JOURNAL OF APPLIED ELECTROCHEMISTRY 21 (1991) 105–110

A zinc–air cell employing a packed bed anode

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Received 25 April 1990; revised 24 July 1990

A cell with a particulate zinc electrode and a monofunctional air electrode has been studied on a laboratory scale. The cell has the feature of relying on solutal natural convection, rather than a pump, for electrolyte circulation. Cells of 80 and 400 cm^2 (air electrode area) have been discharged at constant or stepped current. In two cases cell discharge was halted and restarted after many hours with little or no impact on cell voltage. Based on the laboratory data a preliminary design of a 32 kWh (115 MJ) battery was completed. The projected specific energy of this cell is 79.2 Wh kg^{-1} (637 kJ kg^{-1}), while the peak specific power is 111 W kg^{-1} (20% depth of discharge), meeting of the US Department of Energy targets for a battery for an electric van.

1. Introduction

The zinc–air cell has long been regarded as a candidate for use in electric vehicles because of the moderately high theoretical specific power and energy and the relative ease (compared to the aluminium–air battery, for example) with which the reactants can be regenerated [1–7]. Principal difficulties in realizing a commercial zinc–air cell have been shape change on cycling the zinc electrode [8] and a low capacity of the alkaline electrolyte (without any capacity-increasing additives) to contain (either in solution or suspension) the zinc discharge products [9]. The latter difficulty results in the battery performance being burdened by a large volume of electrolyte and several efforts have been mounted aimed at improving the electrolyte capacity by means of additives (e.g., silicates, lithium hydroxide, D-xylose, sucrose, sorbitol). An additional difficulty with the zinc–air cell that is electrically recharged is the lack of commercial availability of a bifunctional air electrode, forcing reliance on experimental air electrodes, or a third electrode with the complication of switching between electrodes.

The present paper reports on a design for a zinc–air cell where these difficulties appear to have been overcome. The cell uses a particulate zinc electrode where the geometry of the particles, and therefore shape change, are largely inconsequential. The concept behind the cell is one of mechanical recharging. Residual particles and electrolyte are removed from the battery near the end of discharge and replaced with fresh particles and electrolyte. These last are electrically regenerated from cell discharge products in a local or regional facility, using large electrochemical reactors such as fluidized bed reactors [10]. Mechanical recharging, particle regeneration and storage is by slurry handling technology familiar in many industries.

2. The cell

This investigation has used cells of 80 and 400 cm^2 (air electrode area); the smaller cell is illustrated in Fig. 1 but the larger cell is very similar in design. The bed of zinc particles is stationary throughout most of the discharge and is contained between a graphite current feeder and the cell diaphragm. That diaphragm was of Daramic (W. R. Grace Corp.) in most of the experiments but more recently Celgard (Hoechst Celanese Corporation) has proven at least as satisfactory. On the other side of the current feeder from the particles is a space (2 mm wide in the laboratory cells) that serves as an anolyte reservoir and conduit for electrolyte. In operation, a solutal natural convection of anolyte occurs as shown by the arrows in the figure. The electrolyte in the interstices between the particles becomes more concentrated in zincate and therefore denser than that in the conduit, bringing about the necessary convection to avoid anolyte 'saturation' in the bed and to improve mass transfer from the particle surface. No pump is necessary, dispensing with its weight (and that of manifolds, etc.), complexity and energy consumption.

The cathode chamber of the cell consisted of a commercially available air electrode (AE-20, Electromedia Corp.) separated from the diaphragm by 3 mm of electrolyte and backed by a nickel mesh current collector placed on the air side of the electrode. Air was fed to the cell from the laboratory supply via a wash bottle containing 12 M potassium hydroxide. It should be noted that the cell is not optimized. For example the thickness of the graphite current feeder (4 mm) is unnecessarily large from the viewpoint of current conduction and was simply a consequence of the availability of graphite of this thickness. Except as described below the cell was discharged at constant current. A DC power supply (HP-6031A) and a 2.5 Ω

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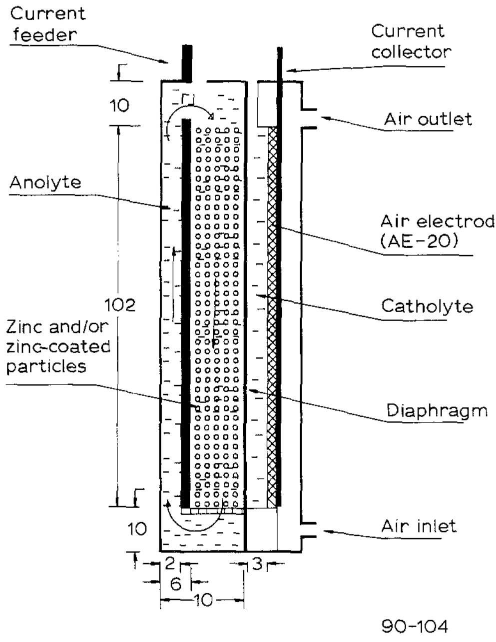

Fig. 1. A diagram of the 80 cm^2 laboratory cell in cross-section. All dimensions in mm.

resistor connected in series with the cell were used. The power supply was supervised by an IBM-AT computer which also stored measurements of cell current and voltage (measured on a Solartron precision voltmeter) at intervals of 5 to 60 s for subsequent printing and plotting.

2.1. *Electrolyte preparation*

In this study all the solutions were prepared from analytical reagent grade chemicals and distilled water. The 45% KOH was from Fisher Scientific. The solutions with additives were prepared by equilibrating either 12 M or 45% KOH with known weight of the additive for 2 days. The smaller cell contained 19 ml of catholyte and 42 ml of anolyte, the larger cell 100 ml of catholyte and 230 ml of anolyte (all to a precision of ± 5%).

2.2. *Pretreatment of particles, separator and air electrode*

Zinc particles, 30-mesh, were soaked in KOH solution for at least 10 min and rinsed with KOH before loading into the cell. Due to wetting and shrinkage, Daramic was soaked in KOH for at least 1 h, whereas Celgard was not pretreated. The air electrode (AE-20) was wetted with KOH solution for at least 6 h.

2.3. *Procedure*

The experimental procedure consisted of placing presoaked zinc particles onto the graphite current feeder with the cell turned into a horizontal position followed by placement of separator and bolting of anolyte and catholyte compartments together in an upright position. This was followed by filling the cell with anolyte and catholyte, turning on air to the cell and waiting until stabilization of open circuit voltage was obtained (3–5 min). Subsequently the power supply was set to withdraw either a constant or stepped current and the voltmeter set to read cell voltage at predetermined intervals (5 to 60 s). Raw data (cell voltage, current, time) and processed data (ampère-hour, power, energy) were stored in a data file for further printing and plotting. This was done until either a preset cut-off voltage or cut-off ampère-hour was reached.

After the experiment was finished the cell was drained and disassembled for visual observation and cleaning. The air electrode was rinsed with distilled water or KOH and stored wet in an airtight plastic bag to prevent drying.

3. Experimental results

All the results reported below were obtained using zinc particles (as opposed to zinc-coated particles) but with a limited electrolyte volume so that approximately half of the zinc was oxidized in the cell during discharge. While operation of a battery of this design using zinc particles appears feasible, a more likely scenario is the use of a zinc-coated particle with a core of less-dense material. In this way the specific power and energy might be increased. Zinc-coated particles have been successfully produced in our laboratory (by fluidized bed electrodeposition) and used in the zinc–air cell, but the pace of experimentation was slowed by the use of these particles. It is argued that, electrochemically, a zinc-coated particle and a zinc particle should behave identically up to the point where the coating is penetrated.

Figure 2 shows two typical discharge curves obtained at a constant current of 1.5 A. (The first run was prematurely halted because the cell capacity was much greater than anticipated from results of previous investigators.) The reproducibility of the results is satisfactory and the discharge curve is an almost smooth decline to a 'knee' at approximately 0.8 V,

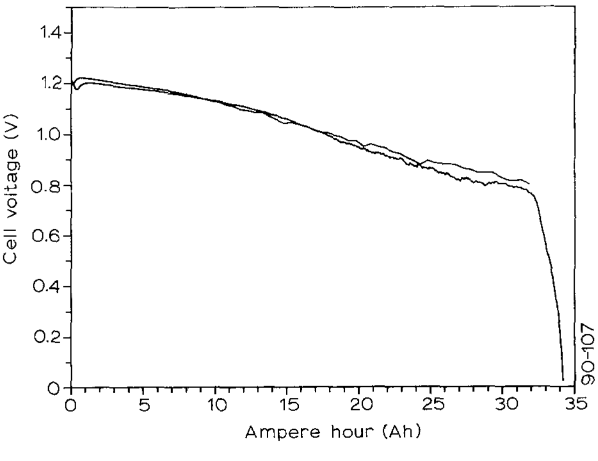

Fig. 2. Reproducibility of the discharge curve in 80 cm^2 cell at 18.8 mA cm^{-2}. Anolyte and catholyte: 12 M; anode: 30 mesh zinc particles; cathode: AE-20 air electrode.

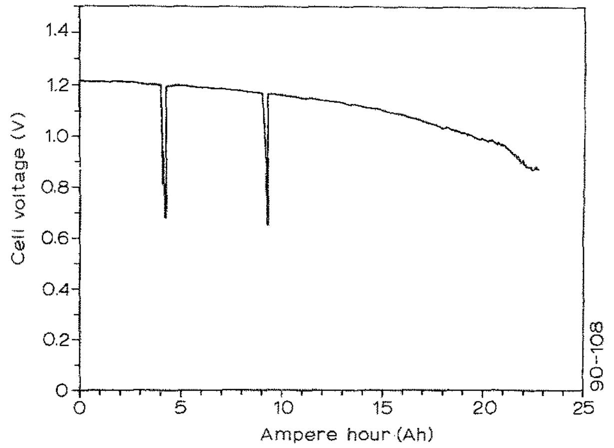

Fig. 3. Result of a discharge experiment where the current density was stepped for 30 s intervals to various values up to 148 mA cm^{-2} at 20% and 40% DOD (where full discharge is defined as the 'knee' in the cell voltage). Anolyte and catholyte: 45% KOH; cathode: AE-20 air electrode; anode: zinc particles. Current density (stepped) from 17 mA cm^{-2} (A = 80 cm^2).

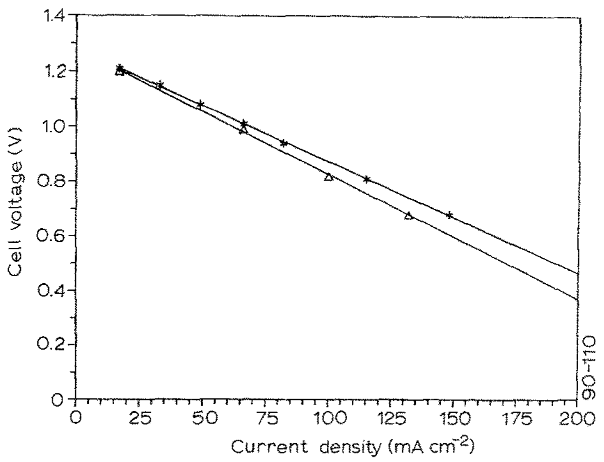

Fig. 5. Cell voltage against current density obtained by stepping the current at (*) 20% and (△) 40% DOD from Fig. 3. Anolyte and catholyte: 45% KOH; anode: 30 mesh zinc particles; cathode: AE-20 air electrode.

followed by a steep plunge to 0 V. In many subsequent experiments discharge was halted at this knee because there appeared to be little advantage in going further. The electrolyte at this point has the appearance of a milky suspension. The migration of this suspension up the space behind the current feeder, to the left in Fig. 2, is evidence of the occurrence of the circulation shown in Fig. 2. As will be seen below, the capacity of the electrolyte, expressed in ampère-hour per unit volume of the electrolyte (anolyte plus catholyte), observed in these experiments was high. Typically this capacity exceeded 500 Ah l^{-1}, a much larger capacity than the 48 to 263 Ah l^{-1} reported by other investigators [11, 12]. Electrolyte samples taken from the cell and centrifuged to remove particles were analyzed and showed 240 g l^{-1} of zinc which is equivalent to 200 Ah l^{-1}. The ability of the cell to yield high ampère hours per litre is therefore a consequence of its ability to continue to function well beyond the point where precipitation has started to occur. In a cell that has been discharged to 0 V the bed interstices were seen to be partly occluded by fine white particles. Consequently it is hypothesized that bed occlusion limits the cell capacity and it is possible that studies of suspension surface chemistry may enhance cell performance.

In Figs 3 and 4, the consequences of stepping the cell current (and therefore the power) to higher levels are displayed. As seen in Fig. 3, on two occasions during a discharge, at otherwise constant current, the current was stepped under control of the computer. The similarity of the rest of the discharge curve to those of Fig. 2 and the fast return of the cell to 'normal' potential following the term at higher power should be noted. These excursions were carried out at 20% and 40% depth of discharge (DOD) where 100% is defined as the knee of the discharge curve. The first of these excursions is shown on an enlarged scale in Fig. 4 where the fast response is even clearer. Plots of plateau voltages versus current density from these excursions appear in Fig. 5 and the power density versus current density curves of Fig. 6 are obtained from the best straight lines passing through the data in Fig. 5 by simply multiplying voltage and current density.

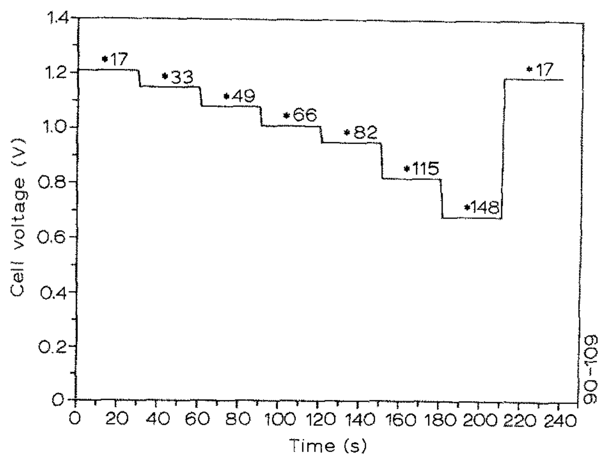

Fig. 4. Enlargement of current step at 20% DOD from Fig. 3. Numbers preceded by asterisks are the current densities during that time interval (in mA cm^{-2}). Anolyte and catholyte: 45% KOH; anode: 30 mesh zinc particles; cathode: AE-20 air electrode.

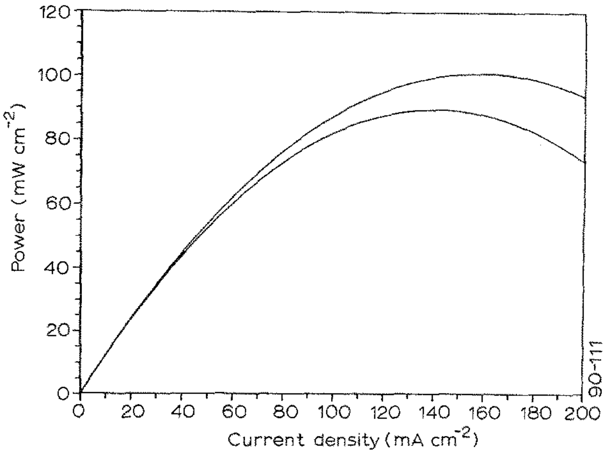

Fig. 6. Power against current density at 20% (upper) and 40% (lower) DOD obtained from Fig. 5. Anolyte and catholyte: 45% KOH; anode: 30 mesh zinc particles; cathode: AE-20 air electrode.

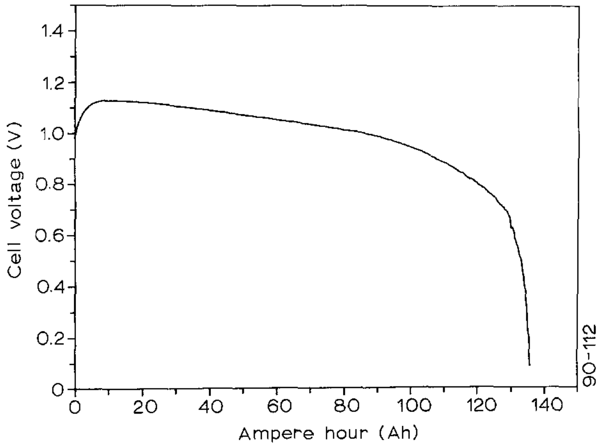

Fig. 7. Discharge curve for the 400 cm^2 cell. Anolyte and catholyte: 12 M KOH; anode: 30 mesh zinc particles; cathode: AE-20 air electrode. Current density: 32 mA cm^{-2}.

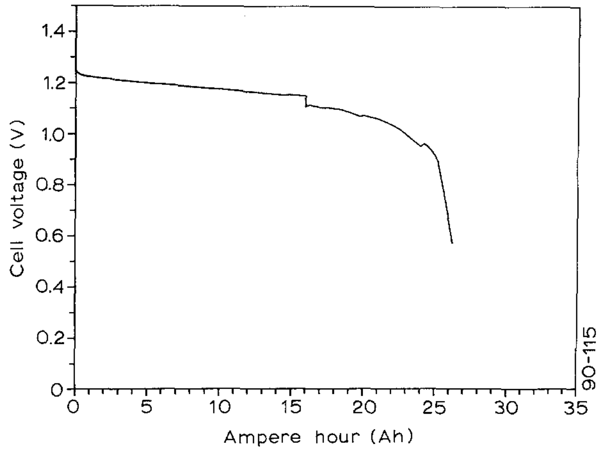

Fig. 9. Discharge curve with 52 h standby. Anolyte and catholyte: 45% KOH (with some additives); anode: 30 mesh zinc particles; cathode AE-20 air electrodes. Current density: 19 mA cm^{-2}.

Figure 7 shows a typical discharge curve for the 400 cm^2 cell. Besides the obviously greater cell capacity the cell shows only a slightly lower voltage than the smaller cell, perhaps because of higher current density and greater voltage drop through the 4 mm thick graphite current feeder. A design exercise based on the laboratory results appears in the next section of this paper. The design is for a 32 kWh (115 MJ) battery and a cell size of 900 cm^2, i.e., somewhat over twice the area of the larger laboratory cell, was selected as yielding a geometry that appeared suitable for an electric vehicle and to be well within the scope of practical scale-up.

Of course, other aspects of cell performance beyond the results presented so far will be significant in electric vehicle applications. Examples are the self-discharge of the cell (and its related ability to function following a period of shutdown) and the long-term stability of the air electrode in the presence of zincate ions.

Figure 8 shows the performance of the cell during a discharge where the circuit was opened, at 14 Ah, for 25 h. A slightly higher voltage on reconnecting the cell is observable. This cell was operated with a Celgard diaphragm and with the perforated plate at the bottom of the bed supporting the particles modified to improve electrolyte circulation. Previously that plate had been a bare printed circuit board (0.8 mm holes) with a nylon mesh (100 mesh) positioned above it to ensure that no zinc particles passed through. The nylon mesh was found to trap the colloidal particles and in the experiment of Fig. 8, and subsequent experiments, it was removed. The cell voltage was initially somewhat higher than those of Figs 3 and 4 while the voltage of the cell at longer times was superior. (The cell was shut down under computer control on reaching 1 V.) Figure 9 shows the results of an experiment where the period on open circuit was longer (52 h). In this case, the electrolyte contained additives, 4 g l^{-1} D-xylose and 20 g l^{-1} LiOH reported by others [9, 11, 13–17] to improve cell capacity. The additives appeared to have little influence on cell voltage prior to the open circuit period but to adversely affect cell performance subsequent to that period.

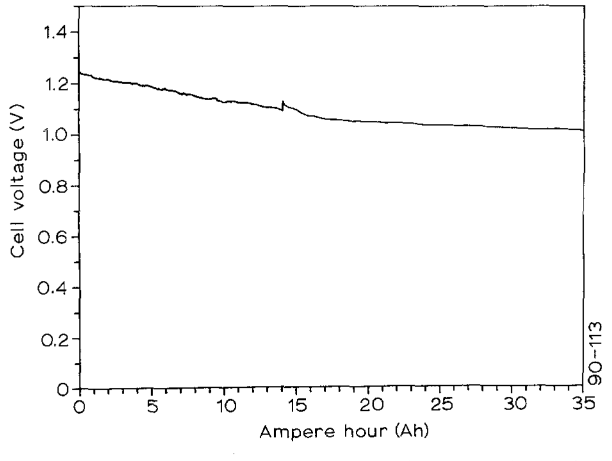

Fig. 8. Discharge curve with 25 h standby. Anolyte and catholyte: 45% KOH; anode: 30 mesh zinc particles; cathode: AE-20 air electrode. Current density: 19 mA cm^{-2}, area 80 cm^2.

A test of the stability of the AE-20 air electrode in the presence of zincate ion was carried out in a separate cell using a nickel anode. The procedure was as follows.

An AE-20 air electrode (50 cm^2) and nickel anode were each glued to a window in a plexiglass sheet and placed 5 cm apart from each other separated by Daramic. The anolyte compartment was filled with supersaturated zincate obtained from a 100% discharged zinc–air cell, and the catholyte compartment was filled with 12 M KOH. Air was used to depolarize the air electrode and the water decomposition reaction started by applying constant current (12.5 mA cm^{-2}). Air electrode voltage was measured with a Hg/HgO reference electrode and recorded with a Soltec two-pen chart recorder as zinc diffused to the catholyte compartment. Cell voltage was also simultaneously recorded with a chart recorder.

After 360 h of operation the cell voltage had changed by only 30 mV, an indication that the air electrode can withstand exposure to zincate-containing strongly alkaline solution. Although the air electrode is exposed to a varying zincate concentration during this experiment, the zincate concentration in an electric vehicle catholyte would also vary, typically over a shorter time period. The result of the experiment is seen as an encouraging one that will ultimately require substantiation by more extensive testing, including tests at constant zincate concentration.

The circulation of electrolyte due to solutal natural convection is an important aspect of the performance of the zinc–air cell described in this paper. That circulation is downward in the bed of particles and would be opposed by any thermally driven natural convection as the temperature of the electrolyte within the bed is raised by the exothermic discharge (and heat generated by internal resistance). A question arises about the performance of a large battery where departure from isothermal behaviour is aggravated by the smaller external surface to volume ratio, compared to laboratory cells. An answer to this question was reached by comparing the performance of the 400 cm^2 cell with and without 100 mm of polystyrene thermal insulation. With insulation the cell temperature rose 7 K during discharge, compared to 2 K without insulation. However, the discharge curve for the insulated case was little different from the non-insulated case, indicating that solutal convection was still dominant.

4. A design for a 32 kWh battery based on the laboratory cell

A 32 kWh (115 MJ) battery was designed based on the laboratory cell performance. It was assumed that the cells would be operated at a mean voltage of 1.1 V with 1.0 V marking the end of a discharge. A capacity of 68 mAh cm^{-2} air electrode was assumed (well below the 322 mAh cm^{-2} achieved in the laboratory). These assumptions lead to a necessary electrode area of 428 000 cm^2. A battery consisting of four modules connected in parallel was envisioned, each module being comprised of 120 cells each with 892 cm^2 electrodes. Selecting a mean current density of 32 mA cm^{-2} yields a battery current of 114 A and mean power of 13.7 kW. Calculating from Fig. 6 the peak power is 44.9 kW achieved at 86 V, 523 A and 20% DOD.

The laboratory cell thickness is 3.7 cm. However, a thickness of 1 cm appears practical (2 mm for outer frame), without any change in bed, conduit, diaphragm and electrolyte volumes, by changing the thickness of the current feeder and construction materials. Selecting a cell height of 26 cm (the height of the 400 cm^2 laboratory cell) results in a battery of 70 cm × 78.6 cm horizontal dimensions. Estimates of the weight of various battery components and of the air supply/scrubbing system appear in Table 1, along with the total weight. Performance figures based on these estimates appear in Table 2 together with US Department of Energy (DOE) target figures for a battery for an electric van. It is seen that the projected performance exceeds DOE targets. It should be noted that the design has not been optimized. For example a reduction in bed thickness and increase in electrode area is likely to result in a 32 kWh battery with still higher peak power but of higher cost due to the greater air electrode area.

A second parameter that has not been optimized is particle size. The particles used in the experiments reported here are approximately 600 μm in size. Larger particles would result in a bed presenting less resistance to electrolyte circulation but less area (per unit bed volume) available for mass transfer. It is suggested, therefore, that there is scope for improvement of this cell beyond the satisfactory performance that it already displays.

Table 1. Projected weight of 32 kWh (115 MJ) zinc–air battery

Specification	*Weight (kg)*
Frame	
Outer (from 2 mm plexiglass)	22.8
Inner (from 1 mm plexiglass)	81.2
	(A) 104.0
Air system	
Air electrode (based on AE-20)	27.2
Intake funnel	0.2
Filter and housing	1.0
Humidifier/scrubber	1.3
Air pump	2.0
Shroud	3.0
Valves	1.0
	(B) 35.7
Anode current collector	(C) 82.7
Total auxiliary (A + B + C)	222.4
Electrolyte	147.7
Zinc	33.9
Total	404

Table 2. Characteristics of an advanced 32 kWh (115 MJ) zinc–air battery

Design parameters	*This cell*	*DOE targets*
Voltage (V)	1.1[a]	
Current density (mA cm^{-2})	32[b]	
Electrolyte capacity (Ah l^{-1})	582[c]	
Electrolyte weight (kg)	147.7	
Zinc weight (kg)	33.9	
Auxiliary weights (kg) (substrate, frame, air electrode, air scrubbers)	222.4[d]	
Total weight (kg)	404	
Energy density (Wh kg^{-1})	79.2	60–120
Power density (W kg^{-1})	97.5 @ 40% DOD[e] 111.1 @ 20% DOD[e]	80–130

(a) Selected as average to end of near flat portion of discharge curve.
(b) Arbitrarily selected, current densities up to 150 mA cm^{-2} have been demonstrated.
(c) Achieved in 80 cm^2 cell with additives.
(d) Based on estimate of Ross for a comparable cell (US patent 4,842,963)
(e) Achieved in 80 cm^2 cell.

5. Concluding remarks

A zinc–air cell has been described wherein the zinc was in the form of particles that underwent partial electrodissolution during cell discharge. A commercially available air electrode was used. A significant feature of the cell was its reliance on solutal natural convection, avoiding the use of an electrolyte pump.

The paper described the discharge of the laboratory cells under conditions of constant or stepped current. Results were reported for both 80 and 400 cm^2 cells. Based on these results a preliminary design of a 32 kWh battery was carried out. The designed battery meets DOE targets for an electric van.

The cell is the subject of a patent application.

Acknowledgment

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution, Energy Storage Division, of the US Department of Energy under Contract No. DE-AC03-76SF00098.

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