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A ZINC-AIR CELL EMPLOYING A PACKED BED ANODE

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ABSTRACT

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 cm² and 400 cm² (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 battery was completed. The projected specific energy of this cell is 177 Wh/kg, while the peak specific power is 238 W/kg (20% depth of discharge), well in excess of Department of Energy targets for a battery for an electric van.

INTRODUCTION

The zinc-air cell has long (1-7) 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 aluminum-air battery, for example) with which the reactants can be regenerated. 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 (10). 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 (9). Mechanical recharging, particle regeneration and storage will be by slurry handling technology familiar in many industries.

THE CELL

This investigation has used cells of 80 cm² and 400 cm² (air electrode area); the smaller cell is illustrated in Figure 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 is unremarkable, consisting 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 molar 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. The system by which this was achieved is shown in Figure 2. A DC power supply (HP-6031A) and a 2.5 ohm 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 seconds for subsequent printing and plotting. The experimental procedure was as follows:

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 12M or 45% KOH with known weight of the additive for two days.

Pre-treatment of particles, separator and air electrode

30-mesh zinc particles were soaked in KOH solution for at least 10 minutes and rinsed with KOH before loading into the cell. Due to wetting and shrinkage, Daramic was soaked in KOH for at least one hour, whereas Celgard was not pre-treated. The air electrode (AE-20) was wetted with KOH solution for at least six hours.

Procedure

The experimental procedure consisted of placing pre-soaked 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 minutes). Subsequently power supply was set to withdraw current either in constant or stepped current and the voltmeter to read cell voltage at predetermined intervals (5 to 60 sec.). Raw data (cell voltage, current, time) and processed data (ampere-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 ampere-hours were 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 air-tight plastic bag to prevent drying.

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 3 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, followed by a steep plunge to zero volts. 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 and in a cell that has been discharged to zero volts 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 Figures 4 and 5, the consequences of stepping the cell current (and therefore the power) to higher levels are displayed. As seen in Figure 4, 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 Figure 3 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 where 100% DOD is defined as the knee of the discharge curve. The first of these excursions is shown on an enlarged scale in Figure 5 where the fast response is even clearer. Plots of plateau voltages versus current density from these excursions appear in Figure 6 and the power density versus current density curves of Figure 7 are obtained from the best straight lines passing through the data in Figure 6 by simply multiplying voltage and current density.

Figure 8 shows a typical discharge curve for the 400 cm² 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 4mm-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 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 longterm stability of the air electrode in the presence of zincate ions.

Figure 9 shows the performance of the cell during a discharge where the circuit was opened, at 14 Ah, for 25 hours. A slightly higher voltage on reconnecting the cell is observable. This cell was operated with a Celgard diaphragm and with the perforated plate supporting the particles modified to improve electrolyte circulation. The cell voltage was initially somewhat higher than those of Figures 3 or 4 while the voltage of the cell at longer times was superior. [The cell was shut down under computer control on reaching 1 volt.] Figure 10 shows the results of an experiment where the period on open circuit was longer (52

hours). In this case, the electrolyte contained additives, 4 g/l D-xylose and 20 g/l LiOH reported by others (10-16) to improve cell capacity. The additives appeared to have little influence on cell voltage prior to the open circuit period but to adversely effect cell performance subsequent to that period.

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 12M KOH. Air was used to depolarize the air electrode and the water decomposition reaction started by applying constant current (12.5 mAcm^{-2}). Air electrode voltage was measured with a Hg/HgO reference electrode and recorded with a Soltec 2-pen chart recorder as zinc diffused to the catholyte compartment. Cell voltage was also simultaneously recorded with a chart recorder.

After 360 hours 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.

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). The question arises as to the performance of a large battery where departure from isothermal behavior 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 80 cm² 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.

A DESIGN FOR A 32 KWH BATTERY BASED ON THE LABORATORY CELL

A 32 kWh battery was designed based on the assumption that laboratory cell performance could be achieved in a large battery. Specifically it was assumed that the cells would operate at a mean voltage of 1.1 volts with 1.0 volt marking the end of discharge. The cells were assumed to achieve the same capacity (322 mAh/cm² air electrode) as in the laboratory. These assumptions lead to a necessary electrode area of 108,000 cm². Selecting an electrode area

of 900 cm² therefore leads to 120 cells for a battery voltage ranging from an initial 177 volts to 120 volts at end of discharge at a discharge current of 28.8 A. At this discharge current the mean power is 3.5 kW and, calculating from Figure 7, the peak power is 11.3 kW achieved at 84 V volts, 133 A and 20% DOD.

The laboratory cell thickness is 3.7 mm. However, a thickness of 1 mm appears practical (2mm 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 cm² laboratory cell) results in a battery of 70 cm by 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 Dept. of Energy 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 μ m in size. Larger

Table 1
Projected weight of 32 kWh zinc/air battery

Frame		
Outer (from 2mm plexiglass)	5.7 kg	
Inner (from 1mm plexiglass)	20.3	
	<hr/>	
	26.0	
Air system		
Air electrode (based on AE-20)	6.8 kg	
Intake funnel	0.2	
Filter and housing	1.0	
Humidifier/scrubber	1.3	
Air pump	2.0	
Shroud	3.0	
Valves	1.0	
	<hr/>	
	15.3	
Anode current collector	22.8 kg	
Total Auxiliary		64.1
Electrolyte		83
Zinc		33.9
Total		<hr/> 181 kg

Table 2
Characteristics of an Advanced 32 kWh Zinc-Air Battery

	<u>Novel Cell</u>	<u>DOE Targets</u>
Design Parameters		
Voltage (V)	1.1^a	
Current Density (mA cm⁻²)	20^b	
Electrolyte Capacity (Ah/l)	582^c	
Electrolyte Weight (Kg)	83	
Zinc Weight (Kg)	33.9	
Auxiliary Weights (Kg) (substrate, frame, air electrode, air scrubbers)	64.1^d	
Total Weight (Kg)	181	
Energy density (Wh/kg)	177	60-120
Power density (W/kg)	193 @ 40% DOD^e 238 @ 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 cm² cell with additives
- (d) Based on estimate of Ross for a comparable cell (US patent 4,842,963)
- (e) Achieved in 80 cm² cell

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.

CONCLUDING REMARKS

A zinc-air cell has been described wherein the zinc was in the form of particles that underwent partial electro-dissolution 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 cm² and 400 cm² cells. Based on these results a preliminary design of a 32 kWh battery was carried out. The designed battery exceeds DOE targets for an electric van. A mathematical model incorporating solutal convection in a cell of this type and mass transport controlled electro-dissolution of zinc has been developed and will be the subject of a later publication. That model displays qualitatively the features of the laboratory cell.

The cell is the subject of a patent application.

ACKNOWLEDGMENT

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90-104

Fig. 1 A diagram of the 80 cm² laboratory cell in cross section. Dimensions in mm.

90-101

Fig. 2 A diagram of the experimental apparatus

Fig. 3 Reproducibility of the discharge curve in 80 cm^2 cell at 18.8 mA cm^{-2}

Fig. 4 Result of a discharge experiment where the current density was stepped for 30 second intervals to various values up to 148 mA cm^{-2} at 20% and 40% DOD (DOD is defined as forming a "knee" in the cell voltage).

Fig. 5 Enlargement of current step at 20% DOD from Fig. 4

Fig. 6 Cell voltage vs. current density obtained by stepping the current at 20% and 40% DOD from Figure 4

Fig. 7 Power versus current density at 20% and 40% DOD obtained from Fig. 6

Fig. 8 Discharge curve for the 400 cm² cell

Fig. 9 Discharge curve with 25-hour standby

Fig. 10 Discharge curve with 52-hour standby. Note that electrolyte contains some additives

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