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Zinc Bromine Battery Technology for Electric Vehicle Applications

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Abstract:

The zinc bromine battery is a high energy density battery that utilizes low cost materials in its construction. It has a relatively high energy density (60 to 70 Wh/kg of battery weight) and is modular in design. It operates at ambient temperature and has unique operating characteristics that are advantages for electric vehicle applications. This paper describes the design, and construction, of a 391 volt, 35 kWh zinc bromine battery for an electric vehicle. This research project resulted in the construction of the "California 1" battery, the highest voltage zinc bromine battery ever to be constructed for used in an electric vehicle.

Introduction

The zinc bromine battery described in this paper was constructed from 4 fifty-four-cell stacks in series (total of 216 cells) and two polyethylene electrolyte storage tanks. The stacks and tanks were constructed by Powercell Corporation for use in a UC Davis electric vehicle that was designed for competition. The battery has a measured "C over 3" capacity of 35 kWh and was named the California 1 (CA1) in recognition of . this technology's applicability to the 1998 ZEV mandate in California.

The author of this paper have been actively researching the use of zinc bromine technology for electric vehicle use since 1989 (1, 2, 3, 4,). This research summarized in Table 1 includes two 5 kWh laboratory modules attaining a specific energy of 56 Wh/kg (3 hour rate) and a peak power of 56 W/kg at 50% DOD, three 22.5 kWh batteries systems attaining a specific energy of approximately 61 Wh/kg at the 3 hour rate and two high voltage 35 kWh batteries. Other independent results for a 5 kWh zinc bromine battery can be found in the reference (5).

Table 1 Zinc Bromine Battery Research

Project (Nominal kWh)	# of Cells and Configuration	Nominal OCV	Battery Weight	Complete EV Power System Weight*
5 kWh	32 Cells	58	100 kg	na
Texas #3 22.5 kWh	144 Cells, two parallel strings of 72 cells	130	375 kg	440 kg
California #1 35 kWh	216 Cell in Series	389	518 kg	606 kg
California #2** 30 to 35 kWh	216 Cell in Series	389	425 to 475 kg	500 to 556 kg

* Includes battery containment, cooling system, cables and controls.

** The California #2 battery is currently being designed for installation in a US Electricar S10 truck. The lead acid batteries that it will replace are nominally 20 kWh in capacity and weigh 832 kg with a EV power system weight of approximately 950 kg.

Zinc Bromine Battery Technology

The zinc bromine battery is an ambient-temperature, flowing-electrolyte battery that utilizes zinc bromide as its electrolyte. The electrolyte is aqueous and undergoes the following reactions charge and discharge.

Table 1. Zinc Bromine Battery Reactions

Electrode	Charge	Discharge
Negative	$Zn^{++}(aq) + 2e^- \rightarrow Zn(s)$	$Zn(s) \rightarrow Zn^{++}(aq) + 2e^-$
Positive	$2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$	$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$

Theoretical energy density for the zinc bromine couple is 440 Wh/kg. A schematic of a single cell is shown in Figure 1. During charge metallic zinc reduces on a solid electrode surface (polyethylene plastic with a carbon filler for electronic conduction) and bromine evolves (oxidation). Discharge is the reverse reaction. Unlike conventional batteries, the electrolyte (and reactive materials) is stored in containers separate from the so called electrode surface. In fact the electrode material (zinc and bromine) are carried in the electrolyte as ions. The electrolyte is a solution of zinc bromide (molarity greater then 2) with quaternary salt additives. As the zinc plates on plastic it forms an electrode while the bromine returns to the electrolyte tank. The quaternary salts form a strong association with bromine, reducing its vapor pressure without adversely affecting its electrochemical properties. The dense brominated liquid (complex) naturally settles at the bottom of the electrolyte tank. During discharge the quantity of returning complex to the stacks is metered by a controllable valve.

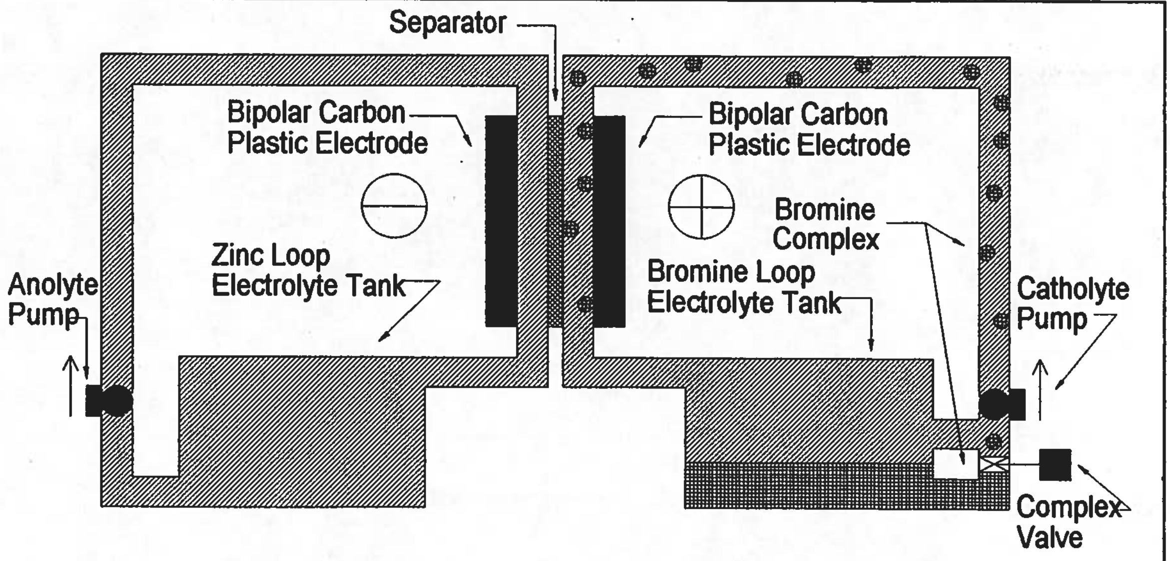

Figure 1. Schematic of the Zinc Bromine System

In the cell the electrolyte from each of the electrolyte tanks is not allowed to mix but is separated by a microporous separator. The separator allows cations and anions to cross between the two electrolyte streams thus completing the electrochemical circuit. Due to the separation of the reactant carrying electrolyte from the stacks where the reaction takes place the battery energy and power density can be adjusted. In principle this is achieved by changing the quantity of electrolyte carried or by increasing the number of cells in the battery.

The California 1 Battery

The California 1 battery design consists of two stack towers, two electrolyte tanks, an electrolyte pumping system, a control system, and a cooling system. Each stack tower consists of two individual 54 cell bipolar stacks that are nominally 100 amp hours at C/3 discharge rate. The CA1 battery system, schematically shown in Figure 2, consists of two electrolyte tanks that supply electrolyte to the stacks. Both are constructed of heavy plastic. No electrochemical reactions occur in the tanks. In addition, the anolyte tank (defined during discharge) has a water to electrolyte heat exchanger built into it. The water is circulated externally to standard car radiator and electric fan. The circulated water is controlled controlling the electrolyte temperature in one tank

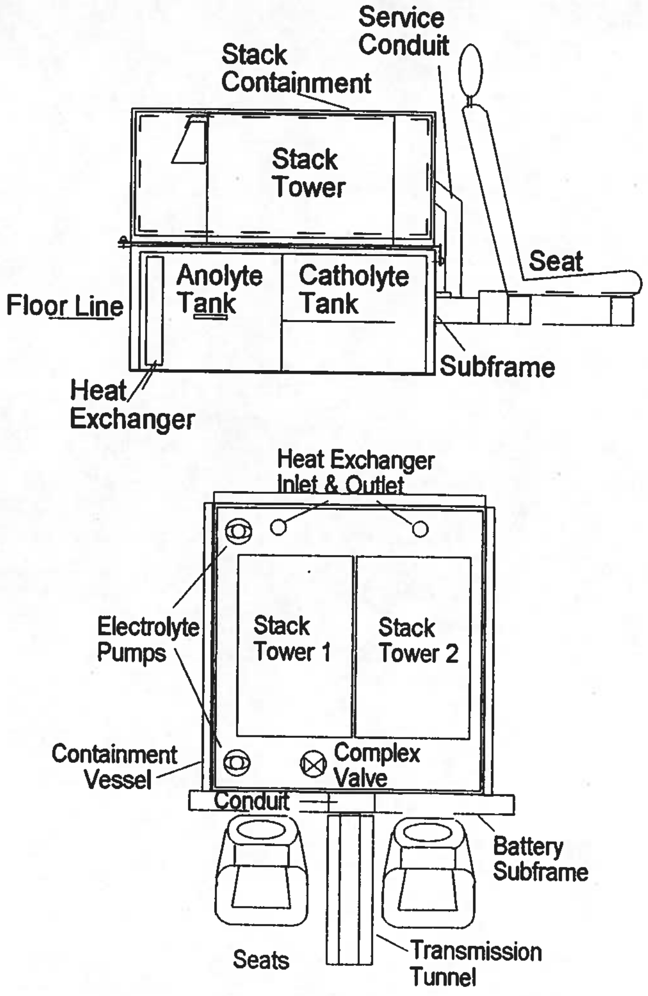

Figure 2. Schematic of CA1 Battery System

The stacks consist of a number of bipolar cells made up of a plate of conductive plastic (bipolar electrode plate) and a microporous separator. The anolyte side of the bipolar plate has shallow grooves on the plastic; on the catholyte side a carbon paper is bonded to the conductive plastic to significantly increase surface area and reduce over-potential. The electrolyte is circulated by two independent pumps. A battery management system monitors temperature and current and controls the electrolyte pumping system, cooling system and safety systems. The entire battery is held by a containment vessel that supports and isolates the battery from the rest of the electric vehicle.

California 1, Design and Performance

The CA1 battery was designed specifically for an electric vehicle that utilized a Geo Prism chassis and Hughes Dolphin drive system (50 KW). The vehicle project name Endura and was designed to compete in the annual Phoenix electric vehicle race. By carefully considering the chassis weight, propulsion operating voltage, the vehicle power and energy needs, the battery capacity and number of cells were determined. Special consideration was given to the electrolyte manifold design to reduce shunt currents. Table 2 provides engineering data of CA1.

Table 2 CA1 Battery Specifications

Chemistry:	Zinc Bromide	
Configuration:	Two Electrolyte Tanks Four 54 Cell Stacks	
Electrolyte:	2 x 100 liters	
$ZnBr_2$ molarity:	≈ 2.5	
OCV 100% SOC:	391	Volts
Charge Capacity @ C/3 Rate	-104.6	Ahr
Energy Capacity @ C/3 Rate:	-34.1	kWh
Max. Power 50% SOC:	≈ 40	kW
Weight:		
Electrolyte	300	kg
4 Stacks (wet)	164	kg
Electrolyte Tanks	40	kg
Electrolyte Pump System	7	kg
Miscellaneous	7	kg
Battery Total	518	kg
Battery Containment Vessel	55	kg
Cooling System	20	kg
Cables, relays, fuses, Comp.	13	kg
Power System Total	606	kg
Charge Method:	Constant Current	
Nominal Charge Rate:	30	amps DC
End of Charge Voltage:	432	volts
Nominal Charge Power:	12	kW
Nominal Charge Time:	5 hours 0 to 100% SOC	

The discharge profiles in Figure 3 were obtained by discharging the battery through a resistor. The current varied from 39 amps to 27.5 with an average of 34.9. Near the end of 3 hours the resistor value was changed and resulted in the sudden increase in current and drop in voltage. The Figure 3 plots show a load voltage changing from 370 to 240 volts. This wide voltage swing was accommodated by re-programming the motor drive. At a C/3 rate, the battery energy density was measured at 65.8 Wh/kg and a power system energy density of 56.3 Wh/kg.

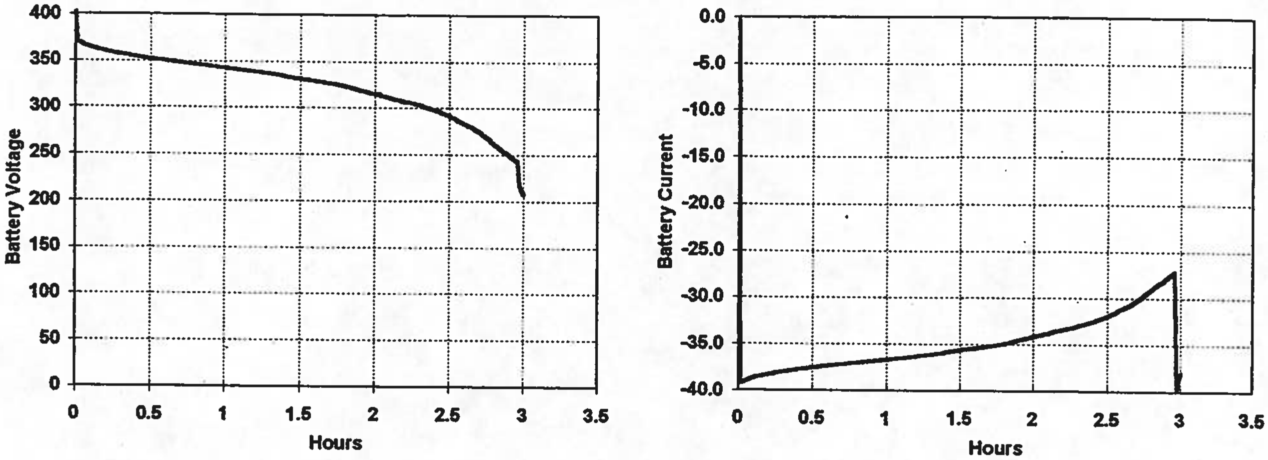

Figure 3. CA1 Performance for C/3 Discharge
-104.6 Ahr. -34.1 kWh, Battery

Before the battery could be used in competition it under went an extensive safety review (6). The conclusion was that the design of this advanced battery had no higher risk associated with it than conventional lead acid battery technology. Using the CA1 battery the Endura electric vehicle placed third in the feature race in Phoenix. In April 94, Endura competed in the World Clean Air road Rally, a three day event in the Los Angeles basin. Out of a field of 54 vehicles, including natural gas and hybrids, the Endura took first place with 690 points of a possible 700 (a first day range of over 160 miles in LA traffic). The nearest class competitor was at 545 points. In May 1994, Endura competed in the American Tour de Sol, a six day cross country road rally for electric vehicles. In a class of twenty one, Endura took second place (5 minutes behind 1st place) in the American Commuter division and first place overall for a student-built vehicle (single charge range of 175 miles). In these three competitive events the car accumulated over 2000 miles and the CA1 battery was cycled approximately 20 times.

Conclusions

The CA1 battery represents the successful demonstration of a high voltage zinc bromine battery.. Its high energy density makes it possible to break the 100 mile range barrier while still having a payload capability. This technology appears to be a viable, potentially low cost battery that can be used in the near term to help meet California's ZEV mandates

The specific performance parameters measured on the CA1 battery are as follows:

- A total energy of 34.1 kWh with a specific energy of 65.8 Wh/kg. This energy level was achieved in the laboratory at a C/3 rate. Typical on the road discharges were in the 30 to 33 kWh range. Further increases in energy density are possible by reductions in weight and an increases in electrolyte reactant utilization.

- The CA1 battery provided approximately 40 kW of power at a 50% state of charge. This gives a specific power of approximate 77 W/kg of battery weight or 244 W/kg considering only the wet cell stack weight. The specific power battery can be further increased by reductions in overall weight, by changes in the cell stack to electrolyte tank weight ratio, by changes in the cell design and by changes in the electrolyte composition. It is interesting to note that although the power density value of the CA1 design was relatively low, the Endura car was always at or near the top in qualification runs which compared acceleration or hill climbing.
- Complete recharging can be accomplished within 5 hours. The approach was simply to provide a constant current charge with no taper. A typical overcharge of 15 to 30% was used.
- The CA1 containment and controls account for 17% of battery system weight. This compares with lead acid battery pack containment cables and control weight of 14% (7). Due to the higher energy density of the CA1 battery, the actual system component weight (containment and controls) is less compared to lead acid technology on a kWh bases.
- Shunt currents between the common electrolyte cells was found to be approximately 1 ma and thus near negligible. Due to the common electrolyte for all cells, shunt currents exist due to the voltage gradients that naturally occur in the electrolyte. These shunt currents create zinc deposit imbalance between cells. The CA1 battery manifold design reduced these currents to a minimum..
- Thermal control was achieved by a water to electrolyte heat exchanger in one of the electrolyte storage tanks and a standard automotive radiator. Electrolyte circulation maintained temperature throughout to within 2 C°.
- Stack and cell balancing was achieved by completely discharging the battery, all zinc being "striped" for the stacks. This procedure is opposite but not unlike an equalization charge for lead acid batteries.

Several distinct advantages unique to zinc bromine technology were also determined:

- The modularity design of the zinc bromine battery allowed a custom fit and weight for the target vehicle. The electrolyte tanks can be shaped to meet unusual volume requirements.
- General handling was accomplished by draining the electrolyte and disassembling the basic components and moving them by hand.
- The zinc bromine battery can be completely discharged and short-circuited with no damage. In this state maintenance or repair it can be easily and safely done. Long term storage or transport (including air shipment) is also done in this state.

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7 Author estimate for US Elecitricar S10 truck, lead acid pack weight of 832 kg, containment tank, cables, controls weight of 118 kg.