

material can accommodate the whole compartment producing a high energy density battery.

Considerable efforts have been devoted towards the development of metal-air batteries. Metals that have been considered are lithium, calcium, magnesium, aluminum, zinc and ferum. However, the zinc-air electrochemical system has received the most attention. Despite its abundance and low cost, zinc possesses attractive electrochemical behaviour; among others, low equilibrium potential, high electrochemical equivalence, compatibility with aqueous electrolyte, reasonably good shelf life, high reversibility and it is the most electropositive metal which is relatively stable in caustic alkali electrolyte [Huot, 1997; Linden, 1995; McBreen, 1984]. The development and properties of the zinc-air electrochemical system and its components will be reviewed in **Chapter II** [Othman and Arof, 1999; Othman and Arof, 2000].

Zinc-air batteries must utilize a porous air electrode to permit air passage. Thus they are susceptible to water loss and the electrolyte drying out, especially for the non-circulating electrolyte type. The AER Energy's zinc-air battery incorporated a built-in patented air diffusion manager, among others to overcome this problem [Cheiky, 1990; Pedicini, 1994; Pedicini et al, 1996; Pedicini, 1997]. Studies on lead-acid batteries utilizing gelled electrolyte (jelly-type) showed encouraging results, viz., enhanced battery life and performance, negligible water loss and no topping-up needed, improved cycle-life and high charge acceptance [Dietz et. al,

1985; Vinod and Vijayamohanan, 1994; Vinod and Vijayamohanan, 2000; Vinod et. al, 1998]. In alkaline batteries, additives such as carboxymethylcellulose (CMC), poly(vinyl alcohol) (PVA) and polytetrafluoroethylene (PTFE) have been used to thicken the electrolyte. However, there was no attempt to employ a jelly-like alkaline electrolyte in a zinc-air electrochemical system to minimize the water evaporation from the cell. Further, as the alkaline electrolyte is retained in jelly granules, better electrolyte-carbon/catalyst-air interfaces will be provided and the occurrence of flooding avoided. Thus the present work was initiated in **Chapter III** with an attempt to utilize the aqueous potassium hydroxide electrolyte in the gel or jelly-like form in the zinc-air cell [Othman et. al, 2000a; Othman et. al, 2001], in view of the performances potential mentioned above. Hydroponics gel was selected due to its well known highly water absorbent property and has long been used in hydroponics technology. The gel is capable of storing solutions from 20 up to 100 times its weight, or more, depending on types. As it is mixed with an aqueous solution, it expands into loosely bound elastic jelly granules. Moreover, the gel is easily available from the local market and less expensive. The fabricated zinc-air cells were characterized according to their open circuit voltage, operating voltage and power density profiles, and discharge capability to ascertain the viability of the gelled KOH electrolyte. X-ray Diffraction (XRD) measurements and Scanning Electron Microscopy analysis were also undertaken on both the zinc anode and the air cathode to establish any side effects between the gel and the electrodes or the electrolyte.

Zinc-air cells have been fabricated employing a simple design using a thin zinc plate as the anode (which is of classical design), a potassium hydroxide (KOH) electrolyte immobilized by hydroponics gel and a commercially available carbon-based air cathode sheet. The discharge capabilities of the fabricated cells were comparatively low, which was presumably attributed to the limited free electrolyte nature of the gelled electrolyte. The aim of the work in **Chapter IV** is to address the probable limiting factors mentioned above with the use of an electrolyte reservoir so as to improve the cell discharge capabilities. Agar in its gelatinized form was utilized as the electrolyte reservoir [Othman et. al, 2001a; Othman et. al, 2002]. The use of agar in its gelatinized form was inspired by the fact that agar in its natural form serves as a water reservoir in the algae cell wall [Concidence, 1983; Lapedes, 1977]. It was anticipated that the agar layer would induce a better and more uniform surface area contact with the KOH electrolyte jelly granules and, improve as well as maintain the wettability of the electrodes. These in turn would lead to an increase in the electrode rate capability and active material utilization, thus improve the cell discharge capacity.

The remaining aspects of the improvement of the zinc/gelled-electrolyte/air cell that are to be considered in the present work are the use of a porous zinc electrode and employing a substantially higher concentration of the KOH electrolyte. By providing an enhanced and intimate interfacial area per unit volume, the porous electrode increases the kinetics and mass transfer of the electrochemical reaction. This would lead to the decrease in the current density, better electrode rate

capability, minimizing the energy loss, improved active material utilization, thus enhancing the cell discharge capacity. Thus the work in **Chapter V** was focused on the fabrication of a porous zinc anode from zinc-graphite-gelatinous agar paste, its optimization and application in the zinc-air cell [Othman *et. al*, 2002a]. Besides, a higher KOH concentration of 6 M was also employed, as the concentration of 2.8 M used throughout this work was comparatively low. Despite the use of a natural biodegradable polymer in the electrode fabrication, the electrode preparation technique adapted in this work is simple, fast and does not require either elevated heat treatment or a mould and hydraulic press.

In **Chapter VI**, a cyclic voltammetry characterization was performed on the zinc and air electrodes in gelled electrolyte to verify the consequence of gelling and the use of the hydroponics gel, on the electrode kinetics and make comparison to their properties in aqueous electrolyte. Cyclic voltammetry analysis was also performed on the electrode coated with a thin agar layer in gelled KOH as its application had been demonstrated beneficial to the zinc-air cell discharge capabilities [Othman *et. al*, 2001a; Othman *et. al*, 2002; Othman *et. al*, 2002a].

The various aspects of the fabrication, components, cell design and performance of the alkaline zinc-air cell developed throughout the present study will be discussed in **Chapter VII**, before finally being summarized in **Chapter VIII**.

## References

- Cheiky, M.C.*, "Metal-air battery power supply", United States Patent 4,913,983 (1990)
- Concidine, D.M.*, (Editor), Van Nostrand's Scientific Encyclopedia, 6<sup>th</sup> ed., Van Nostrand Reinhold Co. (1983) pg. 907-909, 1437
- Dietz, H., Garche, J. and Wiesner, K.*, "The effect of additives on the positive lead-acid battery electrode", J. Power Sources 14 (1985) 305-319
- Huot, J-Y*, "Advances in zinc batteries", in: New Materials for Fuel Cell and Modern Battery Systems, Proceedings of the 2<sup>nd</sup> International Symposium on New Materials for Fuel Cell and Modern Battery Systems, Savadogo, O. and Roberge, P.R. (Editors), Ecole Polytechnique de Montreal (Pub.) (1997) pg. 137-165
- Lapedes, D.N.*, (Editor-in-Chief), McGraw-Hill Encyclopedia of Science and Technology, Vol. 1, McGraw-Hill Inc. (1977) pg. 128
- McBreen, J.*, "Rechargeable zinc batteries", J. Electroanal. Chem. 168 (1984) 415-432
- Othman, R. and Arof, A.K.*, "High energy density zinc-air batteries", in: Proceedings of the Workshop on Current Problems in Batteries, 25-30 October, 1999, Dept. of Physics, University of Malaya, Arof, A.K. (Editor), Penerbit Universiti Malaya, Kuala Lumpur (1999) pg. 49-58
- Othman, R. and Arof, A.K.*, "High energy density zinc-air electrochemical power source: A review", in: Electrochemical Power Sources. Material and Characterization, Arof, A.K., Mohamed, N.S., Subban, R.H.S., Ali, S.A.H. and

Yahaya, M.Z.A. (Editors), Penerbit Universiti Malaya, Kuala Lumpur (2000) pg. 141-152

*Othman, R., Yahaya, A.H. and Arof, A.K.*, "Zinc-air primary cell employing hydroponics gel as gelling agent", in: EEC'2000, Proceedings of Regional Conference on Electrical Engineering in the New Millennium, 8-9 August, 2000, Dept. of Electrical Engineering, Kuala Lumpur (2000a) Paper D(06)

*Othman, R., Basirun, W.J., Yahaya, A.H. and Arof, A.K.*, "Hydroponics gel as a new gelling agent for alkaline zinc-air cell", J. Power Sources 113 (2001) 34-41

*Othman, R., Yahaya, A.H. and Arof, A.K.*, "Zinc-air cell with KOH-treated agar layer between electrode and electrolyte containing hydroponics gel", in: New Materials for Electrochemical Systems IV, Savadogo, O. (Editor), Extended Abstract of the 4th International Symposium on New Materials for Electrochemical Systems, 9-13 July, 2001, Montreal, Quebec, Canada, Ecole Polytechnique de Montreal (2001a) pg. 300-303

*Othman, R., Yahaya, A.H. and Arof, A.K.*, "Zinc-air cell with KOH-treated agar layer between electrode and electrolyte containing hydroponics gel", J. New Mat. Electrochem. Systems 5 (2002) 177-182

*Othman, R., Yahaya, A.H. and Arof, A.K.*, "Zinc-air cell employing porous zinc electrode fabricated from zinc-graphite-natural biodegradable polymer paste", J. Appl. Electrochem. 32 (2002a) 1347-1353

*Pedicini, C.S.*, "Diffusion controlled air manager for metal-air battery", United States Patent 5,356,729 (1994)

*Pedicini, C.S.*, "Diffusion controlled air vent for a metal-air battery", United States Patent 5,691,074 (1997)

*Pedicini, C.S., Sieminski, D.P., Skeggs, L.T., Young, J.E. and Cherry, E.C.*, "Air manager system for recirculating reactant air in a metal-air battery", United States Patent 5,560,999 (1996)

*Vinod, M.P. and Vijayamohanan, K.*, "Effect of gelling on the open circuit potential against time transients of Pb/PbSO<sub>4</sub> electrodes at various states of charge", J. Appl. Electrochem. 24 (1994) 44-51

*Vinod, M.P. and Vijayamohanan, K.*, "Effect of gelling on the impedance parameters of Pb/PbSO<sub>4</sub> electrode in maintenance-free lead acid batteries", J. Power Sources 89 (2000) 88-92

*Vinod, M.P., Vijayamohanan, K. and Joshi, S.*, "Effect of silicate and phosphate additives on the kinetics of the oxygen evolution in valve-regulated lead/acid batteries", J. Power Sources 70 (1998) 103-105