CHAPTER II

High Energy Density
Zinc-Air Electrochemical Power Source:
A Review

2.1 Introduction

An electrochemical power source that utilizes oxygen as the cathode active material possesses many attractions. Prominently, oxygen is readily available and inexhaustible from the ambient air, thus resulting in a lightweight electrochemical power source with a free cathode reactant. Since the cathode reactant is not incorporated into the air-electrode type electrochemical system, its capacity is mainly determined by the anode reactant. Hence the volume of the whole system can be used by the anode reactant, producing a high energy density electrochemical power source.

In view of this performance potential, much effort has been devoted towards the development of metal-air electrochemical power systems. Other advantages of the metal-air type of system include [*Hamlen, 1995*] flat discharge voltage, the capacity is independent of load and temperature within the operating range, long dry storage, ecological friendly and low cost on metal use basis. Although progress has been made with this system over the decades, a number of significant limitations still remain. Among others; the electrolyte drying out and carbonation once exposed to air, air-cathode flooding, low power output, limited operating temperature range due to its aqueous-based electrolyte and metal anode corrosion in a caustic alkali electrolyte.

Metals that have been considered for use in the metal-air electrochemical power source are aluminum [*Doche et. al, 1997; MacDonald and English, 1990; Mukherjee and Basumallick, 1993; Niksa and Wheeler, 1988*], cadmium [*Wagner, 1968; Wagner, 1972*], calcium [*Charkey and Dalin, 1966*], cobalt [*Akuto et. al, 2001*], ferum [*Anderson and Ojefors, 1974; Cnobloch et. al, 1974; Kannan and Shukla, 1991*], gallium [*Jahn and Plust, 1963*], lithium [*Abraham and Jiang, 1996; Abraham and Jiang, 1996a; Littauer and Tsai, 1974*], magnesium [*Charkey and Dalin, 1966; Hamlen et. al, 1969; Kent and Carson, 1966*] and zinc [*Appelt and Malanowski, 1979; Appleby and Jacquier, 1976/77; Foller, 1986; Goldstein et. al, 1999; Jiricny et. al, 2000; Muller et. al, 1994; Muller et. al, 1998; Wei et. al, 2000*]. Another unique metal-air system is sodium amalgam-air [*Yeager, 1963*], which operates at the high temperature of 135°C. Some of the properties of the metal-air cells that have received considerable attention are listed in Table 2.1.

Table 2.1. Metal-air cells properties. After *Hamlen* **(1995)**.

Metal Anode	Electrochemical Equivalent of Metal ($Ah\ g^{-1}$)	Theoretical Cell Voltage (V)	Valence Change	Theoretical Specific Energy of Metal ($kWh\ kg^{-1}$)	Practical Operating Voltage (V)
Li	3.86	3.4	1	13.0	2.4
Ca	1.34	3.4	2	4.6	2.0
Mg	2.20	3.1	2	6.8	1.2-1.4
Al	2.98	2.7	3	8.1	1.1-1.4
Zn	0.82	1.6	2	1.3	1.0-1.2
Fe	0.96	1.3	2	1.2	1.0

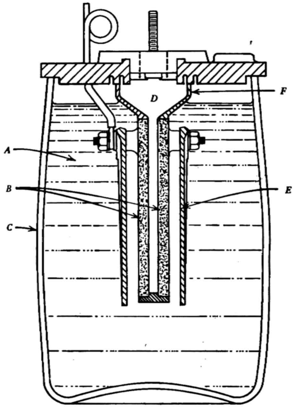
In comparison with its counterparts, zinc possesses several advantages. It is the most electropositive metal that is relatively stable in caustic alkali electrolyte and it is the most active metal that can be electrodeposited from an aqueous bath [*Huot, 1997; Linden, 1995; McBreen, 1984*]. These attractive electrochemical properties of zinc, besides its abundance and low cost, make it the most widely used active material in primary battery industry. Its presence in the commercial market has been over a century. Moreover, zinc is compatible with most conventional positive electrode materials, which makes it an effective anode material for a large number of primary and secondary batteries. The comparison of various types of zinc batteries is given in Table 2.2.

2.2 Present Status of Zinc-Air Batteries

A wide variety of zinc-air batteries have been developed. At present, they are commercially available in primary and electrically rechargeable types, whereas the mechanically rechargeable prototype offers a promising prospect in the near future. Primary cells have been in commercial production since the 1920's in the form of large wet cells (up to 2000 Ah) for remote power such as railway signaling, marine navigation lighted aids (buoys) and lighthouses [*Schumacher,1971*]. Solar cells and other secondary cells now substitute many of these applications. Figures 2.1 and 2.2 illustrate the examples of the early wet cells.

Table 2.2. Comparison of various commercial zinc batteries. After *Huot* **(1997)** and *Linden* **(1995a)**.

Electrochemical System		Properties		
			Practical Energy Density	
Type	IUPAC	OCV (V)	Gravimetric ($Wh\ kg^{-1}$)	Volumetric ($Wh\ L^{-1}$)
Carbon zinc	$Zn / NH_4Cl / MnO_2$	1.5	85	165
Alkaline manganese	$Zn / KOH / MnO_2$	1.5	125	330
Mercury cell	$Zn / KOH / HgO$	1.3	100	470
Air cell	$Zn / KOH / O_2$	1.5	350	1050
Silver cell	$Zn / KOH / Ag_2O$	1.6	120	500
Nickel zinc	$Zn / KOH / NiOOH$	1.6	60	120
Zinc bromine	$Zn / ZnBr_2 / Br_2$	1.6	70	60



A: Electrolyte

B: Carbon panels on perforater metal

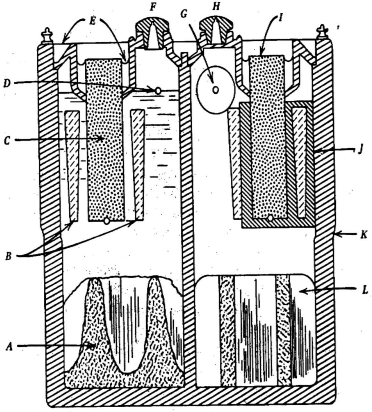
C: Glass jar

D: Air chamber

E: Zinc anodes

F: Plastic frame

Figure 2.1. A typical early zinc-air wet cell used for railway signal. After *Cahoon and Holland* **(1971)**.



A:	Lime cake after activation
B:	Zinc anode
C:	Carbon cathode
D:	Electrolyte-level indicator
E:	Top seal
F:	Filler plug
G:	Cast hydrated alkali with lime
H:	Filler plug with frangible seal
I:	Removable seal over carbon
J:	Cast hydrated alkali cylinder with lime addition
K:	Composition case
L:	Lime-cellulose cake

Figure 2.2. A general-purpose zinc-air wet cell, cross-sectional view of activated (left) and nonactivated (right).

After *Cahoon and Holland* (**1971**).

Currently, zinc-air button cells are used almost exclusively in miniature hearing aids, for both behind-the-ear and in-the-ear types. The button cells exhibit very good performance and have replaced both the mercuric oxide and silver oxide button cells of equivalent design. Compared to the mercuric oxide and silver oxide cells, the zinc-air cell is approximately 40 % lighter but possesses twice the capacity at the same operating voltage and besides, it is environmentally benign. Figure 2.3 illustrates this energy density advantage by comparing the construction of a zinc-air to a conventional button cell. Other primary zinc-air battery applications include pagers, voice transmitters, portable battery chargers, continuous power-on appliances and medical monitoring devices such as telemetry. The most common zinc-air button cell sizes (International Electrotechnical Commission (IEC) standards) are PR70, PR41, PR48 and PR44. Table 2.3 lists the commercially available zinc-air button cell and its properties.

The industrial low rate zinc-air batteries are of prismatic configuration. The design employs a flat plate electrode and a molded plastic case [*Putt and Merry, 1992*], as depicted in Figure 2.4. It is used in low voltage railroad track signal circuits and in lighted aids to navigation. In all these applications, the batteries are usually discharged at low current densities over long periods. Under deep discharge, the cell's performance is easily affected by the passivation of the zinc anode [*Bender et. al, 1995*].

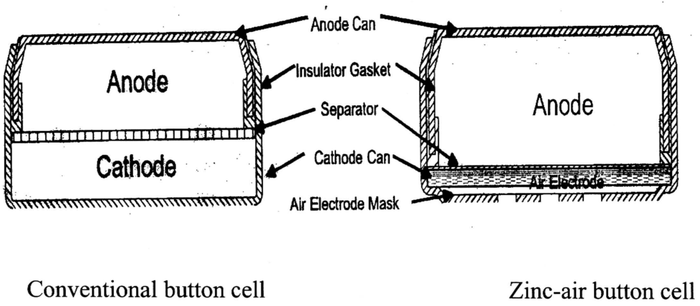


Figure 2.3. Comparison of a conventional button cell and a zinc-air button cell illustrating the energy density advantage of the latter.

Table 2.3. Commercial zinc-air button cells and their specifications.

Button Cell Size		Nominal Voltage	Dimension	Weight (Approximate)	Capacity (At rated load)	Rated Load
IEC [1]	ANSI [2] / NEDA [3]	V	Diameter (mm) x Height (mm)	g	mAh	Ω
PR63	7012ZD	1.4	5.8 x 2.15	0.2	33	
PR70	7005ZD	1.4	5.8 x 3.6	0.3	50-75	2200-3000
PR41	7002ZD	1.4	7.8 x 3.6	0.5	105-140	1300-1500
PR48	7000ZD	1.4	7.8 x 5.4	0.8	210-270	1300-1500
PR44	7003ZD	1.4	11.6 x 5.4	1.8	510-620	602-620
PR1662	7007Z	1.4	15.6 x 6.2	3.7	900-1100	470
PR2330	--	1.4	23.2 x 3.0	4.1	700-1050	50

[1] International Electrotechnical Commission Standards
[2] American National Standards Institute
[3] National Electronic Distributors Association

Note: These data are obtained from the product specification sheet of Energizer®, ZeniPower™, Ray-O-Vac, Toshiba and Panasonic.

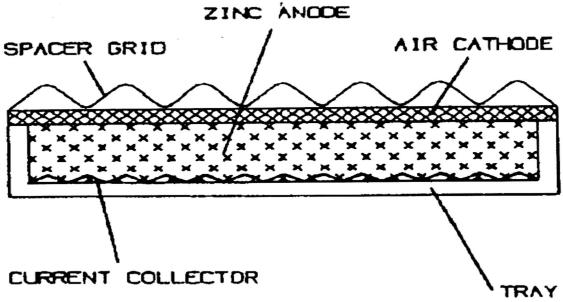


Figure 2.4. Zinc-air cell of prismatic design. After *Putt and Merry* (1992).

Most recently Electric Fuel Corp. introduced primary 3300 mAh zinc-air batteries for the cellular telephone market, the first kind of disposable type [*Goldstein et. al, 1999*]. The big advantage despite the fact that they are not rechargeable, is that their working capacities are several times that of present lithium-based types.

Both primary and secondary zinc-air batteries are in principle the same; both consist of a zinc anode, a caustic alkali electrolyte typically potassium hydroxide and a carbon based air cathode that is exposed to air. Further, during discharge in both types of batteries, the zinc anode is oxidized and oxygen from the ambient air is reduced at the carbon cathode. The difference is that the air cathode of the secondary battery permits the reaction to be reversed, i.e. oxygen is evolved at a reasonable rate during recharge, and the catalyst embedded in the air cathode must be resistant to oxidation due to the oxygen evolution during recharge.

AER Energy Resources Inc. under license from Westinghouse Electric Corp., Pittsburgh and Dreisbach Electromotive Inc. (DEMI), Santa Barbara [*Oman and Gross, 1995; Riezenman, 1995*] first introduced commercial electrically rechargeable zinc-air batteries for portable computer notebooks into the market. The AER energy system consists of zinc-air cells and a patented air manager which allows air flow to the cells during discharge and blocks air flow to the cells during charge and when not in use. Its conceptual battery design is depicted in Figure 2.5. The air manager system ensures that the airflow generates the required power and does not excessively dry the air cathode. Further as the airflow is blocked when there is no current drain, it would extensively reduce the self-discharge. The air cathode incorporates proprietary catalysts that are capable of absorbing oxygen into the battery on discharge and of expelling oxygen on recharge. They are claimed to produce a 150 Wh kg^{-1} energy density [*Harris and Schimpf, 1994; Schimpf 1995*]. The AER zinc-air battery system is a rectangular plate design, external, weighs 1361 g (3 lbs.) and its voltage is adjustable from 12 to 17 V [*McCormick, 1996*]. Nevertheless, to date there is no reported progress on this battery system.

The zinc-air battery ranks among the promising candidates for electric vehicle propulsion. Its theoretical specific energy density is several times higher compared to other counterparts. Several power systems considered at present for electric vehicle propulsion are listed in Table 2.4. Apart from the limitations associated with the air cathode, the development of electrically rechargeable zinc-air batteries has been frustrated by the problems of the zinc electrode. The lifetime of the zinc electrode is short and unpredictable when it is subjected to charge-discharge cycles [*McLarnon and Cairns, 1991*].

A new refuelable or mechanically rechargeable concept overcomes these issues. Zinc shape change and dendritic growth are essentially eliminated, the large voltage losses at the air electrode and its fast degradation due to oxygen evolution during charging is mitigated, and the battery cycle life is determined primarily by the life of the air electrode.

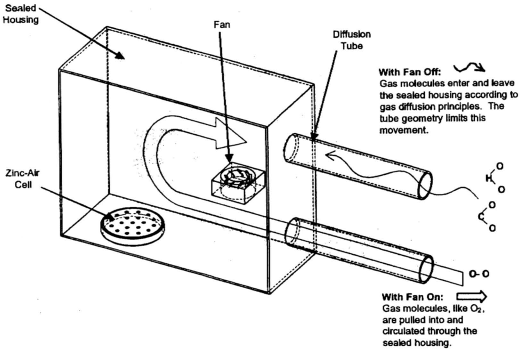


Figure 2.5. AER zinc-air battery design which employs a diffusion air manager. After *AER Energy Resources Inc.* **(2001)**.

Table 2.4. Comparison of various power systems developed for electric vehicle.

Power Source/System	Specific Energy Density[a] (Theoretical) Wh/kg	Specific Energy Density (Present Achievement) Wh/kg
Petroleum	80700[b]	20200[b*]
Zn –Air	1084	175[c]
Zn-Bromine	428[d]	200[b]
Na-S	758[e]	90-100[f]
Li-Ion	600	102[g]
NiMH	217	80[b]
Lead Acid	170	30[b]

[*]Considering a 25 % efficient engine; [a]*Will* (1998), or otherwise stated; [b]*Oman and Gross* (1995); [c]*Goldstein and Koretz* (1998) [d]*McBreen* (1981); [e]*Cairns* (1981); [f]*Braithwaite and Auxer* (1995); [g]*Iwahori* et al (2000)

Electric Fuel Limited (EFL) employed mechanically replaceable zinc cassettes, which when charged contain the zinc metal (Figure 2.6). After discharge the cassettes that now contains zinc slurry can be replaced with fresh cassettes in 30 seconds. A central electro-winnowing recharging facility is needed to restore the zinc electrode and thus no material is wasted. Figure 2.7 shows the schematic of Electric Fuel system operation. A 146 Wh kg^{-1} 650-kg unit has been tested in 3.5-ton German Deutsche Post Mercedes Benz vehicles and gave them 300-km range with a single charge and 110 km h^{-1} top speed [*Goldstein and Koretz, 1993; Goldstein and Koretz, 1998; Goldstein et al, 1999; Harats et al, 1995; Oman and Gross, 1995*].

Another refuelable zinc-air battery design utilizes zinc pellets 0.5-0.8 inch diameter suspended in KOH electrolyte [*Chesworth, 2001; Will, 1998*]. The prototype battery system developed by Metallic Power Inc., California, however, needs an extra component of electrolyte management unit to circulate the electrolyte and remove the reaction product to a special container. The refueling process, which at present takes 10 minutes, involves pumping the zinc pellets into the emptied battery hopper and removing the zinc oxide waste.

A list of developers known to be active in the zinc-air electrochemical system research and development activities, and their current achievements is presented in Table 2.5.

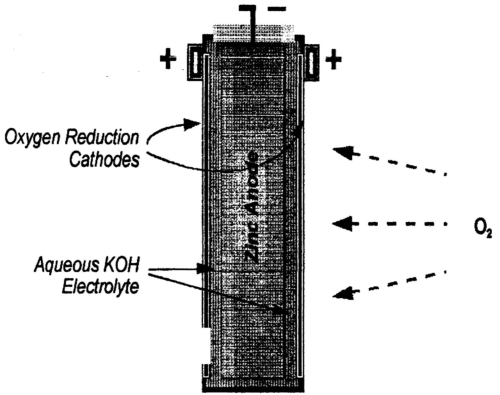


Figure 2.6. A mechanically replaceable zinc cassette developed by Electric Fuel Ltd.. After *Harats et. al.* **(1995)**.

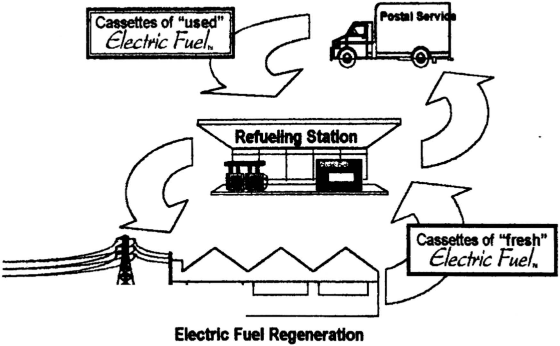


Figure 2.7. Schematic of the Electric Fuel system operation. After *Goldstein* et. *al.* **(1993)**.

Table 2.5. Developers of zinc-air technology. After *Clark and Kinoshita* **[1994]**.

Group	**Zinc-Air Concept**	**Principal Technology Features**
AER Energy Resources, Inc.	Electrically recharged	Developed batteries for portable applications (operating life 400 hr) -advanced air management system controls air flow -2.7 kg, 88 Wh kg^{-1}, 11-14 V operating voltage -0.8 kg, 130 Wh kg^{-1}, 4.75-6 V operating voltage
Dreisbach ElectroMotive, Inc. (DEMI)	Electrically recharged	Demonstrated zinc/air – lead/acid (or Cd/NiOOH) hybrid system in compact car (Honda) and van (Chrysler) -135 Wh kg^{-1} zinc-air battery
Electric Fuel Ltd.	Mechanically recharged	Demonstrated cold-start operation after storage at –20°C Developed patented monofunctional air electrode and high utilization zinc electrode of compacted porous zinc Demonstrated in van a 310 V battery (650 kg) -420 km range at constant 60 km h^{-1} -300 km with postal cycle Demonstrated in a Mercedes postal van (3500 kg) for 1-1.5 years -110 kWh battery
Lawrence Berkeley National Lab. (LBNL) / University of California, Berkeley (UCB)	Mechanically refuelled	Developed design concept for hybrid battery system for Chrysler van utilizing mechanically refuelled zinc-air battery Demonstrated hydraulic refuelling of zinc particles -Projected 50 kWh battery with 178 Wh kg^{-1} (156 Wh l^{-1})

Table 2.5. (continued)

Group	Zinc-Air Concept	Principal Technology Features
LBNL / UCB	Electrically recharged	Demonstrated electrical recharge in spouted bed zinc-air cell -charge and discharge at 83 mA cm^{-2} with 45 wt% KOH containing 64.3 g l^{-1} ZnO
Lawrence Livermore National Lab. (LLNL)	Mechanically refuelled	Designed 12-cell bipolar stack (12 V at 100 A, 440 Ah) for demonstration in hybrid battery system that is on-board electric bus
MATSI, Inc.	Recyclable primary and electrically recharged	Fabricated and tested 5-cell primary batteries -70-cm^2 cell; 360 Wh kg^{-1} -300-cm^2 cell; 464 Wh kg^{-1} Obtained more than 350 charge/discharge cycle in lab.-scale cell with flowing electrolyte in porous zinc electrode
Westinghouse Electric Corp.	Electrically recharged	Developed technology to fabricate 400-cm^2 air electrodes by machine Demonstrated over 180 charge/discharge cycle on bifunctional air electrode in full EV-size cells Developed low cost pasted zinc electrode

2.3 Reaction Mechanisms of Zinc-Air Cell

The overall cell reactions can be summarized as follows [*Crompton, 2000; Hamlen 1995*]

At cathode: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$ $E^0 = +0.40$ V (2.1)

At anode: $2Zn \rightarrow 2Zn^{2+} + 4e$ (2.2)

$2Zn^{2+} + 4OH^- \rightarrow 2Zn(OH)_2$ $E^0 = -1.25$ V (2.3)

$2Zn(OH)_2 \rightarrow 2ZnO + 2H_2O$ (2.4)

Overall: $2Zn + O_2 \rightarrow 2ZnO$ $E^0 = +1.65$ V (2.5)

The oxygen reduction process is complex and it involves a rate-limiting stage, which affects reaction kinetics and finally the cell performance. This stage relates to the formation of hydroperoxide ions HO_2^- [*Bender et. al, 1995; Vincent et. al, 1984*],

Stage 1: $O_2 + H_2O + 2e \rightarrow HO_2^- + OH^-$ (2.6)

Stage 2: $HO_2^- + H_2O + 2e \rightarrow 3OH^-$ (2.7)

Only the initial stage is reversible [*Vincent et. al, 1984*]. The decomposition of the hydroperoxide ion, i.e. stage two, is the key rate-limiting stage. Catalytic compounds are needed to accelerate this reaction. These catalysts are typically transition metal compounds such as oxides and organometallic complexes, noble metals and their compounds, and mixed metal compounds including rare earth metals [*Vincent et. al, 1984*]. Besides, the hydroperoxide ions may undergo other reactions with the current collector to form metal-oxygen bonds which, in turn, may be reduced. Also the ion itself may decompose to reform oxygen,

$$2HO_2^- \rightarrow 2OH^- + O_2 \tag{2.8}$$

Incorporating manganese dioxide into the air electrode might remove the hydrogen peroxide from the intermediates by the following cyclic reaction [*Crompton, 2000*],

$$MnO_2 + H_2O_2 + 2H^+ \rightarrow Mn^{2+} + 2H_2O + O_2 \tag{2.9}$$

$$Mn^{2+} + 2H_2O \rightarrow Mn(OH)_2 + 2H^+ \tag{2.10}$$

$$Mn(OH)_2 + H_2O \rightarrow MnO_2 + 2H_2O \tag{2.11}$$

However, for secondary applications MnO_2 might not be suitable due to its instability towards oxygen evolution on recharge.

The reactions of the zinc electrode have been subject to a large number of investigations. However, there is still no general agreement on its precise mechanisms during charge and discharge. The following mechanisms have been proposed [*Falk and Salkind, 1969*]. During initial stage of discharge in a basic solution, zinc is oxidized to a solid form either zinc oxide or zinc hydroxide,

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e \qquad (2.12)$$

or

$$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e \qquad (2.13)$$

Then these compounds dissolve to form complex zincate ions,

$$ZnO + 2OH^- + H_2O \rightarrow Zn(OH)_4^{2-} \qquad (2.14)$$

or

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-} \qquad (2.15)$$

and when the solution becomes saturated with zincate ions, it is no longer able to dissolve the passivating ZnO or $Zn(OH)_2$ compound formed on the electrode until finally the discharge reaction ceases. In a compact cell design with minimum amount of electrolyte used, a high surface area zinc electrode is employed to permit all the zinc to be efficiently oxidized prior to the passivating film formation [*Cretzmeyer et. al, 1977*].

Whereas the reactions during charging are believed to be [*Falk and Salkind, 1969*]

$$Zn(OH)_4^{2-} \rightarrow Zn(OH)_2 + 2OH^- \qquad (2.16)$$

and followed by

$$Zn(OH)_2 + 2e \rightarrow Zn + 2OH^- \qquad (2.17)$$

2.4 Cell Components and Design

The zinc-air cell comprises a caustic alkali electrolyte, a zinc anode and a carbon electrode that must be sufficiently porous and gas-permeable to 'breathe air', yet close enough to resist electrolyte penetration. An electrochemical power source performance is very much dependant on its cell design, type of separator and, the anode, cathode and electrolyte formulation. A detailed account of the various types and designs of the cell component will be given in the following sections.

2.4.1 Zinc Anode

The zinc anode has a theoretical capacity of 0.82 Ah g^{-1}. In conventional wet cells, zinc anodes are utilized in a massive or plate form. However, cast zinc cannot sustain current as high as powdered zinc. Now the anode of the zinc-air button cells is in the form of zinc paste, i.e. zinc powder mixed with a gelling agent and electrolyte. In general, there are three types of zinc electrode preparation, namely, the compressed dry powder process, the slurry or paste method and the electroformed method. Regardless of type of preparation, the objectives are to produce a high porosity electrode, a high surface area and also good distribution of alloying element added particularly to raise the hydrogen overvoltage on zinc [*Falk and Salkind, 1969*]. The zinc anode may be prepared in the charged or discharged state. The former comprised of metallic zinc and the latter state is made from a mixture of zinc oxide and additives that can only be used in an alkaline electrolyte.

In the compressed dry powder process, a mixture of zinc metal or zinc oxide, binding agents such as fine Teflon powder or poly(vinyl alcohol) (PVA), which may also contain a corrosion inhibitant agent (traditionally being mercuric oxide), is placed in a mold and compressed around a current collector. The pressure applied is a function of porosity desired and types of mixture employed. A high porosity electrode is a prerequisite for high discharge rate applications, whereas a low porosity electrode would result in a high energy density electrode suitable for low rate applications [*Falk and Salkind, 1969*].

The paste or the slurry preparation technique is usually used to fabricate a dry, charged and a high rate zinc electrode. Powdered zinc oxide is mixed with water or KOH solution and, with or without gelling agents such as carboxymethylcellulose (CMC). The resulting paste is applied onto a suitable metal grid, dried and finally formed against a positive electrode in preferably 5% KOH solution. It is then washed and dried [*Falk and Salkind, 1969*].

Whereas in the electroforming method, the zinc electrode is electrodeposited from a zincate bath, typically being the cyanide bath, or may also be plated from a slurry of zinc oxide in alkaline solution onto a metal substrate, with subsequent rinsing and drying processes [*Falk and Salkind, 1969*].

Zinc, as other metal electrodes, suffers from acidic or caustic alkali electrolyte attacks. Zinc reacts with the electrolyte and hydrogen is liberated,

$$Zn + 2OH^- + 2H_2O \rightarrow Zn(OH)_4^{2-} + H_2 \qquad (2.18)$$

The rate of this reaction increases with increasing temperature and decreasing KOH concentration [*Falk and Salkind, 1969*]. Amalgamation used to be the ultimate means of zinc electrode corrosion protection. Mercury increases the hydrogen overvoltage and induces a more uniform corrosion because it gives rise to a uniform equipotential surface [*Schumacher, 1971a*]. The initial level of mercury was as high as 8-wt % of the zinc electrode. The gradual reduction and expected elimination of mercury in view of the environmental concerns posed a new challenge to inhibit the anode corrosion. Alternative approaches that have been worked out are zinc alloying and electrolyte additives. The most used alloying elements were bismuth, indium, aluminum and calcium [*Huot, 1997*]. The addition of inorganic additives such as gallium, bismuth, indium, calcium and aluminum oxide was also observed to inhibit cell gassing [*Huot, 1997*].

2.4.2 Air Cathode

The air cathode has been the subject of intensive studies particularly in the development of fuel cells, due to its attractions of being lightweight and theoretically of infinite capacity. The performance of fuel cells and alkaline air-depolarized cells is very much dependant on the effective functioning of the air cathode. The voltage losses under open circuit and both during discharge and charging are mainly due to the air cathode. An air cathode must possess the following significant features [*Chakkaravarthy et al, 1981*]; porosity for air diffusion, non-wettability to prevent water permeation, good conductivity to minimize the internal resistance of the battery, and good mechanical strength for the purpose of transportation and fixing rigidly into the battery.

The air electrode is normally in the form of a porous conducting solid such as carbon [*Berl, 1943*] or nickel [*Jahn and Plust, 1963; Thacker, 1969*], and impregnated with catalytic material. However, active carbon has long been preferred because of its stability and low cost. A more recent air cathode design consists of laminated structures of fibrous carbon supported by nickel-plated mesh. The carbon is blended with a catalyst and wet proofing agent while the exposed surface of the electrode is coated with a gas permeable hydrophobic layer such as Teflon, paraffin or PTFE to prevent leakage of electrolyte [*Hamlen 1995*]. The use of fibrous carbon structures substantially enhances the active surface area and yet reduces the electrode weight.

Reduction of oxygen at the air electrodes is unique in that it must occur in the vicinity of three adjacent phases (refer to Figure 2.8); namely solid (electron conductor), gas (oxygen) and liquid (water) [*Cretzmeyer, 1977*]. From the airside, air (oxygen) diffuses through the porous electrode towards the opposite electrolyte side. Whereas from the electrolyte side of the porous electrode, some solution fills the pores in the surface layers of the electrode, and the diffused oxygen dissolves in the electrolyte at this point and participates in the electrode reaction by donating or accepting electrons. Thus a stable gas-liquid interface is crucial in air electrode design to prevent the electrolyte from penetrating beyond the surface layers of the porous structure, a phenomenon known as flooding.

The occurrence of flooding affects the air electrode performance in two ways [*Hoare, 1968*]. First, the loss of the high surface area of the catalytically active layer results in the loss in current density. Second, the increase in the diffusion path of the gaseous reactant to the catalyzed reaction sites induces an increase in polarization, lowering the rate of the electrode reaction. Several concepts and procedures have been adapted in the air cathode design to overcome this problem [*Chakkaravarthy et. al, 1981; Hoare, 1968*];

i. maintaining the gas under enough pressure to keep the electrolyte in the surface layers of the porous electrode

ii. use of dual pore electrode i.e. the electrode layer facing the electrolyte having smaller pores compared to the pores of the body structure

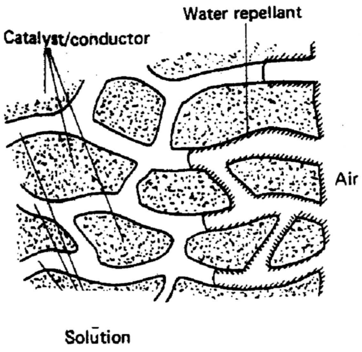


Figure 2.8. Schematic view of the solid-liquid-gas interfaces (triple interface zone) in an air electrode.

After *Vincent* et. *al.* **(1984)**. .

iii. use of double skeleton catalyzer (DSK); it combines the excellent catalytic activity and the low sensitivity to impurities of Raney nickel with the mechanical strength and good electrical conductivity of a porous metal electrode.

iv. immobilizing the electrolyte in a solid matrix; such as the electrolyte being held fixed in an asbestos disk placed between the electrodes.

v. wet proofing the electrolyte side of the porous electrode with hydrophobic material such as paraffin wax in petroleum ether, polyethylene or polytetrafluoroethylene (PTFE).

In the alkaline zinc-air electrochemical system, the air cathode is capable of supporting current density in the range 100 to 150 mA cm^{-2} when supplied with pure oxygen, whereas when utilizing the ambient air it is capable of supplying 25 to 30 mA cm^{-2} current density [*Schumacher, 1971*]. Although carbon is a poor catalyst for oxygen decomposition in alkaline electrolyte, the air cells incorporating the porous carbon electrode perform well for very low current drains [*Chakkaravarthy et. al, 1981*].

2.4.3 Electrolyte

The choice of electrolyte depends on several conditions such as the high efficiency of the zinc anode oxidation, polarization of both anode and cathode, and physical properties such as conductivity, freezing point, surface tension and vapour pressure [*Bender et. al, 1995*]. Principally, the electrolyte can be either alkaline or acidic. However, for a zinc-based cell and most of the metal-air batteries, the majority of the requirements are met by a caustic alkali such as sodium or potassium hydroxide aqueous systems particularly the enhanced performance of the air cathode at high pH electrolytes [*Cretzmeyer et. al, 1977; Schumacher 1971a; Vincent et. al 1984*]. Moreover, the caustic alkali solutions are stable, highly soluble and favourable over a wide temperature range. Their high conductivity over the normally used concentration range contributes to the low impedance and higher volumetric or gravimetric electrical output of the alkaline cells. Sodium hydroxide (NaOH) is cheaper than the potassium hydroxide (KOH) on a bulk basis and especially when equimolar concentrations are considered. However, KOH possesses better conductivity and a lower freezing point. The latter makes it more suitable for lower temperature operations. The lowest freezing point (eutectic) of aqueous KOH is registered at 31.5 wt. %, which is -67 °C, while for aqueous NaOH a minimum freezing temperature (eutectic) of –28°C is obtained at 19 wt. % [*Dean, 1973*]. The comparison of the principal properties of the aqueous KOH and NaOH electrolytes is illustrated in Figures 2.9 and 2.10. Mixed electrolytes have also been proposed to combine the low cost of NaOH with the better conductivity and low temperature tolerance afforded by KOH [*Schumacher, 1971a*]. On the other hand, cells employing alkaline electrolyte absorb carbon dioxide from the atmosphere. Precipitation and blockage of carbonate crystals in the pores of the air cathode may result in the decreased performance of the air cathode.

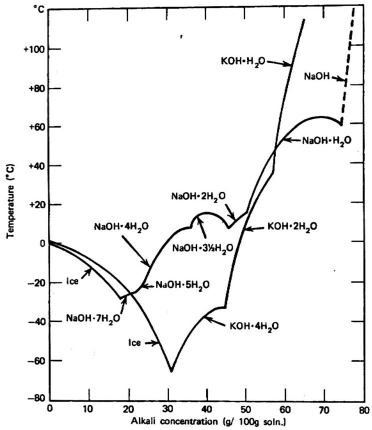
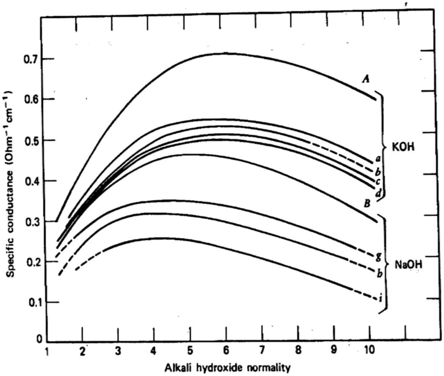


Figure 2.9. Freezing points of aqueous KOH and NaOH electrolytes. After *Schumacher* (**1971a**).



(A) KOH
- a. 1.0 mole ZnO : 4.33 mole KOH
- b. 1.0 mole ZnO : 3.71 mole KOH
- c. 1.0 mole ZnO : 3.37 mole KOH
- d. 1.0 mole ZnO : 3.00 mole KOH

(B) NaOH
- g. 1.0 mole ZnO : 4.05 mole NaOH
- h. 1.0 mole ZnO : 3.03 mole NaOH
- i. 1.0 mole ZnO : 1.76 mole NaOH

Figure 2.10. Conductivity curves of NaOH-ZnO and KOH-ZnO solutions at 30 °C. After *Schumacher* (**1971a**).

It has been suggested that the optimum KOH concentration for zinc anode discharge is 35 to 37 wt.% [*Harats et. al, 1995*]. The study is based on the conductivity of the discharged species and the maximum passivation time for the horizontal zinc electrode. The highest permissible KOH concentration considering the possibility of partial crystallization is 50 wt. % [*Falk and Salkind, 1969*].

For ease of handling and fabrication, the electrolyte is usually immobilized with a gelling agent. Materials that have been employed are starch [*McComsey and Felegyhazi, 1995; Scarr and Hunter, 1995*], cellulose and its derivatives [*Appelt and Malanowski, 1979; Cahoon and Holand, 1971; Morehouse et. al, 1961*], vinyl polymers such as poly(vinyl alcohol) [*Huot, 1997; Naylor, 1995*], and polytetrafluoroethylene (PTFE) [*Ikeya et. al, 1993; Vassal et. al, 1999*].

Zinc oxide is one of the most important electrolyte additives in alkaline zinc batteries. It has the beneficial effect of reducing the zinc electrode solubility [*Falk and Salkind, 1969; Keily and Sinclair, 1981*]. On the other hand, it has a negative influence on the electrical performance of the battery. Among others, the addition of zinc oxide would decrease the electrolyte conductance and the limiting current density. Another important additive is hydrated lime or calcium hydroxide. Its role is to regenerate the exhausted electrolyte and also to reduce zincate solubility. The lime combines with the $Zn(OH)_4^{2-}$ oxidation product and produces calcium zincate that has a low solubility in the electrolyte. At the same time, hydroxyl ions are released into the bulk of the electrolyte. As the lime is exhausted, the zinc starts to consume the electrolyte, decreasing the electrolyte alkalinity and passivating the zinc.

The circulating electrolyte system (CES) has also been employed especially to minimize problems encountered in zinc replating in secondary cell design. Further, CES can also assist the thermal management system. Other advantages include the ease of replacement of the spent electrolyte in the mechanically rechargeable battery and the reduction in IR loss due to oxygen bubble formation during the charging of the battery [*Blurton and Sammells, 1979*]. In its basic design the electrolyte is circulated through each cell during operation and the spent electrolyte is passed to a settling tank where the discharge products can be precipitated out and stored for the eventual recharge of the battery. Its major disadvantage is the increase in the complexity of the system. Figure 2.11 illustrates the C.G.E. (Compagnie Générale d'Electricité) circulating zinc-air system that utilizes a tubular electrode design (Figure 2.12) [*Appleby and Jacquier, 1976/77*].

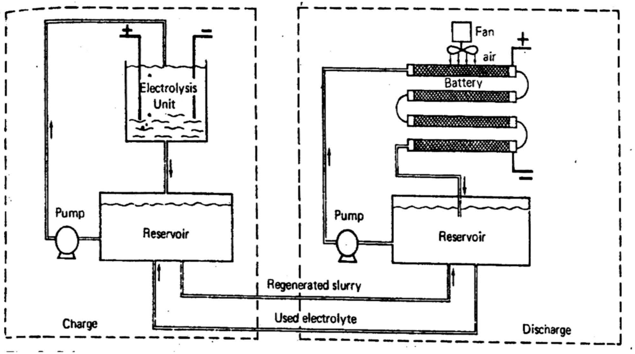


Figure 2.11. Schematic diagram of the C.G.E. circulating zinc-air system. After *Appleby and Jacquier* **(1976/77)**.

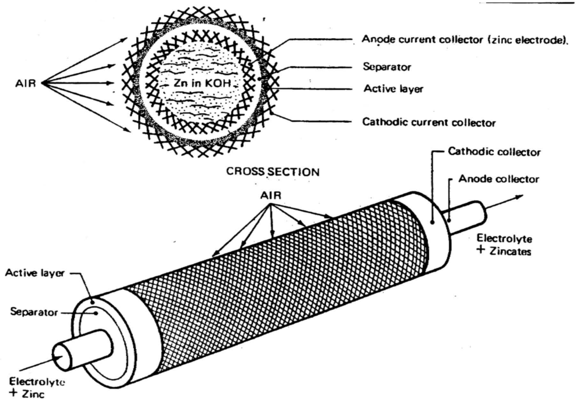


Figure 2.12. General schematic view of the C.G.E. tubular electrode. After *Appleby and Jacquier* **(1976/77)**.

The rapid advancement in the development of solid-state electrochemical cells has initiated a new trend in metal-air batteries. A solid polymer electrolyte has been introduced for application in metal-air batteries [*Abraham and Jiang, 1996; Abraham and Jiang, 1996a; Vassal et. al, 2000*]. *Abraham and Jiang* (1996) constructed the Li-oxygen cell employing non-aqueous Li-polyacrylonitrile (PAN)-based plastisized polymer electrolyte (12 w/o PAN-40 w/o ethylene carbonate, EC–40 w/o propylene carbonate, PC-8 w/o lithium salt, $LiPF_6$). The cells studied have demonstrated specific energy of between 250-350 Wh kg^{-1} rated at 0.1 mA cm^{-2}. On the other hand, *Vassal et. al* (2000) studied a water-containing alkaline solid polymer electrolyte obtained from copolymer of epichlorohydrin with ethylene oxide and KOH as the conducting salt, with P(ECH-co-EO)/KOH composition of 44 wt.% / 56 wt.%, for use in zinc-air and nickel-metal hydride cells. The zinc-air cell performed well up to 14 mA cm^{-2} at 0.8 V discharge voltage measured at room temperature, while at 60°C it could withstand 30 mA cm^{-2} current density in decarbonated air. They also observed comparable zinc-air cell performance with the use of polyethylene oxide (PEO)/KOH solid polymer electrolyte, which was developed earlier for application in nickel-cadmium [*Fauvarque et. al, 1995; Guinot et. al, 1998*], nickel-zinc [*Fauvarque et. al, 1995; Guinot et. al, 1998*] and nickel-metal hydride cells [*Vassal et. al, 1999*]. Other alkaline solid polymer electrolytes that have been investigated are poly(vinyl alcohol) (PVA)-KOH-H_2O [*Lewandowski et. al, 2000; Mohamad et. al, 2002*] and PEO-PVA-KOH [*Yang, 2002*]. Solid polymer electrolyte offers the advantages of good mechanical strength, the ability to deform and allows the construction of a thin and compact cell design, and the elimination of the electrolyte leakage problem.

2.4.4 Separator

At first sight, the separator of an electrochemical cell merely serves as an electronic insulation between the positive and negative electrodes without materially increasing the internal resistance of the cell. The choice of separator however, contributes to the performance and life of a cell. It affects the high rate capability of the cell, as well as the charging properties, low temperature performance, charge retention and cycle life. In general, a separator material must possess minimum electrolytic resistance and high electronic resistance, should be as thin as possible for minimum internal resistance and maximum cell space for electrodes, be sufficiently flexible to be wrapped around the electrode and at the same time be capable of withstanding pressure, stress, vibration and shock, and last but not least be at a commercially reasonable cost [*Falk and Salkind, 1969*]. A wide variety of materials have been used to fulfill the various requirements of different types of systems, which differ from one electrochemical system to another. For future application in electrically rechargeable zinc-air battery in particular, the following properties are crucial for the separator material [*Chakkaravarthy et. al, 1981*],

i. be inert to oxidation by the evolving oxygen during charging;
ii. be stable in the electrochemical cell where high potentials are applied across the matrix during charging;

iii. be chemically inert to potassium hydroxide for extended periods of time and at temperatures of up to 50°C;

iv. possess high absorption and wettability for the electrolyte;

v. have a fine porous capillary structure to hold the electrolyte in the pores and limit the oxygen gas cross diffusion;

vi. have a high bubble pressure;

vii. be sufficiently porous to meet the electrolyte storage needs and have a low electrical resistance;

viii. be able to retard zinc dendrite growth and shape change, i.e. the separator must be permeable to H^+, OH^- and K^+ ions but impermeable to Zn^{2+} and ZnO_2^- ions.

Usually, a single type of separator material cannot meet the requirements desired for a particular system. In that case multiple separators of different types are needed. At present, plastic separator materials are widely employed in most of the electrochemical cells in the form of thin, porous sheets, woven, felted or extruded [*Falk and Salkind, 1969*].

Cells may also be fabricated without utilizing the separator, for instance, a cell container with a groove design at the inner side that permits the electrodes to be inserted at a suitable distance without the risk of contact between the electrodes. Usually the cell is provided with large amount of electrolyte to minimize the maintenance. This design, however, can only be applied to cells intended for applications where the volume is not of primary concern.

2.4.5 Bipolar Cell Design

A bipolar cell design is assembled from positives consisting of two single plates facing back to back, an ordinary single negative placed in between the two positives and separated by plastic rods or sheets (see Figure 2.13). This construction possesses the advantage of higher volumetric capacity. This design does not permit the use of very thin electrodes hence it is not suitable for high rate applications.

2.5 Cell Performance

Unlike other electrochemical systems, the zinc-air cell is anode-electrolyte limiting. By accommodating the required quantity of zinc and electrolyte, a very large capacity power source can be fabricated. Besides, unlike other positive electrodes, the capacity of a properly designed air electrode is unconstrained in its size and weight [*Chakkaravarthy et. al, 1981*]. The zinc - air cell has a theoretical specific energy density of 1085 Wh kg^{-1}, which is based on the theoretical cell voltage of 1.65 V and assuming the final reaction product of ZnO [*Appleby and Jacquier, 1976/77; McBreen, 1981; Rand, 1979*]. Practical values of 300 Wh kg^{-1} and 90 Wh kg^{-1} have been achieved for primary and secondary cells respectively [*Muller et. al, 1994*].

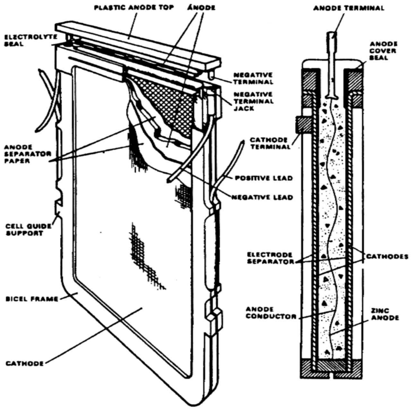


Figure 2.13. Zinc-air cell of bipolar (or dual) cathode design. After *Will* **(1984)**.

The nominal open circuit voltage (OCV) for a zinc-air cell is 1.4 – 1.5 V. Depending on the external load, the initial discharge at 20°C ranges from 1.5 to 1.35 V [*Bender et al, 1995*]. As the air cathode is not chemically altered during discharge, the cell voltage remains quite stable with 0.9 V the typical end voltage. Thus, the discharge curves are relatively flat. Below the limiting current, the cell is capable of discharging approximately the same capacity. However as the discharge current approaches the limit, polarization of the cell voltage increases hence the cell delivers less than the rated capacity. The discharge rate is dependent upon the rate at which air can be admitted. Usually, for high discharge applications air blowers are needed.

The charge-discharge efficiencies are dominated by the large voltage losses of the air cathode where the state-of-the-art of the voltaic efficiency at C/5 to C/4 discharge rates is 1.15/1.2 V i.e. 52.3% [*Will, 1998*]. The zinc-air cell is also sensitive to electrical abuse. It cannot be quick-charged, and might be permanently damaged if it is discharged below 0.9 V.

2.6 Unresolved Problems of Rechargeable Zinc-Air Batteries

Primary zinc batteries are the most widely used power sources for portable applications with moderate energy consumption. The development of long life secondary zinc batteries has been frustrated by the problems encountered with the zinc electrode. Coupled with the air electrode and employing aqueous-based electrolyte, the quest for an electrically rechargeable zinc-air battery is a formidable challenge, from both the technical and scientific perspectives. Various aspects and issues in relation to the realization of an electrically rechargeable zinc-air battery will be discussed in this section.

2.6.1 Zinc Anode

The zinc electrode is the limiting factor in all alkaline zinc batteries. The method and rate of charge, zinc anode design and thickness, and the quantity of electrolyte are among the factors that determine the life of the zinc electrode. The renowned modes of failures of the zinc electrode are the redistribution of the zinc active and the formation of unwanted zinc electrode morphologies (dendrites, filamentary growths and nodules) after repeated charge-discharge cycling [*Himy, 1995; McLarnon and Cairns, 1991*]. These problems have been linked to two important characteristics of zinc, viz., considerable solubility of the zinc discharge products in the alkaline electrolyte and its rapid electrochemical kinetics. Zinc hydroxide and zinc oxide, the discharge products of zinc-air cell electrochemical reaction, have considerable solubility in potassium hydroxide electrolyte and thus diffuse away from the reaction sites. This phenomenon leads to zinc electrode reshaping and surface densification with discharge-charge cycles. The upper side and edges of the electrode change faster while the bottom side of the electrode becomes thicker due to the zinc ions preferentially replating on the bottom parts of the electrode [*Himy, 1995*]. This results in a reduction in the electrode's active area and a corresponding loss in energy storage capability. Thus, the lifetime of the zinc electrode is short and unpredictable, causing fast capacity drop with cycling.

Numerous inorganic and organic additives have been investigated to improve the secondary zinc electrode capabilities, primarily to limit the discharge product solubility and mobility. One of the widely studied additives is calcium hydroxide. Despite its role in replenishing the alkaline electrolyte through the release of hydroxyl ions, the complexation with the zincate ions forming substantially insoluble calcium zincate compound $Ca(OH)_2.2Zn(OH)_2.2H_2O$, effectively trapped the zincate ions within its structure [*Wang and Wainwright, 1986*],

$$Ca(OH)_2 + 2Zn(OH)_4^{2-} + 2H_2O \underset{decomposition}{\overset{formation}{\rightleftarrows}} Ca(OH)_2.2Zn(OH)_2.2H_2O + 4(OH)^- \tag{2.19}$$

During charging, as the calcium zincate is close to the reaction site, it will provide an ample supply of zincate within the electrode structure for the zinc reduction and the conditions for dendrite formation will not be reached [*Wang, 1990*]. This accounts for the observed reduced shape change and improved cycle life of Zn/NiOOH cells [*Gagnon, 1986*]. However, the incorporation of calcium hydroxide is found to be most effective in 20 w/o KOH concentration. At higher concentrations the electrode shape change and solubility increases, hence affecting the capacity retention and cycle life [*Gagnon, 1986*]. Other adverse implications of calcium hydroxide addition are reduced zinc active material utilization and accelerated passivation [*Gagnon and Wang, 1987*]. Besides, as the formation of calcium zincate compound is a relatively slow reaction while its decomposition, on the other hand, is relatively fast, the high-rate charge-discharge processes may limit the effectiveness of calcium hydroxide addition

[*Wang and Wainwright, 1986; Wang, 1990*]. A maximum benefit of calcium zincate can be obtained under normal charge-discharge rate and is more pronounced at lower KOH concentrations i.e., up to 22 w/o, because the rate of increase of ZnO concentration with increase in KOH concentration is smaller below this concentration [*Sharma, 1986; Wang, 1990*]. Calcium zincate compound does not form above KOH concentrations of 34 w/o, [*Sharma, 1986; Wang, 1990*]. In another recent development, calcium zincate itself has been tested as the negative electrode in Zn/NiOOH cell [*Yu et. al, 2001*].

The choice of KOH concentration in alkaline zinc batteries gives rise to a dilemma between optimum performance at higher concentrations (20-35 w/o) that increases zincate species solubility, or reduced shape change at lower concentrations (as low as 10 w/o) [*Gagnon, 1991*] at the expense of the cell performance. Thus an alternative approach is to employ lower KOH concentrations in combination with supporting electrolyte to compensate for the reduced electrolyte ionic conductivity. Among the supporting electrolytes investigated are potassium fluoride (KF) [*Adler et. al, 1993; Thornton, 1981; Thornton and Carlson, 1980*], potassium chloride (KCl) [*Kujas, 1962*], potassium bromide (KBr) [*Kujas, 1962*], potassium borate (K_3BO_3) [*Schneider and Dominiczak, 1973; Thornton and Carlson, 1980*], potassium phosphate (K_3PO_4) [*Thornton and Carlson, 1980*] and potassium carbonate (K_2CO_3) [*Adler et. al, 1993; Jost, 1969*]. *Adler and co-workers* (1993) employed a novel ternary electrolyte $KOH - KF - K_2CO_3$ that significantly reduced the rate of zinc active material redistribution over the electrode area as compared to *KOH, KOH-KF* and $KOH\text{-}K_2CO_3$ electrolytes. A sealed 1.35 Ah Zn/NiOOH cell constructed with the ternary electrolyte showed a capacity-loss rate of 0.09% per cycle and could sustain over 500 deep-discharge cycles before reaching 60 % of initial capacity.

Another common feature arising from the charge-discharge cycling is the dendrite growth that could protrude the cell separator, causing internal short-circuiting. A number of factors can be looked into to minimize this problem, if not with complete elimination. One of the ways is to develop a foolproof dendrite resistant separator or the modification of the zinc electrode by the inclusion of dendrite inhibiting additives. The separator could be made with pore size smaller than the zincate ions so as to limit the migration of the active material away from the zinc electrode. However, the reduction in pore size is usually accompanied by an increase in the electrolyte resistivity and the decrease in water permeability. It is believed that batteries employing microporous separator that possesses high water and electrolyte permeability should exhibit less shape change because it minimizes the electrolyte and zincate ion concentration gradient within the battery, but at the risks of dendritic shorting and zinc oxide deposition within the separator pores. On the other hand, the use of a membrane separator could provide a much lower rate of active material migration and probably no deposition of zinc oxide within the separator, but at the expense of high rates of electrode shape change resulting from poor mass transfer, due to the electro-osmotic pumping effects [*Choi et. al, 1976; Choi et. al, 1976a; McBreen, 1972*]. Besides, the membrane separator is also vulnerable to chemical attack because the polymer used in the membrane separator must contain hydrophilic functional groups that are capable of interacting with the electrolyte and these same functional groups tend to reduce the resistance of the polymer to chemical attack [*Lundquist, 1983*]. The separator material with pore size of 300 Å could satisfactorily retain dendrite penetration while sufficiently maintaining its permeability [*Lundquist, 1983*]. *Sato et. al* (1983) have developed a separator that is resistant to zincate ion penetration and at the same time sustains its ionic conductivity. The separator consists of nylon non-woven cloth coated with poly(vinyl alcohol) (PVA) containing boric acid (H_3BO_3). The nylon cloth acts as a substrate as PVA itself is mechanically weak. *Himy and Wagner* (1980) fabricated a composite separator, which consists of a polyolefin microporous separator (average pore size 100 Å to 500 Å) coated with nickel by means of sputtering technique. Nickel with its hydrogen overpotential in alkaline electrolyte which is lower than that of zinc might slow down the dendrite propagation. As the dendrite reaches the separator, nickel oxidizes and dissolves the dendrite tip,

micro dendrite tip (anode): $$Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e \tag{2.20}$$

nickel coating (cathode): $$2H_2O + 2e \rightarrow H_2 + 2OH^- \tag{2.21}$$

overall reaction: $$Zn + 2H_2O + 2OH^- \rightarrow H_2 + Zn(OH)_4^{2-} \tag{2.22}$$

However, this separator design demands enough water reserve for the cell, which means lower electrolyte concentrations, to compensate for the water lost whenever zinc dendrites make an encounter with the nickel coated polyolefin separator.

Another possible approach is to modify the zinc electrode by, for example, alloying or introducing a dendrite-inhibiting agent into the electrode or electrolyte. Some metal oxides were reported to improve zinc electrode cycle life. During the charging process when zinc ions are reduced to metallic zinc, the metal oxide or metal ion additive is also reduced. The particulate metal forms a conducting network within the electrode structure that substantially enlarges the current collector active surface area. This simple procedure might reduce the zinc overvoltage reaction by providing an oxide-forming metal if the electrode is overcharged. There have been considerable candidates investigated for this purpose, among others; bismuth oxide (Bi_2O_3) [*Biegler et. al, 1983; McBreen and Gannon, 1985; Sato et. al, 1983*], cadmium oxide (CdO) [*Biegler et. al, 1983; Wagner and Himy, 1976*], lead oxide (PbO) [*Wagner and Himy, 1976*], magnesium oxide (MgO) [*Binder and Odar, 1984; Jerabek, 1971*], neodymium hydroxides ($Nd(OH)_3$) [*Zhu, 1997*], a mixture of lead oxide (PbO) and indium hydroxide ($In(OH)_3$) [*McBreen and Gannon, 1981*], a mixture of mercury oxide (HgO) and titanium oxide (TiO_2) [*Shivkumar et. al, 1998*], a mixture of Bi_2O_3, PbO and CdO [*Skelton and Serenyi, 1997*] and mixtures of thallium oxide (Tl_2O_3) and PbO, or Tl_2O_3 and CdO [*Wagner and Himy, 1976*].

Alternatively the dendritic growth might be mitigated through controlled charging [*Himy, 1995a*]. It has been established that growth of zinc dendrites occurs during electrodeposition under conditions of diffusion control, that is high charge rates of 100 mA cm^{-2}, whilst under activation control, which is low charge rates of 15-20 mA cm^{-2}, a dense, adherent mossy form of zinc is produced [*Himy, 1995a; Naybour, 1968*]. Therefore, in the charging process, the potential must be carefully selected below the threshold of overcharge on the zinc electrode. An interrupted current charging technique might also essentially reduce dendrite formation [*Himy, 1995a; McLarnon and Cairns, 1991; Sato et. al, 1983*]. Another benefit obtained from this high current short pulse charging is a uniform distribution of zinc electrode charging, which results in reduced shape change. Generally, in this charging mode, the pulsed current amplitude is about five times the value in constant current mode charging, but its average value is about the same, while the rest period is about four times the pulse duration [*Himy, 1995a*]. However, for a particular power system and design, these parameters might need to be optimized.

For a more complex system, the use of flowing electrolyte could substantially reduce the electrolyte concentration gradient and limit the thickness of the diffusion layer [*McLarnon and Cairns, 1991*]. These would result in more uniform electrochemical reactions, improved efficiency, an increase in limiting current density and cell life, a reduced shape change and obviate the dendritic bridging [*McLarnon and Cairns, 1991; Stachurski and Yardney, 1976*]. In this particular system design, the zinc active material could be either in the form of flow-by electrode [*Adams et. al, 1981; Caprioglio and Weinberg, 1971*] or made of an unconsolidated stream of zinc particles [*Appleby et. al, 1975; Appleby and Jacquier, 1976/77*]. The former has been prepared by electrodeposition onto a planar metallic substrate [*Adams et. al, 1981*] or onto a porous foam material that produces a high porosity electrode [*Iacovangelo and Will, 1985; Ross, 1989*]. The latter might exist in the form of zinc powder-KOH colloidal suspension or zinc-coated glass/polymer spheres [*Backhurst et. al, 1969; Doniat, 1979*].

2.6.2 Air Electrode

The main problems associated with the air cathode are related to its stability and efficiency during the charging process. Even noble metal catalysts such as platinum reveal significant dissolution or deep surface oxidation, which are detrimental to their catalytic efficiency [*Bagotzky et. al, 1982; Thacker, 1969*]. Attempts have been made to introduce an auxiliary (third) electrode to be used during charging in order to protect the air electrode from oxidation and degradation [*Gumucio, 1965; Postula and Thacker, 1970; Hattori et. al, 1973*]. Though the air electrode does not participate in the charging cycle, placing the third electrode between the anode and cathode still exposes the air electrode to the degradation due to the possible contact with the cross-diffused evolving oxygen. Thus *Hattori et. al* (1973) positioned the third electrode away from the air electrode, i.e. inserting the anode between the air cathode and the third electrode. Nevertheless, the chief setback of the use of a third electrode for charging is that it needs mechanical switching and hence the size and cost of the switch would be another factor to consider. Therefore, obviously a bifunctional air electrode would be far better where both the oxygen reduction and evolution are carried out on the same electrode.

Various bifunctional air electrode catalysts have been tested, using Ag [*Carlson and Ojefors, 1980*], mixed oxides [*Swette and Ginner, 1988*], noble metals [*Motoo et. al, 1984*], organometallic compounds [*Gupta et. al, 1989*], perovskite-type oxides [*Kudo et. al, 1975; Manoharan and Shukla, 1985; Matsumoto et. al, 1977*] and many others. Among those, some perovskite-type oxides appear to be promising for their high activity and comparatively low cost, such as $La_{0.2}Sr_{0.8}Fe_{0.2}Co_{0.8}O_3$ [*Matsumoto et. al, 1980*] and $La_{1-x}Sr_xCoO_3$ (x = 0.2, 0.4) [*Matsumoto et. al, 1980a*]. *Shimizu et. al* (1990) made significant progress in the development of a bifunctional air electrode when they proposed a bifunctional electrode using $La_{0.6}Ca_{0.4}CoO_3$ as the catalyst. The electrode showed a high bifunctional performance, i.e. anodic current density of -3000 mA cm^{-2} and cathodic current density of 1000 mA cm^{-2} at –125 mV and 700 mV vs. Hg/HgO respectively, in 30 w/o KOH at 25°C. The catalyst is considered to decompose effectively the hydroperoxide radicals. Further, the electrode was stable for 100 charge-discharge cycles at a current density of 100 mA cm^{-2}. The Paul Scherer Institute in a joint effort with the Swiss Federal Institute of Technology and the Lawrence Berkeley National Laboratory utilizing the $La_{0.6}Ca_{0.4}CoO_3$ the catalyst, has further improved the air bifunctional electrode performance. Employed in a 0.8 Ah zinc-air cells, 450 charge-discharge cycles were obtained at C/3 rate of discharge and C/6 rate of charge [*Muller et. al, 1994*].

2.6.3 Aqueous-based electrolyte

The main advantages of aqueous-based electrolyte power systems are low cost with high conductivity. Water, being the electrolyte solvent, is the most natural, abundant and totally environmentally friendly. Nevertheless, its chief disadvantage is the relatively low decomposition potential, which is theoretically only 1.23 V. Using electrode materials of high hydrogen and oxygen overvoltage, cell voltage up to 2 V is possible [*Beck and Ruetchi, 2000*]. In the maintenance-free (sealed) lead acid battery, the oxygen produced at the positive electrode during overcharge diffuses to the negative electrode and is reduced to water [*Bose and Hampson, 1987; Mrha et. al, 1989*]. This oxygen-cycle renders the battery tolerant to overcharge. However, this approach is not likely in metal-air batteries due to the fact that they are open systems. As the air electrode must be sufficiently porous to permit air access, the system is susceptible to water loss due to water evaporation and, moreover, during overcharging. AER Energy Resources Inc. has developed electrically rechargeable zinc-air batteries that have to incorporate a recirculating air manager system that makes the battery less susceptible to water loss. It also includes a catalyst element that catalyzes the recombination of the oxygen and hydrogen gases generated while charging [*Cheiky, 1990*; *Pedicini, 1994*; *Pedicini et al, 1996; Pedicini, 1997*].

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