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Zinc-Air Battery – Powering Electric Vehicles to Smart Active Labels

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Abstract—***The present paper reviews the development of zinc-air battery. Due to its high energy density advantage, the electrochemical system has been extensively studied and developed. However, major problems associated with the electrochemical system remain a formidable challenge, the utmost being to develop an electrically rechargeable zinc-air battery. Efforts made to overcome or mitigate the limitations concerned can be conceptually classified either as solving problems or seeking solutions. The changing paradigm from the electrically rechargeable system to the mechanically rechargeable system is illustrated as an example. Emerging innovations in smart active labels - flat, flexible and functional devices, particularly in healthcare industry, instigated the authors to develop zinc-air battery as a prospective micro-power source for smart active labels. The thin battery technology developed, in collaboration between IIUM and BPPT, is of low cost, comprises of green electro active materials, and able to operate in quasi-neutral electrolyte. These features fulfil the criteria for the battery to be incorporated into disposable smart active labels.***

I. INTRODUCTION - A BREATHING BATTERY

Metal-air batteries are popularly dubbed as *breathing batteries*. They are unique in that they utilize oxygen from the ambient air as one of the electroactive materials. Hence this provides them with a practically inexhaustible and free oxygen supply from the ambient air. Since the atmospheric oxygen does not require storage, it reduces the battery weight and simplifies the battery design. Consequently, the metal active material can accommodate the whole battery compartment producing a lightweight, high energy density battery.

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 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 (Hamlen, 1995). Although progress has been made with this system over 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 aluminium, cadmium, calcium, cobalt, ferum, lithium, magnesium and zinc (Othman, 2003).

In comparison with other metals, 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 (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 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.

II. ELECTROCHEMICAL PROPERTIES OF ZINC-AIR CELL

The overall cell reactions of a zinc-air cell can be summarized as follows (Crompton, 2000; Hamlen 1995)
At cathode:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad E^0 = +0.40 \text{ V} \qquad (1)$$

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

$$2Zn^{2+} + 4OH^- \rightarrow 2Zn(OH)_2 \quad E^0 = -1.25 \text{ V} \qquad (3)$$

$$2Zn(OH)_2 \rightarrow 2ZnO + 2H_2O \qquad\qquad\qquad (4)$$

Overall:

$$2Zn + O_2 \rightarrow 2ZnO \qquad E^0 = +1.65 \text{ V} \qquad (5)$$

Based on the theoretical cell voltage of 1.65 V and considering ZnO as the final reaction product, zinc-air cell has theoretical specific energy density of 1085 Wh kg^{-1} (Appleby et al., 1976; Cairns, 1981). 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).

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 (Oman 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. 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 (Will, 1998).

III. PRESENT STATUS AND CHALLENGES

A wide variety of zinc-air batteries have been developed since Alfred Smee (1840) first described a primary, acidic zinc-air cell in the literature. At present, commercial zinc-air batteries are mostly of primary type while the electrically rechargeable types are still troubled with rapid capacity fading of zinc electrode and stability of air electrode.

3.1 Primary zinc-air battery

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 signalling, marine navigation lighted aids (buoys) and lighthouses (Cahoon et al., 1971). Solar cells and other secondary cells now substitute many of these applications. Currently, zinc-air button cells are used almost exclusively in miniature hearing aids. The construction of high energy zinc air button cells is made possible by the use of very thin air electrodes and Teflon insulation. 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. Other primary zinc-air battery applications include pagers, voice transmitters, portable battery chargers, continuous power-on appliances and medical monitoring devices such as telemetry. In all these applications, the batteries are usually discharged at low current densities over long periods. In 1999, Electric Fuel Corp. introduced a primary 3300 mAh zinc-air battery, of prismatic design, for the cellular phone market (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 batteries. However, the non-rechargeable paradox put the product at disadvantage.

3.2 Secondary zinc-air battery

The development of electrically rechargeable zinc-air batteries has been frustrated by the problems associated both with the air cathode and zinc anode. AER Energy Resources Inc. (2001) under license from Westinghouse Electric Corp., Pittsburgh and Dreisbach Electromotive Inc. (DEMI), first introduced electrically rechargeable zinc-air batteries for portable computer notebooks into the market but without much success. Most probably this was due to the battery system's external design and weighty form (1.36 kg). The following section highlights the main obstacles towards realizing a rechargeable system.

3.3 Zinc anode

The main issue concerning zinc electrode is its short and unpredictable lifetime, causing fast capacity drop with cycling. This problem is as a result of zinc electrode shape change and the formation of unwanted zinc morphologies (dendrites, filamentary growths and nodules) after repeated charge-discharge cycling (Mc Breen, 1984; Mc Larnon and Cairns, 1991). Two important characteristics of zinc; high solubility of the zinc oxidation products in the alkaline electrolyte and its rapid electrochemical kinetics, are the root cause of the problem. During initial stage of discharge in a basic solution, zinc is oxidized to a solid form either zinc oxide or zinc hydroxide (Falk and Salkind, 1969),
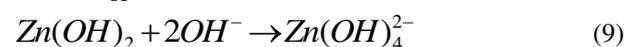
$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e \qquad (6)$$

or

$$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e \qquad (7)$$
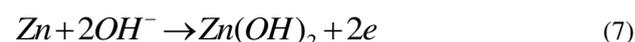
Then these compounds dissolve to form complex zincate ions,

$$ZnO + 2OH^- + H_2O \rightarrow Zn(OH)_4^{2-} \qquad (8)$$

or

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-} \qquad (9)$$
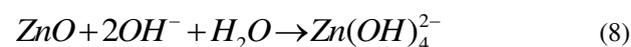
Numerous inorganic and organic additives have been investigated to limit the discharge product solubility and mobility. One of the widely studied additives is calcium hydroxide (Wang, 1990). However, the incorporation of calcium hydroxide is found to be most effective in 20 w/o KOH concentration. At higher concentrations the electrode shape change and solubility increases, hence affecting the capacity retention and cycle life (Gagnon et al., 1987).

Another common feature arising from the charge-discharge cycling is the dendrite growth that could protrude the cell separator, causing internal short-circuiting. One approach is to develop a foolproof dendrite resistant separator. The use of a membrane separator instead of a microporous 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 (Gagnon et al., 1987; Choi et al., 1976; Mc Breen, 1972; Lundquist, 1983).

3.22 Air Electrode

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: $O_2 + H_2O + 2e \rightarrow HO_2^- + OH^-$ (10)

Stage 2: $HO_2^- + H_2O + 2e \rightarrow 3OH^-$ (11)
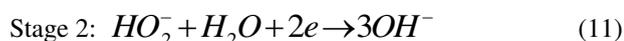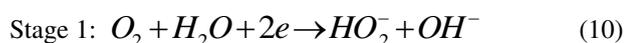
Only the initial stage is reversible (Vincent et. al, 1984). The decomposition of the hydroperoxide ion, i.e. stage two, is the key rate-limiting stage. Catalytic compounds are needed to accelerate this reaction. These catalysts are typically transition metal compounds such as oxides and organometallic 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,

$$2HO_2^- \rightarrow 2OH^- + O_2 \quad (12)$$

Another main issue concerning the air electrode is the catalyst stability during charging. During recharge oxygen is evolved at the air electrode. Therefore, the catalyst embedded in the air cathode must be resistant to oxidation when oxygen is produced at the air electrode. Even noble metal catalysts such as platinum reveal deep surface oxidation, which are detrimental to their catalytic efficiency (Hamlen, 1995). Another attempt is to introduce an auxiliary (third) electrode to be used during charging in order to protect the air electrode from oxidation and degradation (Postula et al., 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 (Hattori et al., 1973).

3.3 A mechanically rechargeable system – A changing paradigm

An innovative concept of refuelable zinc-air power system or 'mechanical charging' is introduced to overcome the issues involving the zinc anode and air cathode. As a result, the 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.

John Cooper of the Lawrence Livermore Laboratory patented a refuelable zinc-air battery in 1993 (Cooper, 1995; Cooper and Krueger, 1997). The battery is charged with an alkaline electrolyte and zinc pellets which are consumed into zinc oxide and potassium zincate during the discharge process. Refuelling aka 'charging' involves draining and replacing the spent electrolyte and adding a new charge of zinc pellets that takes about 10 minutes. This short refuelling time is particularly attractive for electric vehicle (EV) applications. Metallic Power Inc. of California also developed a prototype of refuelable zinc-air battery system for EV propulsion (Goldstein and Koretz, 1998). The battery system design consists of zinc pellets 0.5-0.8 inch diameter suspended in KOH electrolyte. An electrolyte management unit circulates the electrolyte and remove the reaction product to a special container.

Electric Fuel Limited (EFL), on the other hand, employed mechanically replaceable zinc cassettes. After discharge the cassettes that now contain 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. 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 et al., 1999).

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 electrochemical systems. The success of EFL's mechanically rechargeable zinc-air system further instigated the realization of a practical electric vehicle. Its innovative solution eliminated the need to solve the long-standing issues pertaining to both zinc and air electrodes. However this approach requires investment in new infrastructures which will definitely disadvantaged its widespread acceptance.

IV. ZINC-AIR BATTERY AS MICRO-POWER SOURCE FOR SMART ACTIVE LABELS

Healthcare industry ranks among the largest industries worldwide. Emerging do-it-yourself healthcare initiatives are driving innovations in "smart active labels" i.e. flat, flexible and functional devices (Chan, 2000; Trček et al., 2001; Demongeot et al., 2002; Kardas et al., 2006; Naszladya et al., 1998). These new display-type plastic smart card devices include among others blood glucose monitors, drug-delivery patches, cosmetic patches, Radio Frequency Identifications (RFIDs) data loggers and surveillance devices, sensors and displays. These devices require flexible thin-film batteries that perform best at body temperature and humidity, contain no hazardous materials, safe and environmentally friendly.

Zinc-air battery fulfils the requirements as the prospective micro-power source for "smart active labels", in particular the disposable type medical microchips application. The authors have developed a thin, high energy density zinc-air battery utilizing MCM-41 inorganic membrane technology. MCM-41 material belongs to a group of mesoporous materials known as M41S (Saputra et al., 2011). This class of material is characterized by its hexagonally ordered, uniform nano-channels with large surface area (Kresge et al., 1992). A functional prototype of Zn/MCM-41/air cell measured 1 cm^2 area x ca. 300 μm thick and weighed 50 mg, possessed electrochemical characteristics of comparable performance with commercial cell, namely, open circuit voltage of 1.5 V, limiting current density of 42 mA cm^{-2}, optimum power of 40 mW cm^{-2}, and volumetric energy density of 840 Wh l^{-1} rated at 20 mA (Saputra and Othman, 2012). Zinc-air system is also capable to operate in quasi-neutral electrolyte (Jindra et al., 1973), for instance in phosphate buffer electrolyte of pH 6.5.

V. CONCLUSION

Although commercial zinc-air cells have been in production since 1920s, the electrochemical system is still receiving considerable interest but of opposite energy density requirements. In high energy density applications, zinc-air system is being developed for powering electric vehicles. Since the system is not electrically rechargeable, the mechanically rechargeable concept is currently adopted. However this approach requires investment in new infrastructures which will definitely disadvantaged its widespread acceptance. On the other hand, zinc-air system is also explored for applications in microscale MEMS devices which usually consume power in the microwatt range. This prospective application is very promising since the cell could be made very thin with high power density. Though it is not rechargeable, there are numerous throw-away or single use applications which need on board micro power source such as the cosmetic and drug delivery patches.

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