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# Further studies of a zinc–air cell employing a packed bed anode
# Part I: Discharge

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The zinc–air cell employing a packed bed anode, described previously [2], has been the subject of further investigation. A 76 cm$^2$ (air electrode area) laboratory cell has been used to determine cell performance under a varying load corresponding to the Simplified Federal Urban Driving Schedule. The results were then used as a basis for the conceptual design of a 55 kW (peak power) battery. Projected specific energy of the battery was 110 Wh kg$^{-1}$ and projected specific power 97 W kg$^{-1}$ under SFUDS discharge. These values were increased to 228 Wh kg$^{-1}$ and 97 W kg$^{-1}$ when capacity is important and to 101 Wh kg$^{-1}$ and 150 W kg$^{-1}$ when power is important, based on the results of discharge experiments at 45° C. Preliminary experiments were carried out to determine the long term stability of the air electrode in this application, to measure self discharge of the zinc and to test the practicality of mechanically recharging the cell.

## 1. Introduction

The ease with which the zinc may be regenerated, operation at near-ambient temperatures and moderately high specific power and energy, make the zinc–air battery a candidate for application in electric vehicles. Difficulties in employing this battery as an electrically rechargeable storage device include shape change of the zinc on cycling and the fact that bifunctional electrodes are at an early stage of development. The use of a copper foam substrate, to avoid the first difficulty, has been suggested by Ross [1]. An alternative approach, in which the zinc was present in the form of zinc (or zinc-coated particles) which were mechanically introduced into the cell, was described by two of the present authors previously [2, 3]. A commercial monofunctional air electrode was used and electrolyte flow was achieved by solutal natural convection, rather than by pumps.

Earlier work on the use of zinc particles can be found in the literature [5–7] but the particles were employed in slurry electrodes while packed bed electrodes are the subject of the present investigation.

The present paper reports on additional experiments on laboratory cells intended to develop these concepts. The main topics of interest are the performance under the Simplified Federal Urban Driving Schedule (SFUDS), performance of the cell at 45° C, and the behaviour of air electrodes after exposure to electrolyte for several months. A design exercise for a battery delivering 55 kW SFUDS peak power was completed, based on the laboratory results. Additional topics investigated included the self discharge of the zinc particles, and the feasibility of mechanical recharging. A subsequent paper (Part II) reports on experimental investigations of the regeneration of zinc particles.

## 2. Experimental details and apparatus

Most of the results described in this paper were obtained using the cell depicted in Fig. 1. Because the cell was described in detail previously [2], the present description is brief. The zinc (in most cases 30 mesh zinc from Fisher Scientific) was present as 300–600 μm particles forming a packed bed between the current feeder (usually 4 mm graphite) and diaphragm (usually Celgard 5550). Anolyte (initially 45% KOH from Fisher Scientific and J. T. Baker Inc.) permeates the bed and occupies an additional volume behind the current feeder, the latter volume serving as an upflow channel for solutal natural convection as the electrolyte in the bed becomes denser during discharge. The air electrode employed in most of this work has been AE-20 from Electromedia Corporation; it is placed in contact with a stagnant catholyte (45% KOH on one side and a nickel mesh current collector on the other). The cell was discharged through a Keithley 228A bipolar power supply controlled by a microcomputer. The microcomputer stored cell voltage and current measured by a Solartron computing voltmeter, as well as processed data such as power, energy and current density as a function of time. Air was taken from the laboratory supply via a wash bottle containing 45% KOH.

The usual discharge procedure (described in detail

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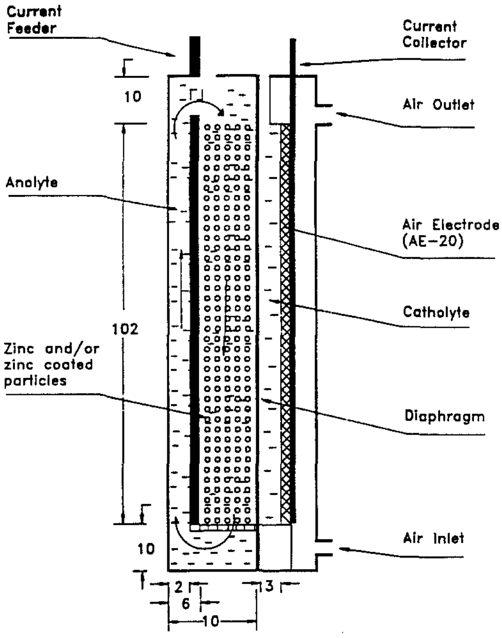

Fig. 1. Schematic of 80 cm$^2$ laboratory Zn–air cell (XBL 902-524) (Dimensions in millimetres).

previously) consisted of wetting the air electrode and zinc particles and assembling the cell with the particles in place on the current feeder. The air supply was turned on and, following an interval of 3–5 min, for stabilization of open circuit voltage, the discharge commenced. Except as described below, no attempt was made to control the cell temperature during discharge. Discharge was halted at a preselected cell voltage, usually in the range 0.8–1.0 V (thought to represent the cell voltage at the practical end of discharge of a battery based on this cell). The cell was then disassembled, inspected and cleaned.

## 3. Results and discussion

### 3.1. *Cell materials*

While graphite has been used extensively in this investigation as a current feeder material, copper may be a better choice. This is illustrated in Fig. 2 where the cell voltage on discharging the cell at constant current (2A) is compared for current feeders of 4 mm thick graphite and 1.6 mm copper. Because the latter is less fragile and yields higher cell voltage, it is an obvious choice for a current feeder, although optimization of thickness would precede development of full-scale batteries.

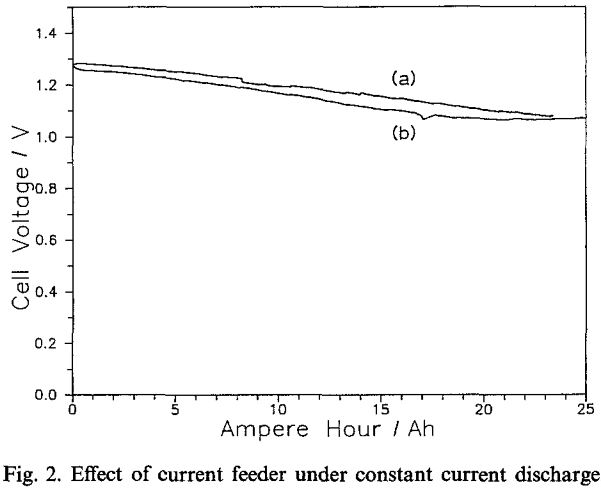

Fig. 2. Effect of current feeder under constant current discharge, graphite against copper. Anolyte/catholyte: 45% KOH; anode: 30 mesh zinc; cathode: AE-20 air electrode. $I = 2$ A, $A = 78$ cm$^2$. (a) 1.5 mm copper current feeder, and (b) 4.0 mm graphite current feeder.

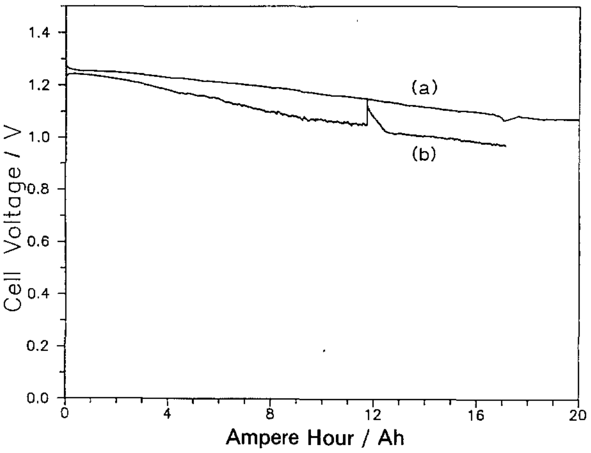

Fig. 3. Effect of particle shape under constant current discharge, zinc particles against zinc coated copper shot. Anolyte/catholyte: 45% KOH. $I = 2$ A, $A = 76$ cm$^2$. Cathode: AE-20 air electrode. Anode: (a) 0.5–0.6 mm zinc particles (irregular shapes), and (b) 0.5–0.6 mm zinc coated copper shot (regular shapes).

To speed the experimental work, particles that are entirely zinc have been used in most of this investigation. Zinc-coated particles would be more likely in practical application and in the present work the relative amounts of zinc and anolyte were selected so that only a fraction (approx. 10–15%) of the zinc dissolved, mimicking the electrochemical behaviour of a zinc-coated particle. One experiment was carried out using zinc-coated copper shot (0.5–0.6 mm dia.) generated as described in Part II. Figure 3 compares the discharge curve of this experiment with that for pure zinc particles. The former included an overnight shutdown of approximately 14 h. That shutdown appears to have had only a minor effect on the subsequent discharge, a result consistent with earlier work [2] and suggesting that a vehicle equipped with this type of battery could be parked without special precautions. The cell voltage for the zinc-coated particles is somewhat inferior to that for the Fisher particles; this may be because the latter are irregular, presenting a greater surface area per unit volume to the electrolyte and minimizing the collapse of the bed as discharge proceeds.

A comparison between two air electrodes (AE-20 from Electromedia Corp. and AC65-1072 from Alupower Corp.) is provided in Fig. 4 where cell voltages at constant current are plotted. AE-20 is a three-layer gas diffusion electrode. There is an active carbon reaction layer (which is catalysed with modified cobalt macrocycle), a hydrophobic Teflon bonded layer and a silver coated nickel mesh current collector on the air side of the electrode. AC65-1072 is a four-layer gas diffusion electrode. There are two reaction layers,

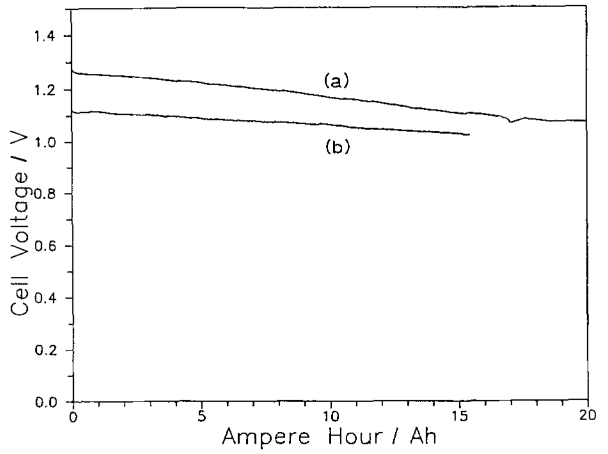

Fig. 4. Effect of air electrode under constant current discharge, AE-20 against AC65-1072. Anolyte/catholyte: 45% KOH; anode: 30 mesh zinc; $I = 2$ A, $A = 76$ cm$^2$. Cathode: (a) Electromedia: AE-20 air electrode, and (b) Alupower: AC65-1072 air electrode.

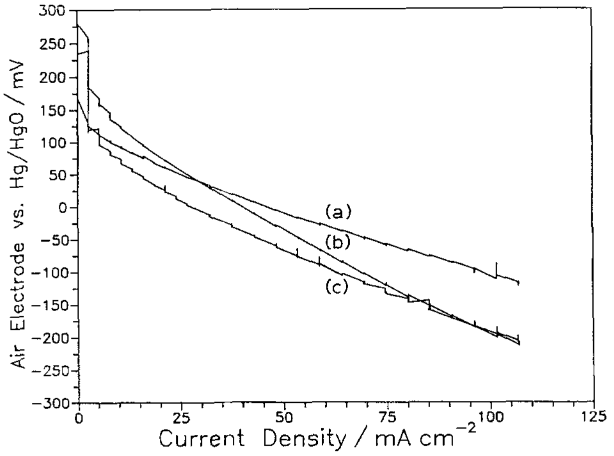

Fig. 5. Effect of longtime exposure on air electrode polarization. AE-20 air electrode exposure test. (a) 1 h wetting in 45% KOH; (b) 5.5 months wetting in 45% KOH; and (c) 5.5 months wetting in 45% KOH + 10 g dm$^{-3}$ Zn$^{2+}$.

which are mixtures of carbon black and other chemicals, a current collector, and a microporous Teflon film. The current collector is between the two carbon layers, Teflon is the outer layer on the air side of the electrode. Both air electrodes are used for oxygen reduction and hydrogen oxidation in neutral and alkaline solutions and were intended for use in aluminium–air cells; the results for a different application may not reflect the true potential of these materials. Both electrodes have been subjected to SFUDS testing, as described below, and the Alupower electrode was unable to sustain more than 0.4 h of operation compared to 6.9 h for the AE-20 electrode.

Two AE-20 air electrodes have been exposed to electrolyte for long periods. The electrodes were mounted on a plexiglass electrode holder which was attached to a grooved plexiglass plate forming a sealed rectangular container. After filling with the electrolyte, the ports were sealed to prevent carbon dioxide contamination from the air.

After 5.5 months the electrodes were removed and placed in a cell filled with 45% KOH where their voltage with respect to a mercury/mercuric oxide electrode was measured. The air electrodes were used as cathodes and zinc particles were placed in a "bag" made of multi-layer nickel to form an anode; thus a galvanic cell was established. The polarization curves for these electrodes and a fresh electrode appear in Fig. 5. There has been sufficient change in polarization, particularly for the electrode exposed to zincate ions, to require further exposure testing of these electrodes. Some discolouration of electrolyte was observed as KOH concentration and time of exposure increased and zincate concentration decreased. Such discolouration was not observed in 45% KOH saturated with zincate during two months of exposure.

### 3.2. *Modified SFUDS discharge*

Discharge of an electric vehicle battery at constant current or power is an unlikely occurrence. Various discharge schedules have been suggested to better simulate the abstraction of energy from a vehicle battery. Among the most demanding of these is the Simplified Federal Urban Driving Schedule. The schedule consists of the repetition of a 6 min cycle. During each cycle the vehicle accelerates from rest four times. The first three accelerations are to 39.6 km h$^{-1}$ and the last to 87.5 km h$^{-1}$. Each acceleration is followed by a deceleration to rest and intervals at rest. Based on estimates of vehicle mass (including battery mass) and frontal area, the equivalent battery power can be calculated and is plotted in Fig. 6a, taken from the report of Idaho National Engineering Laboratory [4] in which the schedule is described. The periods of negative power represent regenerative braking of the vehicle. In the present investigation the schedule was modified to eliminate regenerative braking. While it is possible that further development of air electrodes would lead to sufficient bifunctionality to permit brief periods of regenerative braking, the AE-20 electrode is rapidly degraded by application of the unmodified

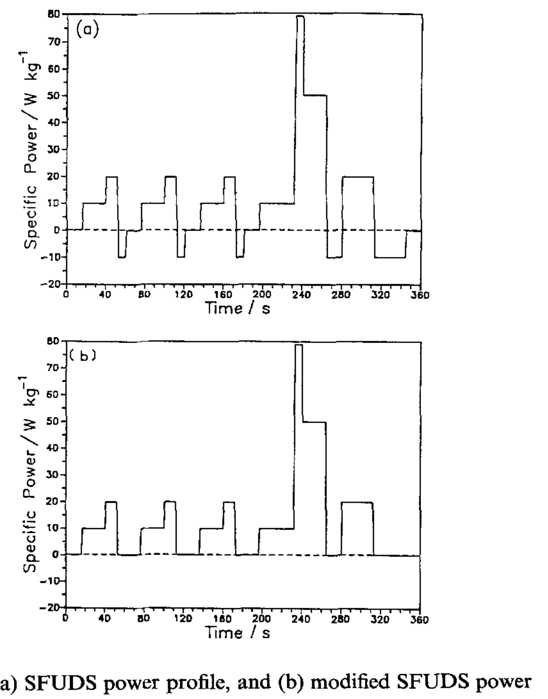

Fig. 6. (a) SFUDS power profile, and (b) modified SFUDS power profile.

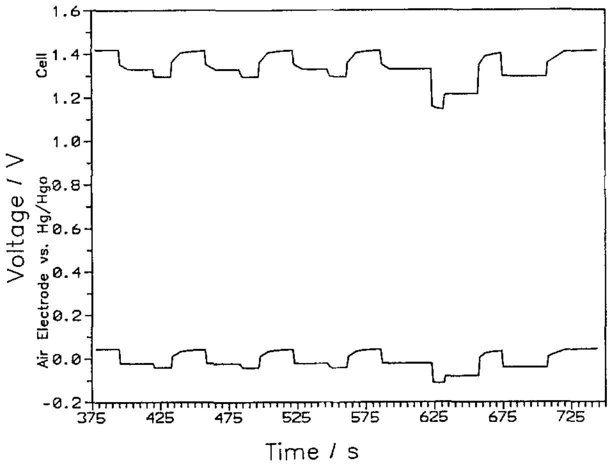

Fig. 7. Air electrode and cell voltage during a modified SFUDS discharge.

SFUDS. The modified schedule shown in Fig. 6b was therefore used in this investigation.

Under control of the microcomputer, the modified SFUDS power was demanded of the laboratory cell and the cell was able to match the demand for the first 6.9 h of discharge. The power requested by the computer was based on the design exercise described below (case 1). A power of 8.06 W from the laboratory cell corresponds to 55 kW for the designed battery and the cell achieves the 8.06 W peaks throughout (and beyond) the 6.9 h period. However, after 6.9 h, the cell voltage fell to 0.8 V at 8.06 W, corresponding to a battery voltage below 120 V which was regarded as a minimum in the design exercise. This point was therefore treated as the end of discharge, even though the cell was not fully discharged in an electrochemical sense.

In some SFUDS discharges a reference electrode was incorporated into the cell (a Luggin capillary placed near the air electrode and connected to a mercury/mercuric oxide electrode) and Fig. 7 displays the cell voltage and air electrode voltage versus time during slightly more than one SFUDS cycle. From this type of data polarization curves were constructed and appear in Fig. 8. It appears that polarization of the air electrode makes a significant contribution to the decline of cell voltage at the higher current densities. Plots of this type permit the calculation of power per unit electrode area; resulting curves appear in Fig. 9. While these curves are the result of a degree of extrapolation (beyond approximately 100 mA cm$^{-2}$) they suggest that higher powers can be obtained in the cell than exploited in the SFUDS discharge, if lower cell voltage is acceptable.

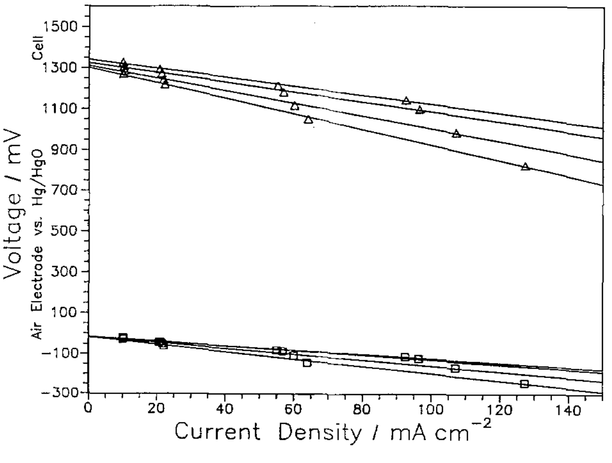

Fig. 8. Polarization curves for cell and air electrode as a function of depth of discharge obtained from Fig. 7. Curves (top to bottom) at 0.1, 2, 5 and 6.9 h.

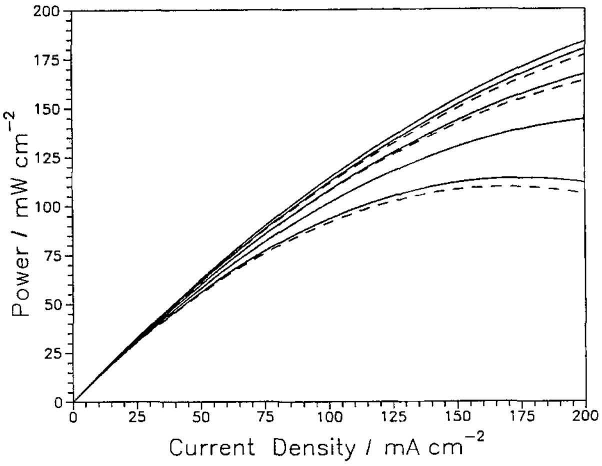

Fig. 9. Comparison of power against current density curves for room temperature and 45° C modified SFUDS discharge. Anolyte/catholyte: 45% KOH; anode/cathode: 30 mesh zinc/AE-20. Solid at 45° C (0.1, 2.5, 6, 10, and 15 h at discharge). Dashed at 22° C (room temp.), (0.1, 2.5, and 6 h at discharge).

Heat is generated during discharge and must be dissipated, or increase in battery temperature tolerated. Dissipation of heat is facilitated if the battery operates satisfactorily at above ambient temperature. Runs were carried out in which heating tape and an on-off controller were used to maintain the cell temperature at 45° C. To avoid drying the air electrode, the air wash bottle was also maintained at 45° C. Keeping the power demand out of the battery the same as before, the cell was discharged at 45° C. The result was that the cell was able to sustain the SFUDS power at higher voltages for much longer duration (15 h as opposed to 6.9 h) which implies longer range for the vehicle. Figure 9 compares power curves for room temperature and 45° C experiments. Having a projected long vehicle range encouraged an attempt at a higher power experiment to see if higher powers could be obtained while still meeting the specific energy requirements. The cell was discharged at 12.5 W peak power corresponding to 85 kW for the battery design described below. The end of discharge occured at 6.3 Ah.

### 3.3. *Cell design*

Conceptual designs of a 55 kW (SFUDS minimum peak power) battery were carried out. The designs assumed that the energy and power per unit area of air electrode are the same in the battery as in the laboratory cell under modified SFUDS testing (for example, 8.06/12.5 W per 76 cm$^2$ peak power). The battery was also designed with the same ratio of electrolyte volume to zinc mass as employed in the laboratory cell. That

*Table 1. Estimated mass of components of 55 kW battery*

| | |
|---|---|
| Electrolyte/kg | 328 |
| Zinc/kg | 63 |
| Frame | |
| Outer (from 2 mm plexiglass)/kg | 17 |
| Inner (from 1 mm plexiglass)/kg | 70 |
| Air system | |
| Air electrode (based on AE-20)/kg | 22 |
| Intake funnel, filter, housing, air pump, humidifier/scrubber, shroud, valves/kg | 17 |
| Current feeder/collector/kg | 48 |
| Total/kg | 565 |

ratio was somewhat arbitrarily selected and it should be recognized that alteration of battery characteristics (for example, upward in specific power and downward in specific energy) can be achieved by changing the ratio.

Table 1 lists the mass of the various parts of the battery and it should be noted that the principal mass is that of the electrolyte. Although the mass of some other components, (for example, the outer frame or the air delivery system) were only estimated, they are sufficiently small that errors introduced are not likely to be significant. Table 2 describes the anticipated performance of this battery for three cases. The extrapolation from an 8/12.5 W laboratory cell to a 55 kW battery is not as extreme as it first appears. The cells in the battery would be 960 $cm^2$ in cross sectional area, that is only one order of magnitude larger than the laboratory cell. The stacking of these cells to form the 55 kW battery is largely a matter of electrical connection. The energy density and specific energy are sufficient to provide a satisfactory range for an electric vehicle before (mechanical) recharging. For example, when used in the IDSEP van [4] a range of 240, 498 and 221 km would be expected under the SFUDS driving schedule for cases 1, 2 and 3, respectively. Both case 1 and 2 are superior in power density, specific power, energy density and specific energy to a conventional lead acid battery; higher powers have been reported for advanced lead acid batteries. Case 3 shows that power densities similar to those of lead acid batteries can be obtained with much higher energy densities if the cell is discharged at higher temperatures (i.e., 45° C), which can be achieved using the heat generated during discharge. Further optimization of this zinc–air technology (for example, by use of different particle sizes) or use in a hybrid system would be appropriate.

### 3.4. *Additional experimental results*

An approximate measurement of the rate of self discharge of a battery employing zinc particles was obtained by contacting 20 g of Fisher Scientific zinc particles with 100 $cm^3$ of 45% KOH in a beaker which was occasionally stirred at room temperature. Samples of the solution were withdrawn at intervals of a few days and analysed for zinc by atomic absorption spectrophotometry. The analytical results were then expressed as a percentage of the original zinc that had passed into solution and this is plotted in Fig. 10. This first indication is that the self discharge will not present a difficulty.

The concept of electrolyte flow driven by solutal natural convection had previously been substantiated by visual observation of an upward movement of clouded electrolyte in the upflow channel (on the opposite side of the current feeder from the zinc particles) towards the end of discharge in constant current

*Table 2. Characteristics of designed battery based on SFUDS performance of laboratory zinc–air cell (end of discharge defined by battery voltage reaching 120 V at peak power)*

| *Battery: 4 modules in parallel (0.30 m × 1.55 m × 0.32 m (high) each)* | *Case 1 55 kW ambient* | *Case 2 55 kW 45° C* | *Case 3 85 kW 45° C* |
|---|---|---|---|
| Total mass (including auxiliaries) | 565 | 565 | 565 kg |
| Total volume | 600 | 600 | 600 $dm^3$ |
| Total number of cells | 600 | 600 | 600 |
| Average cell voltage | 1.2 | 1.25 | 1.25 V |
| Open circuit battery voltage | 218 | 218 | 218 V |
| Minimum battery voltage | 120 | 120 | 120 V |
| Energy* | 62 | 128.5 | 57 kWh |
| Average power | 12.5 | 12.5 | 19 kW |
| Peak power* (constrained by minimum battery voltage) | 55 | 55 | 85 kW† |
| Voltage/current† | 180V/80A<br>120V/455A | 188V/80A<br>120V/455A | 188V/80A<br>120V/708A |
| SFUDS energy capacity† | 62 | 128.5 | 57 kWh |
| SFUDS energy density† | 103 | 214 | 95 Wh $dm^{-3}$ |
| SFUDS peak power density† | 92 | 92 | 142 W $dm^{-3}$ |
| SFUDS specific energy† | 110 | 228 | 101 Wh $kg^{-1}$ |
| SFUDS specific peak power† | 97 | 97 | 150 W $kg^{-1}$ |

* Modified SFUDS – Modification is the elimination of regenerative braking.
† End of discharge under modified SFUDS discharge.

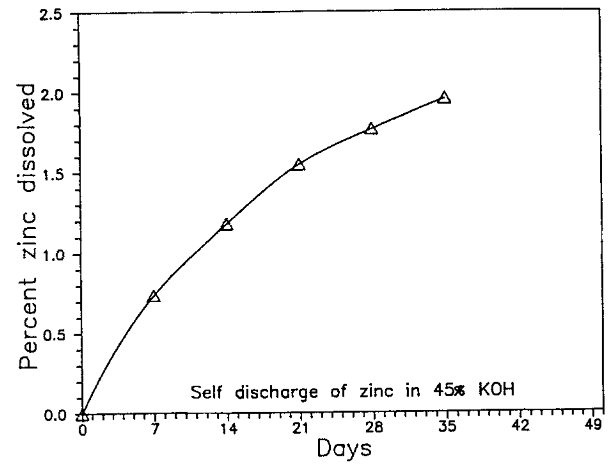

Fig. 10. Self-discharge (chemical dissolution) of 30 mesh zinc particles in 45% KOH.

experiments. Further evidence was provided by analysis of small electrolyte samples for zinc content. The analysis was carried out by EDTA titration using Erichrome Black-T as indicator and the results are depicted in Fig. 11.

The recharging envisioned for a battery based on this technology is mechanical. That is, spent electrolyte and particles are removed from the cells and replaced by regenerated ones. A possible regeneration facility is described in Part II. A demonstration that the mechanical recharging may be feasible was carried out on the laboratory cell. A cell was discharged at 2A for 4 h, following which nearly all of the residual particles and electrolyte were sucked out of the anode side of the cell through a tube passing through a hole in the top of the cell and connected to a water jet aspirator. Without rinsing, fresh particles and electrolyte were placed in the cell through the hole and a second 2A discharge carried out. Following this, a less careful removal of spent electrolyte and particles was carried out using the same tube and aspirator as before but abstracting approximately 90% of the anode chamber contents. Fresh particles and electrolyte were added and a third discharge carried out. Cell voltage is plotted against time for the three discharges in Fig. 12. Differences between the curves are probably smaller than the precision of the measurements.

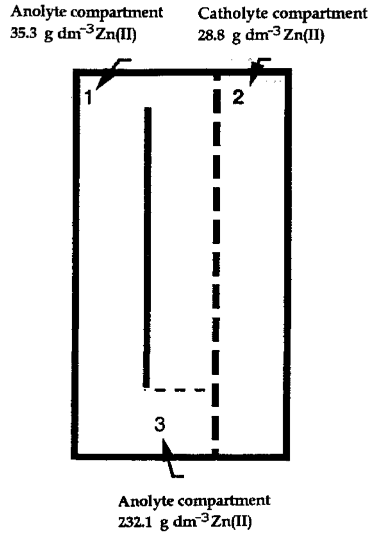

Fig. 11. Zinc concentration at different locations of 80 cm$^2$ laboratory cell.

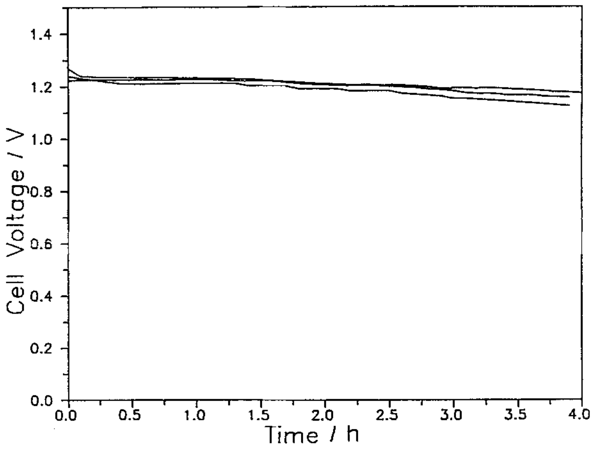

Fig. 12. Cell voltage against time during subsequent mechanical recharging. Anolyte/catholyte: 45% KOH. Anode: 20 mesh zinc; cathode: AE-20 air electrode. $I = 2$ A, $A = 76$ cm$^2$. From top to bottom: (a) first run; (b) 100% of anolyte/particles suctioned out, cell refilled with fresh ones, no rinsing; and (c) 90% of anolyte/particles suctioned out, cel refilled with fresh ones, no rinsing.

## 4. Conclusions

Further experiments have been completed on a laboratory cell that might be scaled up to a battery for electric vehicles. The results suggest:

(i) that copper is a more suitable material than graphite for current feeders

(ii) that the cell can be shut down for hours without impact on subsequent discharge

(iii) that the performance of the cell operated with zinc coated copper particles is comparable with that of the cell operated on zinc particles

(iv) that the AE-20 air electrode from Electromedia Corporation has performed better than one alternative during one test

(v) that after exposure to KOH solutions containing zinc for 5.5 months, an AE-20 electrode showed a somewhat greater polarization than a new electrode

(vi) that the cell can be discharged in conformity with the (modified) Simplified Federal Urban Driving Schedule with satisfactory results

(vii) that, based on the SFUDS discharge, a scale-up exercise predicts specific power of 97 W kg$^{-1}$ and specific energy of 110 Wh kg$^{-1}$, although these numbers can be altered (for example, by changing the ratio of zinc to electrolyte). Operation of the cell at 45° C (rather than close to ambient temperature) should improve thermal management and gives results leading to improved design performance: 228 Wh kg$^{-1}$ and 97 W kg$^{-1}$ for an energy-oriented design and 101 Wh kg$^{-1}$ and 150 W kg$^{-1}$ for a power-oriented design.

(viii) that self discharge of the zinc particles is approximately two percent per month in preliminary experiments

(ix) that the laboratory cell has been evacuated and mechanically recharged (without disassembly) with no apparent impact on cell performance.

## Acknowledgement

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