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APPLIED SCIENCE DIVISION

The Secondary Slurry-Zinc/Air Battery

Final Report

H.B. Sierra Alcázar, P.D. Nguyen, G.E. Mason,
and A.A. Pinoli

July 1989

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THE SECONDARY SLURRY-ZINC/AIR BATTERY

Final Report

July 1989

by

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SUMMARY

Secondary Slurry-Zn/Air Battery

The rechargeability of the slurry-Zn/air battery was demonstrated with a practical recharge cell. Dendritic Zn was deposited on a Mg plate substrate and automatically scraped to regenerate dendritic Zn slurries. Excellent discharge results were obtained with the regenerated dendritic Zn slurry, comparable to those obtained with slurries made with mixtures of Zn powder. The dendritic Zn slurry allowed, however, twice the utilization of Zn in the slurry.

Recharge Studies

The minimum constant current density, MCCD, at which the energy for deposition of suitable dendritic Zn is minimal at a given zincate concentration and temperature, was determined. The MCCD increases with depth of charge, DoC, as well as with temperature. Temperature increases have complicated effects in the energy requirements in that although they decrease the overvoltage (in most of the recharge range) they tend to promote smooth deposition and therefore increase the current density at which dendritic deposition occurs. The use of higher temperatures (70 °C) was found advantageous, except at very low or very high zincate concentrations, where the energy requirements for dendritic Zn deposition were lower at room temperature.

An increase in specific charge results in a decrease of average cell energy density at all DoC. Increasing the specific charge also benefits coulombic efficiency. As expected for constant current deposition during individual scraping periods, most of the hydrogen evolution occurs at the beginning of the period because the active surface is small in the Mg substrate until nucleation and growth of Zn dendrites occurs. Longer scraping periods will average down the impact of the initial inefficiency of constant current density electrodeposition, however, after 300 c/cm² the gains are small.

Discharge Studies

The inherent discharge capacity of LiOH combined with sorbitol and silicate as capacity extension additives to 12 M KOH was determined by determining transition time at the Zn rotating disk electrode (RDE). It was found that at 1000 RPM and room temperature the capacity extension of the combined additives (25 g/l LiOH, 25 g/l SiO₂, and 15 g/l sorbitol) is 305.4 g Zn⁺⁺/l; not as high as the capacity found for LiOH alone in the same conditions (368 g Zn⁺⁺/l at 25 g/l).

Bicell III, with separated catholyte, was built to circumvent air cathode passivation, which appeared to limit discharge capacity. The experiments with Bicell III showed that the cathode does not limit the discharge capacity.

The possibility of improving discharge performance by flowing the Zn slurry on both sides of the anode current collector was explored with Bicell IV, featuring a nylon mesh separator. The cell voltage is dominated by ohmic losses in the electrolyte, and gains made by increased contact of Zn particles to the exmet collector, if any, are overshadowed by IR losses due to the increased gap length between anode and cathode.

The catholyte gap in Bicell IV-a allowed the study of the effect of gas sparging that might occur when very high air flow rates to the cathode cause a pressure unbalance and air is sparged into the electrolyte region. The power vs. current density curves show a specific peak power of 243 and 275 mW/cm² for air and oxygen, respectively. The main reason for the difference is believed to be increased electrolyte resistivity due to air sparging. This phenomena can, in principle, be controlled by balancing the gas and electrolyte pressures.

Better performance characteristics were obtained with Bicell IV-c , with no catholyte compartment.

Battery System Performance

The results at the single cell level were used for modeling purposes. An energy capacity of 125 kWh for a hydraulically rechargeable battery system model and 111 kWhr for a secondary battery system model at an average power of 5.5 KW were estimated in conformity with the IDESP van requirements. The model is based on the results obtained to date with individual charge and discharge bi-cells.

An electrically rechargeable slurry Zn/air system featuring an on-board charge reactor with 20 000 cm² of cathode area is estimated to recharge 340 l of Zn slurry in 8 hours, requiring 387 kWhr (165 kWhr without ohmic losses).

Recommendations

Further R&D in the improvement of the separate charge and recharge processes , in parallel with integration of the cells into a system is recommended to realize the advantages of the slurry-Zn/Air battery.

The power density can be significantly improved by focusing in improving electrolyte conductivity and discharge cell design and

operation. Suggestions for research are evaluating the compromise between conductivity and capacity at KOH molarities lower than 12 M KOH in the presence of capacity extension and conductivity improvement additives.

The discharge cell design and operation aspects that can be improved are the cell geometry, characteristics and exact position of exmet used as anode current collector, and the temperature and hydrodynamic conditions of gas and slurry streams. The optimum design will be dependent on the structure and size distribution of dendritic Zn in the slurry, as well as on the hydrodynamic conditions, that vary with DoD because of the changing physical characteristics of the slurry. A study of these relationships is recommended.

Studies focusing on decreasing the recharge energy in parallel with engineering improvements to the scraped bicell are recommended to improve the recharge process. The improvement of the oxygen evolution anode is a promising way to decrease the recharge energy: new doped nickel oxide anodes have been reported to have significantly improved oxygen evolution kinetics. Hydrogen depolarization of the anode could also result in significant economic gains suitable for central recharge.

The system integration of the charge and discharge reactors remains to be demonstrated and cycle life needs to be tested. The development effort is justified by the pay off of a safe, environmentally benign and cheap secondary battery with performance comparable to advanced battery systems being currently developed to power EV's.

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1 INTRODUCTION

The Slurry Zn/Air Battery Concept

The slurry-Zn/air battery system is a good candidate to power electric vehicles. It can operate either with hydraulic or electric recharge (secondary battery) or with both. Hydraulic recharge can be accomplished at strategically located stations by replacing discharged (spent) electrolyte with a fresh slurry of KOH solution and Zn particles. The spent electrolyte consisting of KOH solution with dissolved zincate ions, micelles and dissolved polymeric species containing ZnO can be electrically recharged at a separate recharge reactor, which can be carried on board. Electrical recharge involves deposition of dendritic Zn on a suitable substrate, such as Mg or glassy carbon plate, either at on-board reactor or at a central-station recharge reactor. Figure 1 shows the concept of the secondary battery with on-board recharge, and Figures 2 and 3 show projected discharge and recharge reactors components. The deposited dendritic Zn can be integrated into the electrolyte (with very low zincate concentration) by mechanical scraping the cathode substrate plates in the recharge reactor. Central station recharge may have access to cheaper sources of energy (i.e. hydrogen to depolarize the anode), but on-board recharge capabilities are necessary before widespread recharge stations are available for EV's.

Figure 1. Diagram of a Secondary Slurry-Zn/Air Battery System.

The advantages of the slurry-Zn/air battery include low self-discharge rate and sustained peak power capability. The slurry system does not suffer the problems of shape change or dendritic growth that affect porous and planar Zn electrodes. Furthermore, the specific energy and specific power of the battery can be tailored to specific applications. Additional advantages of the slurry-Zn/air battery include safety, low environmental impact and potentially low cost.

Figure 2. Diagram of Discharge Reactor. Formed with 172 bicells with a total air cathode active area of 30.96 m².

Overview of R&D

The research effort on the slurry-Zn/air battery made in the first two years of funding (1-2) were focused on the discharge cell and on the recharge cell. For the discharge process, the R&D goals were to find capacity extension additives, select the type of Zn particles and to improve the discharge performance. For the recharge process, the goals were to select a viable method of recharge (either smooth deposition on beads or dendritic Zn deposition and mechanical scraping) and optimize the recharge performance.

Bicells I and II (200 cm² of active cathode area each) were constructed to study the discharge process. The planar design is an engineering advancement over previous tubular configurations (3) which exhibited cathode sealing problems and a low cathode-area-to-volume ratio. Slurries made with commercially available Zn powder and with Zn coated polymeric beads were tested in Bicells I and II, with the Zn powder slurries giving better performance than the slurries based on Zn-coated polymeric beads (4). Slurries based on Zn powder were chosen for further development.

During Phase II, studies with the more compact design of Bicell II demonstrated better slurry hydrodynamics than that obtained with Bicell I. The air or oxygen supplied to Bicell II was also humidified, decarbonated and preheated. A specific peak power (with respect to cathode area) of 830 mW/cm², using pure oxygen as depolarizer, was obtained in Bicell II (5).

Various discharge-capacity extension additives were tested in Bicells I and II. Their operating mechanisms were discussed and classified as Types A, B, C, and D (6). A transition-time measurement was used to evaluate the effectiveness of additives under controlled hydrodynamic conditions at the Zn rotating disk electrode (RDE) (7). The results agreed with the capacities obtained using the bicells discharged at 200 mA/cm².

The addition of 25 g/l of SiO₂ to 12 M KOH extended the discharge capacity further than that obtained with stannate, titanate or aluminate. It is believed that these additives have a Type A mechanism to dissolve zincate ions, aiding in the formation of micelles. Sorbitol was found almost as effective as silicate in improving capacity of the electrolyte. The optimum concentration of sorbitol in 12 M KOH was 15 g/l. Sorbitol is a Type B additive that improves the zincate solubility by stabilizing polymeric chains involving ZnO molecules (8). A combination of 15 g/l sorbitol and 25 g/l silicate yielded a 203 Ah/l discharge capacity at 200 mA/cm², about 20% higher than that obtained with the separate additives (6). Silicate, used as a Type C additive to precipitate ZnO from 3 M KOH, did not improve the discharge capacity significantly. The best capacity extension (228 Ah/l) was obtained with 25 g/l. LiOH·H₂O (7).

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Figure 3. Recharge Reactor. Comprising 13 charge bicells with an active Mg-cathode area of 1538 cm² per cell.

Two recharge procedures were explored. The recharge of Zn coated polymeric beads was attempted with a fluidized-bed cell (1). Buoyancy of the beads caused fluidization problems. Eventually, the bead recharge efforts were abandoned in favor of the Zn powder slurry, which had better discharge performance and promised a more practical recharge. Thus, dendritic Zn deposition and mechanical scraping was the approach chosen to regenerate the Zn powder slurry (9).

Dendritic Zn deposition was studied in a three electrode cell where the evolved hydrogen was collected and measured. Various cathode substrates with a planar geometry were tested and the deposits manually scraped. Glassy carbon (GC) or magnesium metal allowed easy removal of dendrites with Mg requiring somewhat less energy than GC. A cell, with a rotating cylinder cathode that is scraped, was built to develop a practical recharge cell (9). The preferential growth of Zn at the fixed blades, where Zn dendrites accumulated after scraping, caused shorting problems. This design was abandoned in favor of a static, planar cathode, with moving scraper blades.

The projected performances of various slurry-Zn/air battery systems were calculated based on the results obtained with the single cells (4, 10,11). Experiments using both Zn powder and Zn-coated polymeric bead (Sorapec Bead) slurries, with silicate + sorbitol additive were used as the basis for an 11 kW, 300 kg slurry-Zn/air battery model. The best Ragoné curve (for Zn powder slurry and oxygen depolarization) resulted in 105 W/kg and 47 kWh/kg for short range missions and 465 kWh and 24 W/kg for long range missions. An extended description and comparison of various 11 kW systems based on experimental results with bi-cells I and II, and tubular cells from the CGE slurry-Zn/air battery under various additives and polarization conditions was published (4).

Single-cell charge and discharge data (with LiOH additive) for a hydraulically recharged system were used to estimate a specific energy of 91 Wh/kg and 64 kWh for a 700 kg battery system with a maximum power of 60 kW and a cruise power of 5.5 kW (10). A 750-Kg battery system with on-board recharge was also reported (11, 12). The capacity used in this case was 228 Ah/l. The maximum specific peak power in Bicell II continually decreases from above 800 mW/cm² at full charge to 243 mW/cm² at 65% DoD. A peak power of 243 mW/cm² was used to calculate the size of the discharge reactor to meet the requirement of 50-kW peak power at all times. Thus,

1232 bi-cells with 200 cm^2 active area each are required. The estimated weight without the slurry electrolyte was 408 kg, leaving 342 kg (212 l) for the slurry electrolyte. The total volume of the system was estimated to be less than 550 l. The calculated available energy (E^*) at cruising power was 64.67 kWh. For slow recharge, the estimated round-trip efficiencies were >99% coulombic efficiency, 54% voltage efficiency and 47% energy efficiency. Thus, the estimated cost of energy was \$0.14/kg of Zn recharged with off-peak electrical energy at \$0.07/kWh. If the recharge anode is depolarized with H_2 , which costs \$1.67/100 SCF, the cell voltage can be reduced to 0.7 V at 75 mA/cm^2 , and therefore the consumption of electrical energy is reduced and the total cost of recharge energy is then only \$0.06/kg of Zn. This means a cost of only \$0.056/kWh when used for recharge at a central-station.

- 1) Anode Holding Plate (Lucite)
- 2) Anode Current Collector (Copper Exmet)
- 3) Microporous Separator
- 4) Cathode Holding Plate (Lucite)
- 5) Cathode Air Electrode
- 6) Cathode Current Collector and Air Holding Plate (Copper)

Figure 4. Discharge Bicell III

2 EXPERIMENTAL

Discharge

A new discharge cell, Bicell III, was designed with separate anolyte and catholyte compartments as shown in Figure 4. The distance between air cathode and separator was 1/8 in. and the distance from separator to external all of anolyte compartment was 1/4 in.. The anolyte with the Zn particles (slurry) was recirculated to a reservoir with a centrifugal pump. The catholyte in Bicell III was quiescent or flowed into a separate tank with the aid of a second centrifugal pump.

Various separator membranes were tested to prevent or minimize transport of zincate ions into the catholyte. The separator selected for this purpose was Celgard 5550, a polyolefin base film heat-embossed to a nonwoven polypropylene in a dot pattern, and with coated surfactant to render it hydrophilic. Celgard 5550 has a thickness of 19 mils (0.075 mm), and is completely wettable in 12 M KOH. We were unable to operate the cell with two radiation grafted polyethylene microporous films from RAI: a 0.001-in. thick film called Zamm 0 and a 0.002-in. thick film called XSC220E. These films easily ruptured during operation with changes in back-pressure. No rupture problems, however, were found with Celgard 5550.

Some engineering improvements over Bicell II include a modular stack design, easy assembly, and scale-up. Better hydrodynamic conditions were obtained with smaller dimensions (smaller hydraulic diameter of slurry compartment) and improved flow distribution of slurry. An upward flow of slurry with no major eddies was obtained with a three fold branching of the incoming flow into three 1/8 in. input channels at the bottom of each side of Bicell III (with identical three outputs at the top of the bicell).

Operating conditions of Bicell III were similar to that used with Bicell II. Preheated and humidified air or pure oxygen was used to depolarize the cathode. The back pressure of these gases was adjusted (with a column of water at the gas outlet) to match the pressure of the slurry-anode, provided by the fixed-speed centrifugal pump (same pump used for three consecutive years) and a few inches of anolyte column at the cell outlet. The gas flow was measured with a mass flow meter and controlled manually at 5x

with 12 M KOH + 25 g LiOH.H₂O anolyte at 55 °C . The temperature was maintained with a tube preheater (heating tape coiled around a stainless steel tube), a thermocouple in the anolyte region of Bicell III; and a temperature controller.

Figure 5. Discharge Bicell IV-c. 1. Clear faceplate and chamber for circulating anode (Zn-slurry). 2. Anode current collector (copper exmet). 3. Nylon mesh separator. 4. Gas diffusion cathode with built in current collector (Eltech AE100). 5. Air cathode frame and chamber for circulating air or oxygen. The assembly is held together with through-bolts in the perimeter.

Bicell IV was constructed without the separated catholyte compartment which was designed in Bicell III. In order to preserve the stacking advantages, Bicell III was converted to Bicell IV-a by replacing the microporous membrane by a Nitex polyamide nylon separator with 45 % opening. The anode current collector was tested at various positions and eventually moved close to the separator and the separator closer to the air cathode. The distance between cathode and anode current collector was 0.5 in. in Bicell IV-a, 0.25 in. in Bicell IV-b, and nominally zero (only the width of the separator) in Bicell IV-c, see Figure 5. The catholyte compartment, 0.25 in. thick, remained in Bicells IV-a and IV-b, but not in Bicell IV-c.

To prepare Zn powder slurries, a mixture of 75 w/o 100 mesh powder and 25 w/o 30 mesh size powder were added in the amount of 300 g of Zn powder mixture (99.999 % pure) per liter of 12 M KOH (plus additive). Dendritic Zn slurries were prepared with Zn dendrites produced with the scraped bicell. These dendrites were filtered out, rinsed with water and methanol, dried and weighed and stored in nitrogen atmosphere before being added in the amount of 300 g of Zn dendrites per liter of 12 M KOH (plus additive).

Transition Time Measurements

A transition time measurement (TTM) was used to evaluate the discharge capacity extension (DCE) provided by additives under controlled hydrodynamics and constant (controlled) discharge current. The TTM has the advantages of reproducibility, independence from bicell design and slurry characteristics, which are useful in the selection and evaluation of additives to enhance electrolyte capacity. The method is based on the determination of the passivation time (t_p) of a Zn rotating disk electrode in the test electrolyte. A critical current density (i_c) was determined as a function of zincate concentration and additive concentration from the t_p measurements that followed the Sand equation $i_c = k/\sqrt{t_p}$. The concentration of zincate at which the critical current density becomes zero defines the DCE of the additive. Although the current density is constantly flickering for individual Zn particles in the slurry electrode, a ranking correspondence of DCE was found between capacity measured with the bicells and with the TTM.

1 & 12 STAINLESS STEEL FRAME PLATES

2 & 11 CLEAR FACE PLATES

3 7 & 9 FRAME

4 & 6 OPEN BOTTOM FRAME

5 Mg CATHODE WITH SCRAPER

8 NYLON MESH SEPARATOR

10 Ni EXMET ANODE

13 DENDRITIC ZINC COLLECTION SUMP

Figure 6. Exploded View of Charge Bicell with One Active Side. From left to right: 1) stainless steel frame plate, 2) clear faceplate, 3) frame, 4) open-bottomed frame, 5) Mg cathode with scraper, 6) open-bottomed frame, 7) frame, 8) nylon mesh separator, 9) frame, 10) anode (three layers of Ni exmet), 11) clear faceplate, 12) stainless steel frame plate. Assembly is held together with 24 through bolts in perimeter (not shown). Full bi-cell operation requires anode on left side (in configuration symmetrical with right side of this diagram).

Scraped Recharge Cell System

The recharge system consists of the scraped cathode cell, a Zn slurry collection column, a pump for delivery of the Zn to the column and circulation of the electrolyte, a programmable power supply, and a HP85B computer with a data acquisition and control unit (HP 3497A)for both monitoring and controlling the recharge operation.

The scraped cathode cell, shown in Figure 6 consists of a stack of acrylic frame plates which house a magnesium plate serving as cathode, nylon mesh separator and nickel exmet anode. 142 cm² of the Mg plate were exposed on one side of the plate and the rest masked for the initial tests. Anode and cathode potentials were measured with external Hg/HgO references electrodes and Luggin capillaries. At the end of a plating period a novel scraper mechanism is activated. A movable scraper blade is sent down across the active cathode surface. This action forces the zinc dendrites down into the sump of the cell. The polypropylene scraper blade is then automatically returned to its rest position above the cathode area. At the end of this action the circulation pump is activated, and the dendritic Zn as well as the entire recharge cell electrolyte volume is delivered to the collection column.

The collection column is a four-inch ID acrylic tube with a Zn slurry delivery port at the bottom. The Zn dendrites are trapped in the lower portion of the column by a filter element that prevents them from entering the upper section of the column where a port allows the clear electrolyte to return to the recharging cell by gravity. The filter is made of a nylon mesh cloth sandwiched by two nickel exmet supports. The turbulent action delivers the entire recharge cell volume of 2.5 liters in 8 seconds, frees the dendrites of trapped gases as well as breaks them apart. Therefore the Zn particles settle rapidly to the bottom of the column, and the gases are easily vented. The collected Zn is delivered via gravity thru a diaphragm valve for inspection or collection as fuel for the discharge cell.

Data Acquisition and Control System (DACS)

The DACS monitors five key signals of the scraped recharge cell system: anode potential, cathode potential, cell voltage, current signal via shunt resistor, cell temperature and charge passed; all

as a function of elapsed time. Each of these sets of measurements may be taken, printed-out, and stored in as little as five seconds. The data can also be plotted off-line. At the present time, efficiency measurements are limited to either gravimetric determination of the Zn content of the electrolyte by titrimetric or ICP spectrophotometric methods. The DACS controls the current levels as a function of depth of charge (DoC), the scraping periods, and the action of motors and valves necessary for scraping and flushing.

Efficiency Measurements

The recharge of zincate oversaturated electrolyte was studied with a cell in which the evolved hydrogen could be measured. The cathode substrates used were Mg and GC plates where dendritic Zn was deposited and scraped at periodic intervals with a polymeric blade. The anode was a nickel mesh. The cathode potential was measured with respect to a Hg/HgO reference electrode equipped with a Luggin capillary. Anode potentials were also measured with respect to a Hg/HgO reference electrode. A net was used to recover the scraped Zn for examination in a stereo microscope to classify its morphology.

3 RESULTS AND ANALYSIS

Recharge Bicell

The feasibility of a recharge bicell featuring a Mg cathode, automatically scraped at periodic intervals, was demonstrated. The operation of this practical recharge cell was guided by recharge studies that focused on determining the conditions of temperature and current density at which dendritic Zn deposition requires the least energy. The parameters studied included the temperatures, various zincate concentrations, current density and specific charge passed before scraping. The coulombic efficiency at each of these conditions was determined by measuring the evolved hydrogen in a cell with a manually scraped Mg cathode (2). The dendritic Zn slurry obtained in the recharge bicell was successfully pumped and discharged in Bicell IV-c, thus demonstrating the secondary slurry-Zn/Air battery concept.

Morphology of Electrodeposited Zn

Smooth electrodeposits of Zn are unsuitable for operation of the slurry-Zn/air battery because they are difficult to scrape off the Mg or GC substrate cathode. Smooth Zn electrodeposits come off in relatively large plates which can not be broken off by the centrifuge pump and consequently clog slurry lines. On the other hand, electrodeposits with very fine and interlocking dendrites, while easily scraped, come off in large spongy chunks which do not brake down by the centrifuge pump and cause clogging too.

The geometry of electrodeposited dendrites determines their ratios of surface area to weight or volume; it was observed that under a given zincate concentration and temperature, these ratios increase with the average current density. Rather than measuring directly these ratios, the morphology of scraped Zn electrodeposits was classified in a simpler and faster fashion according to the appearance under a stereo optical-microscope at 7x magnification. A scale of 0 to 6, called the "Dendricity Scale", was defined to encompass all stereo-microscope observations, in such a way that larger numbers in the Dendricity Scale correspond to increasing surface area to weight (or volume) ratios. Certain macroscopic features related to the shape and light reflectance of dendrites, are described as additional criteria to classify deposits. Table 1 shows the guidelines for classification and suitability for operation of the slurry-Zn/air battery.

Table 1. Dendricity Scale To Evaluate Structure of Electrodeposited Zn, Scraped off a Mg Cathode of the Slurry-Zn/Air Battery

VALUE	STRUCTURE	SCRAPING	SLURRY PROPERTIES
0	Smooth deposit	Very difficult to scrape.	Large plates of scraped deposits clog slurry lines
1	Moss like deposits	Can be scraped with a plastic blade.	Large lumps that can be broken down by centrifuge. Marginal for use in circulating slurry.
2	Bulbous dendrites	Easily scraped	Suitable for circulating slurry. Globular agglomerations remain, which however do not clog 1/8 I.D. slurry lines.
3	Disk shaped dendrites	Easily scraped	Suitable for circulating slurry
4	Fern leaf like structure. Shiny luster.	Easily scraped	Suitable for circulating slurry
5	Interlocking fern leaf like dendrites.	Easily scraped, but dense mesh structure traps hydrogen bubbles, causing buoyancy.	Unsuitable for circulating slurry. Large sponge like clusters do not break down by centrifuge pump and clog slurry lines. Buoyancy also causes separation problems.

Minimum Constant Current Density for Dendritic Zn Deposition

The minimum constant current density (MCCD) is defined as the current density at which the energy for deposition of suitable dendritic Zn at a given zincate concentration and temperature is minimal. The criterion for suitability is that the scraped Zn deposit is easily fluidized on passing through a centrifugal pump. Presently this criterion is met by the dendritic electrodeposits characterized with values of 2, 3 and 4 in the scale of dendricity. A dendricity value of 1 might be acceptable. Its lower deposition energy requirements make it a good candidate for fluidization experiments and perhaps special design of slurry lines for a practical system, however at this time the minimum dendricity value for determining MCCD was 2.

The MCCD is plotted as a function of zincate concentration and temperature in Figure 7. It can be seen that MCCD increases with depth of charge (DoC) as well as with temperature. At the high zincate concentration of 225 g Zn^{++}/l , increasing the temperature from 23 to 55° C increases the MCCD from 330 to 1010 mA/cm². A further temperature increase to 70 °C results in a MCCD of 1310 mA/cm². This means that to produce dendritic zinc from fully discharged electrolyte one has to choose between either high current density at high (70°C) temperature or low (room) temperature at lower current density. At a lower zincate concentrations, such as 23 g Zn^{++}/l , the same trend is present but MCCD varies only from 50 to 225 mA/cm² for a temperature change of 23 to 70 °C, respectively. The average cathode overpotential is here the time-averaged cathode overpotential during the period of time that takes to pass 300 c/cm². The average cathode overpotential at the MCCD, however, decreases with increasing temperature. Temperature increases have complicated effects in the energy requirements in that although they decrease the overvoltage (in most of the recharge range) they tend to promote smooth deposition and therefore increase the current density at which dendritic deposition occurs.

The specific cathode energy (or average cathode energy density) is defined as the product of the time averaged cathode potential times the constant current divided by the weight of Zn electrodeposited. This half cell specific energy decreases with increasing temperature at zincate concentrations larger than 50 g Zn^{++}/l , as seen in Figure 8. The average cathode overpotentials used to calculate specific cathode energy density in Figure 8 are the lowest at which a dendritic Zn deposit can be obtained at the given

zincate concentrations and temperatures; in other words they correspond to the MCCD's shown in Figure 7. The lowest average cathode overpotentials were obtained at 70 °C, except in about 10 % of the either very concentrated or very diluted zincate concentration range, where recharge (dendritic deposition) requires less energy at room temperature.

Figure 7. Minimum current density (MCCD) for deposition of Zn on Mg substrate as a function of temperature and zincate ion concentration.

Figure 8. Specific Cathode Energy (averaged during a scraping period corresponding to 300 c/cm² at MCDD) vs depth of recharge expressed as zincate concentration in g Zn⁺⁺/l.

Figure 9. Specific Energy vs Concentration of Zincate Ions. Specific energy calculated from cell potentials time-averaged during a scraping period at the indicated specific charge in each curve. Recharge proceeded at MCCD in a cell featuring a Ni anode.

Specific Charge Effects

The specific charge is the amount of charge transferred to the electrodeposit during each scraping period. The average specific cell energy is the energy required to produce a gram of Zn electrodeposit; this energy is calculated by multiplying the time-averaged cell potential by the constant or time-averaged current density. An increase in specific charge results in a decrease of average cell energy density at all DoC as shown in Figure 9. As expected for constant current deposition during individual scraping periods, most of the hydrogen evolution occurs at the beginning of the period because the active surface is small in the Mg substrate until nucleation and growth of Zn dendrites occurs. For the same reason the specific energy is high at the beginning of the cycle. Longer cycles will average down the impact of the initial inefficiency of constant current density electrodeposition, however after 300 c/cm² the gains are small.

Coulombic Efficiency

The coulombic efficiencies were calculated from measurements of the evolved hydrogen and charge passed. Coulombic efficiency was calculated as a function of (a) concentration of zincate (depth of recharge), (b) concentration of discharge additive, (c) coulombs of charge passed (since the last scraping period) from 0 to 300 c/cm², (d) temperature, and (e) stagnant or stirred electrolyte. The structure of the deposit for each of the previous experiments was classified by stereo microscopic observation. In general, very high coulombic efficiencies were obtained for conditions of temperature, zincate concentration, MCCD and specific charge under which a practical recharge cell would operate.

It was found that the effect of temperature on coulombic efficiency is small. For recharge at zincate concentrations 25 g Zn⁺⁺/l it was found to be 97.3 % at 70 °C and 98.9% at 23 °C.

The recharge coulombic efficiency improves at higher zincate ion concentrations. Increasing the specific charge from 30 to 600 c/cm² (108 to 2160 mA Hr) also improves the coulombic efficiency, as shown in Figure 10.

Stirring did not improve coulombic efficiency: higher currents are needed on stirred recharge in order to produce a dendritic Zn deposit, and these higher current densities cause lower coulombic efficiency. No deleterious effects were noted that could be attributed to capacity-extension additives. An indirect benefit of discharge capacity extension is that of extending the recharge range in the region of high coulombic efficiency, thus improving the overall coulombic efficiency.

Figure 10. Coulombic efficiency vs. concentration of zincate ions at various specific charges and at MCDD (minimum current density required for dendritic Zn deposition). Room temperature.

Potential Transients at the Practical Recharge Cell

A typical potential decay in a scraping cycle is shown in Figure 11, the cell voltage and anode and cathode potentials are plotted as a function of time for a DoC corresponding to zincate concentrations of 72 g Zn⁺⁺/l respectively. Note that the current density is maintained constant during the electrodeposition period, but its level is adjusted for each plating period according to the MCCD's which are a function of zincate concentration (DoC) and temperature. It was found for the practical recharge cell that suitable dendritic Zn was obtained when depositing slightly below the MCCD's reported in Figure 7. Thus some improvements in the minimum required energy are to be expected from lowering the required morphology requirements to a mixture of Type 2 and 3 deposits.

Figure 11. Plot of anode and cathode potentials (vs. Hg/HgO) and cell voltage vs. recharging time during one scraping cycle at a zincate ion concentration of 72 g Zn⁺⁺/l and 99 mA/cm² constant current density.

Discharge with Bicell III

The change in zincate concentrations in the anolyte and catholyte during discharge at 100 mA/cm², using Bicell III with Celgard 5550 separator, is shown Figure 12. At low concentrations of zincate in the anolyte, the transport of zincate into the catholyte was minimal. The transfer rate of zincate increased at DoD greater than about 60%; at the anode passivation point, the concentration of zincate (as Zn⁺⁺) was found to be 215.4 g/l in the anolyte and 54 g/l in the catholyte.

Figure 12. Concentration Transients in Discharge Bicell III.

The discharge curve obtained with Bicell III and Celgard 5550 separator is shown in Figure 13. A cell voltage of 1.05 V was maintained, in contrast to the discharge curves obtained with Bicell I and II showing a decaying cell voltage. The anode and cathode potentials are shown in Figure 14 as a function of discharge time. It can be seen that both the anode and the cathode appear to passivate simultaneously. The passivation mechanism of the cathode was previously suspected to be precipitation of ZnO in its pores. At zincate ion concentrations below saturation in the catholyte, however, this mechanism is not plausible. The observed cathode passivation is most certainly caused by the localized high current density resulting from the passivation of extended zones of the anode.

Figure 13. Discharge Curve Obtained with Bicell III and Celgard 5550 Separator.

The objective of building Bicell III with separate anolyte and catholyte was to increase the electrolyte capacity, which was previously believed to be limited by premature cathode passivation. The experiments with Bicell III have shown that the cathode does not limit the discharge capacity. Furthermore, the cathode potential measurements taken in Bicell II (2), are believed to be in error. These measurements showed a decay of cathode potential with discharge time, but now it is believed that the internal Hg/HgO reference electrode used for these measurements was shorted to the anode. In spite of being shrouded with a separator, it seems that fine Zn particles established a bridge to the slurry anode, and what was measured was the cell voltage instead of the cathode potential. The potential measurements taken with Luggin capillaries permanently installed on each side of the separator in Bicell III are reliable and do not show the cathode passivation that the measurements with Bicell II mislead us to believe.

The discharge capacity obtained with bi-cell III at 100 mA/cm², using 0.8 l anolyte and 0.6 l catholyte was lower than that obtained with bi-cell II at 200 mA/cm² using the same fixed-speed centrifugal pump and LiOH additive (25 g/l) in 12 M KOH. Although about the same amount of Zn was dissolved in the anolyte in both cases, the final concentration of zincate in the bi-cell III anolyte was 215.4 g Zn⁺⁺/l, compared with 279 g Zn⁺⁺/l obtained with Bi-cell II. Taking into account the catholyte and anolyte volumes in bi-cell III, the discharge capacity of the combined electrolytes in bi-cell III was only 120.2 Ah/l (146.6 g Zn⁺⁺/l).

The anode potential curve of Figure 14 is flat as expected for a slurry anode. The cell potential of Figure 13 is also flat, in contrast with that measured with Bicells I and II. The explanation is that the cell voltages in Bicells I and II decreased with increasing DoD due to an increase in electrolyte resistivity, which is noticeable at the higher zincate concentrations. In Bi-cell III, the resistivity of the catholyte remained essentially low during discharge, because the zincate concentration did not increase much (see Figure 12). The specific power of Bicell III is, however, significantly lower than that of Bicell II due to the higher resistance of the separator and to the added resistance from a less resistive but longer catholyte path.

Figure 14. Anode and cathode Potentials as a function of DoD in Bicell III

Polarization curves at 100 mA/cm² and a zincate concentration in the anolyte of 47 g Zn/l, taken 1.5 hours after start of discharge with Bicell III, are shown in Figure 15. The separator's IR drop is the voltage measured between reference electrodes with Luggin capillaries near each side of the separator. The curve labeled UNADJUSTED POT. is the cell potential as measured, and the curve labeled ADJUSTED POTENTIAL is the cell potential less the measured IR drop across the Celgard 5550 separator. It can be seen that the IR drop across the separator was only 1/13 of the total cell potential at 50 mA/cm², but at 250 mA/cm² it is more than 1/3 of the cell potential.

Figure 15. Polarization Curves with Bicell III Discharged at 100 mA/cm².

In conclusion, the separated anolyte and catholyte design of the bicell is not practical. The specific power is lower because of the added cell resistance. The discharge capacity achieved with the electrolyte was also lower, mainly due to the added catholyte volume. The separated anolyte and catholyte design adds unnecessary complications but was helpful in gaining a better understanding of the discharge process.

Discharge with Bicell IV

Discharge curves using Bicell IV are shown in Figure 16. Curve A was taken with Bicell IV-a, having a gap of 1/4 in. from air cathode to separator, and 1/4 in. gap from separator to anode current collector (exmet). Curve B was taken with Bicell IV-b, having a gap of 1/4 in. from air cathode to separator, but separator and exmet plate adjacent to each other. Curve C was taken with Bicell IV-c, having exmet separator and air cathode sandwiched together as close as possible. It can be noted that a capacity of 223 Ah/l at 200 mA/cm² was obtained with Bicell IV, an improvement over that obtained with Bicell III and close to that obtained with Bicell II.

The possibility of improving the performance by flowing the Zn slurry on both sides of the anode current collector was explored. Comparing Curves B and C of Figure 16, gains in voltage made by increased number of contacts of Zn particles to the exmet collector, if any, are overshadowed by IR losses due to the increased gap length between anode and cathode. For the same reason Curve A in Figure 11 shows the poorer performance.

Figure 16. Discharge Curves with Bicell IV-a

The catholyte gap in Bicell IV-a allowed study of the effect of gas sparging that might occur with very high air or oxygen flow rates to the cathode. This operation mode can cause a pressure unbalance which sparges gas into the electrolyte region. This effect is illustrated in Figure 17, showing the voltage drop across the Nitex polyamide nylon for oxygen and air depolarization. Both for oxygen depolarization and for air depolarization, 1 milliohm resistance is obtained at low current densities. At current densities higher than 300 mA/cm², however, the IR drop measured across the separator increases, indicating an apparent separator resistance of 4 milliohms. High flow rates of air are needed to maintain the 5x stoichiometric ratio of oxygen at the higher current densities; the increased resistance is believed to be due to increased resistivity of the electrolyte caused by air bubbles sparged in through the air cathode, operating at higher pressures than the electrolyte side. This phenomena can be controlled by balancing the gas and electrolyte pressures. The easiest way to avoid the problem in future designs is to decrease pressure drops in the cathode outlet gas lines with extra outlets and bigger diameters, so that gas pressure in the cathode is effectively controlled by a water column or similar device at the end of the outlet line, and not by pressure drops in the outlet lines themselves, because these pressure drops are flow rate dependent and make balancing more complicated.

Figure 17. Voltage drop across "Nitex" separator in Bicell IV-a

The cell potential obtained with Bicell IV-a was dominated by ohmic resistance both for air and oxygen depolarization. The cell potential showed a straight line decay from 1.42 V at OCV down to 0.5 V at 450 mA/cm² for air and down to 525 mA/cm² for oxygen depolarization. The corresponding specific power vs. current density curves in Figure 18 show a specific peak power of 243 and 275 mW/cm² for air and oxygen, respectively. The main reason for the difference is believed to be increased electrolyte resistivity due to air sparging.

Figure 18. Specific Power vs. Current Density.
Discharge with Bicell IV-a

Polarization curves with fresh air cathodes (A-100 from ELTECH) in Bicell IV-c at various DoD are shown in Figure 19. This run was made with a Bicell IV-c. The ohmic drop changes because of the increase of electrolyte resistivity with increasing DoD. The one point that deviates from ohmic behavior in the polarization curve taken at 45 Ah/l is the one determined at 700 mA/cm². A similar behavior was observed on determinations with Bicell II (2). The explanation for the improvement of peak power at high current density behavior is a decreased electrolyte resistivity due to an increase in electrolyte temperature in the neighborhood of the separator. This temperature increase above the bulk temperature is caused by local heating due to ohmic losses at the higher current densities.

Figure 19. Polarization Curves as a Function of DoD.
Bicell IV-c at 55 °C

The specific peak power resulting from the 45 Ah/l curve in Figure 19 is 670 mW/cm². This value is close to the 800 mW/cm² specific peak power determined with Bicell II at 16 Ah/l. The typical specific peak powers as a function of DoD obtained in subsequent runs with new A-100 air cathodes in Bicell IV-c are shown in Figure 20. The occurrence of high peak powers, as those of Figure 19, which were not reproduced in the subsequent runs shown in Figure 20, suggests that there is potential for improvement. One can surmise that they might be the result of particularly good bicell assembly, or of variations of the air cathode, or subtle operation changes. The conservative specific peak powers of Figure 20 were, however, used for modeling the battery system in the next section.

The minimum Zn powder loading required to maintain 200 mA/cm² discharge without additional polarization due to Zn depletion was determined in Bicell IV-c to be 99 g Zn/l. The anode potential is monitored for this purpose, starting discharge with 300 g of Zn per liter of slurry until the Zn is depleted enough to cause a sharp change in anode potential due to decrease of effective anode area; addition of Zn powder to the slurry returns the anode potential to its previous level. The minimum Zn powder loading in the slurry is the concentration of metallic Zn in the slurry just previous to the onset of this sharp polarization. This can be calculated based on the coulombs of charge passed.

Dendritic Zn Discharge

A dendritic Zn slurry was successfully discharged with Bicell IV-c. The slurry was made with 300 g/l of dendritic Zn, mostly of Type 3 morphology produced in the scraped recharge cell. The cell voltage as a function of DoD is shown in Figure 21. The corresponding specific peak power as a function of DoD is shown with triangle symbols in Figure 20. Not enough dendritic Zn was produced to determine whether it caused a change in electrolyte discharge capacity. Figures 21 and 22 show, however, that the performance with dendritic Zn slurry is similar to that obtained with a slurry containing Zn powder mixture.

The minimum dendritic Zn loading in the slurry required to discharge Bicell IV-c at 200 mA/cm² without increased polarization was found to be 50 g/l, almost half of that required with Zn powder mixture. This can be explained by the finer structure of the dendritic Zn. The density of the dendritic Zn slurry was 4.529 g/

cm³; smaller than the 6.696 g/cm³ density of the slurry made with Zn powder mixture (300 g/l). On visual examination, the specific area of the dendritic Zn was definitely larger than that of the Zn powder mixture.

Figure 20. Specific Peak Power vs DoD. From typical runs in Bicell IV-c at 55 °C. Triangles indicate discharge of a slurry made with dendritic Zn, ovals correspond to Zn powder slurry.

Figure 21. Cell voltage vs. DoD for slurries made with dendritic Zn (solid circles) and powdered Zn (shallow circles).

Discharge Capacity from Transition Time Measurements

The inherent discharge capacity of Zn in 12 M KOH containing LiOH combined with sorbitol and silicate as capacity extension additives was determined from the transition time at the Zn rotating disk electrode (RDE). The critical current densities were extrapolated from a plot of inverse square root of passivation time as a function of zincate concentration. Figure 22 is a plot of the critical current densities versus the zincate concentration. The inherent discharge capacity of the additive combination is the zincate ion concentration, expressed as g of Zn^{++}/l , extrapolated from the curve in Figure 22 at a critical current density value of zero. It was found that at 1000 RPM and room temperature the inherent capacity extension of the combined additives 25 g/l LiOH, 25 g/l SiO_2 , and 15 g/l sorbitol is 305.4 g Zn^{++}/l ; not as high as the capacity found for LiOH alone in the same conditions (368 g Zn^{++}/l at 25 g/l).

Figure 22. Critical Current Density From Transition Time Measurements vs. Zincate Ion Concentration. Zn RDE at 1000 RPM.

4 MODELING THE SLURRY-Zn/AIR BATTERY

Models of the hydraulically rechargeable battery system and of the secondary battery system will be described in this section.

A design concept of a pre-commercial prototype power source for the IDSEP van has been completed. Using a fixed criteria of a 700 Kg battery (see Table 2) with a minimum power of 55 KW for acceleration, most requirements for the IDSEP are met (volume less than 600 l, minimum energy capacity more than 21 KWh, and 120 V minimum voltage). An energy capacity of 125 KWh for a hydraulically rechargeable slurry Zn/air battery system and 111 kWhr for a secondary battery system (hydraulic and on-board electrical recharge) at an average power of 5.5 KW were estimated in conformity with the IDSEP van requirements. The model is based on the results obtained to date in individual charge and discharge bi-cells.

The secondary slurry-Zn/air battery system envisioned consists of two separate stacks of discharge and recharge cells, and optional slurry reservoir(s) of a size compatible with the vehicle mission. This concept is shown in Figure 1. For the purpose of this exercise the amount of Zn slurry (dendritic Zn particles in 12 M KOH) stored in the system was adjusted so that the total weight of the battery system would be 700 Kg. This is for comparison purposes only, since we feel that the range needs of typical EV's, and specifically the IDSEP van could be achieved with less Zn slurry and therefore with a smaller battery system.

In the hydraulically rechargeable slurry-Zn/air battery system, the weight of the Charge Reactor (charge cells) is replaced with an equivalent weight of dendritic Zn slurry to bring the total weight of the system to 700 Kg. The components and estimated weights and volumes for the hydraulically rechargeable and secondary systems are given in Table 1. It can be seen that both systems are limited by weight, since their estimated volumes are less than the maximum 600 l specified for the IDSEP van.

Discharge Stack

A schematic of the discharge stack is shown in Figure 2. It consists of 172 sandwiched discharge bicells with air cathodes measuring 20 x 45 cm (1800 cm² active area per bicell) connected in series. A stack of 43 bicells forms a submodule where the slurry is flowed by an independent pump. Appropriately slot-

ted manifolds at the bottom and top of the four submodules allow circulation of the slurry along each bicell, consecutively, in an upward and a downward direction as indicated in the diagram. It is believed that the geometry of the slots will allow an even distribution of flow along the width of each bicell. This stack arrangement is designed for a maximum voltage of 240 V at open circuit and a minimum of 120 V during operation within the nominally allowed DoD: $D^* = 0.93$.

Table 2. Weight and Volume of Projected Slurry-Zn/Air Battery Systems

	Hydraulic Recharge		On Board Recharge	
	Weight (kg)	Volume (l)	Weight (kg)	Volume (l)
Discharge Cells	120.6	480	120.6	480
174 Bicell + Busses (101.2 kg)				
2 Manifolds (19.4 kg)				
Air System	8.7	30	8.7	30
Intake funnel (0.2 kg)				
Filter & housing (1.0 kg)				
Humidifier/Scrubber (1.0 kg)				
Shroud (7.1 kg)				
Water tank (0.4 kg)				
Valves (1.5 kg)				
Air pump (7.5 kg)				
Electrolyte System	11.6	10	11.6	10
4 Electrolyte pumps (8.2 kg)				
Plumbing (1.2 kg)				
Valves (2.2 kg)				
Charge Cells			25.0	60
Polypropylene Housing (1.7 kg)				
Ni anodes (14) (1.6 kg)				
Mg cathodes (13) (0.3 kg)				
Busses (8.3 kg)				
Zn removal system (4.0 kg)				
Plumbing (0.8 kg)				
Electrolyte holding tank (8.3 kg)				
Miscellaneous	32.3	10	32.3	10
Controls, Sensors (10.0 kg)				
Mountings (22.3 kg)				
Oxygen gained				
Total Dry Weight	177.2	530	198.2	590
Slurry Electrolyte	526.8	330	501.8	315
Total System	700	530	700	590

Charge Stack

A schematic of the charge stack is shown in Figure 3. It consists of 13 charge bicells with an active Mg cathode area of 1538.4 cm^2 per bicell, connected in parallel. The 13 Mg plates and 14 Ni anodes comprising the stack are suspended in a structure that allows collection and exhaustion of evolved gases on top. Scraping of deposited Zn off both sides of the Mg plates is achieved by sliding scraping blades located on the upper part of the structure when not in use. The design envisioned is to have the charge stack suspended inside the slurry reservoir to save container weight and additional pumps and valves. Alternatively it could be independently enclosed. In any case the estimated recharge time is eight hours at MCDD.

Projected System Performance

Two peak power vs. fractional DoD curves calculated for the 700 Kg-battery system are shown in Figure 23. The specific peak power vs. DoD data used for calculation of curve 1 is taken from Figure 20. As can be seen from curve 1 in Figure 23, the requirement of 55 KW peak power is only met in 93 % of the capacity range, while the full capacity is available in a system with no ohmic losses, as shown in curve 2 of Figure 23, calculated from the data of Figure 20 corrected for ohmic losses in the electrolyte.

Plots of energy capacity vs. power data are shown for four cases in Figure 24. Cases 1 and 3 refer to the battery system with on-board charge reactor while cases 2 and 3 refer to a hydraulically chargeable battery (the reactor weight replaced with extra Zn-slurry). Cases 3 and 4 are corrected for no ohmic losses in the electrolyte.

In summary, an electrically rechargeable slurry Zn/air system featuring an on-board charge reactor with $20\,000 \text{ cm}^2$ of cathode area is estimated to recharge 340 l of Zn slurry in 8 hours, requiring 387 kWhr (165 kWhr without ohmic losses). An energy capacity of 125 kWh for a 700 Kg hydraulically rechargeable battery system model and 111 kWhr for a secondary battery system model at an average power of 5.5 KW (peak power density of 71.4 W/Kg) were estimated in conformity with the IDESP van requirements. This results in an energy density of 178.6 Wh/Kg for the hydraulically recharged system and 158.5 Wh/Kg for the slurry-Zn/air battery system with on-board electrical recharge.

Figure 23. Peak Power vs. Fractional DoD for a 700 Kg Slurry-Zn/Air Battery System. Curve 1 is based on experimental results of Figure 20. Curve 2 is based on the 22%-curve of Figure 19.

Figure 24. Ragoné Curves. Curves 1 and 3 correspond to a 700 Kg system with on board recharge. Curves 2 and 4 correspond to a system with only hydraulic recharge. Curves 1 and 2 are calculated from curve 1 in Figure 25. Curves 3 and 4 are calculated from Curve 2 in Figure 25.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The rechargeability of the slurry-Zn/air battery was demonstrated with a practical recharge cell that requires minimal hydraulic and mechanical energy for operation. A dendritic Zn was deposited on a Mg plate substrate from which it was easily, periodically and automatically scraped to regenerate dendritic Zn slurries. Excellent discharge results were obtained with the regenerated dendritic Zn slurry, comparable to those obtained with slurries made with mixtures of Zn powder. The dendritic Zn slurry allowed, however, twice the utilization of Zn.

The inherent discharge capacity of LiOH combined with sorbitol and silicate as capacity extension additives to 12 M KOH was determined from transition time measurements at the Zn rotating disk electrode (RDE). It was found that at 1000 RPM and room temperature the capacity extension of the combined additives 25 g/l LiOH, 25 g/l SiO₂, and 15 g/l sorbitol is 305.4 g Zn⁺⁺/l, not as high as the capacity found for LiOH alone at the same conditions (368 g Zn⁺⁺/l at 25 g/l).

The experiments with Bicell III have shown that the cathode does not limit the discharge capacity. In conclusion, the separated anolyte and catholyte design of the bicell is not practical. The specific power is lower because of the higher cell resistance. The discharge capacity achieved with the electrolyte was also lower, mainly due to the added catholyte volume. The separated anolyte and catholyte design adds unnecessary complications but was helpful in understanding the discharge process.

The possibility of improving performance by flowing the Zn slurry on both sides of the anode current collector was explored. The cell voltage is dominated by ohmic losses in the electrolyte, and gains made by increased contact of Zn particles to the exmet collector, if any, are overshadowed by IR losses due to the increased gap length between anode and cathode.

The catholyte gap in Bicell IV-a allowed the study of the effect of gas sparging when very high air flow rates to the cathode cause a pressure unbalance and air is sparged into the electrolyte region. The power vs. current density curves show a specific peak power of 243 and 275 mW/cm² for air and oxygen, respectively.

The main reason for the difference is believed to be increased electrolyte resistivity due to air sparging. This phenomena can, in principle, be controlled by balancing the gas and electrolyte pressures.

The minimum constant current density (MCCD) at which the energy for deposition of suitable dendritic Zn is minimal at a given zincate concentration and temperature, was determined. The MCCD increases with depth of charge (DoC) as well as with temperature. Temperature increases have complicated effects in the energy requirements in that although they decrease the overvoltage (in most of the recharge range) they tend to promote smooth deposition and therefore increase the current density at which dendritic deposition occurs. The range of MCDD was found 50 to 300 mA/cm² for room temperature charge and 200 to 1300 mA/cm² for charge at 70 °C. The use of higher temperatures (70 °C) was found advantageous, on most of the DoC range, over the room temperature energy requirements, except at very low or very high zincate concentrations.

An increase in specific charge results in a decrease of average cell energy density at all DoC as shown in Figure 9. For 600 c/cm², the energy required to deposit 1 g of Zn varies from 3.1 to 1.7 Wh in the DoC range of 230 to 25 g Zn⁺⁺/l. Increasing the specific charge also benefits coulombic efficiency. As expected for constant current deposition during individual scraping periods, most of the hydrogen evolution occurs at the beginning of the period because the active surface is small in the Mg substrate until nucleation and growth of Zn dendrites occurs. For the same reason the specific energy is high at the beginning of the cycle. Longer cycles will average down the impact of the initial inefficiency of constant current density electrodeposition, however after 300 c/cm² the gains are small.

Coulombic efficiency was calculated as a function of (a) concentration of zincate (depth of recharge), (b) concentration of discharge additive, (c) coulombs of charge passed (since the last scraping period) from 0 to 300 c/cm², (d) temperature, and (e) stagnant or stirred electrolyte. Very high coulombic efficiencies (>99%) and relatively low overpotentials are possible for recharge at low current densities. The coulombic efficiencies are about the same for both Mg and GC substrates: above 99% at high zincate concentrations and down to about 88 % at 51 g Zn/l. These results apply in the current density range from 100 to 750 mA/cm².

The conservative specific peak powers obtained with Bicell IV-

c as a function of DoD (Figure 16) were used for modeling the battery system. An electrically rechargeable slurry Zn/air system featuring an on-board charge reactor with 20 000 cm² of cathode area is estimated to recharge 340 l of Zn slurry in 8 hours, requiring 387 kWhr (165 kWhr without ohmic losses). An energy capacity of 125 kWh for a 700 Kg hydraulically rechargeable battery system model and 111 kWhr for a secondary battery system model at an average power of 5.5 KW (peak power density of 71.4 W/Kg) were estimated in conformity with the IDESP van requirements. This results in an energy density of 178.6 Wh/Kg for the hydraulically recharged system and 158.5 Wh/Kg for the slurry-Zn/air battery system with on-board electrical recharge.

Recommendations

Further R&D in the improvement of the separate charge and recharge processes, and integration of the cells into a system is recommended to realize the advantages of the slurry-Zn/Air battery.

The power density can be significantly improved by improving electrolyte conductivity and discharge cell design and operation. Suggestions for research are evaluating the compromise between conductivity and capacity at KOH molarities lower than 12 M KOH in the presence of capacity extension and conductivity improvement additives.

The discharge cell design and operation aspects that can be improved are the cell geometry, characteristics and exact position of exmet used as anode current collector, and the temperature and hydrodynamic conditions of gas and slurry streams. The cell geometry can be improved with rectangular geometry instead of the square geometry; measures to increase slurry volume in front of the air cathode and to improve slurry flow along the edges of the active cathode area are also likely to improve power density. The optimum design will be dependent on the structure and size distribution of dendritic Zn forming the slurry as well as hydrodynamic conditions that vary with DoD because of the changing physical characteristics of the slurry. A study of these relationships is recommended.

Studies focusing on decreasing the recharge energy in parallel

with engineering improvements to the scraped bicell are recommended to improve the recharge process. The improvement of the oxygen evolution anode is a promising way to decrease the recharge energy: new doped nickel oxide anodes have been reported to have significantly improved oxygen evolution kinetics. Hydrogen depolarization of the anode could also result in significant economic gains suitable for central recharge.

A possible enhancement in the proposed slurry-Zn/Air battery system could be achieved by reducing the water carried for a full mission. Zinc powder and dry KOH could be carried separately, and reconstituted into a slurry with water, obtained from stations at suitable intervals. This mode of operation would diminish self discharge, increase power and energy densities, and improve safety and pollution problems in the case of traffic accidents.

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APPENDIX A

Charge Stack Sizing

The purpose of this Appendix is to describe the experimental basis and calculation procedures used to estimate the size of the charge stack required for the IDSEP on-board charge reactor. The size of the stack depends on the volume of spent electrolyte and time in which it is desired to be recharged. By an iterative process it was found that the approximate volume to be charged was 340 l of spent electrolyte. A convenient recharge time for this volume was arbitrarily set as 8 hours. Additional constraints to the problem were that the minimum energy should be expended in the recharge process (highest coulombic efficiencies), and that the final zincate concentration in the regenerated electrolyte should be less than 25 g Zn⁺⁺/l. The specific charge per scraping cycle was arbitrarily chosen as 300 c/cm². A small improvement in the energy requirements and in the total time of recharge can be expected for larger specific charges, but we chose 300 c/cm² because of the extensive experimental data base we have already gathered with that specific charge.

The minimum current densities (MCCD's) for deposition of dendritic Zinc at various temperatures as a function of zincate concentration used for modeling are those shown in Figure 7. These MCCD's correspond to the lowest energy requirements for deposition of Zn with an acceptable dendritic morphology. For the sake of modeling calculations the 55 °C curve of Figure 7 was numerically represented with three linear regions given by

[Zn ⁺⁺], g/l	MCCD, mA/cm ²
25 - 99.9	$i = 3.3([Zn^{++}] - 25) + 150$
100 - 149.9	$i = 2.0([Zn^{++}] - 100) + 400$
150 - 280	$i = 6.5([Zn^{++}] - 150) + 500$

The plating time as a function of zincate concentration was calculated from the above relationships for each scraping cycle considering increments of 1 g Zn⁺⁺/l until 300 c/cm² were deposited in each cycle. This procedure was repeated for a number of cycles necessary to bring the zincate concentration from 278 to 25 g Zn⁺⁺/l. Adding up the plating times for each scraping cycle gives a total operating time of approximately 47 hours.

The electrolyte volume that 1 cm² of cathode can recharge in a

scraping cycle if the zincate concentration were to be reduced by 1 g Zn⁺⁺/l is:

$$V = (300 \text{ c/cm}^2) (1 \text{ eq}) 65.38 \text{ g} / (96500 \text{ c}) (2 \text{ eq.}) (1 \text{ g/l}) \\ = 0.10163 \text{ l/cm}^2$$

The inverse is the surface area to electrolyte volume, namely 9.84 cm²/l. Since our model calls for 8 hours recharge time, the surface area to electrolyte volume must increase by 47/8, becoming

$$(47) (9.84 \text{ cm}^2/\text{l}) / 8 = 57.8 \text{ cm}^2/\text{l}$$

Multiplying the above figure by 340 l we arrive at the total active area of 19,652 cm², which we rounded to 20 000 cm² in the final model design.

Cathode overpotential is also a function of DoC (zincate concentration). The experimentally determined cathodic overpotential curves were curve-fitted with three linear regions according to the expressions shown below. The interpolated overpotentials were then used to calculate Zn deposition requirements in small DoC increments.

[Zn ⁺⁺], g/l		Cathodic Overvoltage, V
25	- 99.9	$i = 0.00074 ([\text{Zn}^{++}] - 25) + 0.232$
100	- 149.9	$i = 0.00298 ([\text{Zn}^{++}] - 100) + 0.289$
150	- 280	$i = 0.00632 ([\text{Zn}^{++}] - 150) + 0.435$

Anode overpotentials, V_a, were calculated from the Tafel slope and exchange current density for oxygen evolution on a co-precipitated Fe/Ni oxide electrode as reported by . Corrigan (13):

$$V_a = 0.25 \log_{10} (i - 4.5 \times 10^{-9})$$

Anode and cathode potentials were obtained by adding the calculated overpotentials to the open circuit voltages of the electrodes which are respectively 0.303 and -1.35 V vs Hg/HgO. The ohmic losses were calculated at each scraping cycle. The conductivity of the electrolyte, S_c, in (ohms cm)⁻¹, as a function of zincate concentration, Z_c, in g Zn⁺⁺/l, was estimated from a relationship determined from our own measurements:

$$S_c = -9.644 \times 10^{-4} Z_c + 0.3447$$

If a 1 cm gap between anode and cathode is used for the model calculations, the energy required to recharge 340 l is 387 kWhr, of which 222 kWhr are ohmic losses (165 kWhr would be required with no ohmic losses). Correspondingly, 385 kW peak power is needed with a 1 cm gap, compared to 80 kW in the absence of ohmic losses.

The observed voltage drop with DoD is essentially due to ohmic losses resulting from diminished electrolyte conductivity at the higher zincate concentrations. In order to assess the improvement limit obtained from gains in electrolyte conductivity and in cell design, calculations of discharge performance were made with and without considering the ohmic losses.

The size of the recharge reactor was designed so that a reasonable compromise between unused discharge capacity and weight of reactor could be achieved. The discharge capacity of the 12 M KOH electrolyte with LiOH additive determined at 200 mA/cm² in the bi-cell was 228 Ah/l (278 g Zn⁺⁺/l). This is the value considered as 100% DoD. The peak power used for sizing the discharge stack was 190 mW/cm² experimentally determined at 93 % DoD. The cathode area needed is therefore

$$A = 55 \text{ kW} / (190 \text{ mW/cm}^2) = 289,474 \text{ cm}^2$$

This area was divided into 172 cells connected in series, sufficient to provide 120 V at end of discharge and no more than 240 V at any time.

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