CHAPTER VII

Discussion

Since *Smee* (1840) first described a primary, acidic zinc-air cell in the literature, the zinc-air electrochemical power sources have been extensively studied and developed. However, their main constraints remain a formidable challenge. Among the major problems of metal-air batteries in general are those associated with the electrolyte, viz. the water loss and the electrolyte seepage that causes the air electrode flooding [*Hamlen, 1995; Hoare, 1968*]. As the air electrode of the metal-air batteries must be sufficiently porous to permit air diffusion, consequently the system is also susceptible to water evaporation that leads to the electrolyte drying out. The electrolyte seepage through the air electrode pores would finally diminish the triple-interface zone that is essential for the air electrode's optimum performance. Efforts made to overcome or minimize these issues are mostly focused on the air electrode. Among the measures employed in the design and fabrication of the air electrode were the inclusion of a particulate water repelling agent such as wax [*Karlsson, 1983*], polyethylene [*Manoharan and Shukla, 1985; Kannan and Shukla, 1991*], polystyrene [*Matsumoto et. al, 1980*], fluorinated polyacryloester [*Kudo et. al, 1977*] and the majority being polytetrafluoroethylene (PTFE) [*Antolini et. al, 2002; Motoo et. al, 1984*]; the application of a semipermeable hydrophobic membrane on the airside of the electrode such as the Teflon membrane [*Hoge, 1992; Hamlen, 1995*]; the use of double pore electrode structure whereby the electrode layer facing the electrolyte has smaller pores compared to the pores of the body structure [*Kiros, 1996*]; the use of a double skeleton catalyzer (DSK) that 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 [*Justi and Winsel, 1961*]; and maintaining the gas under enough pressure to keep the electrolyte in the surface layers of the porous electrode [*Hoare, 1968*]. AER Energy Resources Inc., introduced a built-in patented air diffusion manager that shields the air electrode from exposure to air during storage, among others to overcome this problem [*Cheiky, 1990*; *Pedicini, 1994*; *Pedicini et al, 1996; Pedicini, 1997*]. While the majority of the efforts focused on the air electrode design and fabrication, not much attention has been devoted to the electrolyte itself to apprehend the problems of the electrolyte drying out and flooding. *Wynveen and Kirkland* (1962) immobilized the KOH electrolyte of H_2-O_2 fuel cell in a solid matrix of asbestos disk between the porous electrodes in an effort to stabilize the gas-liquid interface. It has been observed in gelled (jelly-like) lead acid batteries that the gelling of the electrolyte enhances the life and performance of the battery, namely, the water loss due to overcharging is negligible and no topping-up is needed, improved cycle-life and high-charge acceptance [*Dietz et. al, 1985; Vinod and Vijayamohanan, 1994; Vinod et. al, 1998; Vinod and Vijayamohanan, 2000*]. Thus the present work was initiated with an attempt to utilize the aqueous potassium hydroxide electrolyte in the gel or jelly-like form in the zinc-air cell. The hydroponics gel was used as a new alkaline electrolyte gelling agent to minimize the water loss due to the high water retention of the gel [*Othman et. al, 2000; Othman* *et. al, 2001a; Othman et. al, 2001b; Othman et. al, 2002a; Othman et. al, 2002b*]. Further, as the KOH electrolyte is retained in jelly granules, it would possibly provide better electrolyte-carbon/catalyst-air interfaces and thus the flooding occurrence is minimized. The difficult problem of air electrode wet proofing is also avoided. Hydroponics gel is commonly known as a medium used to store water and soluble nutrients in hydroponics technology where plants are grown in nutrient-rich water rather than soil. The gel was initially in granular form. As it is mixed with an aqueous solution, it expands into loosely bound elastic jelly granules and is capable of storing solutions from 20 up to 100 times its weight, or more, depending on types. Thus the use of hydroponics gel could reduce the amount of electrolyte needed to occupy a particular cell volume. Compared to other polymer-type gelling agents commonly used, cellulose or cellulose derivatives such as carboxymethylcellulose (CMC) [*Cahoon and Holland, 1971 and Morehouse et. al, 1961*], vinyl polymers such as polyvinyl alcohol (PVA) [*Naylor, 1995 and Huot, 1997*], and polytetrafluoroethlyne (PTFE) [*Vassal et. al, 1999 and Ikeya, 1993*], hydroponics gel is cheaper. Further, there is a certain limit where the polymer-type material tends to shield and reduce the capacity of the cell [*Huot, 1997*], whereas hydroponics gel merely absorbs and stores the electrolyte.

Zinc-air cells were initially fabricated adapting a simple classical design to investigate the efficacy of the hydroponics gel as the alkaline electrolyte vehicle. A 0.4-mm zinc foil was utilized as the anode and a commercial air electrode that consists of a laminated structure of fibrous carbon as the cathode. The electrolyte was a 2.8-M potassium hydroxide solution without the inclusion of any additives. Normally, for alkaline zinc batteries, the electrolyte is mixed with a zinc oxide additive. It is particularly useful in limiting the solubility of the zinc oxidation product, i.e. both the zinc oxide and zinc hydroxide [*Falk and Salkind, 1969*]. The solubility of the zinc oxidation product invokes the problem of shape change and rapid capacity fading, which hampered the development of the rechargeable zinc electrode [*McBreen, 1984; McLarnon and Cairns, 1991*]. Considering the scope of the present study that is confined to primary cell, the zinc oxide additive was not included in the KOH electrolyte. A separator was also not included in the cell design as the cell was not in the compact form and the electrodes were essentially distanced apart. The fabricated zinc-air cells were discharged at galvanostatic current drain of 5, 50 and 100 mA. The resulting cell capacities of 229, 165 and 115 mAh, respectively [*Othman et. al, 2001a*], were significantly low than expected from the 36900 mAh (4.5 g x 0.82 Ah g^{-1}) theoretical electrochemical equivalent of zinc metal used. The use of a compact planar zinc foil that possesses low surface area per unit volume might possibly have accelerated the zinc electrode passivation. Another possible contributing factor was the decrease in the KOH concentration to the zinc electrode due to the fact that the electrolyte was entrapped in the gel. Besides, as the gelled electrolyte was in the form of loosely bound semi-solid granules, it might increase the electrode-electrolyte interfacial resistance. XRD and SEM characterization of both electrodes before and after discharge showed that the failure of the cells was not due to any side reaction between the gelled electrolyte and the electrodes. The formation of an insulating zinc oxide layer on the zinc electrode caused the cell operation to cease. The cyclic voltammetry study on the zinc electrode in gelled electrolyte supported the above presumptions pertaining to the low zinc active material utilization. The gelling of the electrolyte induces accelerated zinc passivation, increases the onset of the zinc oxidation and reduces the anodic current density. The hindrances on the zinc electrokinetics are most likely due to the increase in the interfacial ohmic resistance and the electrolyte diffusion transport impedance, as verified by *Vinod and Vijayamohanan* (2000) using the impedance spectroscopy technique on the lead-acid battery employing gelled electrolyte. The cyclic voltammetry study also indicated there were no other reactions than that of the oxidation-reduction reactions of zinc in the alkaline medium.

The use of an electrolyte reservoir between the electrode-gelled electrolyte interface might improve the zinc active material utilization. Even in the electrochemical cells utilizing paste or liquid electrolyte, an electrolyte reservoir or wetting agent was employed. Normally, the electrode is wrapped with an absorbent material such as ALDEX or cellulose-type material [*Himy, 1995*], or in another approach a hydrophilic wetting agent is included into the electrode composition [*Muller et. al, 1995; Muller et. al, 1998*]. It was anticipated that the electrolyte reservoir would promote a higher, better and a more uniform surface area contact with the KOH electrolyte jelly granules and, improve as well as maintain the wettability of the electrodes throughout the cell discharge. Providing an enhanced and more intimate interfacial contact area per unit volume [*Newman and Tiedemann,* *1975 and Bagshaw, 1997*], and preserving the electrode necessarily wet [*Himy, 1995; Muller et. al, 1995; Muller et. al, 1998*], leads to an increase in the electrode rate capability and zinc active material utilization. In this work, agar was introduced as another material that could also be used as an electrolyte reservoir [*Othman et. al, 2001b; Othman et. al, 2002a*]. The use of agar was inspired by the fact that agar in its existing natural form serves as a water reservoir in the algae cell wall. Algal polysaccharides are fibrous material with gel forming properties. The zinc-air cells discharge capacities were improved markedly as a result of applying a thin agar coating between the electrode-gelled electrolyte interfaces. The cell capacities were extended from formerly 229, 165 and 115 mAh, to 497.5, 209 and 131.3 mAh, at rated current of 5, 50, and 100 mA, respectively, when the agar coating was applied onto the zinc electrode. As the agar coating was applied onto both the zinc and air electrodes the cell capacities were further enhanced to 711, 240 and 163 mAh, respectively. These results supported the presumed roles of the agar coating between the electrode-gelled electrolyte interface. The beneficial role of the agar coating on the zinc electrode was further verified by the cyclic voltammetry study. The cyclic voltammogram of the zinc electrode proved that the agar layer eased the hindrances caused by the gelled electrolyte. However, the agar coating did not improve the cathodic current profiles of the air electrode in gelled electrolyte. There seems to be contrasting results on the influence of the agar coating on the cell discharge performance and the cyclic voltammetry observations. Zinc and oxygen is a unique couple, in such that their electrochemical kinetics lies in the opposite ends. Zinc is well known for its rapid electrokinetics [*McBreen, 1984; McLarnon and Cairns,* *1991*] whereas in contrast, oxygen is renown for its slow electrokinetics [*Hoare, 1968*]. It is believed that inserting an additional agar layer between the air electrode and the gelled electrolyte might probably have hindered the slow and complex nature of the oxygen reduction. Therefore, how could the application of the agar layer improve the zinc-air discharge performance? Zinc-air cells are susceptible to water loss and hence the electrolyte drying out due to the permeability of the air electrode. Thus, the air electrode-gelled electrolyte interface is mainly affected. Furthermore, during cell discharge heat is generated and this might accelerate the process. Accordingly, coating the electrode with an agar film would keep the interface necessarily wet throughout the cell discharge and as a result improve the cell discharge capacity.

Another aspect of the improvement of the zinc-air cell employing the gelled electrolyte was the form of the zinc electrode. The previous results were obtained using zinc foil as the anode. The use of the zinc anode in the porous form would definitely enhance the zinc-air cell discharge performance due to the efficient and high surface area obtained from such an electrode [*Jin and Lu, 2001; Kriegsmann and Cheh, 1999; Lindbergh, 1997*]. Porous zinc electrodes were prepared from zinc-graphite-gelatinized agar paste [*Othman et. al, 2002b*]. Once dried, the agar acts as a binder to the electrode. The porous electrode preparation technique employed was simple, fast, using environmentally benign and biodegradable binding material, and did not require either elevated heat treatment or mould and hydraulic press. Graphite was included in view of its favourable effects on the zinc electrode as reported by other workers [*Bass et. al, 1988; Brown, 1983; Duffield et. al, 1987*]. The inclusion of the conductive particulate graphite was reported to improve zinc anode discharge capability, considerably inhibit active zinc dissolution and promote reprecipitation of oxidized zinc species. However, in the present study the inclusion of graphite had an adverse effect. SEM investigation revealed the existence of two distinct layers in the electrode structure when graphite was included. Graphite with its density significantly lower than that of zinc surfaced and formed a graphite-rich matrix. Most likely the graphite-rich matrix obscured the electrode porosity and hence resulted in reduced cell capacity. This phenomenon was further exacerbated due the limited free electrolyte nature of the gelled electrolyte. Though the use of more viscous agar concentration in the preparation of the electrode might blend the zinc and graphite mixture homogeneously, however, it resulted in reduced electrode capacity. At agar concentration higher than 5 mg cm^{-3}, the dried agar formed a film that was thick enough to shield the zinc active material. Thus the porous zinc electrodes were prepared without the inclusion of any graphite content. The zinc-air cells discharge capacities employing the porous zinc anode were remarkably extended. At 50 mA discharge current the cell capacity was extended from 240 to 1349 mAh, an improvement ratio of 5.6. Whereas at 100 mA discharge current the delivered capacity increased by 4.5 times, enhanced from 163 to 734 mAh. Normally, alkaline zinc batteries employed an aqueous KOH concentration in the range 6-10 M (27 to 40 wt. %) [*Bagotzky and Skundin, 1980*]. Thus a 6 M KOH concentration was applied. The delivered cell capacities were substantially extended to 2066 and 1908 mAh at discharge rates of 50 and 100 mA respectively. The corresponding specific energy density of the cell at the rated discharge currents were 443 and 420 Wh kg^{-1} respectively. Although the porous zinc anode possesses high surface area and usually a sufficient amount of KOH electrolyte entrapped within the electrode pores, the application of an agar layer as the electrolyte reservoir to the electrodes was still beneficial to the cell discharge performance particularly for the gelled electrolyte medium. The removal of the agar layer between the electrode-gelled electrolyte interfaces resulted in considerably reduced cell capacity by 52 %. For comparison of the zinc-air cell performance achieved in the present work, quite recently Electric Fuel Ltd. introduced a 3.6 V disposable primary zinc-air battery for cellular phones rated 3300 mAh [*Goldstein et. al, 1999*]. Hence the discharge capacities of 2066 mAh and 1908 mAh obtained in this work from a single 1.4 V zinc-air cell could be considered of comparable performance to the present technology.

Finally, a cyclic voltammetry characterization was performed on the zinc and air electrodes in gelled KOH electrolyte to ascertain the effect of gelling on the electrode kinetics. The immediate consequence of gelling is the decrease in the free electrolyte concentration to the electrode. As anticipated, it caused substantial hindrance to the electrode kinetics, as apparent from the reduced current density of the voltammograms. The starved electrolyte nature of the gelled electrolyte adduced several interesting properties of particular interest in the development of the secondary zinc electrode. The mobility of the zincate species was considerably reduced. The limited free electrolyte was easily saturated with zincate ions thus minimizing the dissolution of the precipitated discharge product. Moreover, the gel structure also possibly retarded the soluble zincate ion migration and trapped it within the gel structure. As a result, the suppression of the zinc oxidation product dissolution and the impediment of the mobility of the zincate species promoted the redeposition of zinc, as is evident from the improved features of the cathodic profile. Both the intensity and the area under the curve of the cathodic peak were notably enhanced in the gelled electrolyte. Another manifestation of the suppression of the zinc oxidation product dissolution was the substantial decrease in the passivation current as a result of gelling. The passivating current is related to the chemical dissolution of the passive oxidation product [*Prentice et. al, 1991; Rehim et. al, 1995*]. It is well known that in order to reduce the problems of shape change and capacity fading on repeated cycling of the zinc anode, the dissolution and migration of the discharge product must be controlled. From this point of view, the use of gelled electrolyte shows potential prospects. Another interesting effect of gelling was its influence on both oxygen and hydrogen gassing on the far positive and negative ends, respectively. The gelling of the electrolyte attenuated both the oxygen and hydrogen evolution reactions. In aqueous based electrolyte batteries, the charging process causes considerable water loss due to the decomposition of the water. By extending the oxygen evolution potential sufficiently high towards the positive end, the electrolyte water loss can be thus minimized. The increase in the hydrogen overvoltage on zinc in alkaline medium is another added advantage, especially without the inclusion of any additives. The losses due to wasteful corrosion could be minimized. These beneficial effects of the use of gelled aqueous based electrolyte have in fact been observed in the maintenance-free lead acid battery [*Vinod and Vijayamohanan, 1994; Vinod et. al, 1998*]. The increase in the hydrogen overvoltage in gelled electrolyte could be attributed to the decrease in the activity of water [*Dirkse and Timmer, 1969*] and the suppression of the zinc dissolution [*Ruetschi, 1967*], which were due to the limited free electrolyte medium. On the contrary, the customized design of the commercial air electrode utilized in this work might not be suitable for use with gelled electrolyte. The air electrode consisted of a laminated structure of fibrous carbon sandwiched against a nickel support and current collector. The fibrous carbon structure inhibited the gelled electrolyte penetration and thus its large surface area design was under utilized. The cyclic voltammetry profile of the air electrode in gelled electrolyte verified that the gelled electrolyte could not even reach the nickel current collector mesh.

For the zinc electrode the coating with an agar layer improved its current density profile, shifted the anodic peak negatively after being drawn out positively, and displaced the cathodic peak towards a less negative value after being shifted negatively due to the electrolyte gelling. These trends substantiated the presumption on the role of agar between the electrode-gelled electrolyte interface. On the other hand, for the air electrode the application of the agar film between the electrode–electrolyte interface did not improve the electrode activity in the oxygen reduction reaction. The additional agar layer might further affect the oxygen reduction process, which is well known for its slow and complex nature. Nevertheless, the application of the agar has been demonstrated to be beneficial in extending the zinc-air cell service life. Coating the electrode with an agar film would keep the interface necessarily wet throughout the cell discharge and as a result improve the cell discharge capacity.

The cyclic voltammetry studies confirmed that the use of the hydroponics gel as a gelling agent did not result in any side reactions with the zinc electrode, air electrode or the KOH electrolyte although the origin of the hydroponics gel was not studied. Hydroponics gel was selected because the gelled KOH was readily and easily prepared upon mixing the gel with the aqueous KOH. It is easily available from the local market and low cost. The cyclic voltammograms of zinc and oxygen in the gelled KOH electrolyte revealed the typical electrochemical reduction-oxidation behaviors in an alkaline medium as vastly reported by other researchers. XRD and SEM observations of the zinc and air electrodes before and after complete cell discharge supported the cyclic voltammetry study results. The failure of the cells at the end of discharge was due to the formation of an insulating zinc oxide layer, which is the end discharge product of the zinc-air cell.

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