CHAPTER IV

The Application of a KOH-Treated Agar Layer as an Electrolyte Reservoir between the Electrode and the Gelled Electrolyte

4.1 Introduction

Earlier investigations on primary zinc-air cells employing hydroponics gel as an immobilizing agent for 2.8-M potassium hydroxide (KOH) electrolyte showed promising results. However, the discharge capability of the fabricated cells was much lower than that expected from a 4.5 g zinc electrode [*Othman et. al, 2000; Othman et. al, 2001*]. Presumably, the following factors might contribute to the low active material utilization; the low surface area of the compact planar zinc electrode and the use of a substantially lower KOH electrolyte concentration. Further, as the KOH electrolyte was in the form of loosely bound semi-solid granules, it may have limited the amount of free KOH electrolyte available to the zinc electrode and also have induced an increase in the electrode-electrolyte interfacial resistance.

The aim of the present work is to address the latter issue, which originated from the use of gelled electrolyte. The electrode-gelled electrolyte interfacial contact and the electrode wettability will be improved by using a thin agar coating as the electrolyte reservoir. 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 [*Concidine, 1983; Lapedes, 1977*].

4.2 Some properties of agar

Agar is a biodegradable polysaccharide polymer extracted from marine algae and is hydrophilic in nature. It comprises mainly neutral polymer agarose, pyruvated agarose and sulphated galactans. The structure of agar is based on a disaccharide alternating repeat structure of 3-linked β-D-galactopyranosyl and 4-linked 3,6-anhydro-α-L- galactopyranosyl units [*Falshaw et. al, 1998; Marinho-Soriano, 2001; Ockerman, 1978; Singh, 1992; Singleton and Sainsbury, 1988*]. The gel forming properties of agar have found useful applications in the medical, agricultural, drug packaging and release, cosmetics and food industries [*Chandra and Rustgi, 1998*].

4.3 Experimental

4.3.1 Zinc-air cell fabrication

The cell components, design and fabrication were similar to those detailed earlier in Section 3.2. The only difference is the application of a KOH-treated, thin, agar layer onto both the electrodes, as depicted schematically in Figure 4.1. In order to study the effect of the agar coating on the cell discharge performance, the cell will be prepared in which (a) both the anode and cathode are coated with the thin agar layer, (b) only the zinc electrode is coated and finally (c) no agar layer is applied on either electrode. The agar layer in its gelatinized form will serve as an electrolyte reservoir to the electrode. This is meant to ease the hindrances due to the high water retentivity of the gel, which resulted in poor active material utilization.

4.3.2 Preparation of the agar solution and KOH-treated agar layer

A purified agar (Bacto-Agar) for microbiological culture media, the extraneous matters, pigmented portions and salts of which are reduced to a minimum, was used in this work. The agar was in fine granular form, mixed with deionized water, stirred and dissolved at 90°C giving a clear solution. An agar solution concentration of 5 mg cm^{-3} was employed. When the agar solution temperature was approximately 50°C, it was poured onto the zinc anode and the air cathode to a quantity just enough to cover the whole area. Once the agar layer gelatinized or solidified, it was soaked with several drops of the aqueous KOH electrolyte. The thickness of the agar coating was less than 1 mm.

4.3.3 Characterization of the zinc-air cell

The fabricated zinc-air cell was characterized according to its operating voltage vs. current drain and power density curves, and discharge profile at constant current of 5, 50 and 100 mA. A LG-50 Galvanostat electroanalytical system was used to perform the experiments.

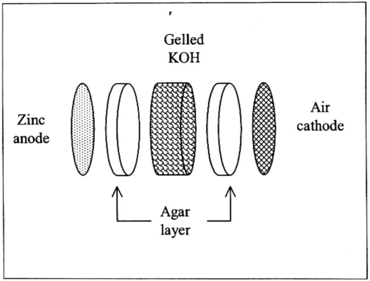

Figure 4.1. Schematic layout of the zinc-air cell preparation employing the agar layer as an electrolyte reservoir.

4.4 Results

Slight changes in the open circuit voltage (OCV) of the zinc-air cell were noticed as a thin agar layer was introduced between the electrode-gelled electrolyte interface. The average OCV increased slightly from 1.45 V to 1.47 V as the agar layer was applied between the zinc anode-electrolyte interface. However, it dropped to 1.42 V after the agar layer has been applied onto both electrodes. The operating voltage vs. current drain curves of the zinc-air cell are shown in Figure 4.2. Improved operating voltage profiles are observed above the 8 mA region for the cell with the agar coating, either onto the zinc anode only or both electrodes. The cell with the agar layer applied onto both electrodes shows the best profile, though in the lower current range its operating voltage is slightly less. The corresponding power density curves are given in Figure 4.3. It is only above the 30 mA range that the distinction is obvious. The discharge performance of the cells at constant current of 5, 50 and 100 mA is displayed in Figures 4.4 to 4.6, respectively. Consistently, the cells employing the agar layer show marked improvement in their discharge performance. The discharge duration improves as an agar layer was applied between the zinc electrode-electrolyte interface, and it is further enhanced when both the electrodes were coated with the thin agar layer. Table 4.1 details the cells discharge performance as the agar layer was applied onto the zinc and air electrodes, at the respective discharge currents.

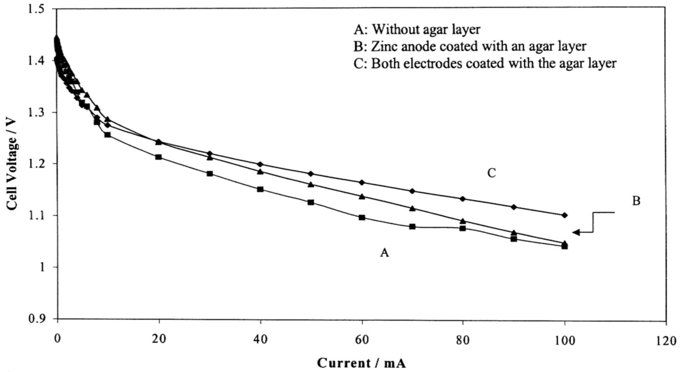

Figure 4.2. The agar coating improves the zinc-air cell operating voltage profiles.

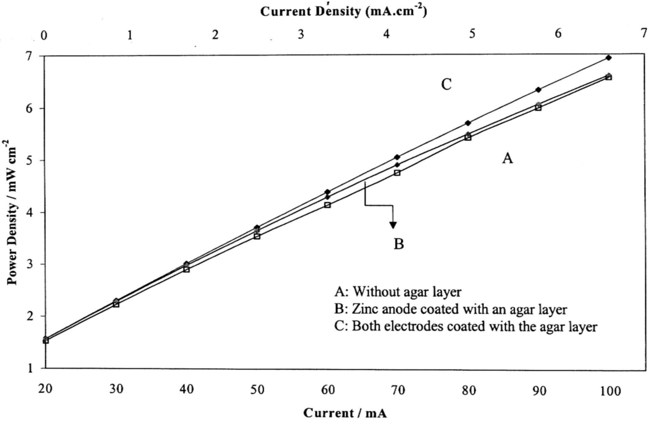

Figure 4.3. The agar coating also improves the zinc-air cell power density profiles.

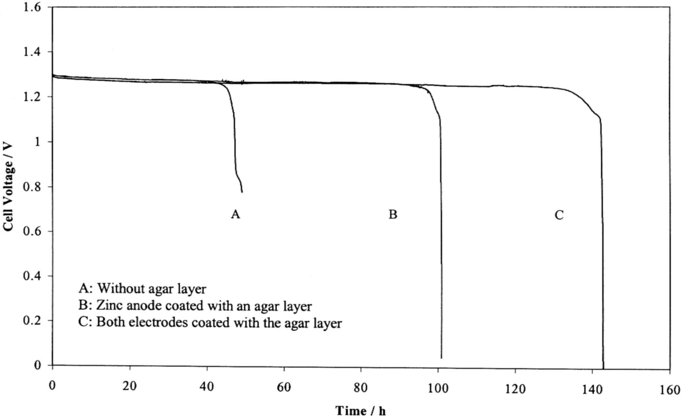

Figure 4.4. Zinc-air cell discharge profiles illustrating the beneficial effects of the agar coating, at discharge current of 5 mA.

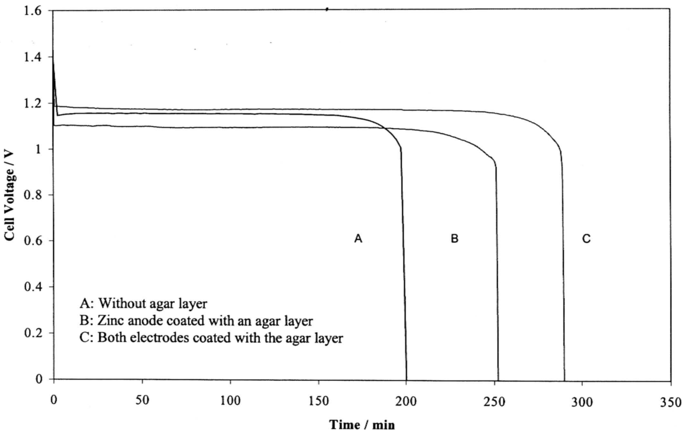

Figure 4.5. Zinc-air cell discharge profiles illustrating the beneficial effects of the agar coating, at discharge current of 50 mA.

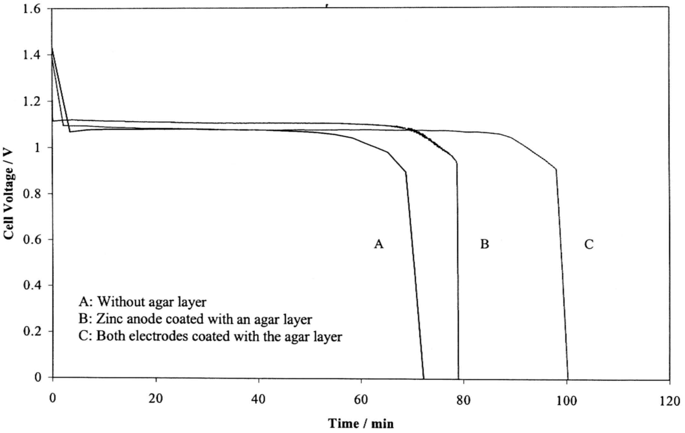

Figure 4.6. Zinc-air cell discharge profiles illustrating the beneficial effects of the agar coating, at discharge current of 100 mA.

Table 4.1. The influence of the agar coating on the zinc-air cells discharge performance.

Discharge Current (mA)	Without agar coating A	Zinc electrode coated with agar B		Both electrodes Coated with agar C		
	Discharge duration (min)	Discharge duration (min)	Increment (%) B-A	Discharge duration (min)	Increment (%) C-B	Overall Increment (%) C-A
5	2826	6030	113	8532	41	202
50	198	251	27	288	15	45
100	69	79	14	98	24	42

4.5 Discussion

An immediate consequence of gelling is the decrease in the freely available KOH concentration to the electrodes, whereby the limited electrolyte becomes easily saturated with zincate ions which thus accelerated the zinc anode passivation. Also the elastic jelly granules are likely to contribute to the increase of the interfacial resistance due to the lack of continuous and uniform electrode-gel electrolyte interface. *Vinod and Vijayamohanan* (2000), applying the impedance spectroscopy method, verified that the gelling of the electrolyte in maintenance-free lead acid battery caused a considerable increase in the interfacial ohmic resistance and the electrolyte diffusion transport impedance. Another notable feature of diffusion transport in gels is the existence of simultaneously competitive diffusion and retention processes [*Lakatos and Lakatos-Szabo, 1998*]. In view of these adverse effects caused by the use of gelled electrolyte, an electrolyte reservoir between the electrode-gelled electrolyte interface could ease these problems. Agar in its gelatinized form was utilized as the electrolyte reservoir. Its use was inspired by the fact that agar is known in its existing natural form to serve as a water reservoir in the algae cell wall [*Concidine, 1983; Lapedes, 1977*]. Algal polysaccharides (which include alginic acid, agar and carageenaan) are fibrous material with gel forming properties. As the agar layer adheres sufficiently to the electrode when it gelatinized, it would form 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. Providing an enhanced and intimate interfacial contact area per unit volume [*Bagshaw, 1997; Newman and Tiedemann, 1975*], 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 active material utilization. Thus in this work, it is anticipated that the improvement in the electrode-gelled electrolyte interface properties would lead to an improvement of the cell discharge capacity.

The cells delivered capacities were essentially extended as the agar layer was applied onto the zinc electrode. It is reasonable to deduce that the further improvement in the cells delivered capacities as both the zinc and air electrodes were coated with the agar layer, were attributed to the agar coating on the air electrode. At 100 mA discharge current the capacity is enhanced from initially 115 to 131.3 mAh and finally to 163.3 mAh, an improvement ratio of 1.4. At 50 mA discharge current, the delivered capacity increases nearly 1.5 times, rising from 165 to 209 mAh and finally to a capacity of 240 mAh. At the lower discharge rate of 5 mA the improvement ratio increases threefold, beginning from 229, increasing to 497.5 mAh and finally the discharge performance improved to 711 mAh. These results suggest that the application of the agar layer improved the electrode-gelled electrolyte interface. Besides, the improvement of both cathode-gelled electrolyte and anode-gelled electrolyte interfaces are equally important. Note that these factors alone significantly contributed from 1.4 up to threefold capacity increment ratio, depending upon the discharge rate.

It might appear that the application of the thin agar layer might further deplete the free electrolyte available to the electrode and also increase the hindrance to the diffusion transport process. Nevertheless, as the agar material is fibrous in nature [*Concidine, 1983*], the microfibre network entrapped the electrolyte and concurrently promoted the electrode-gelled electrolyte interface, as demonstrated from the cell discharge results. However, more elaborate studies are needed to support these observations and presumptions.

The planar zinc anode, due to its low surface area per unit volume and compact form, possesses limited discharge capabilities and hence ineffective active mass utilization. Thus another aspect of the improvement of the discharge capacity of the cell is the utilization of the porous zinc anode because of its efficient and high surface area

4.6 Summary

The application of a thin, KOH-treated, agar layer between the electrode-gelled electrolyte improved the discharge performance of the zinc-air cells markedly. The agar layers served as an electrolyte reservoir and at the same time maintained the wettability of the electrode during cell discharge. These factors alone induced an improvement ratio of 1.4 up to threefold, depending upon the discharge rate.

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