfer rates in a stationary bed of Zn particles. The cell configuration is shown in Fig. 4. This design represents a considerable reduction of the complexity associated with pumping slurries or maintaining a fluidized bed. Also, large discharge capacities have been obtained, >500 Ah/l, which is about twice as large as that obtained using other Zn/air cell designs.

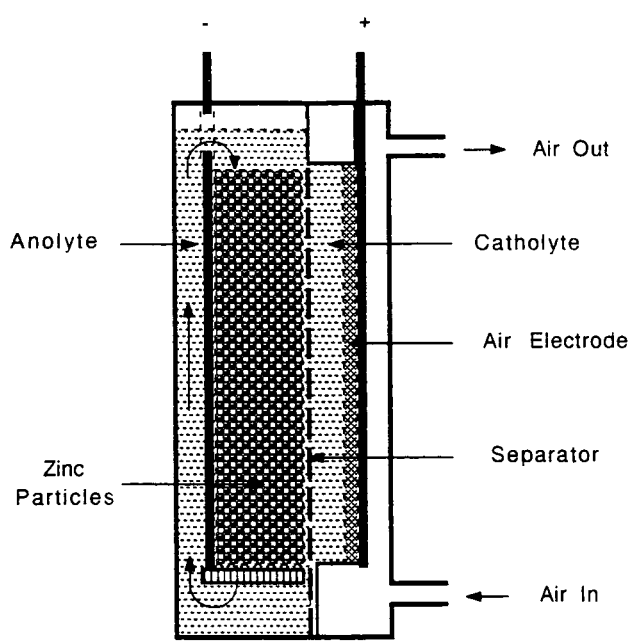

Figure 4. Packed-bed Zn/air cell configuration.

Electrically rechargeable consolidated-electrode cells: The negative electrode in this type of Zn/air cell is typically a porous, polymer-bonded Zn-ZnO sheet, which is similar to the Zn electrode in the static-electrolyte Zn/NiOOH cells described above. The positive electrode can be a bifunctional air electrode, which reduces O_2 during cell discharge and evolves O_2 during cell charge. The short lifetime of bifunctional air electrodes has led to three-electrode Zn/air cell designs, where the Zn electrode is positioned between the O_2-reduction electrode and the O_2-evolution electrode (the so-called third electrode). Cells of this kind were developed by Yuasa Battery Co. (105) to avoid subjecting bifunctional air electrodes to damaging high overpotentials during cell charge. During charge, when the third electrode is evolving O_2, Zn-containing electrolyte is circulated in the gap between the O_2-reduction electrode and the Zn electrode, and Zn-free electrolyte is circulated between the O_2-evolution electrode and the Zn electrode. Zinc is thereby preferentially deposited on the side of the Zn electrode facing the O_2-reduction electrode. During discharge, the O_2-evolution electrode is electrically isolated from the cell. Zinc electrode discharge capacities of 300-400 mAh/cm^2 were obtained.

A novel version of the electrically rechargeable Zn/air cell has been developed at the Lawrence Berkeley Laboratory (106-108). The cell incorporates a porous, flow-through reticulated electrode for Zn deposition/dissolution, and a bifunctional air electrode with a corrosion-resistant graphitic carbon substrate. More than 600 cycles were obtained on the Zn electrode (when cycled opposite a NiOOH electrode), with no apparent structural changes, which demonstrated that this type of cell design can avoid problems such as Zn active material redistribution and dendrite growth. The Zn electrode discharge capacity was ~200 mAh/cm^2, and novel corrosion-resistant carbon materials were used as the substrate for the bifunctional air electrode. Projected Zn/air battery performance parameters were 110 Wh/kg, 140 W/kg and 60% (DC-DC) energy efficiency, and the materials costs were estimated to be ~$20/kWh (106).

The suitability of the various Zn/air battery designs for electric vehicle applications have been analyzed in recent reports. One report concluded that static-electrolyte electrically

rechargeable systems are most appropriate for such applications (109), whereas the other report favored the use of mechanically rechargeable slurry-electrolyte systems (110). Two reviews have addressed Zn/air battery R&D (111,112).

Zinc/Silver Oxide

The Zn/KOH/AgO battery is based on the cell discharge reaction

$$Zn + AgO = ZnO + Ag \tag{1}$$

where the electrochemical and chemical reactions at the Zn electrode are the same as those for the Zn/NiOOH cell, Eqs. (1) and (2). The intermediate species Ag_2O is formed as AgO is reduced during discharge, resulting in a two-plateau cell voltage-time discharge curve. The average cell discharge voltage is about 1.55 V, and the theoretical cell specific energy is 440 Wh/kg. The characteristics of Zn/AgO cells have been described in several reviews (113-115), and the construction of Zn/AgO cells is similar to Zn/NiOOH cells. The AgO electrode is prepared by sintering or pressing Ag powder onto a Ag grid, and a Ag grid is often used as the substrate for the Zn electrode. Cellophane separators are used, along with a nylon wick wrapped around each electrode. The rate of degradation of the cellophane separator decreases as the electrolyte KOH concentration is increased, and the electrolyte composition is ~45 wt% KOH for this reason.

Zinc/silver oxide batteries have been developed by Energy Research (116,117), General Motors (118), Electric Storage Battery (119), Martin Marietta (120-122), and Yardney (123,124). Zinc/silver oxide cell performance exceeds that of Zn/NiOOH cells; specific energies greater than 100 Wh/kg have been demonstrated. Also, Zn/AgO batteries can be discharged at high rates. A full battery discharge can be carried out in only eight minutes, *i.e.*, the 8C rate (114). However, the lifetime of these cells is shorter than Zn/NiOOH cells, particularly so when the Zn/AgO cell is designed to maximize energy content. Zinc/silver oxide cells suffer not only from Zn electrode material redistribution and dendrite shorting, but also from Ag migration and penetration of the separator (114,125).

Zinc/Manganese Dioxide

Primary alkaline cells based on the Zn/MnO_2 couple find a myriad of uses, however attempts to develop a rechargeable $Zn/KOH/MnO_2$ cell have met with only limited success. A fundamental problem is the reaction of soluble Zn species with MnO_2 to form a mixed Zn-Mn oxide phase that is not rechargeable. Recent efforts have focussed on the addition of various oxides to the MnO_2 electrode to alter its physical structure and avoid the formation of the mixed Zn-Mn oxide phase. Compounds such as TiO_2 (126,127) and Bi_2O_3 (128) have been used for this purpose. Other strategies include special heat-treatment regimens for the MnO_2 electrode (129) and the addition of Ag powder to the MnO_2 electrode (130); these procedures are intended to reduce the degree of positive-electrode swelling that accompanies cell cycling.

Zinc/Ferricyanide

The $Zn/NaOH/Na_3Fe(CN)_6$ battery is based on the same negative-electrode reactions as in the Zn/NiOOH battery [Eqs. (1) and (2)], and the following liquid-phase redox reaction at the positive electrode, written for cell discharge:

$$Fe(CN)_6^{3-} + e^- = Fe(CN)_6^{4-} \tag{2}$$

i.e., the reduction of ferricyanide ion to ferrocyanide ion. This system was developed at Lockheed Missiles & Space Co. (131,132) for load leveling and solar photovoltaic energy storage applications. The $Zn/Na_3Fe(CN)_6$ system employed a "flow by" Zn electrode: the Zn active material was deposited as the metal when the battery was charged, and it was stored as soluble $Na_2Zn(OH)_4$ in a reservoir that can be remote from the cell stack. It was proposed to operate the cell stack at temperatures somewhat higher than the ambient-temperature reservoir, thereby promoting the precipitation of ZnO when $Na_2Zn(OH)_4$-supersaturated electrolyte was fed to the reservoir. This scheme led to a more-compact system, although it required solids-handling procedures. A separate reservoir stored the soluble $Na_3Fe(CN)_6$ and $Na_4Fe(CN)_6$ species. Careful control of the electrolyte flow rate was needed to maintain a compact Zn deposit, and periodic

stripping and redeposition of the Zn was necessary to avoid unwanted growths. This system is a hybrid between a true redox battery, where all active materials are soluble in the electrolyte, and a conventional battery. A conceptual diagram of a $Zn/Na_3Fe(CN)_6$ system is shown in Fig. 5.

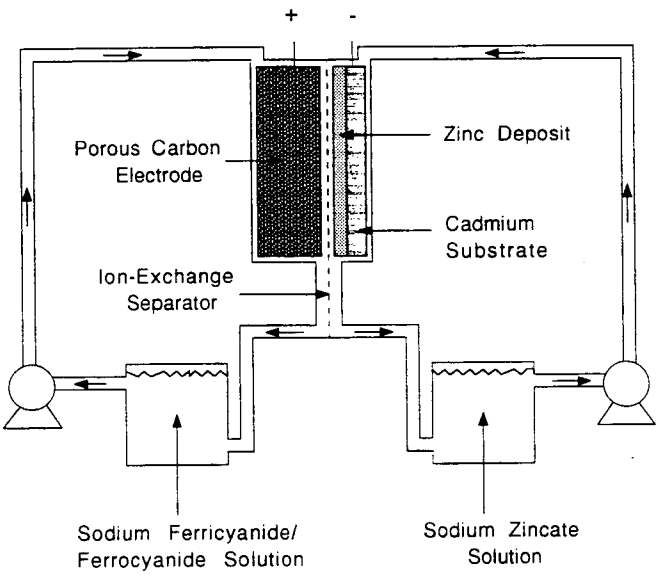

Figure 5. Zinc/Ferricyanide conceptual design.

Lockheed constructed and tested cells as large as 1000 cm^2, although most tests were performed with 60-cm^2 cells. More than 1400 cycles were obtained at ~70% (DC-DC) energy efficiency for a Zn capacity density of 70 mAh/cm^2, using Nafion membranes. Zinc capacity densities as high as 200 mA/cm^2 were obtained in other cells, and cell discharge voltages of about 1.6 V were typical. Alternative, less-expensive membranes and solids-handling procedures were under investigation when Lockheed's effort was discontinued.

RECENT R&D ON SECONDARY CELL COMPONENTS

Zinc Electrode Fabrication

Consolidated porous Zn electrodes have been fabricated by pasting (13,133-135), slurry precipitation (33), powder compression (136), electrodeposition (137), sintering (138-141),

rolling (12,20,142-144) and cementing (145). The electrode may be prepared as a mixture of Zn and ZnO particles, or it may contain only ZnO particles. In the latter case, the electrode must be "formed" by slowly charging it to reduce a portion of the ZnO to Zn. The final Zn:ZnO ratio is selected to provide adequate reserves of ZnO and Zn when the cell is fully charged and discharged, respectively. The Zn-ZnO particle sizes range from 0.1 to 10 μ (146-151). Granular particle shapes are commonly used in polymer-bonded Zn electrodes, however acicular crystalline particles were claimed to give extended Zn/NiOOH cell lifetimes (152). The electrode pore size and pore size distribution are recognized as important parameters in determining electrode performance and capacity loss rates (153,154). An optimum porosity of 64% has been identified (153), and porosities of 60-75% are common for polymer-bonded Zn electrodes. A novel Zn-electrode fabrication recipe uses particles with a layer of ZnO surrounding a Zn core, rather than a mixture of pure Zn and ZnO particles, and a Zn electrode constructed with such particles exhibited an extended lifetime (155). Another unusual construction technique is to encapsulate C_4H_{10} inside hollow polymeric particles, and incorporate the particles in the electrode mix. The C_4H_{10} is released when the electrode is heated, and the resulting porous structure is said to exhibit improved stability (156).

Zinc electrode wetting is enhanced by incorporating fibrous materials in the electrode structure and placing wicking materials (also termed interseparators or absorbers) next to the electrode. Fibers are usually dispersed in the Zn electrode mix, however directionally shrinkable fiber sheets have been used (157). A wide variety of fibrous materials have been investigated, including cellulose (158,159), polyolefin (160), polyamide (161,162), sodium ligninsulfonate (163), acrylonitrile-vinyl chloride (164), glass (165), TiO_2 (166), Al_2O_3 (167,168), carbon (169-171), and Zn (172,173). Fibers are typically used to enhance wetting of the electrode, however hydrophobic polyolefin fibers were used to promote greater access of O_2 to the Zn electrode (160), and mixtures of hydrophobic and hydrophillic fibers have also been incorporated in the Zn electrode (174). An interesting tradeoff in Zn electrode fabrication strategies is the selection of

an optimum degree of wetting for sealed-cell designs. If the electrode is flooded with electrolyte, the transfer of O_2 gas from the NiOOH electrode (evolved during overcharge) to the Zn electrode is impeded, which limits the rate of Zn-O_2 recombination. However, if too little electrolyte is provided, there may be incomplete utilization of the Zn electrode active material.

The order in which the components of the Zn electrode are assembled can also play a role in the performance and longevity of the cell. Many Zn electrode recipes call for layered structures, where the individual layers are of differing composition. For example, incorporating extra metal oxide additive in the outer layer of a Zn electrode appears to extend Zn/NiOOH cell lifetimes, compared to a uniform dispersion of the metal oxide throughout the electrode. Applying thin inorganic (175-177) and organic (178,179) compound coatings to the Zn electrode also appears to be beneficial. Other strategies include placing an electrolyte absorber in the center of the Zn electrode, rather than on the surface (180), using layers of additive-containing Zn active materials with charging voltages that differ from one another by >10 mV (181), and incorporating an outer layer that contains extra wetting agent (182). Each of these strategies tends to extend Zn/NiOOH cell lifetime.

Other electrode fabrication procedures include *a*) non-uniform material dispersions, for example providing extra metal-oxide additives (183-185), polymeric binder (186), rubber (187) or Zn-ZnO active material (188) near the periphery of the electrode, *b*) using porous frames or other means to alter the local ionic conductivity near the edges of the electrode (189,190), and *c*) creating a grooved electrode surface to facilitate the removal of gas bubbles (191).

The Zn electrode current collector must exhibit a sufficiently high electronic conductivity to avoid excessive ohmic potential losses at high current densities, yet be lightweight and inexpensive. Typical current collectors are high-area sheets such as expanded metal Cu foil* (12,31) or perforated Cu foil (12,134,192-194). Solid foil current collectors have been used (20), however

* Manufactured by Exmet Co., Bridgeport CT.

perforated foil current collectors are much more common, and optimum perforation sizes and distributions have been identified (193,194). Sponge (88,106,133,195,196), net (197) and pocket-plate (198) current collectors have also been used. Copper current collectors can be coated with a high-H_2-overpotential metal, such as Pb (31), Cd (199), In (200), Sn (201) or Bi (202) to prevent Cu dissolution during overdischarge. Organic compounds, such as polyvinyl alcohol (203) and carboxymethyl cellulose (204) have also been used as protective coatings for current collectors. A strategy to slow the rate of Zn electrode shape change is to apply $Fe(OH)_2$ at the edges of the current collector (205), thereby increasing the rate of local H_2 evolution at the electrode edges and altering the overall current density distribution. Most current collector designs provide a fine grid structure that supports a uniform dispersion of active material (111). A unusual current collector design uses 30-mm^2 compartments to hold the Zn active material, thereby providing a degree of isolation from adjacent regions of the electrode and slowing the rate of shape change (206). Another unusual current collector design provides thin, vertical polytetrafluoroethylene (PTFE) strips on the current collector (207). These strips create local channels that permit evolved gasses to escape.

Flow-by Zn electrodes have been prepared by electrodeposition onto a planar metallic substrate (131), and high-porosity Zn electrodes have been prepared by electrodeposition onto reticulated (sponge) current collectors (106,195). Unconsolidated Zn electrodes are prepared as assemblies of particles, such as Zn electrodeposited onto Cd-coated plastic particles (101), or dendritic Zn scraped from an inert current collector (98-100,102,103).

Zinc Electrode Composition

The typical Zn electrode composition is >90 wt% Zn plus ZnO, <5 wt% polymeric binder, and <5 wt% metal oxide additive. Numerous inorganic chemical species have been combined with Zn-ZnO to form secondary battery electrodes with improved properties. The touted beneficial effects of these additives include *a*) suppression of H_2 formation, *b*) reduction of Zn

species solubility, *c*) co-deposition of additives to form compact Zn layers, *e.g.*, dendrite suppression, *d*) creation of a metallic substrate that is more conducive to the electrodeposition of compact Zn, *e*) more-uniform current density distribution, *f*) improved wetting of the Zn electrode structure, *g*) increased electronic conductivity of the Zn electrode, *h*) complexation of soluble Zn species to reduce their mobility, *i*) increased utilization of the Zn electrode active material, and *j*) retention of desirable porous structures, *e.g.*, by using "fillers" and "pore-formers." These modifications to the Zn electrode are discussed in the following paragraphs, and Table 3 lists most of the inorganic additives that have been investigated during the past 15 years.

The need to suppress H_2 formation is critical for both primary and secondary Zn batteries. Mercuric oxide has long been the favored primary-battery additive for this purpose. However, environmental pressures have spurred a world-wide effort to identify a less-toxic alternative additive. For secondary battery applications, HgO is an undesirable H_2-suppression additive not only for environmental reasons, but also because it tends to accelerate Zn active material redistribution (259). Numerous metals and metal compounds have been evaluated as H_2 suppressants, and these are identified in Table 3. Of these compounds, the oxides and hydroxides of Cd, Pb, Sn, In, Tl and Bi would appear to be the most popular, based on the frequency of their appearance in the patent literature. Battery developers in the U.S. (General Motors, Yardney, Energy Research) and Japan (Sanyo, Matsushita, Hitachi, Toshiba, Furukawa, *etc.*) have been particularly active in this area. These compounds have been favored not only for their capacity to suppress H_2 formation, but also for their beneficial effect on cell lifetimes. At least two mechanisms have been proposed to explain the improved cell lifetimes observed using such compounds as electrode additives. First, if the additive is present as the reduced metal, it may serve as an ideal substrate that promotes the formation of compact, thin Zn deposits *via* electrodeposition. The compounds of metals more noble than Zn would be expected to be present in their reduced form, which has been shown to be the case for Tl_2O_3 and Bi_2O_3 (91). Second, the incorporation of metallic deposits in the Zn-ZnO mix enhances the electronic conductivity and polarizability of the electrode.

Table 3. References to Investigations of Zinc Electrode Inorganic Additives.

Cation	Pure Element, Oxide or Hydroxide	Halide	Oxyanion
Ag	150,208,209	-	-
Al	167,210	-	-
Ba	185,210-212	213	-
Be	185	-	-
Bi	42,157,203,209,213-226	-	-
Carbon	166,171,206,220,221,235,250,251,253,254 256,262	-	-
Ca	12,13,30,32,33,42,135,157-159,163,164,168, 177,183,191,197,202,203,211,212,218,219, 223-225,227-251	213	219 (carbonate) 252 (silicate)
Cd	21,44,45,148,152,161,168,185,186,188,193, 199,209,211,220,226,236,237,242,250,255-266	-	255 (sulfate)
Ce	220	-	-
Co	268	-	-
Cs	269	-	-
Cu	239,240,267	-	-
Fe	270	-	-
Ga	209,210,222,271,272	-	-
Hg	*	-	-
In	171,175,181,184,209-211,222,226,243-245,252, 259-261,269,271-293	-	-
K	-	-	267 (sulfate)
La	185	-	-
Li	292	-	-
Mg	212,241,267,294-296	-	-

* The references to HgO additions are too numerous to list in this table. See, for example, reference 259 for a discussion of HgO additions to the Zn electrode.

Table 3 (cont'd).

Cation	Pure Element, Oxide or Hydroxide	Halide	Oxyanion
Na	-	-	267 (sulfate)
Pb	12,21,139,158,159,173,209,212,220,222, 236,259,260,267,280,281,297-299	-	-
Rb	289	-	-
Si	182,282	-	-
Sn	209,220,226,246,264,265,283,298,300,301	-	-
Sr	284	-	-
Ti	166,212,220,266,301,303-305	-	-
Tl	135,149,176,181,210,222,226,236,243, 247,259,260,269,285-293,299	-	-
V	220	-	-
Zn	-	302,307	302,306 (titanate)
Zr	139,185,212	-	138 (sulfate)

This effect provides a more-uniform current density distribution and promotes Zn deposition near the current collector, rather than near the separator.

Investigators have long known that Ca is a beneficial additive to the Zn electrode (227-229). When $Ca(OH)_2$ is added to ZnO in alkaline electrolyte, an insoluble calcium zincate compound is formed, thereby "trapping" the soluble $K_2Zn(OH)_4$ species. Investigations (308) have shown that the calcium zincate compound stoichiometry is $Ca(OH)_2.2Zn(OH)_2.2H_2O$. This compound is most effective in reducing $K_2Zn(OH)_4$ solubility in ~20 wt% KOH electrolyte (309), and kinetic studies showed that high-rate charge/discharge processes may be limited by the rate of calcium zincate formation/decomposition (310). Additions of 10%, 25%, and 40% $Ca(OH)_2$ to the Zn electrode were evaluated by Jain *et al* (33); only the intermediate composition gave marked improvement in cell endurance. X-ray analysis demonstrated that the discharged negative electrode was uniformly covered with a calcium zincate compound. The low solubility of calcium zincate in KOH accounts for the reduced rate of Zn redistribution of the 25 wt% $Ca(OH)_2$

electrode. The microstructures of the calcium zincate compound and the ordinary ZnO discharge product are compared in Fig. 6. Other alkaline-earth metal hydroxides such as $Ba(OH)_2$ and $Mg(OH)_2$ have been used, as well as calcium oxide, citrate, carbonate, fluoride and silicate compounds.

Other materials listed in Table 3 include various carbons (acetylene black, graphite, powders, *etc.*), and metal hydroxides, halides, sulfates and titanates. These materials may act to reduce $K_2Zn(OH)_4$ solubility, enhance electronic conductivity, provide an improved substrate for Zn electrodeposition, act as "fillers", and/or improve electrode wetting.

Polytetrafluoroethylene (PTFE) is by far the most commonly used organic additive, and it serves as a binder to impart strength to the Zn electrode. Polyvinyl alcohol (PVA) is also used for this purpose. The other organic compounds that have been added to the Zn electrode may also act as binders, suppress Zn dendrite initiation and propagation, act as fillers, improve electrode wetting, and/or complex soluble Zn species. These materials are listed in Table 4.

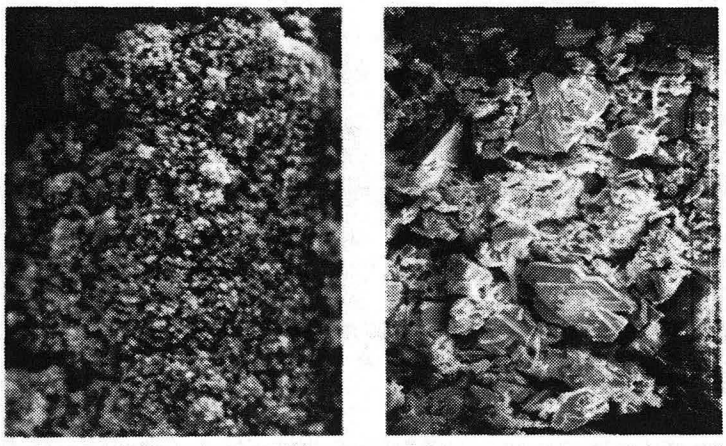

Figure 6. Microstructures of the discharge product on two Zn electrodes. The left-hand side shows the typical ZnO discharge product on a "standard" Zn electrode, and the right-hand side shows the discharge product on a Zn electrode containing 25 wt% $Ca(OH)_2$. The stoichiometry of this product is probably $Ca(OH)_2.2Zn(OH)_2.2H_2O$.

Table 4. References to Investigations of Zinc Electrode Organic Additives.

Compound	References
acrylic acid - ethylene copolymer	312
acrylamide - acrylic acid - methylenebisacrylamide copolymer	317
acrylic acid - diacetone acrylamide copolymer	314
acrylonitrile - vinyl chloride polymer	164
benzene	311
Carbowax	267
carbazole	254
cellulose, cellulose acetate, hydroxyalkyl cellulose, carboxymethyl cellulose	158,220,238,254,267,313,319,320
carboxylated styrene - butadiene	316
calcium citrate	329
calcium glutonate, sodium glutonate	237,326
calcium ligninsulfonate, sodium ligninsulfonate	163,235,330
dextrin	220
methyl methacrylate - acrylonitrile	156
piperonaldehyde	220
polyacetylene	179,263,331
polyacrylate	319
polyacrylamide	315
polyamide	162,307,315,327
polyethylene, polyethylene oxide	53,238,257
polyethyleneimine	318
polymethacrylic acid	324
polystyrene	178,325
polytetrafluoroethylene	numerous references; see, for example, 334-336

Table 4 (cont'd.)

Compound	References
polyvinyl alcohol	53,164,183,191,212,249,257,279,285,307,327,333
polyvinylidene fluoride	163
polyvinyl glycol	324
styrene	311
styrene - maleic anhydride copolymer	332
various surfactants	53
tetraalkylammonium, ammonium compounds	323
thiourea	321
trihydroxybenzene	253
trihydroxyfluorone	322

Electrolyte Composition

The favored electrolyte composition for secondary Zn/NiOOH, Zn/air, Zn/AgO and Zn/MnO_2 cells is 20-45 wt% KOH. The choice of KOH concentration reflects a compromise between conflicting requirements. In general, ~30 wt% KOH is desirable because the ionic conductivity is near a maximum at this concentration. Also, the positive electrodes tend to deliver maximum capacities at high KOH concentrations, and the rate of oxidative degradation of certain separator materials is slower at higher KOH concentrations. Both of these trends favor the choice of high KOH concentrations.

However, the ZnO contained in the negative electrode is highly soluble in concentrated KOH electrolyte, and this high solubility exacerbates Zn redistribution. Therefore, there is a strong incentive to select lower KOH concentrations to reduce Zn species solubility.* The lower limits of KOH concentration that support NiOOH, AgO, O_2 and MnO_2 electrode operation have

* An exception is the strategy for choosing the electrolyte composition in Zn/air cells where the Zn electrode operates as an electrode of the first kind. In this case, the specific energy of the battery is proportional to the quantity of Zn that can be dissolved in the electrolyte, so there is an incentive to choose a high KOH concentration.

not been investigated in detail. However, it has been shown that the NiOOH electrode can function in 15-20 wt% KOH (31). A useful strategy is to operate the cell at as low a KOH concentration that can be tolerated by the positive electrode, and add indifferent supporting electrolyte to provide adequate ionic conductivity. The solubility of Zn species can then be minimized without a significant degradation of battery specific power.

Table 5 lists many of the electrolyte compositions that have been investigated for possible use in secondary Zn cells. Alternative electrolytes, such as those containing fluoride, borate, phosphate, arsenate, and carbonate ions, have been shown to exhibit reduced Zn species solubility and extend Zn/NiOOH cell cycle life. The solubility of ZnO in alkaline-fluoride electrolyte (15 wt% KOH - 15 wt% KF) is only one-fourth of its solubility in 30 wt% electrolyte, and the Zn redistribution rate in model Zn/KOH-KF/NiOOH cells was shown by Nichols *et al* (31) to be a factor of four slower than that of cells cycled in 30 wt% KOH. Zinc electrodes cycled in electrolytes with low KOH content had a desirable porous structure (~0.5 μ particle size).

Most developers of Zn/NiOOH batteries add ~1 wt% LiOH to the KOH electrolyte; the LiOH addition enhances NiOOH electrode charge acceptance. Sodium hydroxide additions to KOH electrolyte have been shown to extend Zn/NiOOH cell lifetimes when the cell is cycled at >50°C (352,353). Table 5 lists the numerous metal oxides that have been tried as electrolyte additives. Many of these additives are only sparingly soluble in aqueous electrolytes, so they probably function similarly to additives included in the electrode mixture. For example, lead salts and certain other compounds are known to suppress Zn dendrite growth when added to the electrolyte. Other electrolyte additives have been investigated as Zn complexing agents, such as EDTA (361) and caprolactam (360). Mixed organic-inorganic electrolytes (CH_3OH-KOH) were used by Dzieciuch *et al* (125) to suppress the solubility of Zn species in Zn/MnO_2 cells, and there has been one study of polymer electrolytes (317).

Table 5. References to Various Electrolyte Compositions used in Zinc Secondary Cells.

Composition*	References
KOH-KF	31,32,307,327,337-340
K_3BO_3, K_2HBO_3, Na_3BO_3, Na_2HBO_3	31,34-36,337,339,341-343
K_3PO_4, K_2HPO_4, Na_3PO_4, Na_2HPO_4	34-36,337,341,342,344
K_3AsO_4	34-36,341,342
KOH-K_2CO_3, NaOH-Na_2CO_3	345-349
KOH-$K_3Fe(CN)_6$, NaOH-$Na_3Fe(CN)_6$	131,132,350
KOH-$In(OH)_3$	278,293,351
KOH-K_2SiO_3, NaOH-Na_2SiO_3	100,102,103,321,337
NaOH additions	352,353
LiOH additions	278,354,355
LiO_2CH additions	356
Na_2S, $Na_2S_2O_3$ additions	321
CdO additions	357
PbO additions	172,358
TeO additions	358
FeO additions	290
GeO additions	288
CoOH additions	293
sorbitol additions	102,103
ammonium compound additions	359
caprolactam additions	360
EDTA additions	361
KOH-CH_3OH	125
polymer electrolyte	317

* Entries labeled "additions" imply additions to aqueous KOH electrolyte.

Most Zn/air cell designs rely on *high* concentrations of Zn in the electrolyte to attain high battery specific energy, so compositions have been selected to provide high Zn species solubility. Silicate additions had been considered to be most effective in this regard*, and it was reported that extremely high Zn concentrations could be obtained in SiO_3^{2-}-containing alkaline electrolytes (362). This report prompted investigations of the structure of such electrolytes, however other studies have confirmed only modest increases of Zn solubilities in SiO_3^{2-}-containing electrolytes (102). The mechanism for enhanced Zn solubility appears to be silicate adsorption on ZnO particles, which blocks further Zn precipitation (363). A recent investigation of alternative agents to enhance the solubility of Zn identified LiOH as a beneficial additive (103).

Iron compounds are generally recognized as harmful contaminants in secondary alkaline Zn cells, because they can catalyze H_2 evolution on the Zn electrode and thereby complicate sealed-cell operation. Methods for the removal of Fe impurities from alkaline electrolytes have been investigated (364).

Separators

Separators provide a barrier to Zn dendrite growth, and can play an important role in determining the transport of species between the negative and positive electrode compartments. A review by Bennion (365) provided a thoughtful analysis of the separator properties that are required for a long-lived Zn/NiOOH cell, and included an extensive bibliography of separator R&D before 1980.

The separators used in secondary alkaline Zn cells range from the coarse screens in $Zn/Na_3Fe(CN)_6$ cells (366), which are primarily intended to alter the electrolyte flow pattern, to highly selective cation-exchange membranes such as Nafion, used in the same cell. Table 6 lists many of the separator materials that have been investigated during the past 15 years. Microporous separators are commonly used in Zn/NiOOH, Zn/AgO, Zn/MnO_2 and Zn/air cells.

* Discussed in the "Fundamental Studies" section of this review.

Table 6. References to Separator R&D.

Type/Composition	References
Organic Microporous Separators	
polypropylene	52,367-369
Vinylon	368
polyethylene	192
polytetrafluoroethylene	370
cellulose acetate - polyphenolquinoxaline	371,372
Nylon	42,103,369,373
polyvinyl alcohol	374,375
cellophane	18,29
polystyrene	376
acrylonitrile-vinyl chloride	224
polyamide	219,248,377
Inorganics and Impregnated/Coated Polyolefins	
metals, metal oxides, metal hydroxides*	21,116-118,172,377-387
polyvinyl alcohol	42,157,223,224,385
H_3BO_3	42,157,223,224,385
H_2O	388
surfactants, gels	389-391
Daramic (SiO_2/polyethylene)	104
inorganic/organic	392,393
asbestos, ZrO_2 cloth	98,106
Ion-exchange Membranes	
radiation grafted	394
supported liquid	395,396
anion exchange	397

* AgO, Al_2O_3, $Ba(OH)_2$, CaO, $Ca(OH)_2$, Cd, CeO_2, CuO, FeO, MgO, $MgSiO_3$, Ni, $Sr(OH)_2$.

The rate of Zn material redistribution is slower in Zn/NiOOH cells using microporous separators, compared to Zn/NiOOH cells using ion-exchange membrane separators (367). Microporous separators provide a barrier to Zn dendrite propagation, but exhibit little selectivity in the transport of ionic species. The separator material pore size and tortuosity play an important role in determining its effectiveness in resisting Zn dendrite penetration; small pore sizes are preferred (367). Polypropylene has been the favored microporous separator material in Zn/NiOOH batteries (12), and cellophane has been the material of choice for Zn/AgO battery separators (114). However, cellophane undergoes oxidative degradation in KOH electrolyte, particularly at lower concentrations (371). Mixtures of cellulose acetate and polyphenolquinoxaline are more stable than cellophane (372). Electrically rechargeable Zn/air cells using bifunctional air electrodes place severe demands on the separator material. The separator must not only provide a barrier to Zn dendrite growth, but also withstand chemical attack by the peroxyl ions generated at the air electrode. Asbestos and ZrO_2 cloth separators have been used in such cells (106).

Composite separator systems have been investigated in an attempt to combine favorable properties of different materials. Microporous polymers have been impregnated or coated with various metals, metal oxides, metal hydroxides, silicates, liquids and surfactants. Metals such as Ni, Cd and Mn (21,116-118,378,379,387) have been coated onto polyolefin separator materials, and they may slow Zn dendrite propagation by oxidizing the tip of the dendrite when it reaches the separator. Other metal compounds may act similarly, provide some selectivity against $Zn(OH)_4^{2-}$ ions, and/or simply serve as "fillers." Surfactants have been used to promote wetting of the separator, thereby increasing its ionic conductivity (389). An interesting composite is the inorganic-organic separator (392). These materials have typically used SiO_2 or Al_2O_3 with a polyvinyl alcohol binder, but they tend to be brittle. Combinations such as polyvinyl pyridine with $MgSiO_3$-$ZrSiO_3$ on an asbestos substrate tend to be more flexible (393).

Ion-exchange membranes have been produced by various methods, including radiation grafting ionic groups onto polymeric substrate materials (394). Cation-exchange groups such as

acrylic ions are typically used (395), although many other negatively charged moieties are suitable. Cell lifetimes have not generally been improved by using cation-exchange membranes, probably because of water transport problems, which may cause rapid active material redistribution* and dehydration of the Zn electrode. Bennion has stated that anion-exchange membranes would be superior to cation-exchange membranes (365). Supported-liquid membranes, which are anion-exchange organic liquids (*e.g.*, crown ethers, hydrocarbons, amines) constrained in a microporous polymeric material (396,397), and chemically prepared anion-exchange membranes have been developed (398). Unfortunately these efforts have not succeeded in producing a stable material, although they represent promising avenues of investigation.

Multilayer separator systems have been developed, with the layers exhibiting different transport properties (25). One variation of this approach used a multilayer, fibrous separator system with the separators aligned so that the fibers were oriented in different directions (399). In another version, the separator layers had different pore sizes, with the smallest pore sizes in the separator layer closest to the Zn electrode (400).

Cell Charging

Numerous investigators have evaluated charging modes that differ from simple DC current. Direct-current charging can lead to high overpotentials on the Zn electrode near the end of charge, which can lead to dendrite formation and cell shorting. The simplest non-DC charge waveform is termed "taper charging," and calls for a constant current early in charge, until a certain cell voltage is reached*, after which a constant cell voltage (and decreasing current) is applied or the charging process is halted (30,401-403). This procedure helps avoid high Zn electrode overpotentials at the end of charge, thereby slowing the rate of Zn dendrite initiation and propagation. The cell pressure has also been used to trigger charge termination (37).

* Osmotic pumping theory of Zn material redistribution, to be discussed in the section on mathematical modeling.

* The inflection point in the charging voltage-time curve may also be used (401).

The use of auxiliary electrodes during cell charging was discussed in a previous section of this review (see references 69-77). Placement of a diode and a properly sized resistor between the Zn electrode and a H_2-absorbing auxiliary electrode has been used to control pressure build-up in Zn/NiOOH cells during charge (405).

Pulse charging has long been recognized as a means of extending the lifetime of secondary Zn cells (406,407). Pulse current, pulse-reverse current, alternating current superimposed on direct current, alternating voltage, alternating voltage superimposed on constant voltage, and other forms of non-DC charging have been investigated (21,32,37,38,39,42,87,127,408-412). The effectiveness of pulse-charging depends on parameters such as the frequency, peak current density (pcd), and on-time/off-time ratios. For example, high-frequency pulse charging was found to have little effect on the lifetime of Zn/NiOOH cells (408), whereas low-frequency pulse-current charging (<10 Hz) has been shown to have a marked effect on Zn/NiOOH cell capacity retention (37,38,412). Katz *et al* (412) analyzed the Zn electrode from a Zn/NiOOH cell pulse-charged at 30 ms on/90 ms off (8.3 Hz) at a pcd of 15.7 mA/cm^2, for 125 deep-discharge cycles. Scanning electron micrographs showed that the pulse-charged Zn electrode had a more densely textured surface than a constant-current charged electrode. This effect may be attributed to the more-numerous nucleation sites generated during pulse-charging (413,414).

The use of vibrating electrodes and other means to agitate the electrolyte during charging was discussed in the earlier section of this review that discussed Zn/NiOOH cell designs. Another novel charging method is to sparge the electrolyte with gas bubbles to mix the electrolyte (415).

FUNDAMENTAL STUDIES

Cell Thermodynamics

The Zn electrode equilibrates with $Zn(OH)_4^{2-}$ ion in strong alkaline electrolyte, as shown on the Pourbaix diagram for this system (416). The activity coefficients for the common alkaline electrolytes used with Zn electrodes have been recently tabulated (417). The rest potential of the Zn electrode in various compositions of alkaline electrolytes has been measured by several workers (418-420), and a recent investigation by Isaacson *et al* covered a range of KOH and $K_2Zn(OH)_4$ (up to and including the $K_2Zn(OH)_4$ saturation value) at various temperatures (421). Chen and Gibbard (422) measured the Zn/NiOOH thermoneutral potential to be 1.86 V, which implies that the cell should be nearly isothermal during charge, but may require cooling during high-rate discharge

Zinc Electrodeposition

Numerous investigators have studied the kinetics of Zn deposition from alkaline electrolyte (423-428), and detailed mechanisms have been proposed. Reported values of the exchange current density for Zn electrodeposition range over two orders of magnitude (1-100 mA/cm^2), probably because of variations in the smoothness of the Zn electrode. Reaction orders in the linear and Tafel overpotential regions have been determined (429-431), and rotating-disk studies of Zn electrodeposition at solid and polymer-bonded porous electrodes have been carried out by Hampson *et al* (433-435), who also extended their investigations to include cycling studies (435). Investigations of the impedance characteristics of Zn electrodeposition led to the conclusion that there is an autocatalytic step involving a Zn surface species (436-438).

Most of these investigations of Zn electrodeposition were carried out at solid Zn electrodes with large volumes of electrolyte. Cyclic voltammograms show that the reduction process in pasted Zn electrodes, in a minimum amount of electrolyte, differs from that at solid electrodes in

$K_2Zn(OH)_4$-containing electrolyte (299). A long-standing question is the mechanism for reduction of ZnO to Zn, which may proceed by a solid-state (439) or solution-precipitation (440,441) mechanisms. There is evidence that the direct solid-state mechanism accounts for only a small fraction of the reduction current (439). There has been one study of ZnO crystallization in $K_2Zn(OH)_4$-containing electrolyte using an isotope tracing method (442).

An interesting phenomenon is the oscillation of the Zn electrode potential observed at high current densities during Zn electrodeposition (443). It was postulated that the oscillations are caused by local depletion of Zn species in the electrolyte. The resulting concentration overpotential leads to H_2 evolution, which stirs the electrolyte and replenishes the local Zn species concentration, thereby establishing a periodic process (444). The H_2 overpotential (445) and rates of H_2 evolution (446) have been measured on Zn and various Zn alloys.

The morphology of Zn electrodeposited from alkaline electrolyte depends strongly on the electrode overpotential and the degree of electrolyte stirring. In general, mossy Zn is obtained at low overpotentials, epitaxial Zn layers are obtained at moderate overpotentials, boulder-type deposits are obtained at high overpotentials, and dendritic Zn is obtained at the limiting current. The indentity and structure of the substrate also has a strong effect on the Zn deposit character. Investigations of Zn electrodeposition on various substrates have been carried out, including Cu, Au, Cd, Zn, Pb, Tl, Sn, In, Ag, carbon and steel (447-455). Studies by McBreen *et al* (447-450) have shown that Cu substrates produce hexagonal Zn deposits oriented parallel to the basal plane; Pb, In and Sn substrates produce compact Zn oriented perpendicular to the basal plane; and Cd substrates produce Zn deposits of intermediate character. These investigations have encouraged the use of Pb and Cd substrates for secondary Zn battery electrodes.

The characterization, understanding and control of Zn dendrite initiation and propagation has been a subject of study in many laboratories, for many years. Recent investigations have focussed on the critical overpotential for Zn dendrite formation (456), and the use of impedance

measurements to characterize dendritic Zn growth (457). Various Pb salts have been effective in controlling Zn dendrites (457-459), along with substances like antimony, glue, polyethylene glycol, surfactants, and various other organic compounds (324,459-462).

Zinc deposition from alkaline electrolytes has been studied using *in situ* Raman spectroscopy (463) and video microscopy (464). The texture of porous Zn electrodes has been characterized by impedance techniques (465-467).

Zinc Electrodissolution

The characteristics of Zn electrodissolution determine the specific power and capacity of both primary and secondary alkaline Zn batteries, and have thus received considerable attention. The kinetics and mechanism of active Zn electrodissolution have been studied by several groups (424,427,468-470). The pasted Zn electrode exhibits only a small overpotential, even during high-current discharge. In general, active Zn dissolution is followed by the precipitation of two different types of films: the so-called Type I film, which is porous and non-passive, and the Type II film, which is coherent and passive. Zinc passivation has been characterized by various techniques (471-479), and the onset of passivation depends strongly on the electrolyte flow rate (103,470,471,479) and the presence of certain ionic species in the electrolyte, particularly SiO_3^{2-} (102,103,362,478-481) and Li^+ (103). A study by Liu *et al* (475) showed that Zn is not likely to passivate in porous electrodes discharged at moderate rates, so long as a high specific surface area is maintained (as the electrode is cycled, material redistribution and "densification" tend to reduce the specific surface area of the Zn active material). Ellipsometry and coulometry have been used to study Type I passive films on Zn in alkaline (482-484) and neutral (485) electrolytes. The effect of CO_3^{2-} ions on Zn electrodissolution has been characterized using cyclic voltammetry (486,487).

A particularly useful experimental apparatus for the study of Type I film formation is a so-called model pore electrode. This electrode is constructed so that a thin film of electrolyte lies on

a planar Zn electrode, and a transparent cover glass permits *in situ* microscopy of the electrode surface as electrodissolution proceeds. This technique was first used by Katan and his co-workers to study Type I film formation on Zn (488-491), and has since been used by others (492,493). The film precipitation is seen as a "front" that moves from the mouth of the pore to its root as the discharge proceeds. Weaver *et al* have extended this technique by using probe beam deflection to measure local concentration gradients in the pore (493). Figure 7 shows a schematic diagram of a model pore cell with probe beam deflection. One optical investigation of Zn particle movement in a restricted electrolyte-filled tube showed that fragmented dendritic Zn clusters could migrate rapidly in an electric field (494). This observation provides a possible mechanism to explain the rapid rate of Zn material movement that is sometimes seen in secondary cells. A related study of Zn species diffusion was done by Kautz and May (495).

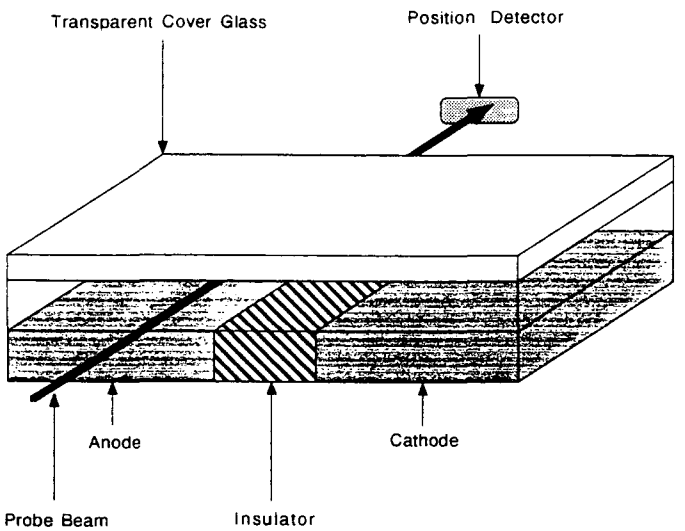

Figure 7. Schematic diagram of a model pore electrode with probe beam deflection to measure local concentration gradients.

Zinc Corrosion

Little fundamental research has been carried out on Zn corrosion in alkaline electrolytes during the past 15 years. An interesting investigation of Zn corrosion showed that Zn alloys that

are corrosion-resistant in sheet or rod form may be susceptible to corrosion when prepared as high-area porous electrodes (496). There has also been a survey of the effect of various additives on Zn porous electrode corrosion rates (497).

Electrolyte Properties

Many of the basic physicochemical properties of KOH-$K_2Zn(OH)_4$ have been tabulated (498). The ionic conductivity of KOH-$K_2Zn(OH)_4$ mixtures has been measured over a wide temperature range (499), and has been recently measured in $K_2Zn(OH)_4$-supersaturated solutions (500). The solubility of ZnO and $Zn(OH)_2$ in KOH is known to be a strong function of the KOH concentration (501,502); it varies approximately as the square of KOH concentration. Electrodissolution of Zn in alkaline electrolytes can produce $Zn(OH)_4^{2-}$ concentrations at least three times the saturation value, and many months may be required for equilibrium to be attained, when ZnO is the final solid product (503). There is a strong incentive to understand the structure of KOH-$K_2Zn(OH)_4$ solutions, to develop means of reducing the Zn solubility (for Zn electrodes of the second kind) and increasing the Zn solubility (for Zn electrodes of the first kind). There has been considerable interest in the structure of the Zn species in concentrated alkali (362,363, 478-481,503-510), including measurements of the electrolyte ionic conductivity (500), uv spectra (506,507), refractive index (493,508), extended X-ray fine structure (363), and Raman spectra (509,510). It is now well established that the $Zn(OH)_4^{2-}$ ion has a tetrahedral structure, with hydroxy-bridged aggregates at high concentrations (510).

Carbonate ions have been considered to be detrimental to the operation of secondary Zn cells (346), however recent work has shown that carbonate additions extend the lifetime of Zn/NiOOH cells (345,347). Good methods have been developed for the rapid determination of the CO_3^{2-} content of alkaline-zinc electrolytes (511), and the carbonation of zincate solutions has been investigated (512).

Mathematical and Phenomenological Models

Perhaps the most vexing problem facing developers of secondary Zn cells is active material redistribution (shape change) on the Zn electrode, and shape change is the focus of many of the mathematical and phenomenological models that have been developed. The shape change problem has been recognized for years, and many of the investigations described in the previous sections of this review may be regarded as "fixes" for shape change. However, none of these "fixes" has worked to the extent that shape change can be controlled in quiescent electrolyte. It is instructive to consider various models that have been proposed to explain the phenomenon of shape change:

1. *Osmotic Pumping.* Choi, Bennion and Newman proposed that electrolyte flows generated by osmotic pressure gradients in Zn/AgO cells with ion-exchange membrane separators lead to Zn shape change (513). During charge, $K_2Zn(OH)_4$-lean electrolyte flows from the center of the cell toward the reservoir region near the edges of the electrode, and during discharge $K_2Zn(OH)_4$-supersaturated electrolyte flows from the reservoir region toward the center of the cell. The net result is a rapid transfer of Zn from the edges of the cell toward the center. A detailed phenomenological model was developed, and experimental measurements on model cells confirmed key aspects of the model (514).

2. *Nonuniform Current Distribution.* McBreen proposed that the degree of nonuniformity of the current density in Zn/KOH/NiOOH cells is unequal between charge and discharge, which leads to concentration differences that vary between charge and discharge (515). Experiments with sectioned electrodes confirmed the nonuniformities in current density distribution.

3. *Autocatalytic Zinc Dissolution.* McKubre proposed that the kinetics of Zn dissolution in KOH electrolyte includes an autocatalytic step, whereby the presence of $Zn(OH)_4^{2-}$ ion catalyzes further Zn dissolution (516). Zn dissolution would be enhanced near electrode edges where the local current density is high, leading to a gradual loss of Zn material from the electrode periphery.

4. *Nonuniform Current Efficiency.* Energy Research Corporation proposed a model whereby the difference between the OH^- concentration near the electrode periphery and the OH^- concentration near the center of the electrode causes H_2 evolution at the electrode periphery during charge, thereby reducing the local current efficiency for Zn electrodeposition (20). During discharge, the Zn dissolution rate is greater near the electrode periphery. The net result is more Zn deposition at the electrode center and less near the periphery.

5. *Local Zinc Oxidation.* Oxygen gas generated at the NiOOH electrode is more readily transported to the periphery of the Zn electrode, compared to the central region of the electrode. The O_2 gas then oxidizes Zn (to soluble ZnO) more rapidly at the electrode periphery, leading to gradual loss of Zn material from the edges of the electrode.

It is possible that there are Zn electrode structures and modes of Zn electrode operation for which each of the models is valid, and it is also possible that shape change is a combination of effects. It is disconcerting that none of the models predicts "reverse" shape change, *i.e.*, movement of Zn from the center of the electrode toward the edges. Figure 8 shows both types of shape change in Zn/NiOOH cells that are identical, save for the electrolyte composition.

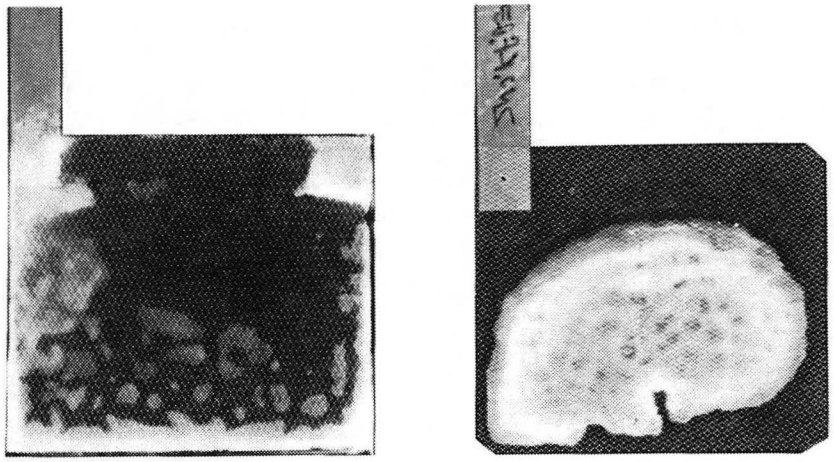

Figure 8. Shape change patterns on Zn electrodes from two different Zn/NiOOH cells. The electrode on the left-hand side was cycled in a Zn/NiOOH cell with 31 wt% KOH electrolyte for 106 cycles, and the electrode on the right-hand side was cycled in a Zn/NiOOH cell with 3.5 M KOH - 3.3 M KF electrolyte for 280 cycles.

Mathematical models of the processes in Zn alkaline secondary cells have addressed transport processes in the vertical direction* (Choi *et al, op.cit.*) and the horizontal direction (517,518). This horizontal-direction model predicted that Zn precipitation could lead to loss of capacity by pore plugging. Miller *et al* have developed a comprehensive one-dimensional (vertical direction) model of the Zn/NiOOH cell that accounts for non-uniform current density distribution (519). Isaacson *et al* developed a two-dimensional mathematical model of the Zn/NiOOH cell that predicts local reaction profiles in the Zn electrode (520). Gu used empirical current-voltage data to predict Zn/NiOOH cell performance as a function of key parameters (521).

Other mathematical models have addressed transport processes in the separators of Zn/AgO cells (522) and the current distribution in Zn/NiOOH and Zn/AgO cells (523-528). Investigators at Argonne National Laboratory used sectioned electrodes to confirm predictions of current density distribution (524), and the results showed a penetration depth of only ~5×10^{-3} cm. It is well known that 1-mm-thick Zn electrodes have high active material utilization, and the movement of a reaction front through the electrode during discharge can explain the discrepancy. There has

* Parallel to the plane of the electrodes.

been one mathematical model of the vibrating Zn electrode (529), which confirms the reason for using such electrodes, *i.e.*, to avoid steep concentration gradients.

Zinc Species Migration to the Positive Electrode

It has been recognized that Zn species migration to the positive electrode in Zn/NiOOH cells can lead to capacity loss (530-532). Proposed mechanisms for the observed capacity loss include mechanical blocking of the NiOOH electrode by precipitated ZnO or $Zn(OH)_2$, formation of a Zn-Ni oxide compound (533), or enhanced swelling of the NiOOH active material caused by the presence of $Zn(OH)_4^{2-}$ in the electrolye-filled pores of the NiOOH electrode (diffusion hindrance). There does not appear to be conclusive evidence to favor one mechanism over another. Chemical analyses of NiOOH electrodes recovered from cycled Zn/NiOOH cells show substantial Zn content (18). X-ray fluorescence analyses of cycled NiOOH electrodes from Zn/NiOOH cells revealed a nonuniform distribution of Zn in the NiOOH electrode, with greater Zn content near the center of the NiOOH electrode (534).

It has also been reported (535) that ZnO precipitates in the air electrode in Zn/air batteries, resulting in unwanted changes in the air electrode wetting properties and pore structure. This problem can occur near the end of charge when the electrolyte becomes less alkaline because of local H_2O generation at the air electrode, and near the end of discharge when the electrolyte can become supersaturated in $K_2Zn(OH)_4$, thereby promoting ZnO precipitation. Zinc precipitation also occurs in AgO electrodes (532) and MnO_2 electrodes (128).

There have been fundamental investigations of the effect of Zn species on the electrochemical behavior of $Ni(OH)_2$ films (536,537).

Cell Cycle-Life Performance

Numerous cycle-life tests of secondary Zn cells are described in the previously cited references to battery development and cell component R&D. Most of these tests were of an empirical

nature, aimed at identifying components and configurations that maximize cell cycle-life performance.

Seiger performed a study of the lifetime of several battery systems as a function of depth of discharge, and concluded that the cycle life of a Zn/NiOOH cell is a strong function of its depth of discharge, with shallow depths of discharge leading to greatly enhanced lifetimes (538). The lifetime of a 95-Ah Zn/NiOOH cell, cycled at various depths of discharge, is shown in Fig. 9, along with the total charge throughput. It can be concluded that cycling a Zn/NiOOH cell at shallow depths of discharge will extend its lifetime, and result in increased energy delivery.

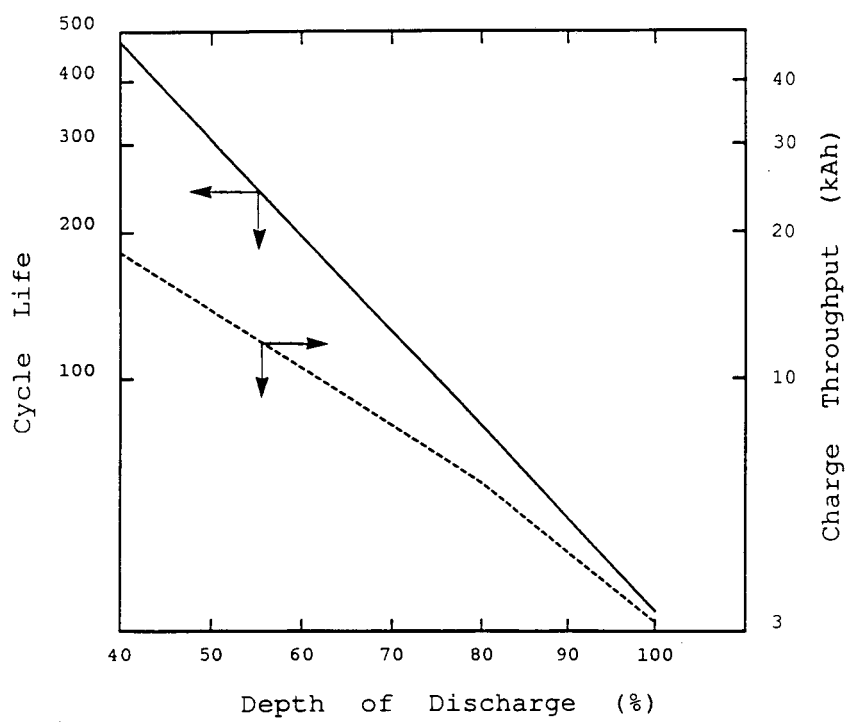

Figure 9. Lifetime and charge throughput of a 95-Ah Zn/NiOOH cell constructed by Yardney Electric Corporation, cycled at various depths of discharge (538).
_____ Cycle life
---------- Charge throughput

Hamby *et al* sampled electrolyte concentrations in secondary Zn cells to test features of the osmotic pumping theory of shape change (439,540). Hendrikx *et al* measured local electrode potentials to estimate the extent of shape change (541) and Isaacson *et al* measured Zn and Cd micro-reference-electrode potentials to derive local KOH and $K_2Zn(OH)_4$ concentrations in a

porous Zn electrode (542). The rate and extent of Zn electrode material redistribution have been measured by several investigators (31,32,514,515,543-548), including cells with controlled current distribution (545), and using radiotracer techniques (547-549).

There have been few reports of controlled test of cells that combine several features that are known to individually extend Zn cell lifetimes. Adler *et al* (32) prepared cells that combine three of the modifications discussed above in a single cell. Pulse-charging, alkaline-fluoride electrolyte, and a 25 wt% $Ca(OH)_2$ electrode can extend the cycle-life of the Zn/NiOOH cell well beyond its present limits. Some data for a pulsed-charged ZnCa/KOH-KF/NiOOH cell are shown in Fig. 10. This cell exhibits superior capacity retention, compared to a Zn/KOH/NiOOH cell charged under constant-current conditions. These results are particularly interesting because the $Ca(OH)_2$ and KF additions were compensated by reducing the Zn and KOH content so that the advanced ZnCa/KOH-KF/NiOOH cell has nearly the same specific energy (Wh/kg) as its standard Zn/KOH/NiOOH counterpart. However, these results are not reproducible, apparently because of difficulty in forming calcium-zincate compounds in fluoride-containing electrolytes; CaF_2 formation is thermodynamically favored over calcium zincate. Cairns *et al* are evaluating other reduced-Zn-solubility electrolytes that favor the formation of insoluble calcium zincate compounds.

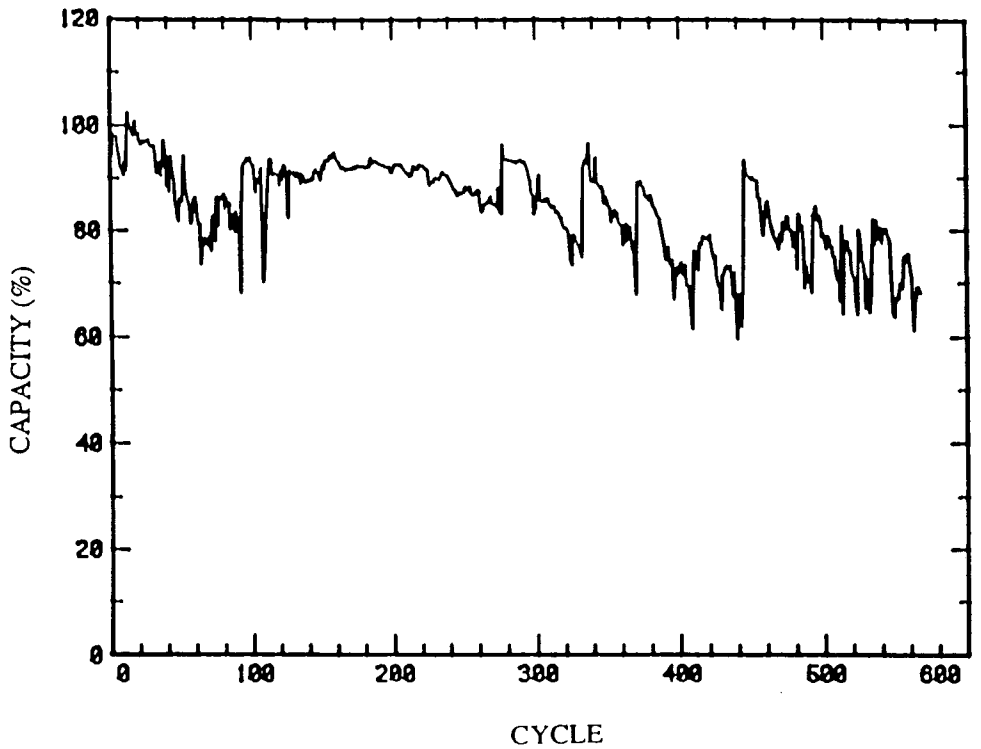

Figure 10. Cycle-life performance of a pulse-charged Zn-Ca/KOH-KF/NiOOH cell (32). Standard constant-current-charged Zn/KOH/NiOOH cells typically lose >30% of their original capacity after about 100 cycles.

FUTURE PROSPECTS

Significant increases in the lifetime of Zn/NiOOH cells have poised this technology for entry into commercial portable power applications, however longer lifetimes are needed before a viable electric vehicle battery can be built. Recent investigations of the pulse power characteristics of NiOOH electrodes (550) confirm that the Zn/NiOOH cell is suitable for high-power applications as well.

Tests of new designs for Zn/air cells suggest that the Zn electrode may not be the life-limiting component. However, the voltage efficiency and lifetime of the bifunctional air electrode must be improved before electrically rechargeable Zn/air cells can be in widespread use. Some interesting new designs of mechanically rechargeable Zn/air cells have been developed, and they will be useful for special-purpose applications.

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Zinc/silver oxide batteries continue to be the system of choice for selected defense applications, however their high cost and short lifetime will continue to preclude their use in commercial markets.

Secondary alkaline Zn cell R&D has made great strides during the past fifteen years. There is strong interest in cells of this type, and we can expect similar advances during the years ahead.

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