CIRCULATING ELECTROLYTE ZINC/BROMINE BATTERY. TEST PROGRAM AND PROCEDURES

P. GRIMES

Exxon Research and Engineering Company, P.O. Box 45, Linden, NJ 07036 (U.S.A.)

The Exxon circulating electrolyte zinc/bromine battery system is being co-developed by organizations in America, Europe, Japan, and Australia. The circulating electrolyte zinc/bromine battery systems have reached the multi-kilowatt hour capacity size ranges. Several 20 kW h and 30 kW h systems have been successfully tested in different modes of operation.

Circulating electrolyte batteries use a test program procedure which considers the circulation system characteristics in addition to the classical test procedures.

The overall operation of the Exxon zinc/bromine battery is based on a circulating electrolyte. Advanced battery designs have been proposed for various couples, such as iron/air, iron/nickel, zinc/chlorine, and zinc/bromine, using electrolyte circulation concepts. Electrolyte circulation is generally useful for feeding reactants, removing products, assisting thermal management, and homogenizing the electrolyte. A particular advantage of circulation of the electrolytes in the zinc/bromine battery is the improved uniformity of the zinc-plating during charging. Although electrolyte circulation increases design complexity, it also allows better performance and higher specific energies.

Bipolar cell design with electrolyte circulation permits compact, high voltage battery stacks. The common electrolyte pathways, however, allow the shuntage of power when the battery is at potential (during charge/discharge or open circuit stand). The shunt power loss is greater with an increase in the conductivity of the electrolytes, cell voltage, number of cells in the stack, and larger dimensions of the system electrolyte channels and manifolds. The pumping power, however, diminishes with the larger channels and manifolds. There are application design tradeoffs between the hydraulic and electrolytic power considerations.

Electrical shunt current control methods have been developed which involve passing appropriate electrical power through the common electrolyte pathways. This nulls the voltage gradients between the cells and the common electrolyte channels and manifolds. The shunt current effects on the battery stack are thereby reduced/eliminated. The power involved in shunt current protection in a well designed system is only slightly higher than the power which would have been lost through shuntage in an unprotected system. As a result, power can now be productively directed into the shunt current protection system.

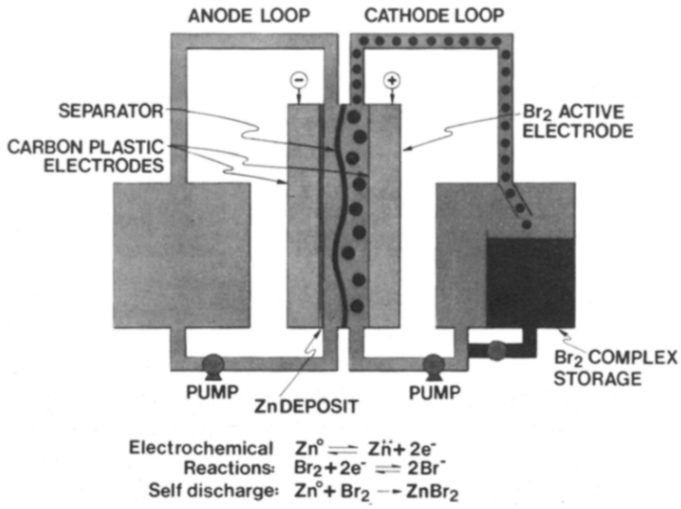

Fig. 1. Schematic of zinc/bromine circulating battery system.

The schematic of a zinc/bromine battery system, shown in Fig. 1, has three main components. The principal component is the electrochemical module, where the actual electrochemistry takes place. The second component is the circulating electrolyte (an aqueous solution of zinc bromide and bromine complexing agents) which is circulating in two streams through the electrochemical module. The third component is the system of pumps and reservoirs which store and circulate the electrolytes. The operation of the zinc/bromine battery is easily understood by following a typical charge/discharge cycle. During charge, zinc is plated at the negative electrode and bromine is evolved at the positive electrode. Bromine associates with the complexing agent to form a second phase, indicated by dots in Fig. 1. This bromine-rich phase is circulated out of the electrochemical module and is separated by gravity in the catholyte reservoir. The bromine is consequently stored away from the zinc, allowing long-term charge retention. During discharge, the catholyte valve is open and the bromine complex is fed back to the module. Consequently, zinc and bromine electrochemically react to form the original solution of zinc/bromide and complexing agents, liberating the energy absorbed during charging. The separator prevents direct mixing of the anode and cathode loops, thereby reducing self-discharge during cycling.

Stack design uses the 1200 cm^2 two-piece unit bipolar cell which has recently been developed. This includes co-extruded bipolar electrodes, which are shown in Fig. 2. In these electrodes, a central conductive plastic is surrounded during the extrusion process by two, non-conductive plastics. Non-conductive plastics are needed at the extremities of this electrode because of shunt current considerations. The injection molded separator used with the larger co-extruded bipolar electrodes is also shown in Fig. 2. In this separator,

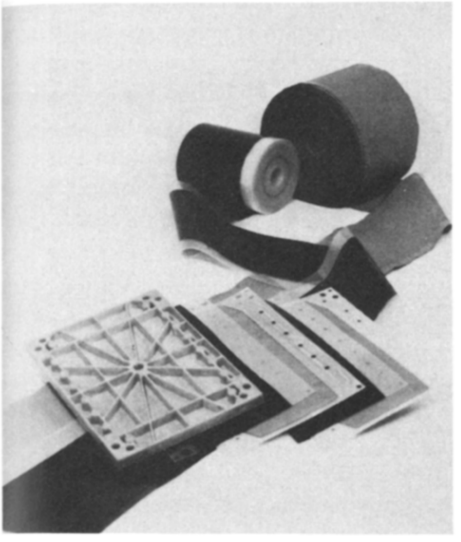

Fig. 2. Components for two-piece cell construction.

an insert of Daramic®* (a microporous separator) which features posts, is surrounded by a non-conductive plastic with various flow distribution channels. These channels distribute the two electrolytes over both faces of its adjacent bipolar electrodes. Closer examination of the flow channels shows that they have been designed to utilize tunnel shunt current projection and high conductivity electrolytes. A stack design, which has a nominal discharge voltage of about 120 V, requires 78 cells in series. A stack of 124 cells produces a system of a nominal 200 V output. A stack array with tunnel shunt current protection is shown in Fig. 3. A common central manifold is located between the two stacks at the positive end of each stack. The extreme ends of the two stacks would, therefore, have a negative polarity and the stacks would be operated in parallel. Both the central and the end feed blocks can be "swiss cheesed" to reduce weight and material for the final deliverable product. The external negative feed blocks are molded from a reinforced polypropylene. The stacks, the central feed block, and the two end blocks are held together by metallic reinforcing rods. Bolts at the extremities of the stack are used for the initial compression of the electrode stacks. However, the actual sealing of the stacks to prevent leaks is done with a sealer. This sealer physically bonds together the electrode frames and the separator frames.

The electrolyte in this design will be comprised of 3 molar zinc bromide, 1 molar quaternary ammonium bromides, and a supporting electrolyte for power applications.

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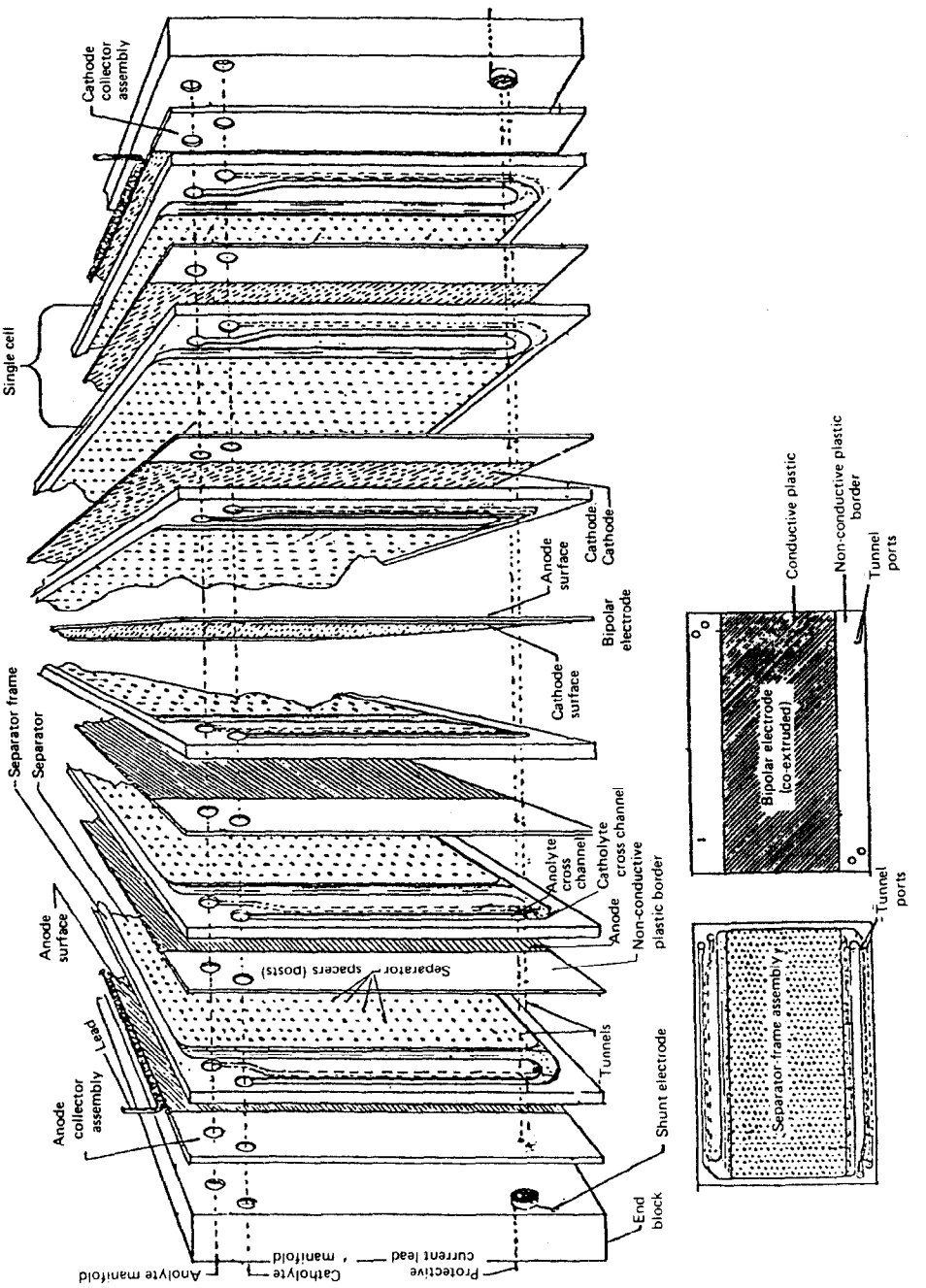


Fig. 2 Exploded view of battery stack.

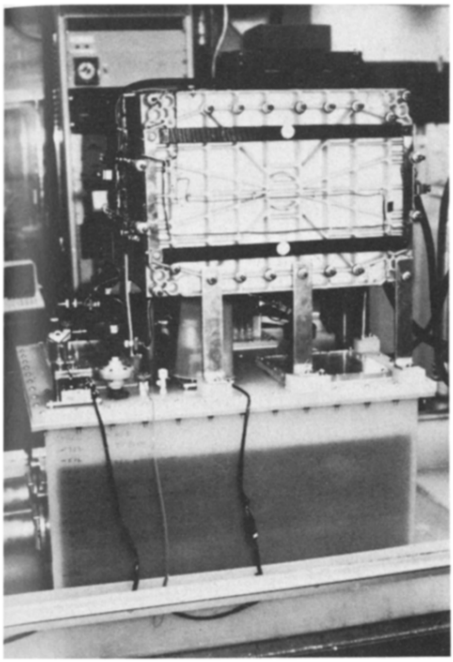
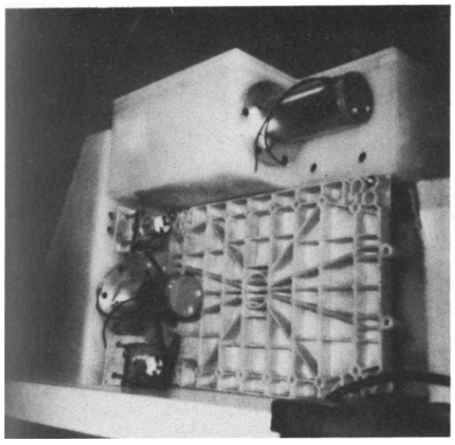


Fig. 4. 20 kW h zinc/bromine battery.



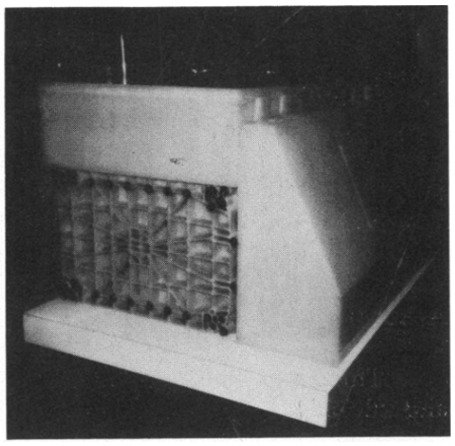


Fig. 5. Reservoirs and stacks for 30 kW h zinc/bromine battery.

Fig. 6. Reservoirs and stack, 30 kW h zinc/bromine battery.

Battery systems of 120 V and 20 kW h capacity and 200 V and 30 kW h capacity are illustrated in Figs. 4 - 6.

In the testing of circulating electrolyte zinc/bromide battery systems, there is an opportunity to consider the monitoring of many parameters and operating variables during charge, open circuit, and discharge conditions:

system voltage and current;
voltage of individual cells or groups of cells (cell blanks);
pump motor voltages and currents;
electrolyte flow rates;
anolyte/catholyte pressures;
shunt current protection currents;
electrolyte temperature;
thermal management temperatures;
state of charge;
battery power and energy input and output;
electrolyte properties.

These systems allow the measurement and monitoring of a wide variety of properties and values, as opposed to conventional cells or batteries of individual cell systems without circulation of electrolyte.

In general, two modes of testing have been used:

(i) Daily cycling with a constant current charge, followed by a constant current discharge to a voltage of one volt/cell and finished by a total discharge through a low resistance load to zero potential.

(ii) Accelerated testing with repeated constant current charge and discharge cycles to a fixed voltage, with periodic total discharge, to a system of zero voltage. Two to four cycles/day are possible with this method.

These tests are aimed at characterization of the batteries and their cycle life.

While accelerated procedures speed up the testing, the results must be used with caution. For example, the diffusion processes and electrolyte species equilibrium are not allowed to reach the degree of completion of the one cycle/day testing. These and other effects could possibly have longer term consequences.

Zinc/bromine batteries have also been successfully tested in power pulsing discharge modes, rapid charging by regenerative braking modes, power feed to utility lines, and federal urban driving cycles.

Acknowledgement

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