

Hydroponics gel as a new electrolyte gelling agent for alkaline zinc–air cells

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Received 20 February 2001; received in revised form 20 April 2001; accepted 21 May 2001

Abstract

The viability of hydroponics gel as a new alkaline electrolyte gelling agent is investigated. Zinc–air cells are fabricated employing 12 wt.% KOH electrolyte immobilised with hydroponics gel. The cells are discharged at constant currents of 5, 50 and 100 mA. XRD and SEM analysis of the anode plates after discharge show that the failure mode is due to the formation of zinc oxide insulating layers and not due to any side reactions between the gel and the plate or the electrolyte. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zinc–air cell; Hydroponics gel; Gelling agent; KOH electrolyte; Zinc oxide crystals

1. Introduction

In this work, zinc–air primary cells are prepared with a low concentration (12 wt.%) of aqueous potassium hydroxide (KOH) electrolyte and a new material, i.e. a hydroponics gel, as an electrolyte gelling agent. Hydroponics gel is a medium used to store water and soluble nutrients in hydroponics technology where plants are grown in nutrient-rich water rather than in soil. Hydroponics gel is attractive due to its capability to store solution from 20 to 100 times by weight. This minimises the weight of the cell. Upon mixture with solution, the gel expands into a loosely bound gel medicine and thus reduces the amount of electrolyte that is required to occupy a particular cell volume. Compared with other polymer-type gelling agents, e.g. cellulose or cellulose derivatives such as CMC [1,2] and vinyl polymers such as PVA [3,4], hydroponics gel is much cheaper. Further, there is a certain limit where polymer-type material tend to shield and reduce the capacity of cells [4], whereas hydroponics gel merely absorbs and stores electrolyte.

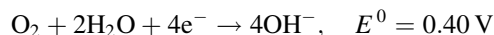
A zinc–air cell has been selected to examine the efficacy of hydroponics gel because this cell system possesses the highest specific energy compared with other zinc-based alkaline batteries. This is mainly due to the unlimited and free supply of oxygen from the ambient air which is not incorporated within the cell. Other advantages of the

zinc–air system include [5] a flat discharge voltage, a capacity which is independent of load and temperature within the operating range, long dry storage, use of an environmentally benign and low cost metal.

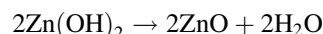
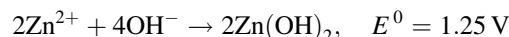
2. Zinc–air cell chemistry

The zinc–air cell has a theoretical specific energy of 1085 Wh kg⁻¹, based on the molecular weight of ZnO (658 Wh kg⁻¹) and the theoretical cell voltage 1.65 V. The overall cell discharge reactions can be summarised as follows [5,6]:

at the positive (cathode) electrode :



at the negative (anode) electrode : $2\text{Zn} \rightarrow 2\text{Zn}^{2+} + 4\text{e}^-$



overall cell discharge : $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}, \quad E^0 = 1.65 \text{ V}$

The oxygen reduction process is complex and involves a rate-limiting stage which affects the reaction kinetics and, finally, the cell performance. This stage involves the formation of hydroperoxide ions O₂H⁻ [7,8]. Catalytic compounds are required to accelerate the decomposition of hydroperoxide ions.

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3. Experimental

3.1. Cell components and fabrication

The zinc–air cell comprised a zinc anode, a caustic alkali electrolyte, and a carbon-based electrode that was sufficiently porous and gas-permeable to ‘breathe air’ but resisted electrolyte penetration. All components were enclosed in a cylindrical plastic casing of dimensions: 28 mm (height), 45 mm (diameter). Both ends were attached with screwed, L-shaped, plastic rings. The container and both rings weighed 12.8 g.

A 0.4 mm thick zinc foil of 99.98% purity was cut into a circular anode plate of 45 mm diameter. A current tab of copper foil (5 mm × 7 mm × 0.1 mm) was soldered to the centre of the plate. The plate was first cleaned with acetone to remove any traces of oil or grease. It was then dipped in 10% nitric acid solution for several seconds to remove any oxide and carbonate layers. Finally, the plate was air-dried, weighed, and stored in a desiccator. The plate and tab weighed 4.67 g.

A commercially available, carbon-based, air cathode sheet was utilised. This consisted of laminated structures of fibrous carbon supported by a nickel-plated mesh that also acted as the current-collector. The air-side of the electrode was coated with a gas-permeable, hydrophobic, Teflon layer. The whole structure was approximately 0.6 mm thick. Similarly, the air cathode sheet was cut into a circular shape (45 mm diameter) with a small portion left for the current tab. The electrode weighed 0.95 g. A cross-sectional view of the air cathode is shown schematically in Fig. 1.

A comparatively low concentration of aqueous potassium hydroxide solution was used (12 wt.%) and hydroponics gel was introduced as an electrolyte immobilising agent. The gel was initially in granular form. On mixing with aqueous potassium hydroxide solution, the gel expanded into loosely bound, jelly granules, 2.18 g of the gel was sufficient to contain 37 ml of potassium hydroxide solution and filled the casing volume (45 cm³).

The construction of the components into a complete cell of monopolar design is shown schematically in Fig. 2. The electrodes were placed snugly on to the L-shaped rings. First, ring with the air cathode was attached to the container.

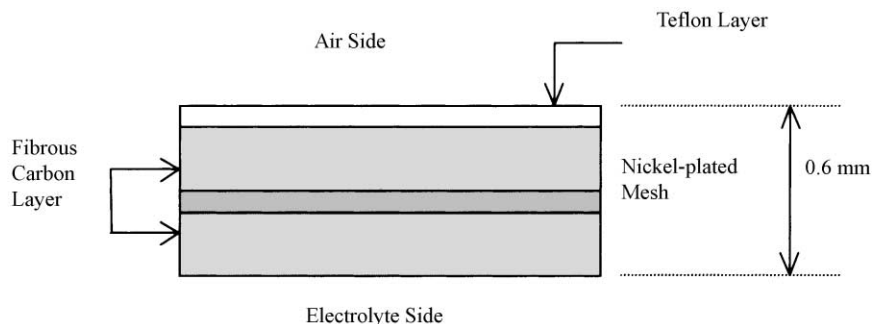


Fig. 1. Cross-sectional view of the air cathode used.

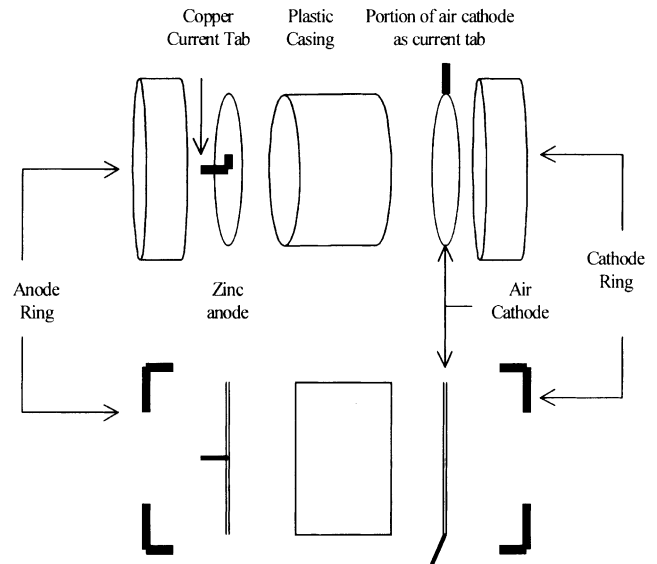


Fig. 2. Layout of the zinc–air cell assembly.

The gelled electrolyte was then introduced. Finally, the container was encapsulated with the zinc anode ring. The interfaces between the components were sealed with an epoxy resin glue. The resulting cell weighed 63.65 g.

3.2. Cell characterisation

The cells were characterised according to their open-circuit voltage (OCV), voltage–current and power density curves, and discharge profiles at constant current. The cell was stored for 24 h prior to discharge testing. The discharge currents were 5, 50 and 100 mA, respectively. A BAS LG-50 galvanostat electroanalytical system was used to perform the experiments.

3.3. Electrode characterisation

X-ray diffraction (XRD) measurements were undertaken on both the zinc anode and the air cathode before assembly in the cell. This involved the use of a Philips X-ray diffractometer XD-5 with Cu K α radiation (1.5405 Å). After the cells were fully discharged, they were dismantled,

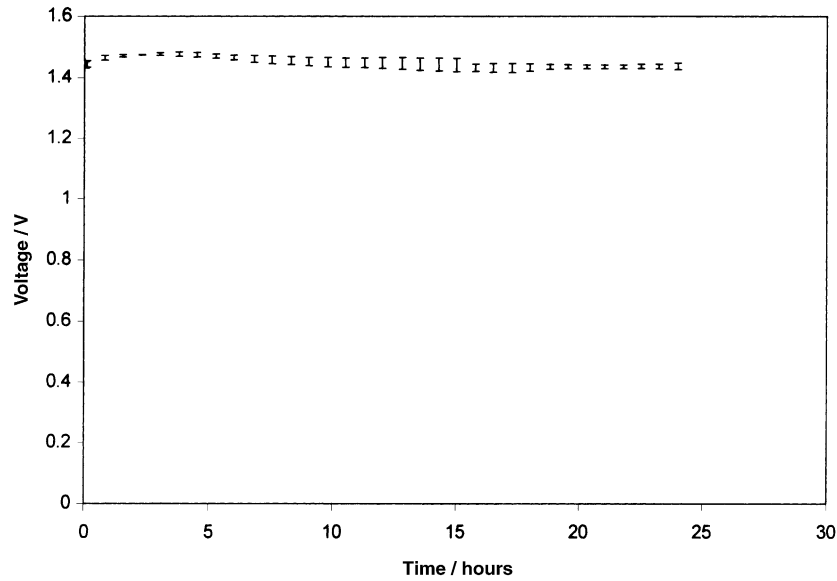


Fig. 3. Zinc-air cell open-circuit voltage during 24 h of storage.

cleaned and air-dried. XRD measurements were again performed on the electrodes. The latter measurements were taken to determine the failure mode of the fabricated cells. Scanning electron micrographs were also taken to support XRD observations.

4. Results

4.1. Cell characterisation

The OCV values of the cells were around 1.45 V. The OCV remained stable, without any significant drop, during

24 h of storage (see Fig. 3). The operating voltage and the power density delivered by the cell as a function of current drain from 10 μ A to 100 mA are given in Fig. 4. The measurements were conducted after 24 h of storage. The cell voltage at each particular current drain was monitored for 10 s and the average value was recorded. The power of the cell was calculated from the measured voltage-current curve.

Discharge profiles at constant currents of 100 and 50 mA are given in Fig. 5 and the profile at a constant current of 5 mA in Fig. 6. The cells are able to sustain the current drains, as demonstrated by the flat discharge curves. The average operating voltage was 1.08, 1.15 and 1.28 V, respectively.

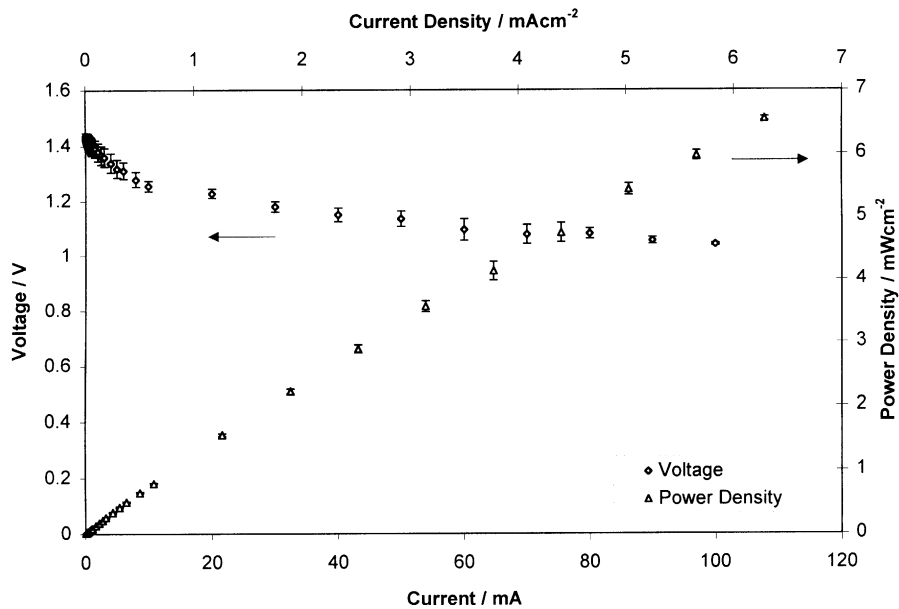


Fig. 4. Zinc-air cell operating voltage and power density as a function of current drain.

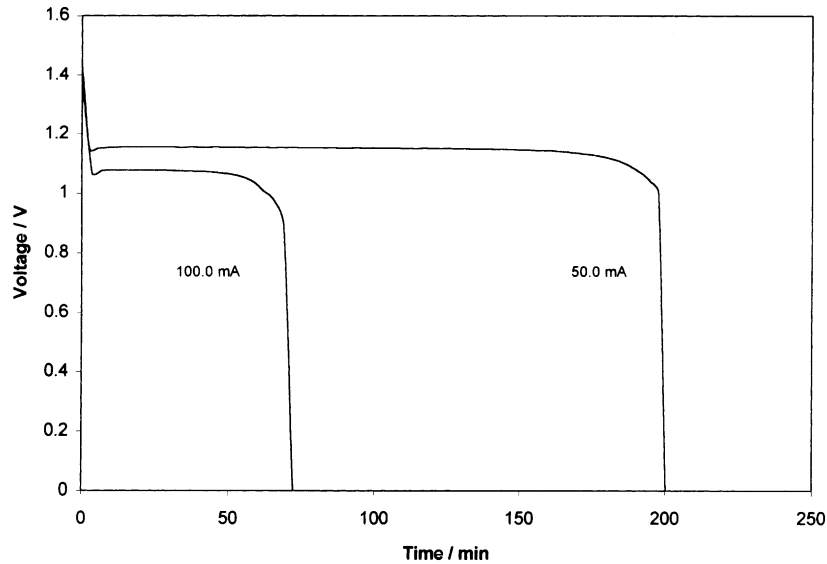


Fig. 5. Constant current discharge profiles at 100 and 50 mA.

The cut-off voltage was around 0.9 V. At a current drain of 100 mA, the discharge lasted for 69 min, i.e. the time interval from beginning of discharge to the cut-off voltage. At 50 and 5 mA, the discharge was sustained for 198 and 2750 min (45.8 h), respectively.

4.2. Electrode characterisation

The XRD pattern for the zinc plate before use is shown in Fig. 7. It conforms to the standard ASTM X-ray data file pattern for zinc [9]. The XRD patterns of the post-discharge zinc plates (Fig. 8) was that for zinc oxide [10,11] which is taken to be the end-product of the discharge. The XRD pattern for the air cathode before use is given in Fig. 9.

Three peaks are detected at 2θ angles of 18.2, 44.6 and 52°. Later, the fibrous carbon layers were separated from the nickel-plated mesh, and XRD measurements were performed on each material (see Figs. 10 and 11, respectively). Therefore, from the peaks detected in Fig. 9 the 18.2° peak is attributed to the fibrous carbon material whereas the 44.6 and 52° peaks are assigned to the nickel-plated mesh. The XRD pattern of the air cathode after usage remained unchanged.

Electron micrographs of the zinc anode plate taken after complete discharge showed that a long needle-like layer of zinc oxide covered the plate, as shown in Figs. 12–14 at 1000, 5000 and 10,000× magnifications, respectively. The above XRD results are in agreement with these observations.

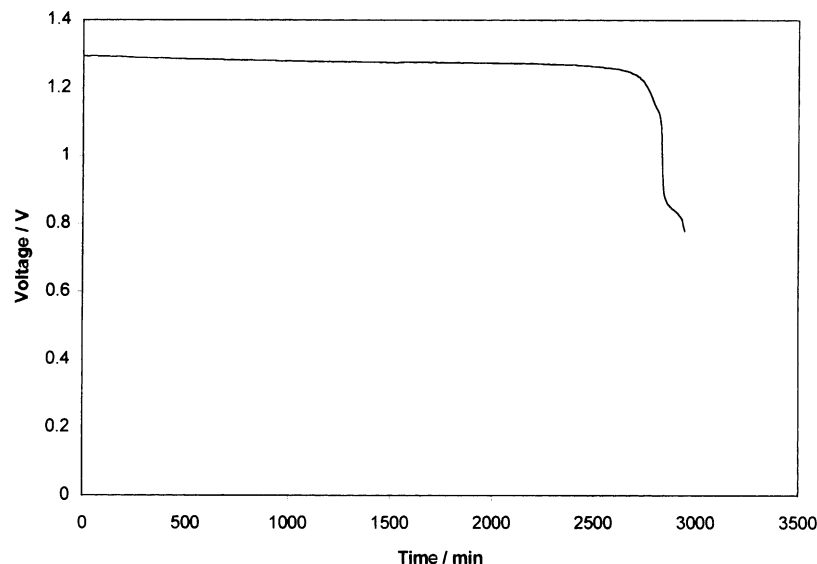


Fig. 6. Discharge curve at constant current of 5 mA.

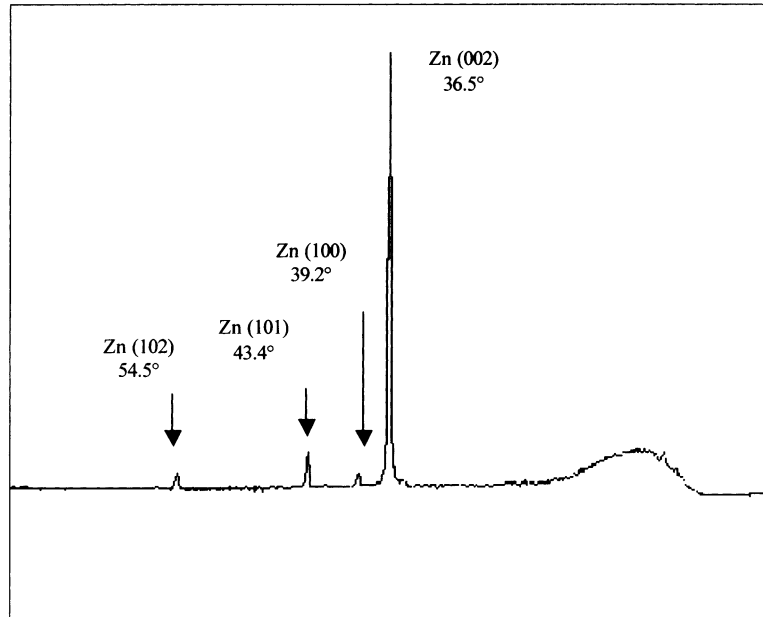


Fig. 7. X-ray diffractogram of the zinc anode plate before use.

5. Discussion

Zinc–air cells have been fabricated employing a comparatively low concentration (12 wt.%) aqueous potassium hydroxide and hydroponics gel as the electrolyte gelling agent. OCV measurements over a period of 24 h does not show any sign of fast self-discharge. The cell close-circuit operating voltage in the 10 μ A to 100 mA current range is in agreement with reported data [6,7]. The cells are capable of

delivering 5, 50 and 100 mA constant current drains with resulting capacities of 229, 165 and 115 mAh, respectively. The use of hydroponics gel as an alkaline electrolyte gelling agent does not affect the oxidation–reduction reaction of the zinc–air cell, as evident from the discharge capability of the cells. It should be noted that the resulting capacities are much lower than that expected from the 4.5 g zinc electrode. Presumably, this is because the electrode has a compact planar form. Further, the concentration of potassium hydroxide

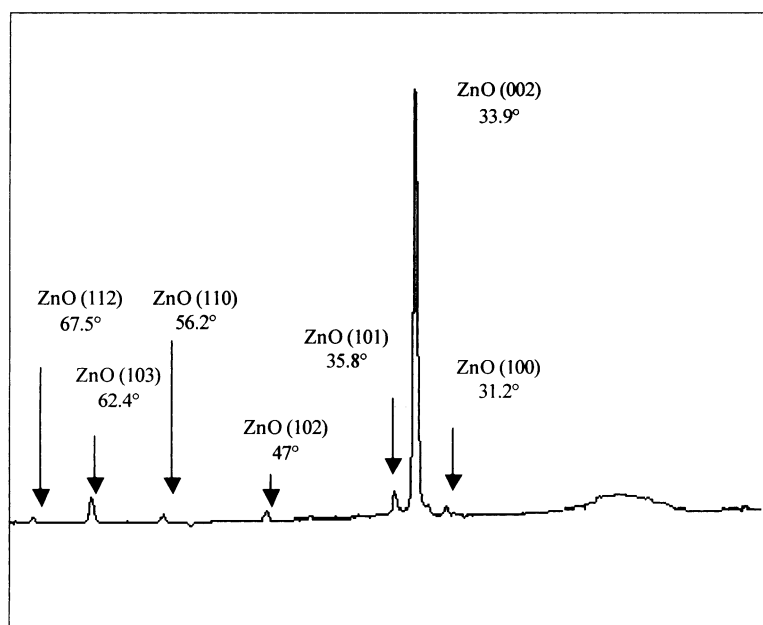


Fig. 8. The typical X-ray diffractogram obtained from the zinc anode after complete discharge which matches to the zinc oxide pattern.

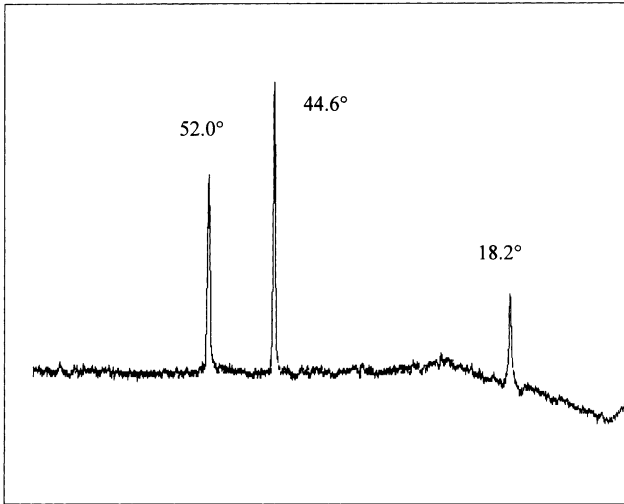


Fig. 9. XRD pattern of the air cathode sheet. The sheet consists of fibrous carbon layers, nickel-plated mesh and Teflon membrane.

electrolyte was only 12 wt.%. Normally, zinc-based batteries employ a potassium hydroxide concentration in the range 27–40 wt.% (6–10 M) [12]. Thus, the use of a highly porous and expanded zinc electrode and potassium hydroxide of substantially higher concentration would definitely improve utilisation of the zinc active material.

XRD results show that the failure of the cell at the end of discharge is due to the formation of an insulating layer of zinc oxide rather than any side reactions of the hydroponics gel with the zinc or the electrolyte. Electron micrographs show that a long needle-like layer of zinc oxide crystals is formed on the electrode. This supports the XRD observations.

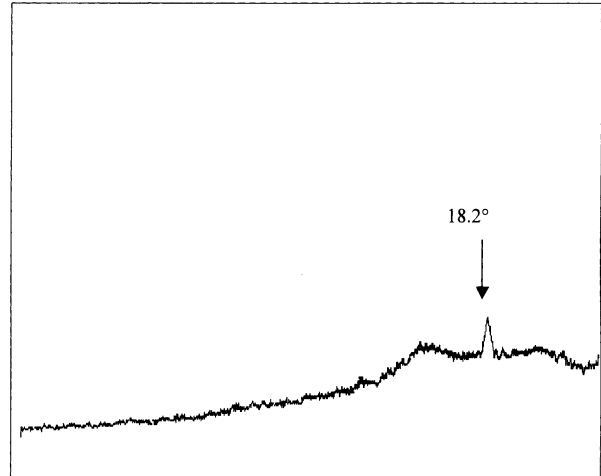


Fig. 10. XRD pattern of fibrous carbon material (from air cathode sheet).

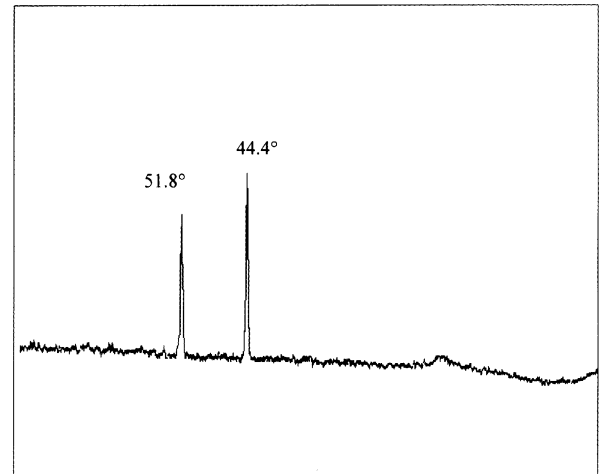


Fig. 11. XRD pattern of nickel-plated mesh (from air cathode sheet).

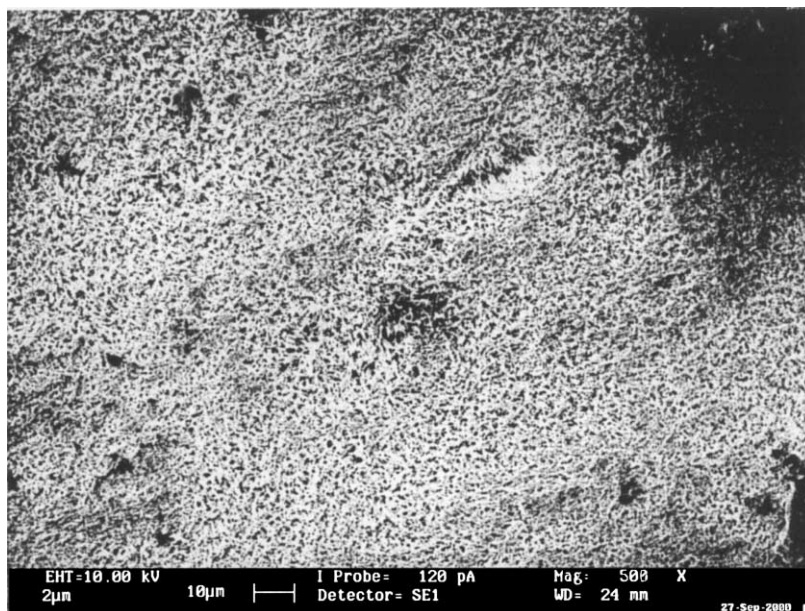


Fig. 12. Scanning electron micrograph of the zinc anode plate after complete discharge displays the carpet-like zinc oxide layer.

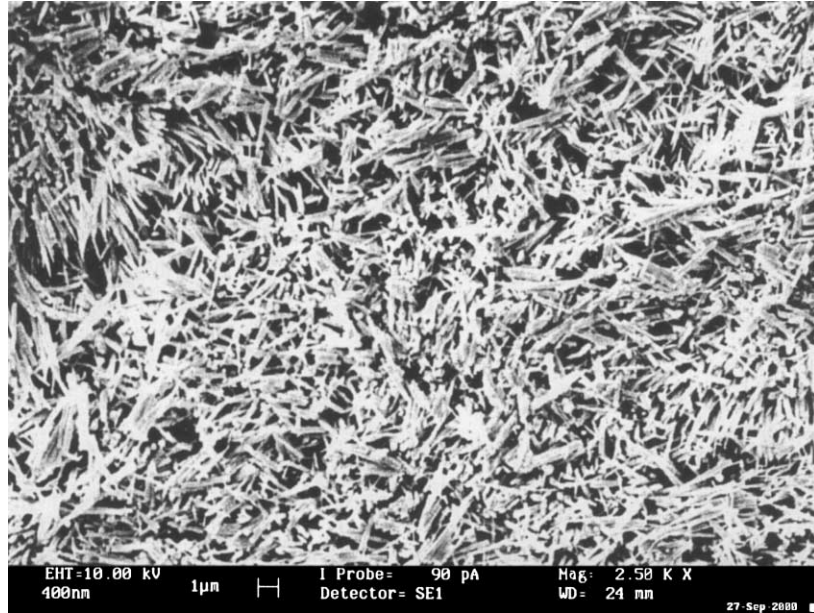


Fig. 13. Scanning electron micrograph of zinc anode plate after discharge at higher magnification reveals the needle-like zinc oxide crystals.

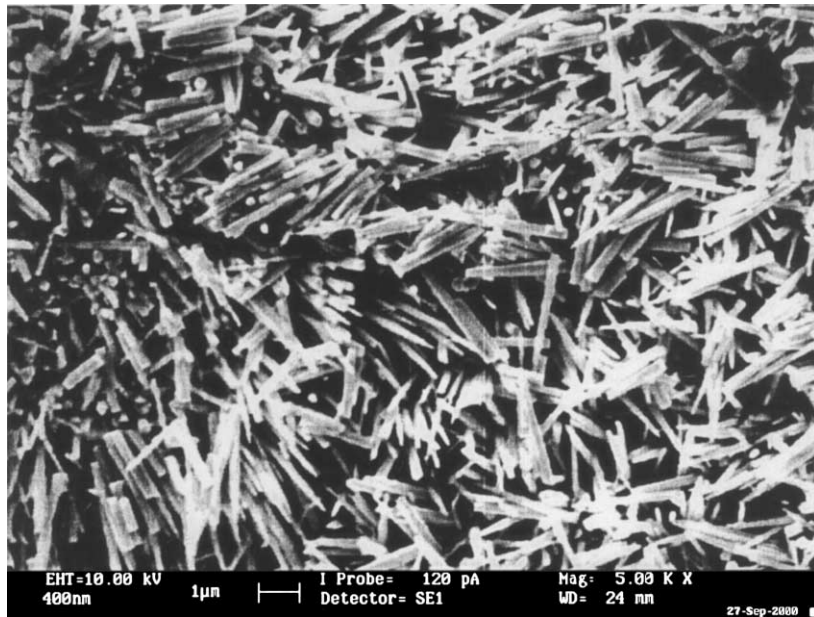


Fig. 14. Zinc oxide needle-like crystal structures at 10,000 \times magnification.

6. Conclusions

Hydroponics gel is a promising alternative electrolyte gelling agent for zinc batteries and very likely for other alkaline electrolyte batteries such as nickel–metal-hydride. Primary, monopolar, zinc–air cells which use a hydroponics gel as the electrolyte immobilising agent have been fabricated and found to be capable of sustaining discharge loads of 5, 50 and 100 mA with corresponding capacities of 229, 165 and 115 mAh. The discharge capability of the cells and XRD analysis show that the inclusion of

hydroponics gel into the aqueous potassium hydroxide electrolyte does not affect the electrochemistry of the zinc–air cell.

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