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DEVELOPMENT OF ZINC-BROMINE BATTERIES FOR
UTILITY ENERGY STORAGE

First Annual Report for the Period September 1, 1978—August 31, 1979

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Gould Laboratories
Rolling Meadows, Illinois

U. S. DEPARTMENT OF ENERGY

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**DEVELOPMENT OF ZINC-BROMINE BATTERIES
FOR UTILITY ENERGY STORAGE**

FIRST ANNUAL REPORT

For the Period

1 SEPTEMBER 1978 - 31 AUGUST 1979

RONALD A. PUTT

MAY 1980

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PREPARED FOR THE

**U.S. DEPARTMENT OF ENERGY
DIVISION OF ENERGY STORAGE**

UNDER CONTRACT EW 78C 02 4984

and

**ELECTRIC POWER RESEARCH INSTITUTE
ENERGY MANAGEMENT AND UTILIZATION DIVISION**

UNDER CONTRACT EPRI RP635-2

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1. EXECUTIVE SUMMARY

A major design improvement was made during the program which has proved crucial to the successful scaleup of the zinc-bromine battery, that being conversion from a monopolar to a bipolar cell design. The bipolar design has been shown to be superior with respect to cost, performance and simplicity. Conversion from the monopolar to bipolar cell design was achieved at the 8kWh submodule level with a minimal perturbation on the hardware construction and testing schedule; two monopolar and one bipolar submodules were built and tested within the twelve month contract period. A cost and design study was also performed for purchased materials and components of an 80kWh, stand-alone, zinc-bromine battery module.

The one year program had as its goals the construction and testing of full size cell hardware, in the form of three 8kWh submodules, and a cost/design study of an 80kWh module. Supporting studies were included for developing the basic electrochemistry of the system. The program was based on technology developed during a 28-month contract with EPRI (RP635-1) which began in March of 1976 (Ref.1). The system design which evolved during that program comprised a monopolar cell stack using titanium electrodes and a microporous separator (DARAMIC®, W.R. Grace), circulation of electrolyte through both the negative and positive sides of the cell stack, and storage of electrolyte and bromine (the latter in the form of a liquid polybromide complex) externally to the cell stack.

Two monopolar, 8kWh submodules of that design were built during the present program. Despite poor electrochemical efficiencies, the reasons for which are discussed below, one of the submodules achieved over 160 deep discharge cycles in continuous, hands-off, automatic cycling, indicating the inherent "cyclability" of the system.

There were two major problems with the monopolar design which became evident in construction and testing of the 8kWh submodules. First, we could not find a cost effective means of producing the highly conductive (i.e. titanium-clad copper) current lead-in tabs required for the electrodes. Second, there would be corrosion of the titanium negative electrodes during cell reversal at end-of-discharge unless an expensive electrical bypass is provided for each cell, in conjunction with a complicated electrolyte formulation for inhibiting corrosion.

The bipolar design suffers neither of these problems. Current collection is required only at the end plates, which can be made much thicker than the internal electrodes for that purpose at a reasonable cost, and the carbon bipolar electrode is not corroded during cell reversal. One disadvantage of the bipolar design is that the voltaic performance of the flat, non-porous bromine electrode is not as good as it is for the porous, flow-through bromine electrode of the monopolar design; and special provisions are required to bring its performance up to the design value.

Based on the clear advantages of the bipolar design, the emphasis was shifted to that concept in time for construction and initial testing of an 8kWh bipolar submodule. This was possible because the rest of the system (i.e. the bromine storage subsystem, the plumbing circuit and other minor auxiliaries) which was developed for the monopolar submodule was directly applicable to the bipolar submodule as well.

A cost and design study for an 80kWh module resulted in a cost estimate of \$54/kWh (1979\$) for purchased materials and components, based on 2500MWh of annual production. A complete battery manufacturability study was not performed, owing to the unlikelihood that the 80kWh module will be commercialized for utility energy storage. Rather, a much larger module size (e.g. 1MWh) is being considered to take advantage of economies of scale and to increase the reliability of a 100MWh installation.

The cost data are realistic, owing to the large extent of commercial production technology already in use to make batteries for testing and the emphasis on using off-the-shelf components wherever possible. For examples, the electrode frames and grid spacers are injection molded, and the separators are cut to size and punched using production die-cutting equipment. And the separator material is commercially available (DARAMIC®, W.R. Grace & Co.), as are the schedule 80 polypropylene plumbing and magnetically-coupled, sealess pumps for the flow systems.

Studies were also performed in support of battery design, construction and testing. These included zinc deposition studies, a multicomponent transport analysis, a thermal management study, modeling of the bromine storage subsystem, titanium corrosion studies and accelerated erosion testing of electrodes.

The original, one year program reported on herein has been extended an additional two years for building and testing an 80kWh module, based on the encouraging developments in the bipolar cell design concept.

Update

The work presented herein was concluded in October, 1979. Preparation, editing and approval of this report has carried into August, 1980. In the meantime, development of the bipolar design has proceeded very well. Cycle testing of the cell components has shown no life-limiting decay mechanisms to date. A cell submodule (nominal 2kWh) of full-size electrodes (1 ft^2) has accrued over 200 continuous cycles in a hands-off, automatic routine with steady efficiencies in the range 53-56%. And initial testing of a full-size, 8kWh submodule has demonstrated energy efficiencies of 65-67%.

Much work remains to bring the submodules to full capacity and design efficiency, and to reduce the battery cost. Nonetheless, the zinc-bromine battery shows increasing promise for meeting the performance and cost goals for utility energy storage.

2. INTRODUCTION

A. BACKGROUND OF THE PROGRAM

Gould Inc. was awarded a one year contract, commencing September 1, 1978, to build and test prototype 8kWh zinc-bromine battery submodules and to perform a cost and design study of an 80kWh module. This followed a 28 month EPRI contract (RP635-1) which established the technical and economic feasibility of the zinc-bromine battery for utility energy storage (Ref.1), in which Gould was able to demonstrate the system's design simplicity, high efficiency, long cycle life and ease of scaleup, all of which are requirements of a battery for the utility application.

At the outset of the program it was believed that the 80kWh module being designed could also serve as the prototype for the BEST facility battery; 100 such modules would provide the required 5-10MWh of installed capacity for that demonstration program. Since then our thinking has changed, because the BEST Facility Batteries Group has recommended (Ref.2) that "mature hardware (e.g. full-scale cells and modules)... of the type and size ultimately anticipated in commercial energy storage installations" should be tested at the BEST facility. The 80kWh module size is not likely to be cost effective for the utility application; economies of scale will probably dictate a much larger module.

Nonetheless, the desirability of building and testing an intermediate-sized advanced battery module (i.e. larger than laboratory scale but smaller than a commercial module) was recognized by the program sponsors, DOE and EPRI. While requiring less investment in development time, hardware and facilities than a commercial-size module, the intermediate-size module will provide a realistic demonstration of the system characteristics, which will become of increasing importance as commercialization draws nearer. Further, intermediate-size modules can be more conveniently installed for field testing at selected sites than

could full scale modules. The capacity range selected, i.e. 80kWh, is a reasonable choice; the resulting module dimensions (4 ft wide x 8 ft long x 5 ft high) allow its construction and movement about standard laboratory facilities without the need for a high bay area or heavy equipment moving capabilities.

In the following section an overview is provided of the module design which has evolved during the program, along with a discussion of the major design considerations.

B. OVERVIEW OF THE 80kWh MODULE DESIGN

The 80kWh, stand-alone module comprises ten identical 8kWh submodules of the bipolar electrode configuration, electrolyte circulation systems (pumps, tanks and plumbing) for both the negative and positive electrolytes, and a bromine storage system.

At the outset of the program a monopolar electrode configuration was employed. However, testing of the two 8kWh monopolar submodules built since then showed that there was no cost effective way to supply current to each electrode individually with acceptably small voltage losses. Consequently we proceeded to develop a bipolar submodule design, which we now favor. In this design a thin carbon plate serves as the bipolar electrode. Zinc deposits on the negative side during charge, and bromine forms on the other.

Electrolyte is flowed along both the positive and negative faces of the electrodes. Microporous separators maintain the positive and negative electrolytes distinct within the cell stack. Flow of electrolyte along the electrodes is required to supply electrode reactants and for enhancing smooth zinc deposition on the negative electrode during charge. These flows are provided by two circulation systems, one common to the negative sides of the submodules, the other

common to their positive sides. The flow loops also contain pumps, storage tanks and additionally a bromine storage system for the positive loop. The only major difference between the two electrolytes is that the bromine concentration on the negative side is approximately one tenth of that on the positive side, to minimize self-discharge.

The bromine formed at the positive electrodes during charge is taken up in a second, liquid, polybromide phase, which is stored externally to the submodules. The polybromide is dispersed into the electrolyte via a static mixing device through which both phases are pumped prior to entry into the submodules.

Each submodule is rated at 40A and 40V on discharge (5 hour rate); the module current and voltage combinations which are thus possible lie in the range 40A, 400V (series connected) - 400A, 40V (parallel-connected), depending on how the submodules are arranged electrically. For this module design, submodule pairs are connected in series, and these pairs are interconnected in parallel to provide 200A at 80V on discharge.

After a brief discussion of the report format we will turn to an in-depth description of the module and its components.

C. REPORT PREVIEW

The report is organized under four headings, i.e. module design (including construction considerations), submodule testing, optimization studies and a cost summary, which is placed last to promote continuity of the other three sections. Appendices provide the details of the cycle test data base, a quantitative procedure for ZONYL®, a theoretical model of the bromine storage system, transference number measurements for zinc bromide, and a theoretical model for ionic transport through microporous separators.

The next section, which presents the module design, begins with a more detailed description of the module followed by individual discussions of the system components.

3. DESIGN OF THE 80kWh STAND-ALONE MODULE

A. INTRODUCTION

The 80kWh module comprises a number of distinct components, which are described in detail below. First, however, an overall description of the module design is presented to acquaint the reader with the terminology and to establish relationships between the components and their functions.

The design which evolved for the 80kWh module (Figure 1) is, in many ways, an adaptation and scaledown of the 400kWh module design developed during the previous EPRI contract (Ref.1). The building block of the module is the 8kWh submodule (or cell stack); ten of these are

FIGURE 1
80 kWh ZINC-BROMINE BATTERY MODULE LAYOUT*
(* PLUMBING OMITTED FOR CLARITY)

connected electrically to one another in a series-parallel arrangement (five parallel strings each having two submodules in series) to provide 80kWh of capacity and 16kW of power at the five hour rate (200A at 80V). Since the submodules require electrolyte circulation on both their negative and positive sides, two plumbing circuits are provided; the submodules are connected hydraulically within each loop, once again in a series-parallel fashion. That is, there are five parallel branches each having two submodules in series, to match the flowrate-head characteristics of the circulation pumps.

The negative side flow loop (Figure 2) contains, in addition to the submodules, an electrolyte storage tank (and within it an immersed coil heat exchanger) and a circulation pump. The positive electrolyte is

FIGURE 2
ZINC-BROMINE BATTERY FLOW SYSTEM

pumped concurrently with the liquid polybromide through a static mixing device, which disperses the polybromide as fine droplets in the electrolyte. This mixture then flows to the submodules and then, via two outlets from the submodule, to the settling tanks. Two outlets are provided from the submodules to rid them of trapped air, which exits at

the top, and the polybromide which, being the denser liquid phase, exits at the bottom. In the settling tank the polybromide returns via gravity to its sump from which it is recirculated to the static mixer via the polybromide pump. The electrolyte, freed of most of the polybromide, is itself pumped through the static mixer once again via the positive electrolyte pump.

All three flow circuits (positive, negative, polybromide) are in operation during both charge and discharge at preset flowrates. There are no system differences, in fact, between charge and discharge, and switching from one mode to another can be done simply and instantaneously. The only moving parts are the three pump impellers. On open circuit stand, the pumps can be shut off to save energy. Auxiliary systems external to the module, namely the power conditioning and cooling systems, were not considered in the module design and will not be discussed herein.

This completes the overview of the module design. The following sections provide the design details of the module's component parts.

B. THE SUBMODULE

The submodule, or cell stack, (Figure 3) is the building block of the module and the most important component. Its nominal capacity (8kWh) is based on a design ampere-hour capacity of 200Ah and an average discharge voltage of 40V. The specific electrode capacity is 2000Ah/m² by design and the average cell voltage is 1.6V.

The submodule comprises a filter-press stack of 26 bipolar carbon electrodes, each a square of 0.09m² (~ 1ft²) area, mounted in a polypropylene electrode frame. The frame, in addition to holding the electrode in position and sealing its edges from leaking currents, also provides the important function of directing electrolyte flow to and from the electrode surfaces.

ZINC-BROMINE CELL STACK COMPONENTS

FIGURE 3

Between each pair of electrodes there is a microporous separator, DARAMIC®, to limit the rate of self-discharge. Since the separator is non-rigid, polypropylene spacing ribs are provided on each side to hold it off the electrode surfaces. The two end plates provide the multiple functions of compressing the cell tightly to prevent leakage, serving as plumbing connections for electrolyte flow and collecting the electrical current from the two end electrodes. The end plates are made of polypropylene as well.

The individual components of the cell stack will be discussed next in more detail, including their design criteria, materials of construction and manufacture. The reader should refer to Figure 3 for a pictorial representation of the components and their relationships to one another.

1. The Bipolar Electrode

The bipolar electrode is a dense carbon sheet. The criteria used in selection of this material are as follows:

- It must be thin (1mm) to insure that the submodule energy density is high enough so that the battery footprint requirement of 8kWh/ft^2 can be met.
- It must be non-porous (0.01% open porosity) to prevent appreciable self-discharge of the electrode via leakage current.
- It must be electrochemically and physically stable for the bromine electrode reaction on one side and the zinc electrode reaction on the other.
- It must be electrocatalytic for the bromine electrode reaction. A linear polarization constant (b) of $1\Omega\text{-cm}^2$ or less (electrode polarization = b times the current density) is desired for both charge and discharge.

- It must be sufficiently strong to resist cracking by the slight torsional stresses applied by cell stack clamping.
- It must be inexpensive (\$5/ft²).

Titanium is suitable in all categories but that of electrochemical stability; the negative side of the electrode becomes irreversibly oxidized at end of discharge when cell reversal occurs. That is, since the cell is negative limited by design (to remove all the zinc), when all the zinc is discharged the next consecutive oxidation reaction occurs. For a carbon electrode that reaction is bromide oxidation, which is acceptable, but for untreated titanium the substrate itself is oxidized, causing pitting and eventual electrode failure. A protective catalytic coating such as ruthenium dioxide prevents this at the beginning of cycle life, but we have found that this coating is eroded away by repetitive zinc deposition.

The carbon electrode material selected for use has demonstrated all of the required properties. Additionally, it is easily bonded into its frame (to prevent electrolyte and current leakage around the edges) by sand-blasting the surface to roughen it, then cleaning it to remove the resulting carbon dust. The electrode is then placed in the frame and a jet of hot air is applied to the carbon, melting those surfaces of the frame in contact with the electrode. Upon cooling, the polypropylene adheres strongly to the carbon, forming a continuous, leak-free seal.

2. The Electrode Frame

The polypropylene electrode frame serves to hold and locate the electrode, carry the flowing electrolyte to and from the electrode, distribute the flow across the electrode and isolate the positive and negative electrolytes from each other and the external environment. On the negative side, flow enters the bottom and exits the top via long narrow channels at either end that resist shunt currents. Notches are placed on either side to positively locate the spacer grid. Tapered

recesses are located around the perimeter of the frame at five points. These properly position the frames during cell stack assembly.

On the positive side the flow enters from the left and right, flowing across the face of the electrode. Electrolyte and trapped air exit out the top and polybromide-laden electrolyte exits the bottom. Each of these four ports utilizes a tortuous path to reduce shunt currents (see Section 5 for the design details of these).

Injection molding of the electrode frame is required to produce the quality required, and to simplify implementation of the design features described above. Injection molding also provides the higher volume part fabrication capability which will be required for module construction. The prototype tooling can be modified as required through the use of mold inserts.

3. Spacing Grids

Plastic grids are placed on either side of the electrode to space the separator away from the electrode surfaces. These grids consist of parallel vertical ribs joined by crossribs and are injection molded of polypropylene. The tapered edge of the negative grid (Figure 4) contacts the negative face of the electrode and is designed to maximize the active electrode area and to minimize dendrite formation along the rib. The positive grid is similar, but the ribs are notched to allow both horizontal electrolyte flow and to increase the open area of the separator. The rib spacing is chosen to provide as much open area for ionic current flow as possible while preventing excessive bowing of the separator in the flow channels between ribs.

4. Separator

The microporous separator, DARAMIC®, is located between electrodes to limit the transport rate of bromine from the positive side to the negative side, and thus limit self discharge. It is obtained as a continuously extruded sheet 0.030" thick from W.R. Grace & Co. This

FIGURE 4
SPACER GRID CONFIGURATION

sheet material is punched on a steel rule die to provide the required openings for electrolyte flow and then cleaned in acetone to remove residual hydrocarbon oils added during manufacture. The separators are then soaked in distilled water prior to cell assembly to prevent them from shrinking on drying.

5. End Plate Assembly

Two end plate assemblies, one on each end of the stack, are provided to firmly clamp down the stack components. These have connections for electrolyte flow and electrical current to the stack. The assembly comprises a molded plastic block and a carbon plate to serve

as the end electrode. This plate is much thicker than the interior electrodes (0.375" vs 0.035") to provide for uniform current conduction from a center tap to the entire electrode face. The center tap consists of a titanium-clad copper rod which is mechanically fastened to the carbon plate; this exits the plastic block through a round hole having an O-ring seal to prevent electrolyte leakage.

The electrolyte plumbing connections to the plastic end block are via standard tapered pipe threads. A hole pattern around the block periphery provides for clamping down the cell stack with through-bolts. These run from one end plate to another outside the frames of the electrode stack; they thus can be made from carbon steel rather than titanium for cost saving, since they are not in contact with the electrolyte.

This completes the description of the mechanical components of the submodule. The following headings discuss the other components and systems which, along with the submodules, comprise the 80kWh module.

C. ELECTROLYTE

The electrolyte solution comprises the active species zinc and bromide, potassium chloride supporting electrolyte, and water, the solvent.

The electrolyte composition and quantity are designed to provide adequate quantities of species for the electrode reactions and to minimize the internal resistance of the battery. The design specifications are as follows:

COMPOSITION

2M zinc bromide

1M zinc chloride

3M potassium chloride.

VOLUME

400ℓ each on the positive and negative sides.

These specifications were derived from theoretical modeling and experimentation, which are discussed fully in Appendix A. Briefly, the zinc chloride is an inexpensive source of excess zinc ions for the negative electrode, and potassium chloride is added to reduce the electrolyte resistance. Since the electrolyte is circulated through the submodules, the total electrolyte volume can be much larger (here five times) than that contained within the submodules. The design electrolyte volumes are optimized to obtain as high an electrolyte utilization as possible to minimize its cost, without allowing the concentration of either zinc or bromide ions to drop below 0.5M at end of charge.

An additional specification on the electrolyte is a pH of 2-4 for acceptable zinc morphology (Ref.1). The pH must be artificially controlled via an auxiliary subsystem, which is addressed later on in this section.

D. BROMINE STORAGE

Bromine is generated at the positive electrodes during the charge half cycle and consumed during discharge. Without bromine complexation, the bromine concentration on the positive side at the end of charge would be so high (several molar) that excessive self-discharge would result, and near the end of discharge its concentration would be so low that the positive electrodes would polarize excessively.

Control of the bromine concentration in the positive electrolyte is accomplished by complexing the bromine in a second, liquid, polybromide phase using selected quaternary ammonium salts. This polybromide phase is stored externally to the cell stack and is intimately mixed with the electrolyte to exchange bromine. Control of the aqueous phase bromine concentration within an acceptable range is thus achieved.

A static mixer (Figure 5) is used to mix the electrolyte and polybromide phases. The static mixer was chosen over other designs e.g. spray towers and stirred tank mixers, because of its compactness,

FIGURE 5

STATIC MIXER (COURTESY KOCH ENGINEERING)

simplicity of design, efficiency of mixing and ease of control. It disperses the polybromide phase (refer again to Figure 2) in the electrolyte as droplets of very nearly uniform size by subjecting the two phases, which are pumped cocurrently through it, to frequent and rapid

changes of direction. The electrolyte-dispersed polybromide mixture is then pumped into the submodules, where bromine transport between phases occurs.

Most of the polybromide phase flows out of the submodules with the electrolyte to the settling tank, where the heavier polybromide falls to the bottom and then to the polybromide sump, the lowest point in the system. The polybromide which settles out of the electrolyte within the submodules drains to the settling tank via the bottom outlets on the positive side. Polybromide flow to the mixer is provided by the polybromide pump, which takes a suction on the sump.

E. PLUMBING AND PUMPS

Electrolyte and polybromide circulation between the storage tanks and the submodules are via schedule 80 polypropylene pipe and magnetically coupled, centrifugal pumps of polypropylene construction. Most plumbing connections are accomplished with socket welding, except for flange or union connections for the pumps, tanks and submodules to simplify installation and removal. While polypropylene pipe has yet to be qualified for this form of bromine service, no failures or deteriorations have been observed in the pumps or plumbing since they were first introduced eighteen months ago. Two-inch main headers and one-inch branch feeders were selected because pressure drop calculations showed that no more than 1-2% of the module energy efficiency will be consumed by pumping the electrolyte through these.

There are five pairs of submodules, one submodule physically located above the other in each pair. The electrolyte flow is in series through each submodule pair, resulting in five parallel flow paths.

The design total flowrate on both the negative and positive sides is 25gpm; this was determined previously (Ref.1).

F. SUPPORT STRUCTURE

A steel structure supports the module components above a 4' x 8' polypropylene industrial pallet. The structure consists of steel channel uprights and horizontal beams that carry the load with steel channel crossmembers for lateral stability. This structure is joined with the polypropylene pallets at dual parallel zee bars. These act to solidify the assembly into a single unit and give it the required strength and stability. These zee bars also act as attachment points should the module have to be hoist-lifted. The structure, after being welded into a single unit, is cleaned, primed and then painted with an epoxy-based paint to protect the structure against corrosion from electrolyte leakage.

G. pH CONTROL SYSTEM

The electrolyte pH range, by design, is 2-4. This range was selected for the following reasons:

- (1) at lower pH values, i.e. a higher hydrogen ion concentration, can cause excessive hydrogen gassing at the negative electrode can result, and
- (2) at higher pH values the zinc morphology becomes mossy and less dense, rather than compact and crystalline as desired. Also, there is a possibility that zinc hydroxide will precipitate and plug the flow channels.

Since hydrogen formation proceeds at an appreciable rate (but less than 0.01% of the applied current density) at the negative electrode even at pH values higher than 2, the electrolyte pH rises with time, and an artificial means of pH control must be employed. This is accomplished using a proprietary subsystem which is physically much smaller than the other module components. Since its cost is also a minor component of the total system cost, no further mention of this unit will be made in this report.

This completes the description of the module. We will now discuss the testing of submodules which has been performed to date.

4. TESTING

The overall goal of battery testing is to demonstrate battery performance which meets or exceeds the requirements for a utility energy storage battery. The specific performance targets are as follows:

- energy efficiency > 70%
- cycle life > 2500 deep discharge cycles
- "hands-off" cyclability

To meet that objective, a testing program was established which comprises two parts. One involves cycle and performance testing of small (3Wh) laboratory cells to determine the inherent efficiency and lifetime qualities of the zinc-bromine couple. The other involves evaluational testing of submodules built during the program, to verify and optimize design concepts.

Cycle testing of 3Wh cells has demonstrated both high efficiencies (approaching 70%) and long cycle lives (1000) of the basic electro-chemical cell. Submodule testing provided us the data we needed to decide in favor of the bipolar design, over the monopolar, and it has also demonstrated the hands-off cyclability of the system on a practical scale. Both phases of the testing program will be discussed individually below.

A. CYCLE TESTING

The cycle testing of 3.2Wh cells will be discussed in three sections, Purpose and Protocol, Database Description, and Experimental Results.

1. Purpose and Protocol

The purpose of the long term cycle testing is to demonstrate the cycle life of cells employing alternative electrode substrates and electrolyte preparations in a rigidly controlled and closely scrutinized experiment. The goal of this testing is to reach 2500 charge/discharge cycles without failure.

The test units are 3.2Wh cell systems (Figure 6). Small cells are suitable for these tests, because durability is considered to be an intensive property of the materials. Cycle testing full scale hardware, which will be eventually done anyway, would confound the results unnecessarily at this stage with scale-up problems. All testing is performed at room temperature; a positive electrolyte flowrate of 0.50 ml/sec and a negative electrolyte flowrate of 2.00 ml/sec are specified, as these are scaled down values of the design flowrates for the

FIGURE 6

3.2 Wh CELL FOR CYCLE TESTING

submodule. Electrolyte volumes are 0.5-1l on each side, which is in excess of that required by the cells. This is for operational convenience; bromine storage is via dissolution in the excess electrolyte volume on the positive side to remove the complication of providing for

the polybromide phase in these small test systems. Each cell is charged at a current of 0.4A (corresponding to $50\text{mA}/\text{cm}^2$ on the 8cm^2 electrodes) for 3.5 hours, and then discharged through a 2Ω resistor until zero voltage is reached. Four hours are allowed for discharge.

During the testing the following are permissible routine maintenance steps:

- Monitor and adjust the...
 - electrolyte pH through the addition of HBr.
 - concentration of any additive.
 - electrolyte volume to replace losses due to leakage.
 - electrolyte bromine concentration.
- Replace faulty equipment external to the cell such as tubing, pumps, reservoir or cycler as required.
- Disassemble and inspect each cell after every 500 cycles to check for wear or deterioration of the internal components.

The following discussion describes the steps taken to determine cell failure. Following the first 50 cycles, 5 consecutive cycles are checked and averaged to determine the baseline efficiencies for each cell. (The voltage and current efficiencies are measured by graphical integration of the voltage and current recordings, respectively. The energy efficiency is calculated as the product of these.) This is done to remove the effects of any initial operational fluctuations. Subsequent failure is then determined as follows:

Disassemble the cell after charge if:

- Shorting occurs in 5 consecutive cycles, or
- Voltage efficiency averaged over 5 consecutive cycles is less than 95% of the established baseline, or
- Coulombic efficiency averaged over 5 consecutive cycles is less than 95% of the established baseline.

The disassembled cell is inspected for electrode deterioration or errors in construction. Construction errors are corrected and the test continued; electrode failure terminates the test. The cycle number and failure conditions are then noted. If the test is to continue,

- Reassemble and discharge the cell.
- Disassemble and inspect the cell again; terminate the test if electrode damage exists. If the electrodes are intact, reassemble the cell using the same electrodes and electrolyte but a different cell housing and resume cycling.

The cell numbering system used to identify a particular cell under test consists of two digits, the first representing the cell housing and the second the trial number. The materials and conditions under test generally varied from one trial to the next for the same cell.

2. Database Description

With a goal of 2500 cycles it was obvious that numerous data would be generated during the course of the long term cycle testing program. A computer database was created for efficient storage and retrieval of these data. This database, which is on the NCSS NOMAD database management system, contains the life history of all the cycle test cells that have been in operation as well as a description of each cell. By use of various list commands all the data accumulated can be extracted, screened and compiled in an easy-to-read format. Appendix B contains the schema description for the database.

3. Experimental Results

The cycle testing program commenced in September of 1978. Cells 51 and 61 were the first ones placed under test, as these represented the baseline materials and conditions (titanium electrodes, potassium chloride-supported electrolyte) for the monopolar cell design which was favored at that time. Cell 61 had a negative electrode pre-anodization

in sodium bicarbonate because preliminary experiments indicated that it would protect the substrate from excessive wear, but otherwise the two cells were identical. Continuous cycling since then (Figures 7A, B) has revealed no degradation in electrochemical performance.

The other cells were placed under test one by one when different materials, pre-treatments, or electrolytes which could beneficially impact lifetime or performance were identified in screening tests. These were then compared against the baseline cells, 51 and 61.

The first such cell was number 41. Corrosion studies (see Section 5) had shown that addition of potassium methyl sulfonate to the electrolyte provided protection of the titanium negative electrode on cell reversal, so it was evaluated in cycle testing for its effect on cycle life. After less than a month of testing it was voluntarily terminated because the additive concentration was not correct. Cell 42 was started in its place with new but otherwise identical materials and the proper (~3M additive concentration. Its performance (Figure 7C) is very similar to that of the baseline cells.

When activity began on the bipolar design, the durability of carbon as a zinc deposition substrate came into question. Cell 31 was fitted with a negative electrode made of a thin carbon sheet (not the presently preferred material) available in the laboratory; otherwise it was identical to the baseline cells. After several months of testing the carbon cracked when the current collection screw was tightened down, and it was replaced with the preferred carbon electrode material, backed up by titanium foil to prevent a similar occurrence of cracking. The cell was re-numbered 32 and placed on continuous cycle testing. Once again its performance to date has been similar to that of the baseline cells.

Cell 21 was assembled with a titanium negative which had been coated with titanium carbide, a material which showed resistance to corrosion on cell reversal. After 100 cycles of erratic performance it was shut down and taken apart. Inspection showed that the coating had been completely eroded away, so the test was terminated. In its place,

FIGURE 7A
CYCLE TEST CELL DATA - CELL 51

Positive Electrode: Porous Titanium
Negative Electrode: Planar Titanium
Electrolyte: 2m ZnBr_2 /4m KCl

Average Energy Efficiency: 65.6%
Regression Coefficient: 0.000921
Std. Error of Reg. Coeff.: 0.00259

FIGURE 7B
CYCLE TEST CELL DATA - CELL 61

Positive Electrode: Porous Titanium
Negative Electrode: Planar Titanium
Electrolyte: 2m ZnBr_2 /4m KCl

Average Energy Efficiency: 68.5
Regression Coefficient: 0.000160
Std. Error of Reg. Coeff.: 0.00305

FIGURE 7C
CYCLE TEST CELL DATA - CELL 42

Positive Electrode: Porous Titanium
Negative Electrode: Planar Titanium
Electrolyte: 2m ZnBr_2 /4m KCl/2.7m KCH_3SO_3

Average Energy Efficiency: 65.0%
Regression Coefficient: -0.0159
Std. Error of Reg. Coeff.: 0.0173

cell 22 was started with titanium electrodes identical to those of the baseline cell, but with an electrolyte formulation which included both sodium perchlorate and sodium chloride as supporting electrolytes. This formulation was chosen also as a result of its ability to prevent titanium corrosion on cell reversal. Its performance is also similar to that of the baseline cells.

Cell 11 had a design modification to allow the use of polybromide to store the bromine on charge, as a durability test for the polybromide itself. Several operational difficulties were encountered, however, which precluded continuous cycling. Its replacement, cell 12, had the baseline cell components but yet another electrolyte formulation for titanium corrosion protection, which involved the use of zinc and sodium chloride as supporting electrolytes. However, after less than 100 cycles, the cell began to short out cycle after cycle. Disassembly and inspection revealed no design or construction flaws with the cell which would cause this. Upon re-assembly the shorting problem persisted, so the test was terminated. That particular electrolyte formulation was assessed to be conducive to dendrite shorting, and was thus eliminated from further consideration.

Cell 13 was next placed in operation as a durability test for ZONYL®, the fluorosurfactant which was found to be effective as a zinc dendrite inhibitor. Operating with baseline materials except a ZONYL® concentration of 50-100ppm, this cell exhibited excessive polarization and thus low voltaic efficiencies. The additive, in addition to causing the unacceptably poor efficiencies, required frequent (weekly) additions to maintain its concentration in the proper range. These two difficulties militate against its use in zinc-bromine batteries.

Cycle testing of these cells will continue. Additional cells are being started to expand the scope of the test program to the cell components of the bipolar design. Under the next heading attention will be directed to the testing of submodules.

B. SUBMODULE TESTING

Testing of 8kWh submodules has directed us in design optimization, and it has demonstrated the cyclability of the 8kWh submodule. Two monopolar and one bipolar submodules were built and tested during the past year. Since the emphasis was only recently shifted to the bipolar design, the vast majority of meaningful test data is for the monopolar submodules. The following describes the test fixtures and procedures, followed by a discussion of results to date.

1. Test Fixture Description

a). Flow system for 8kWh submodule testing. (See Fig. 8).

The submodule is connected to two flow loops that transport and store the electrolyte and bromine. The negative side consists of a pump, a polypropylene tank for electrolyte storage and the necessary polypropylene plumbing to connect these together and to the submodule.

FIGURE 8
FLOW SYSTEM FOR SUBMODULE TESTING

On the positive side, in addition to the electrolyte pump, there are a pump and a static mixer that mix the polybromide phase with the positive electrolyte as they enter the submodule. Bromine transfer between phases occurs there. After passing through the submodule, the flow is to a settler located downstream, where the more dense polybromide phase is removed from the electrolyte. The settler is a section of polypropylene pipe with caps welded to each end and a fiber mesh core on the interior which helps to collect the polybromide droplets and settle them to the bottom of the tank from where they drain to the sump. The supernatant electrolyte leaving the settler returns to the mixer via the positive electrolyte pump. The polybromide phase drains by gravity into the sump, which is the lowest point in the system. The polybromide is pumped via a third pump to a junction with the positive electrolyte system just upstream of the mixer.

All of the plumbing on both electrolyte flow loops is polypropylene. Molded elbows, tees, valves, unions and couples are socket welded to the pipe.

The 8kWh submodule test fixture is a totally self-contained unit except for the electrical connections for charging and discharging the battery and powering the pumps. This unit is not readily transportable, however, as it is not free-standing; it is in a chemical fume hood for testing.

2. Test Program

Testing of the submodules has proceeded under three categories, operability, leakage and performance.

a. Operability Testing

This is the first level of testing. It is basically a pass/fail evaluation, the results of which determine whether to proceed with further testing of the component or system or to replace it.

At this stage, the items are tested for functionality prior to assembly. Items such as pumps, valves, flowmeters, contacting devices and auxiliaries are tested to eliminate defective components. The results of these tests are recorded on a checklist and are of a pass/fail nature.

b. Leakage Testing

Measurements of fluid leakage are an important part of the quality assurance evaluation. The nature and extent of leakage influences component design and materials selection, and provides a measure of the quality control in parts fabrication. To an extent, leakage checks determine operability. If a plumbing fitting leaks at all, it is replaced immediately. On the other hand, submodule leakage is often tolerated if the rate is sufficiently small or if extensive teardown and reassembly are required to eliminate the leak. Leakage test results are taken into account in design modifications for subsequent hardware construction.

Items that are to be leak tested are listed below, together with a short description of the appropriate test.

Flow System: Leaks are detected by circulating water through the system; a part passes or fails the test depending on the absence or presence of visually detectable leaks.

Items to be checked:

- socket welded pipe fittings
- threaded pipe fittings
- pump housings

Submodule: The submodule integrity is checked prior to its installation in the system by means of a static test at eight feet of head, using water as a test fluid.

The following items are visually checked for external leakage:

- plumbing connections
- electrode tab seals (monopolar)
- frame to separator seals
- through-bolt holes

The internal seals between the negative and positive electrolyte compartments are checked by measuring the cross-over flowrate from the negative to positive side under a head differential of eight feet of water. The crossover rate is then compared to permeation data for the separator material; if it is excessive (i.e., five times the permeation rate), the cell is disassembled for inspection and repaired as necessary.

c. Preliminary Performance Testing

(1) Measurement of the degree to which the components achieve their design goals is performed on the following items:

Submodule

Electrical Integrity (monopolar)

- Measure electrical resistance from tab-to-tab on each electrode. (Each electrode has one tab on either side).
- Measure tab-to-bus resistance for each tab on each electrode. (A positive and negative bus exist on each side of the cell).
- Measure electrical resistance between positive and negative bus to detect the presence of a short.

These tests are performed by means of four-terminal resistance measurements on the cell prior to installation of the electrolyte. The measure of performance is the voltage drop at rated current.

Hydraulic Performance:

Measure flowrate/pressure drop characteristics of both the positive and the negative sides.

Flow System:

Measure the head as a function of flowrate. Check for pump cavitation.

Bromine Storage System:

Measure the polybromide carryover rate from the settler at various flowrates. This test involves sample collection of the aqueous phase on the downstream side of the settler during the first charge/discharge cycles of the integrated system.

(2) Test Hardware

Cycling is primarily done by means of time-controlled cyclers. Specialized tests are run by manually operated switchboxes and power supplies.

For data acquisition, the chief parameters of interest are cell voltage and current, cell temperature, electrolyte flow, pH and bromine concentration (anolyte and catholyte). All but cell voltage and current data are presently gathered manually and typically only 2-3 times per cycle.

Acquisition of voltage and current data is accomplished by a Fluke 2240B datalogger. Data scans are activated internally in the datalogger by a timer, by exceeding an alarm limit, by a sudden change of a cell parameter, or by remote request via the serial interface. Manual requests for data are also possible by means of front panel controls. Logged data are stored on magnetic tape by a Techtran 817 data cassette

recorder, for later transfer to an HP9835 desktop computer for data reduction and storage on a floppy disk. Upon accumulation of a reasonable amount of data (generally weekly) a printout and/or plot is generated for data analysis. The reduced data are then placed into files within the NCSS timesharing system where they are easily accessible, not only by Gould personnel but also by DOE/EPRI Project Managers.

(3) Results to Date

(a) 8kWh Monopolar Submodule Testing:

Testing the monopolar submodules showed that, while the efficiency of that design is below specification, the submodules can be routinely cycled in a hands-off, round-the-clock manner. The results of testing the three submodules built to date are presented below.

Submodules #1 and #2 are of the monopolar configuration. Submodule #2 was originally built and tested in March of 1979. Since then, the submodule was taken apart because of excessive external and internal leakage. It has been rebuilt using modified negative frames and new separators.

After assembly of the two submodules, they were separately checked for external leakage and internal crossover rates. Neither submodule exhibited external leakage. Internal crossover rates of the submodules were as follows:

	<u>Crossover rate (ml/h/cm head/cm² area)</u>
Submodule #1	0.87×10^{-3}
Submodule #2	0.96×10^{-3}

For submodule #2, this was a major improvement over the first time it was built (the rate then was 13.7×10^{-3}). For both submodules there was an ~40% lower crossover rate than with the 320Wh cells of the 1.28kWh battery (1.51×10^{-3} ml/h/cm head/cm² area, Ref. 1), which is being used as the standard for separator permeability.

Another pre-cycling test performed on the monopolar submodules was the measurement of the electrode tab to tab potential drops (Table 1). A major difference between submodules #1 and #2 is in the welding of the tabs on the positive electrodes. Submodule #2 had the tabs spot-welded onto the exmet grid on which the porous titanium matrix is supported. For submodule #1, the tabs were TIG welded onto the exmet grid with the weld bead actually fusing into the porous titanium. TIG welding of the tabs decreased the potential drop by ~25%. The negative electrodes of #1 also showed an ~8% decrease in potential drop as compared to submodule #2 for no apparent reason.

Initial electrochemical cycling was performed at $20\text{mA}/\text{cm}^2$ to a loading of $80\text{mAh}/\text{cm}^2$. The average efficiencies of both submodules compare as follows:

	<u>SUBMODULE EFFICIENCY</u>		<u>DESIGN EFFICIENCY</u>
	<u>#1</u>	<u>#2</u>	
VOLTAIC	41%±2	42%±2	85%
COULOMBIC	81%±3	78%±4	85%
ENERGY	35%±2	36%±2	72%

TABLE 1

ELECTRODE TAB-TO-TAB POTENTIAL DROPS(mV), MONOPOLAR SUBMODULES

	Submodule #1		Submodule #2	
	<u>Positives</u>	<u>Negatives</u>	<u>Positives</u>	<u>Negatives</u>
Mean	239	121	317	132
Standard Deviation	43	7	26	9
Minimum/Maximum	183/293	112/139	281/378	110/146

The coulombic efficiencies were below the design value by 4-7%, but this can be remedied by incremental design improvements. The voltaic efficiencies, however, were 43-44% below the design value and this led to the eventual shift in emphasis to the bipolar design.

There were two sources of excessive voltage loss in the submodule. The electrode tab which carries the current from the bus bars to the electrodes was the predominant one, and the other was the positive electrode itself, whose measured conductivity lay well below its design value. These losses were anticipated during the design of the submodules; the design called for the use of a titanium-clad copper composite material for the tabs, which would provide adequate conductivity. Titanium alone was not satisfactory because of its relatively poor conductivity, which is 20-25 times less than that of copper. However, both submodules were built with solid titanium tabs because the composite material of the proper thickness and geometry was not readily available. In fact, while working with the various suppliers of such composite material, we learned that its fabrication in this geometry would be very difficult and expensive, so much so that the cost target for the submodule could not be met.

Similarly, for the positive electrode we sought a conductive screen to support the porous titanium structure. Here we explored the feasibility of coating a copper screen with titanium via various techniques such as powder-pack and chemical vapor deposition. Test specimens prepared for us by various suppliers all quickly failed in bromine exposure tests; the titanium coating could not provide adequate protection for the chemically reactive copper core beneath it. As with the titanium tabs, we assembled the submodules using a titanium screen to support the positive electrode structure, and excessively large voltaic losses resulted.

It was the lack of suitably conductive materials for the electrodes and tabs which made the monopolar design impractical in full size hardware. At the outset of the program we had identified several promising approaches to solving the conductivity problem, but all of them

proved impractical. At this point, the decision was made to pursue the bipolar design which, although it has its own distinct problems, has the advantage of not requiring current collection from each electrode.

Despite the poor voltaic performance of the monopolar submodules, they were placed on continuous cycle testing to evaluate their behavior in hands-off, automatic cycling. Submodule #1 was shut down after fifty cycles because of electrolyte leakage in the flow system which could not be easily accessed for repair. Submodule #2, however, continued to cycle on a hands-off, round the clock basis. Over 160 cycles were obtained in this fashion. Operator attention consisted mainly of periodic sampling the electrolyte to monitor the pH and bromine concentration.

The cycling was performed with a self-contained, automatic battery cycler. Data acquisition encompassed continuous monitoring and recording of voltage and current via a Fluke Datalogger, which wrote on a Techtran digital recorder. Periodically, and off line, the raw data were played back to a Hewlett Packard desktop computer which calculated capacities and efficiencies.

The efficiency of the submodule decreased with time. Based on the observed increase in bromine concentration in the negative electrolyte, it was apparent that an internal leak developed in the submodule. However, the system as a whole operated as designed for five months after the beginning of the test.

(b) 8kWh Bipolar Submodule Testing:

Because of the small amount of time available for testing the bipolar submodule, the testing performed was limited to electrolyte leakage and electrode integrity checks. The first time the submodule was assembled it had considerable leakage of electrolyte both externally and

internally from one side to the other, so electrochemical testing was precluded. Upon disassembly and inspection we observed numerous causes for the leakage and several electrodes were cracked. These pointed out deficiencies in the stack design as well as some critical errors in the plastic electrode frame configuration arising from incorrectly cut injection mold tooling.

The testing performed did, however, serve an important purpose. A complete re-design of the electrode frame was prepared which eliminated the problems encountered with the original design. Because the time span from tool re-design to receipt of injection-molded parts was several months, assembly of the first as-modified bipolar submodule lay beyond the scope of the present report.

In summary, submodule testing made a major impact on the development program; the information we gained from it allowed us to re-direct the effort toward the bipolar configuration because of the insurmountable problems encountered with the monopolar design. It has been an excellent example of the need to introduce hardware engineering early on in a development program, so that practical constraints can be placed on the choice of materials and designs and thus effectively focus the development effort.

The following section discusses those studies which have supported the design and construction programs discussed above.

5. SUPPORT STUDIES

The battery design and testing programs have required a substantial amount of theoretical analysis and laboratory experimentation, which we group under the topic of support studies. These include studies on zinc deposition, the bromine storage system, thermal management, electrode corrosion, and electrode, frame and electrolyte design. Each study is discussed individually below.

A. ZINC DEPOSITION STUDIES

The growth of dendrites on the negative electrode during battery charging places a practical limit on the amp-hour capacity of the zinc-bromine battery. If these dendrites grow long enough to penetrate the separator and touch the positive electrode, internal shorting occurs and continued charging is at a reduced current efficiency. Limiting the capacity to prevent dendrite shorting places a lower limit on the per-kWh cost of the battery. That is, the battery cost, in \$/kWh, is inversely proportional to its capacity. Because of the importance of keeping the battery cost down, the studies of zinc deposition have received major emphasis.

The goal of these studies is to define the proper conditions to achieve dendrite-free zinc deposition at charge capacities of 200-300 mAh/cm². The lower limit is based on cost considerations, while the upper limit is what would be achievable at the design current density (40 mA/cm²) over a seven to eight hour charge period.

In the past year there has been a considerable addition to our knowledge of the factors affecting zinc deposition. Experiments have shown that the pretreatment of the titanium substrate has a strong influence on the zinc deposit quality. For example, electrodes initially etched in hydrochloric acid showed poor or inconsistent deposit qualities, while those etched initially in sulfuric acid showed

reproducibly good deposit qualities. In addition electrodes left idle for a period of 2-3 weeks yielded deposits of consistently poorer quality.

Perhaps more important is the finding that a small addition of DuPont's ZONYL® fluorosurfactant allows reproducibly flat, non-dendritic zinc deposition at loadings as high as 300 mAh/cm^2 . In fact, these deposits have been of the highest consistent quality ever obtained. However, ZONYL® results in unacceptable cell polarization and requires frequent makeup to maintain its concentration in the proper range, thus militating against its use in the zinc-bromine battery.

The zinc deposition studies are carried out on four 3.2Wh cells which share the same electrolyte reservoir and flow system (Fig. 9). Statistically designed factorial experiments are performed on a daily basis, to assess the effects of various treatments on deposit quality. Such quality is determined by disassembling the cells after charge, inspecting the deposit, and assigning a number from 1 to 10 according to the following guidelines:

FIGURE 9
FLOW SYSTEM FOR ZINC DEPOSITION STUDIES

Rating deposit quality (based on an 8cm^2 electrode area).

- 10 Flat, smooth
- 9 Flat, rough
- 8 Slight flow lines
- 7 Medium flow lines
- 6 Sharp flow lines/nodular
- 5 One dendrite
- 4 Two-five dendrites
- 3 Six-ten dendrites
- 2 Eleven-twenty dendrites
- 1 Twenty dendrites

Thus quantified, the results are amenable to statistical analysis.

A detailed account of the experiments conducted in the past year is given below.

1. Substrate Pretreatment

A 2^3 factorial experimental design was used to determine the significant factors in substrate pretreatment which would affect zinc deposit as follows:

Factors:

A) Etching process

- + 50% HCl (60°C , 15 min)
- 50% H_2SO_4 (80°C , 60 sec)

B) Cleaning process at end of charge

- +50% HCl (23°C until deposit removed)
- $\text{ZnBr}_2(2\text{M})/\text{Br}_2(2\text{M})$ (23°C , until deposit removed)

C) + Deposits at $300\text{mAh}/\text{cm}^2$

- No deposition

Experimental Design:

Electrode No.*	FACTORS		
	A	B	C
41	-	+	+
42	+	+	+
43	-	-	+
44	+	-	+
45	-	+	-
46	+	+	-
47	-	-	-
48	+	-	-

*Note: The electrode numbers run sequentially from experiments conducted in previous programs.

The procedure consisted of plating zinc on electrodes 41-44 on a daily basis to a loading of 300 mAh/cm². The cells were then taken apart, and the deposits were examined for quality. Electrodes 45-48 did not undergo deposition but they were subjected to the zinc removal treatments just as electrodes 41-44. To allow assessment of their performance in zinc deposition, two successive depositions were performed on electrodes 45-48 during runs 19 and 20. Thus one could determine whether trends in zinc deposit quality were due to repeated depositions, repeated cleaning treatments, or both. The results are presented graphically in Figures 10A-D.

Generally both sets of electrodes (42,46) and (44,48) originally etched in hydrochloric acid showed poor or inconsistent performance, but electrodes etched in sulfuric acid showed reproducibly good zinc deposit quality. Also, the electrodes used in the studies on a daily basis showed deposits of better quality than electrodes which had been left idle for relatively long periods of time (2-3 weeks).

The explanation for the latter observation may involve the phenomenon of surface oxide film formation on titanium. The composition of the film will depend on the immersion history of the electrode. The surface film present on an electrode cycled regularly is perhaps more conducive to good deposition than one which is left idle in the same

ZINC DEPOSITION STUDIES – SUBSTRATE PRETREATMENT

FIGURE 10A

ELECTRODES ETCHED IN
SULFURIC ACID; CLEANED IN
HYDROCHLORIC ACID

Electrodes (41, 45)

Runs 19, 20 and 34, 35 performed on electrode 45;
all other runs performed on electrode 41

FIGURE 10B

ELECTRODES ETCHED IN
HYDROCHLORIC ACID; CLEANED IN
HYDROCHLORIC ACID

Electrodes (42, 46)

Runs 19, 20 and 34, 35 performed on electrode 46;
all other runs performed on electrode 42

FIGURE 10C

ELECTRODES ETCHED IN
SULFURIC ACID; CLEANED IN
ZINC BROMIDE/BROMINE SOLUTION

Electrodes (43, 47)

Runs 19, 20 and 34, 35 performed on electrode 47;
all other runs performed on electrode 43

FIGURE 10D

ELECTRODES ETCHED IN
HYDROCHLORIC ACID; CLEANED IN
ZINC BROMIDE/BROMINE SOLUTION

Electrodes (44, 48)

Runs 19, 20 and 34, 35 performed on electrode 48;
all other runs performed on electrode 44

electrolyte. Because of the change to the bipolar design with carbon electrodes, however, this question was not pursued any further.

2. Surfactant Additive

The use of surfactants to improve the morphological quality of electrodeposited metals is commonplace. Their application as dendrite inhibitors in rechargeable zinc halogen batteries has been discouraged because of their rapid decomposition in the battery environment, which necessitates frequent makeup and periodic electrolyte purification. There is a class of fluorinated surfactants, however, which is known for its chemical stability; ZONYL® (DuPont) is one of these. An investigation was carried out to evaluate the feasibility of using an agent such as ZONYL® to promote non-dendritic zinc deposition in the zinc-bromine battery. While it was very effective in preventing dendrites, the agent was found to behave similarly to other surfactants, requiring frequent makeup.

A 2^2 factorial experiment was performed to evaluate the performance of ZONYL®, at a concentration of 100ppm in an otherwise standard electrolyte solution, as a leveling agent for two electrode loadings and two flowrates, as follows:

Factors:

A) Loading (mAh/cm^2)

+ 300

- 200

B) Flow (Reynolds No.)

+ 30

- 15

Experimental Design:

<u>Electrode No.</u>	<u>Factors</u>	
	<u>A</u>	<u>B</u>
51	-	+
52	+	+
53	-	-
54	+	-

The procedure consisted of plating zinc on electrodes 51-54 daily according to the experimental design. The cells were then taken apart, and the deposits examined and rated. The electrodes were then stripped of zinc by immersion in a 2M ZnBr_2 /2M Br_2 solution until the following day. The results are shown graphically in Figures 11 A-D. After 33 runs none of the cells had shorted out and none of the zinc deposits got a rating below 6. However, a steady degradation of the zinc deposit quality was observed thereafter with no differences attributable to flow rates but significant differences attributable to loading level. An analysis of variance (Table 2) confirmed this conclusion. (Note that although we were dealing with a 2-factor experiment, for the purpose of statistical analysis the run number was considered a factor; thus a 3-factor experiment was assumed with factor C = run number, factor B = flow rate, and factor A = loading level).

Analysis of the electrolyte solution at this point revealed a surfactant concentration (See Appendix ? for the test method) of $0.0031\% \pm 0.0003$, down from an initial concentration of 0.01%; this loss of ZONYL® could account for the uneven quality of deposits obtained after run 33.

Just before run #56 the ZONYL® concentration was brought back up to the original concentration of 0.01 wt.%. Right after the addition we noted a period of stabilization which lasted for 3-4 runs in which deposits were characterized by sharp flow lines on the edges (this occurrence was also seen at the start of the original 2^2 factorial experiment). This period was followed by very good deposits in all four cells (Table 3). There was, as suspected, little or no difference between the deposits of electrodes 51 and 53 (low loading) before and after addition of ZONYL®. Significant differences, revealing the effectiveness of ZONYL®, were seen in the deposits of 52 and 54 (high

ZINC DEPOSITION STUDIES ADDITION OF ZONYL FSN

2² FACTORIAL EXPERIMENT

FIGURE 11A
ELECTRODE NUMBER 51

FIGURE 11B
ELECTRODE NUMBER 52

FIGURE 11C
ELECTRODE NUMBER 53

FIGURE 11D
ELECTRODE NUMBER 54

loading) before and after the concentration adjustment. This is reasonable, because it has been known that the deposit quality generally degrades as the loading is increased, so the quality for the higher loading would be more affected by the leveling agent.

The zinc deposits obtained with ZONYL[®] were, without question, of the highest consistent morphological quality ever obtained in the zinc deposition studies performed at Gould. However, as discussed in the cycle testing section, the classical problem of agent depletion and decomposition applies to ZONYL as well, and for those reasons its use in high efficiency, low maintenance, long-lived zinc-bromine batteries is not considered practical.

TABLE 2
ANALYSIS OF VARIANCE
Zinc Deposition Studies - Addition of ZONYL
2² Factorial Experiment

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	Variance Ratio, F
1. A (Loading Level)	79.20000	1	79.2000	141*
2. B (Flow rate)	0.0000	1	0.0	0
3. AB (Interaction)	0.16384	1	0.16384	0.3
4. C (Replications)	278.24536	54	5.15269	9*
5. AC	70.23999	54	1.30165	
6. BC	11.50000	54	0.21296	
7. ABC	9.33636	54	0.17290	

TOTAL 448.68545 219

Grand Mean = 7.15454 (Runs #1-3, 50-51 and 56-58 were not included in this analysis)

Error (Residuals) = AC+BC+ABC = 0.562 (162 d.f.)

F_{.05}(1,162) = 3.91

* Significant

TABLE 3
T-TEST: 2² FACTORIAL EXPERIMENT
ZINC DEPOSITION STUDIES - ADDITION OF ZONYL
CELL NO.

	51 7.6	52 5.2	53 8.0	54 5.0
Average Deposit Quality before Adjustment of ZONYL Concentration (runs #51-54)				
Average Deposit Quality after Adjustment of ZONYL concentration (runs #59-63)	8.4	8.4	8.6	7.8
Pooled Variance	0.55	1.75	0.90	2.60
94% Confidence Intervals for Difference	0.8+1.1	3.2+1.9*	0.6+1.4	2.8+2.3*

* Significant differences in deposit quality.

B. BROMINE STORAGE SYSTEM MODEL

The bromine storage system comprises a static mixer, the polybromide pump and storage tank, the electrolyte settling tank, and the necessary plumbing to connect these. The electrolyte and the polybromide are pumped from their respective tanks cocurrently through the static mixing device in which the polybromide becomes dispersed as fine ($\sim 1\text{mm}$) droplets in the electrolyte. This dispersion is then carried to the submodule, where bromine is picked up by the polybromide dispersion (on charge) or released (on discharge).

Design of the bromine storage subsystem requires specification of the optimal flowrates and complexing agent quantity to maximize performance and minimize cost. To assist the design, a theoretical model (see Appendix D) has been developed to characterize the performance of the bromine storage system for an 8kWh submodule incorporating a static mixer. With it, we have been able to quantitatively predict the effects of varying the design parameters on battery performance.

For example, increasing the flowrate above the design point does little to enhance interphase bromine transport at a considerable penalty in pumping power. Increasing the amount of residual polybromide above the design quantity provides for a flatter bromine concentration swing, which is desirable, at a higher installed cost for the battery. Lowering the discharge current also flattens the bromine concentration swing. The harmful effect predicted for bypassing part of the electrolyte flow around the mixer has been an important outcome as it has discouraged us from considering bypass as a design option.

Figure 12 is a diagram of the bromine storage system; Figures 13 A-C show the important results of the study. What we seek is a bromine concentration swing from a maximum of 20g/l at start of discharge to a minimum of 5g/l at end of discharge. The results are discussed below for various combinations of parameters about the design point.

FIGURE 12
BROMINE STORAGE SUBSYSTEM MODEL

Doubling the flowrate has very little effect on the bromine concentration in the aqueous phase (Figure 13A, Curves 1 and 2); however, the pumping power required to double the flowrate is eight times larger, which is unacceptable. If the bromine/organic complexing agent ratio is changed from 2.75 to 2.50 (Figure 13B, curves 1 and 3, respectively), the bromine concentration swing is less severe, which is desirable. However, an increase in the amount of complexing agent results in increased cost for the battery, which may offset the benefit gained.

Figure 13C shows the effect of reflux, i.e., the bypassing of some of the electrolyte around the settler. This was considered because it improves the performance of the settler (lower throughput). The higher the reflux ratio, (curves 4 and 5), the lower the bromine concentration is at end of discharge; in fact, the lower limit of 5g/l is exceeded for both reflux ratios.

In summary, Curve 1 represents the design conditions at the present time, which are subject to change by factors such as cost of complexing agent, bromine partition properties, dependence of cell performance on bromine concentration, operational constraints, etc. With the model we can easily assess the impact of changes in these as the program progresses.

FIGURE 13A
POSITIVE ELECTROLYTE BROMINE
CONCENTRATION PROFILES, PREDICTED

FIGURE 13B
POSITIVE ELECTROLYTE BROMINE
CONCENTRATION PROFILES, PREDICTED

FIGURE 13C
POSITIVE ELECTROLYTE BROMINE
CONCENTRATION PROFILES, PREDICTED

For the 80kWh module, the design will be an essentially linear scaleup of the 8kWh submodule. It should be straightforward and we do not foresee any major problems.

C. THERMAL MANAGEMENT OF THE ZINC-BROMINE BATTERY

Because the energy efficiency of the battery is less than 100%, waste heat is generated during battery operation which, if not removed, would raise the battery temperature above its thermal limit. A cooling system is thus required to maintain the module temperature within its design limits of 20-50°C. A thermal management study has been performed on the zinc-bromine battery to allow proper design of a heat exchanger for waste heat removal.

In designing a heat exchanger for the zinc-bromine battery, the following specifications and data must be at hand:

- Design Operating Temperature

An operating temperature of 50°C has been selected for the battery. At that temperature, the ionic conductivity is 40% higher than at room temperature. Also, at 50°C, the temperature difference for heat transfer will be larger. At temperatures much higher (>60°C), however, degradation of the bromine complexing agent may occur.

- Materials of Construction for the Heat Exchanger

Because the battery electrolyte is highly corrosive, the choice of construction material for the heat exchanger is limited to titanium.

- Physical and Thermal Properties of the Electrolyte and Process Water

The heat capacity, thermal conductivity and viscosity of process water are, of course, handbook data. The viscosity of the electrolyte has already been measured (Ref.1). Heat capacity and thermal conductivity data for the electrolyte are not yet available but can be approximated from published data for similar systems.

- Process Water Temperature

Its temperature will depend upon the geographic location of the battery, but we will assume that it is 30°C.

- Heat Generation Rate

The heat generation rate of the battery has been measured. Before presenting the results, however, a brief discussion of the computation is given below; for a detailed treatment consult Reference 3.

The rate of heat flow ($-q'$) from the battery to its surroundings can be written as a derivative either with respect to the reaction progress variable (ξ) or with respect to time. For isothermal operation we write:

$$-q'_{\xi} = -T(\partial S/\partial \xi)_{P,T} + nF(E-V_i) \quad \text{Discharge}$$

$$-q'_{\xi} = +T(\partial S/\partial \xi)_{P,T} - nF(E-V_i) \quad \text{Charge}$$

or

$$-q'_t = I[-(T/nF)(\partial S/\partial \xi)_{P,T} + (E-V_i)]$$

with the convention that $I > 0$ for discharge and $I < 0$ for charge.

The quantity $(E-V_i)$ is the overpotential;

ξ is the reaction progress variable for the cell reaction and has units of moles. For the initial, fully charged state of the battery, $\xi = 0$ whereas for the final, fully discharged state of the battery, $\xi = 1$.

We need to know the intrinsic entropy change and the overpotential of the cell at the design current density of 40mA/cm².

The design overpotentials on discharge are tabulated below. The discharge half-cycle was chosen for the design of the heat exchanger, since the battery's reversible, or thermodynamic heat, is exothermic then. This provides the worst case conditions for design of the heat exchanger.

DESIGN OVERPOTENTIAL (η) AT 40mA/cm²

η concentration $\text{Br}_2 + 2\text{Br}^-$	10mV
η activation $\text{Br}_2 + 2\text{Br}^-$	25mV
η activation $\text{Zn} + \text{Zn}^{++}$	30mV
η ohmic	<u>125mV</u>
η Total	190mV

The intrinsic entropy change $\partial S/\partial \xi$ can be calculated using the equation

$$(\partial S/\partial \xi)_{P,T} = \left[\frac{(\partial H/\partial \xi)_{P,T} - (\partial G/\partial \xi)_{P,T}}{T} \right]$$

$$\text{where } (\partial H/\partial \xi)_{P,T} = -nF [E - T(\partial E/\partial T)_{\xi,P}]$$

$$\text{and } (\partial G/\partial \xi)_{P,T} = -nFE(\xi)$$

where E is the reversible cell potential.

A measurement of the cell potential (EMF) as a function of the reaction progress variable is sufficient to determine the intrinsic entropy change, which, in combination with the value of the overpotential, will give us the heat generation rate.

The practical thermal efficiency of the zinc bromine battery can be calculated from the relation

$$\epsilon = -nFV_i(\text{avg})/\Delta H$$

where a constant current discharge is assumed and $V_i(\text{avg})$ is the average discharge voltage.

The EMF measurements were made using an H-cell configured as follows:

where m_1 ranged from 0.5 to 4.0 mol/kg, $m_2 = 4.0$ mol/kg, and m_3 was either 0.04 or 0.17 mol/kg.

After filling the cell with the appropriate electrolyte and placing the electrodes in position, the whole H-cell assembly was placed in a thermostatically controlled circulating ethylene glycol bath. The potential was measured at zero current with a $5\frac{1}{2}$ digit high input impedance multimeter calibrated against a Guildline, Model 4577, $7\frac{1}{2}$ digit precision multimeter. About 70-90 minutes were required for temperature equilibration prior to measurement of the EMF. Measurements were made at 273, 293, 313 and 333°C for the concentrations shown in Table 4.

The EMF results are shown in Table 5; these were fitted to a quadratic expression in the temperature by the method of least squares and the following quantities were calculated:

$$(\partial G/\partial \xi)_{P,T}, (\partial H/\partial \xi)_{P,T}, (\partial S/\partial \xi)_{P,T}, \Delta G, \Delta H \text{ and } \Delta S$$

(The change in state to which ΔG , ΔH and ΔS refer is the discharge of the battery between known initial and final states). These are shown in Tables 6 A-D.

TABLE 4				
H-CELL EXPERIMENT				
Zn(Hg) - 2 phase/ZnBr ₂ (m ₁) + KCl (m ₂)/ZnBr ₂ (m ₁) + KCl (m ₂) + Br ₂ (m ₃) / Pt				
ZnBr ₂ (m ₁)	KCl(m ₂)	Br ₂ (m ₃)	Reaction Progress Variable ξ (mole)	
0.5	4.0	0.17	0	Fully charged battery
0.5	4.0	0.04	0	
2.0	4.0	0.17	0.43	
2.0	4.0	0.04	0.43	
3.0	4.0	0.17	0.71	
3.0	4.0	0.04	0.71	
3.5	4.0	0.17	0.86	
3.5	4.0	0.04	0.86	
4.0	4.0	0.17	1	
4.0	4.0	0.04	1	Fully discharged battery
T = 273°K,		293°K,	313°K and 333°K	

TABLE 5						
EMF vs ξ						
Zn(Hg)-2 phase/ZnBr ₂ (m ₁) + KCl(m ₂)/ZnBr ₂ (m ₁) + KCl(m ₂) + Br ₂ (m ₃)/Pt						
ξ	Br ₂ g/l	EMF (Volt)				
		273°K	293°K	313°K	323°K	333°K
Interpolated						
1	20	1.7627	1.7568	1.7508	1.7473	1.7439
1	5	1.7452	1.7392	1.7318	1.7276	1.7230
0.86	20	1.7681	1.7634	1.7576	1.7541	1.7504
0.86	5	1.7517	1.7449	1.7392	1.7349	1.7309
0.71	20	1.7754	1.7703	1.7653	1.7623	1.7593
0.71	5	Not Determined	1.7530	1.7471	1.7433	1.7398
0.43	20	1.7952	1.7917	1.7874	1.7851	1.7827
0.43	5	1.7772	1.7715	1.7668	1.7635	1.7605
0.0	20	1.8612	1.8676	1.8711	1.8723	1.8728
0.0	5	1.8456	1.8492	1.8494	1.8492	1.8481

TABLE 6A

ξ	Br_2 g/g	$(\partial G/\partial \xi)_{P,T}$ cal/mol				
		273°K	293°K	313°K	323°K Interpolated	333°K
1	20	-81296	-81024	-80747	-80589	-80429
1	5	-80489	-80212	-79871	-79675	-79465
0.86	20	-81545	-81328	-81061	-80899	-80728
0.86	5	-80788	-80475	-80212	-80014	-79829
0.71	20	-81881	-81646	-81416	-81277	-81139
0.71	5	not determined	-80848	-80576	-80402	-80240
0.43	20	-81964	-82633	-82435	-82331	-82218
0.43	5	-81725	-817-2	-81485	-81336	-81194
0.0	20	-85839	-86134	-86295	-86349	-86374
0.0	5	-85119	-85285	-85294	-85284	-85234

TABLE 6B

	Br_2 g/g	$(\partial H/\partial \xi)_{P,T}$ cal/mol				
		273°K	293°K	313°K	323°K	333°K
1	20	-8475-	-85073	-85433	-856-3	-85797
1	5	-83823	-84741	-84719	-86230	-86761
0.86	20	-84072	-84884	-85765	-86217	-86692
0.86	5	-84367	-84824	-85396	-85645	-85922
0.71	20	-84810	-85096	-85423	-85580	-85751
0.71	5	not determined	-85308	-85340	-85317	-85308
0.43	20	-84861	-85253	-85668	-85889	-86120
0.43	5	-85113	-85304	-85548	-85636	-85746
0.0	20	-81208	-82753	-84381	-85248	-81638
0.0	5	-82320	-83938	-85622	-86535	-87467

TABLE 6C

$\partial S/\partial \xi = [(\partial H/\partial \xi)_{P,T} - (\partial G/\partial \xi)_{P,T}] / T$						
cal/mol°K						
ξ	Br ₂ g/l	273	293	313	323	333
1	20	-12.65	-13.82	-14.97	-15.54	-16.12
1	5	-12.21	-15.46	-18.68	-20.29	-21.91
0.86	20	- 9.26	-12.14	-15.03	-16.46	-17.93
0.86	5	-13.11	-14.84	-16.56	-17.43	-18.30
0.71	20	-10.73	-11.77	-12.80	-13.32	-13.85
0.71	5	-15.22	-15.22	-15.22	-15.22	-15.22
0.43	20	- 7.57	- 8.94	-10.33	-11.02	-11.72
0.43	5	-11.61	-12.29	-12.98	-13.33	-13.67
0.0	20	+16.96	+11.54	+ 6.11	+ 3.41	+ 0.71
0.0	5	+10.25	+ 4.60	- 1.05	- 3.87	- 6.70

TABLE 6D

$\Delta H, \Delta G, \Delta S$						
	Br ₂ g/l	273°K	293°K	313°K	323°K	333°K
ΔH cal/mol	20	-84034	-84679	-85372	-85656	-86105
ΔH cal/mol	5	-84460	-84968	-85531	-85722	-85983
ΔG cal/mol	20	-82598	-82799	-82648	-82555	-82451
ΔG cal/mol	5	-81946	-81934	-81736	-81598	-81460
ΔS cal/mol °K	20	- 4.136	- 6.416	- 8.703	- 9.841	-10.992
ΔS cal/mol °K	5	- 8.743	-10.353	-11.966	-12.464	-13.737

Since the operating temperature of the zinc bromine battery has been selected at 50°C we have calculated the thermal properties of the battery at that temperature.

Table 6D gives, for a fixed bromine concentration of 5 g/l, $\Delta G = -81.598\text{kcal/mole}$ and $\Delta H = -85.722\text{kcal/mole}$. Thus the overall reversible thermal efficiency of the zinc/bromine battery is 0.9519; since this value is less than unity, the battery will release heat even during a reversible discharge.

It is interesting to examine not only the overall thermal efficiency but also the instantaneous thermal efficiency at each stage of the discharge process. Figure 14 shows the values of ϵ'_{th} at constant pressure and at a temperature of 323°K (50°C). The curve shows that the maximum of reversible heat emission occurs at $\xi = 1$, when the cell is fully discharged. This type of plot, when the heat owing to inefficiencies is included, is useful in battery design, for it clearly shows in which parts of the discharge cycle the greatest and least emissions of heat will occur.

For reversible isothermal operation the heat flow $-q\xi$ from the battery to the surroundings is $-T (\partial S/\partial \xi)_{P,T}$. Figure 15 shows, for example, the reversible emission of heat by the battery at 323°K as a function of state of charge.

In Figure 16 the rate of heat flow $-q'_\xi$ for isothermal operation of the battery at 323°K is shown as a function of overpotential. This figure clearly illustrates the facts that the battery evolves heat at all potentials on discharge, while on charge heat may be absorbed or emitted. At a certain overpotential, which depends on the state of charge, the battery neither absorbs nor emits heat. This thermoneutral overpotential is shown for two states of charge.

FIGURE 14
REVERSIBLE DIFFERENTIAL THERMAL EFFICIENCY AT 323° K
 $\epsilon'_{th} = (\partial G / \partial \xi)_{P,T} / (\partial H / \partial \xi)_{P,T}$

FIGURE 15
EMISSION OF HEAT FOR REVERSIBLE OPERATION OF
THE ZINC BROMINE BATTERY AT 323° K

FIGURE 16
DEPENDENCE OF HEAT FLOW FROM THE ZINC BROMINE BATTERY
ON OVERPOTENTIAL AT 323° K

Finally, calculations for the heat exchanger design are shown in Table 7. An estimate for the size of the heat exchanger for an 80kWh zinc/bromine battery is 0.17m^2 ; a heat exchanger of this size could be easily incorporated into the 80kWh module, and its projected cost is on the order of \$1/kWh.

TABLE 7

HEAT EXCHANGER DESIGN

80 kWh BATTERY

A. Heat Generation at 323°K

$$q' = I[-(T/nF) (\partial S/\partial \xi)_{P,T} + (E-V_i)]$$

$$(-T/nF) (\partial S/\partial \xi)_{P,T} = 142\text{mV}$$

$$\begin{aligned}\text{Overpotential } (E-V_i) &= 190\text{mV} \\ \text{Discharge} &= 5 \text{ hours} \\ \text{Current } (I) &= 10,000\text{A} \\ q' &= 3.32 \text{ kW}\end{aligned}$$

B. Heat Exchanger Calculations

Assume	: Isothermal Discharge
Material	: Titanium Coil
Overall heat transfer coefficient (U)	= $1 \text{ kW/m}^2\text{°C}$
Process Water Temperature	= 30°C
Electrolyte Temperature	= 50°C
Heat Exchanger Area	= $\frac{3.32 \text{ kW}}{\frac{1\text{kW}}{\text{m}^2\text{°C}} \times 20\text{°C}} = 0.17\text{m}^2$
Cost	= Approx. \$70 (~\$1/kWh)

D. CORROSION STUDIES

The monopolar cell design, utilizing titanium electrodes, was preferred during the first nine months of the program. Supporting studies such as this one were performed to solve problems associated with the use of titanium as an electrode material. In this study we have screened various electrode treatments and electrolyte formulations for inhibiting electrode corrosion. We have found that proper electrolyte formulation, coupled with a bypass diode or switch for each cell, provides the corrosion protection required.

In a series string of cells, reverse polarity of the negative electrode would occur in a cell that became stripped of all zinc. This cell reversal condition may result in severe corrosion of the titanium negative electrode if no precautions are taken. One approach is to place a diode or a contactor in parallel with the cell. The diode will conduct the entire string current at a forward potential of 600 to 900mV, depending on which kind of diode is used.

Both of the above techniques have cost/performance tradeoffs. Use of a contactor would limit the potential drop across the cell to $\leq 200\text{mV}$, but its use requires a voltage scanner and an actuating relay. A Schottky diode with a forward potential drop of $\sim 600\text{mV}$ would be preferable to a silicon diode (900mV), but would cost more.

The silicon diode may have been the ultimate choice because of its low cost. During cell reversal, it would limit the negative electrode substrate potential to +2 volts vs the normal hydrogen electrode; even at this potential pitting corrosion can occur. To prevent this, several approaches have been considered to induce passivation of the substrate. They include: (1) providing a protective coating (2) changing the titanium substrate composition, and (3) changing the electrolyte formulation.

Before discussing these methods in detail, it is appropriate to describe how the passivation behavior of a titanium electrode can be assessed experimentally. The specimen is etched in 50% sulfuric acid at 70 to 80°C for about 1 minute, then rinsed with distilled water and soaked in the test solution overnight. The electrode is then placed in a cell filled with the test electrolyte and fitted with a zinc counter electrode and a silver-silver bromide reference electrode. The reference electrode is placed in a Luggin capillary filled with a saturated solution of high purity potassium bromide; its measured potential is +0.072V vs the normal hydrogen electrode (NHE). The titanium electrode is then held at +2.0V with respect to the NHE and the cell current is measured and recorded vs time using an X-Y recorder in conjunction with a potentiostat and a function generator. If the current decreases rapidly as a function of time, one can assume that passivation has occurred (see Figure 17).

FIGURE 17
TITANIUM CORROSION CURRENT
IN PROTECTING AND UNPROTECTING ELECTROLYTES

1. Examination of Oxyanion Additives

In a study by Koizumi and Furuya (Ref.4) the effects of various oxyanions such as sulfate, nitrate and phosphate on titanium in sodium bromide solutions were investigated. The results of the study indicated that the breakdown potential of titanium was shifted in a more positive direction, as desired, in the presence of these additives. The bromide

ion concentrations investigated by Koizumi and Furuya ranged from 10^{-2} M to 1M, which were lower than the concentration range of interest to us, but nevertheless their work provided a good basis for investigating these oxyanion additives.

Carbonates and phosphates were not considered because of the insolubility of their respective zinc salts. Nitrates were dismissed because of the reduction of nitrate to nitrite at the negative electrode and its reoxidation at the positive electrode, thus lowering the coulombic efficiency of the cell. However, perchlorate and methyl sulfate seemed to be good candidates.

A test of a 4m NaClO_4 /2m ZnBr_2 solution revealed that perchlorate possessed protective properties. Several other electrolyte formulations were then investigated in a similar fashion.

Two titanium substrates were prepared for each solution by the standard procedure, which involves etching in 50% sulfuric acid followed by soaking in their respective solutions for 24 hours before testing. The results are presented in Figure 18, which maps the three regions of protection behavior. An additional experiment was conducted with the substrates tested in solution J. Zinc was electroplated on the substrate until 5 coulombs of charge had been registered on the coulometer of the potentiostat. The polarity of the cell was reversed and the zinc was removed from the substrate. At the end of this simulated discharge the voltage across the cell dropped to zero. The substrate was then subjected to a +2.0V potential vs NHE for five minutes. The entire process was carried out twice for each of two previously tested substrates. The current vs. time curves for these tests show that in each case the perchlorate solution continued to protect the titanium substrate through a charge/discharge sequence.

Equally good results were obtained for a solution of 4m potassium chloride, 2.67m potassium methyl sulfonate and 2m ZnBr_2 and led to the testing of this electrolyte formulation in a long-term test cell (#42).

FIGURE 18
CORROSION PROTECTION OF TITANIUM
IN VARIOUS ELECTROLYTES

2. Examination of Zinc Chloride as an Additive in the Zinc-Bromine Battery Electrolyte.

Zinc chloride is added to the electrolyte to provide the excess zinc ions required to achieve a charge to full capacity, since zinc chloride is less expensive than zinc bromide. The effect of zinc chloride on the corrosion behavior of titanium was thus of interest to us. Subsequently we learned that it has a beneficial effect in inhibiting titanium corrosion.

We observed that, in every sodium chloride-supported solution containing 1M zinc chloride, the titanium test electrodes were protected at 2V vs NHE, even for those solutions which were not protective without zinc chloride.

When potassium or ammonium chloride was substituted for sodium chloride to increase the conductivity of the electrolyte, corrosion occurred. Increasing the concentrations of potassium or ammonium chloride did not inhibit corrosion. Thus, sodium and chloride ions appear to be important contributors to corrosion inhibition of titanium.

3. Examination of Alternate Titanium Alloys in Cell Reversal

Samples of two RMI Company alloys were evaluated for their performance under cell reversal conditions. RMI personnel suggested these alloys because of their better resistance to corrosion in other environments. The composition of the alloys together with the presently used grade of titanium are reviewed in the table below:

<u>Nominal Composition</u>	<u>WEIGHT PERCENT</u>		
	<u>Fe</u>	<u>O</u>	<u>N</u>
Present Grade 2 Titanium	0.30	0.25	0.03
Low Iron Titanium	0.03	0.19	0.011
Titanium + 0.02% Yttrium	0.07	0.05	0.008

Three samples of each alloy and four samples of grade 2 titanium were etched as before, rinsed in distilled water, and stored for at least 24 hours in 4m KCl, 2mZnBr₂ solution at a pH of 2.0. The samples were then subjected to a potential of +2.0V vs NHE for 300 seconds in the test cell. In all cases the substrates corroded rapidly, and further experiments with these alloys were not considered necessary.

4. Examination of Protective Coatings

a. Silver/Silver Bromide Protective Coating

An experiment was conducted to determine whether a silver bromide coating would protect titanium against corrosion in cell reversal. Attempts at electroplating silver directly upon titanium from a potassium cyanide/silver cyanide solution, a standard silver plating bath, produced uneven coatings. By first plating copper upon titanium and then silver

upon the copper, uniform films of silver were deposited. Test electrodes electroplated with silver in this manner were then dipped for 10 seconds in a solution of bromine in water to form a thin film of silver bromide. The test electrodes were then placed in the test cell and held at a constant potential of +2.0V vs NHE for approximately 300 seconds. The electrolyte in the cell was a standard solution of 4m KCl and 2m ZnBr_2 at a pH of 2. An unplated electrode, used as a control, corroded as expected. The silver plated substrates released bromine initially but corrosion ensued with the peeling away of the silver/silver bromide film. Further study of this coating was not performed.

b. Titanium Carbide as a Protective Coating

Coatings of titanium carbide have been claimed to protect titanium in zinc-halogen batteries. Titanium electrodes coated with titanium carbide by an electron beam technique were tested under cell reversal conditions in the usual way in a standard 4m KCl/2m ZnBr_2 electrolyte. The coating of titanium carbide did protect the substrate under the test conditions, but repeated zinc plating and stripping on the substrate resulted in complete breakdown of the titanium carbide film (Cell #21 described under Long-Term Cycle Testing). This technique was also shelved.

5. Analysis of Anodic Films on Titanium Substrates

Four titanium electrodes were etched in 50% sulfuric acid, rinsed in distilled water and stored for 24 hours in 4m KCl/2m ZnBr_2 at a pH of 2.0. Each electrode was then polarized at a potential of +2.0 volts vs NHE for a specific amount of time. A fifth electrode was left unetched and was not polarized. The table below lists the electrodes and the length of their exposure to the test cell environment.

<u>Electrode</u>	<u>Exposure at +2.00V vs NHE</u>
1	No treatment
2	15 sec
3	60 sec
4	180 sec
5	To completion of corrosion of surface.

The four polarized electrodes were rinsed with distilled water after exposure. All five electrodes were then submitted to the surface physics laboratory of Gould Laboratories-Electric and Electronic Research for examination by SEM and Auger spectroscopy.

It was noted that corrosion of titanium would start at several spots which would expand outwardly as nearly perfect circles eventually joining each other to cover the entire surface of the electrode. Depending on the exposure time, the spots would be either blue (15-60 sec) or white (60 sec and above). Scanning electron micrographs show the surface morphology of the blue and white corrosion spots, and of the adjacent, non-corroded area (see Figures 19 A and B).

The Auger spectra of both the corroded and the non-corroded areas showed the presence of Ti, C, O and traces of S, Cl and Fe. The blue and white spots are of identical composition, but with different thickness. Auger elemental depth profiles, however, reveal a definite difference between the two areas in that the carbon content at the surface of a corroded spot is much greater than on a non-corroded area. While one could surmise that the presence of carbon enhances corrosion, confirmatory work was not pursued because of the move to the bipolar design.

PITTING OF TITANIUM ELECTRODES

FIGURE 19A
BLUE CORROSION SPOT WITH ADJACENT NONCORRODED AREA

FIGURE 19B
WHITE CORROSION SPOT WITH ADJACENT LESS CORRODED AREA

E. NEGATIVE ELECTRODE EROSION STUDIES

One of the concerns in the use of a non-reacting substrate to support the zinc deposition/stripping process occurring at the negative electrodes during battery operation is the mechanical wear, or erosion, of that substrate by the forces of zinc crystallization. We have devised an accelerated stress test which, under the premise of the experiment, indicates that both titanium and carbon wear sufficiently slowly such that 2500 full discharge cycles can be performed on the battery without failure of the negative electrodes.

A testing program was initiated to study negative electrode erosion. Operating on the premise that the plating and stripping of zinc on and off the negative electrode causes most of the wear on the substrate, the following experiment was performed. Two electrodes were placed in a sealed vessel to which 125 ml of electrolyte were added. The electrodes were connected to a potentiostat programmed for a ten minute cycle of 1A anodic/cathodic current. For five minutes one of the electrodes was a negative electrode; after five minutes the roles were reversed and the other electrode became the negative, and the zinc plated on the first one was stripped. The plan was to accrue 2500 plating and stripping cycles on each electrode pair.

This accelerated stress test has provided useful information on the desirability of the candidate substrates. Weight losses or gains and dimensional changes were noted; profilometer traces were also obtained for plated and unplated areas of several carbon electrodes tested in this program.

Listed below are the four experiments which were completed.
(Figures 20 A-J).

Exp.#	Electrode A	Electrode B	Diode#
1	Airco-Speer(C)	*(C)	No
2	*(C)	*(C)	No
3	Titanium	*(C)	Yes
4	Titanium	*(C)	Yes

(C) Carbon

* Electrode of proprietary origin.

The diode is used to bypass the current around the cell to prevent anodic pitting of the titanium.

To avoid introducing uncontrolled variables a uniform procedure was used for treatment of the electrodes:

- (1) The electrode's dimensions were 3/8 in. x 6 in.
- (2) The carbon electrodes were cleaned in 50% HCl for 30 minutes then rinsed in water for 30 minutes. The titanium electrodes were cleaned in 50% H₂SO₄ followed with the same water rinse.
- (3) All electrodes were dried at 105°C to constant weight.
- (4) The electrodes were wrapped with Teflon tape 2 inches from the bottom, to insulate the edges and space appropriately, then inserted in the electrolyte and cycled.
- (5) At the end of 2500 cycles all electrodes were treated as per steps 1-3 using 50% HCl at this point to clean the titanium electrodes.
- (6) The surface roughness of plated and unplated sections of the carbon electrodes was measured at the end of the test using a profilometer.

The results are presented in Table 8. Weight losses were on the average less than 10% and did not exceed 14%. Overall the electrodes were dimensionally stable. Though the surface roughness of the carbon electrodes did increase with cycling as shown in Figures 20 A-J no degree

FIGURE 20A
UNPLATED AREA

NEGATIVE ELECTRODE SURFACE PROFILE
EXPERIMENT NO. 1
CARBON ELECTRODE OF PROPRIETARY ORIGIN

FIGURE 20B
PLATED AREA

FIGURE 20C
UNPLATED AREA

NEGATIVE ELECTRODE SURFACE PROFILE
EXPERIMENT NO. 1
AIRCO-SPEER CARBON ELECTRODE

FIGURE 20D
PLATED AREA

FIGURE 20E
UNPLATED AREA

NEGATIVE ELECTRODE SURFACE PROFILE
EXPERIMENT NO. 2
CARBON ELECTRODE OF PROPRIETARY ORIGIN

FIGURE 20F
PLATED AREA

FIGURE 20G
UNPLATED AREA

NEGATIVE ELECTRODE SURFACE PROFILE
EXPERIMENT NO. 3
CARBON ELECTRODE OF PROPRIETARY ORIGIN

FIGURE 20H
PLATED AREA

FIGURE 20I:
UNPLATED AREA

NEGATIVE ELECTRODE SURFACE PROFILE
EXPERIMENT NO. 4
CARBON ELECTRODE OF PROPRIETARY ORIGIN

FIGURE 20J
PLATED AREA

of significance could be assigned to this result. Based on this preliminary information, all the electrodes tested are expected to survive 2500 full cycles. Full cycle testing will be performed, of course, to confirm this.

TABLE 8

NEGATIVE ELECTRODE EROSION STUDIES

Experiment No.	Weight Loss or Gain (g/cm^2)		Change in Thickness (mm)	
	Electrode A	Electrode B	Electrode A	Electrode B
1	+0.027 g/cm^2 (4% of plated area weight)	+0.0086 g/cm^2 (7% of plated area weight)	No Change	No Change
2	Electrode Misplaced	+0.0057 g/cm^2 (4% of plated area weight)	Electrode Misplaced	No Change
3	Zinc Deposit Still Present	-0.025 g/cm^2 (14% of plated area weight)	+0.01mm	-0.06mm
4	No Change	-0.0098 g/cm^2 (7% of plated area weight)	No change	-0.01mm

Surface roughness of the carbon electrodes increased with cycling in all cases as shown in the profilometer traces (Figure 20).

F. BIPOLAR ELECTRODE STUDIES

The choice of the bipolar design over the monopolar required that we embark upon a comprehensive program to characterize the performance of the thin carbon sheet which serves as the bipolar electrode. Three properties of particular importance are its electrochemical performance as a bromine electrode, its permeability, or open porosity, and its mass transport behavior in a flow-by electrolyte circulation configuration. We have found that the electrode of present preference performs adequately in all three areas of concern. Its electrochemical performance is somewhat below specification, but surface treatment has a marked effect. The open porosity is well within specification, in fact it is practically nil. And the mass transport of bromine on discharge is adequate provided the polybromide phase is dispersed in the electrolyte. These three topics are discussed more fully below.

1. Electrode Activation Overpotential

Carbon is an effective substrate for the bromine electrode reaction, just as ruthenized titanium. However, the surface area available for reaction on planar carbon is at least one order of magnitude smaller than that of porous titanium. In other words, the local current density on the carbon would be much higher as compared with the porous ruthenized titanium electrode; a larger activation overpotential would thus be required to drive the electrode at the same apparent current density. A preliminary experiment has been performed to obtain the current-voltage relations of the bromine electrode reaction on the carbon electrode.

The experiment involved comparing the activity of several electrodes after different treatments. The electrolyte was a two phase system; 2M potassium bromide and 2M potassium chloride constituted the aqueous phase; the polybromide phase at a bromination level of 2 was present as well. The reference electrode was silver-silver bromide; the electrolyte was stirred by a magnetic stirrer.

The results of the experiment are tabulated as follows:

Electrode Polarization Comparison
(design value is $<1\Omega\text{-cm}^2$)

Substrate Preparation	Polarization constant, $b(\Omega\text{-cm}^2)*$
Untreated	10
Etched in nitric acid	10
Sand blasted	1.8

*Note: this relates overpotential to current density as follows:

$$\Delta V = b.i$$

From this table, it is obvious that the carbon electrode is good but not to specification as a bromine electrode. One should also notice that the electrode's performance depends strongly on the treatment. To further activate the carbon will require a systematic investigation in the future.

2. Electrode Permeability Study

The open porosity of the bipolar electrode is very critical to the coulombic efficiency of the battery. Calculations indicate that 0.004% open porosity would result in 1% coulombic efficiency loss. The open porosity of the material was investigated by the following experiment. The setup is as shown in Figure 21. The carbon specimen was tested under a head of 8 ft of water, in which was dissolved concentrated potassium permanganate as a dye. The permeation rate through a material with 0.004% open porosity should vary with the number of openings, as shown in the following table:

Number₂ of Openings
in 1cm²
(open porosity = 0.004%)

Expected Permeation Rate
(under 8 ft of water head)

1
100
10,000
1,000,000

5.0×10^4 cm³/day
500.0
5.00
0.05

Under the extreme case assumption of 1,000,000 openings in 1 cm², one would expect 0.25cc to permeate over a period of 5 days, which would be evident as visible coloring of the water in the collecting flask. However, no trace of permeation was observed, so the conclusion is that the open porosity of the material is much less than 0.004%, and thus less than a 1% coulombic efficiency loss through the bipolar electrodes can be expected.

3. Concentration Overpotential

Some preliminary testing indicated that a flow-by planar bromine electrode cannot discharge efficiently (low concentration overpotential) at a current density higher than 10mA/cm² unless the flow rate is greatly increased or the bromine concentration is excessively high (-1M). The problem with a high flow rate is the consumption of excessive pumping power and that with a high bromine concentration there is a high rate of self-discharge.

FIGURE 21
EXPERIMENTAL SET-UP FOR PERMEABILITY TESTING

The thickness of the boundary layer determines the rate of bromine transport to the electrode surface. In order to increase the transfer rate of bromine to the electrode surface for reaction, the thickness of the boundary layer must be reduced. Methods available to decrease the boundary layer thickness include (1) increase the flow rate, (2) roughen the surface, (3) modify the rib configuration, or (4) introduce the polybromide phase.

A 6.4Wh cell and a 64Wh cell have been constructed to evaluate the methods for reducing mass transport resistance. Both the positives and negatives of these two cells are flow-by planar carbon electrodes. We have found that, by circulating the polybromide phase as an emulsion in the electrolyte, the cells can operate at $30\text{mA}/\text{cm}^2$ without significant concentration overpotential. This will have a major beneficial impact on cell design and cost, since only one electrode member (i.e. the planar carbon) will be required, as compared with previous designs involving porous, flow-through positives. One disadvantage of flowing the polybromide as an emulsion through the cell stack is that, being less conductive, the polybromide will increase the internal resistance somewhat, but this will be more than offset by the advantages imparted.

G. ELECTRODE FRAME STUDIES

The magnitude of leakage currents in a bipolar electrode stack is determined by the resistance of the channels in the frame as well as by the number of frames per battery stack. In order to reduce the leakage current, the resistance of these channels should be increased. However, increasing the resistance of the channel also means increasing the pumping energy to force electrolyte through them. In order to optimize the channel design, a simple model has been developed. This model includes the consideration of leakage currents and pumping energy loss under the constraint of physical design feasibility. From this model, the design of the channels, as shown in Figures 22 A and B, was obtained.

FIGURE 22A
ELECTRODE FRAME: NEGATIVE SIDE

FIGURE 22B
ELECTRODE FRAME: POSITIVE SIDE

In order to utilize the whole electrode surface, the electrolyte must be evenly distributed over it. For the negative electrode, this can be achieved by purposely narrowing down the size of the inlet flow slots (Figure 22A). The pressure drop through these is about 10 times larger than that of the inlet channel to the farthest slot. This insures uniform flow across the electrode. The trapped air bubbles can be expelled by introducing the electrolyte from the bottom to the top.

For the positive electrode side frame design, the flow channels are more complicated. In order to expel the polybromide and the trapped air at the same time, two outlets are provided (Figure 22B). Two inlets are also provided for the sake of uniform flow distribution.

The uniformity of flow distribution to each electrode is quite good, since the pressure drop provided by the tortuous channels is on the order of 200cm head while the pressure drop through the main channel is on the order of 1cm head; a very uniform distribution to each electrode frame is thus expected.

H. ELECTROLYTE STUDIES

Basic data on the zinc bromide electrolyte have been previously obtained for the density, ionic resistivity, viscosity and activity coefficients (Ref.1). This information was necessary for optimizing the electrolyte formulation. Since completion of this work, additional data have been obtained on the fate of the bromide ions in the polybromide phase and the transport behavior of zinc during cycling.

1. Bromide Ions in the Polybromide Phase Are Available for Reaction at the Positive Electrode.

In review, we use a polybromide phase to complex the bromine produced during battery charging. This is accomplished in a two-phase contacting device in the positive electrolyte flow loop. The polybromide comprises a quaternary ammonium bromide (Q^+Br^-) and bromine, in a molar ratio of 1:1 for a fully discharged battery.

The electrolyte is an aqueous solution of zinc bromide and potassium chloride, the potassium salt acting as supporting electrolyte.

The concept, up to now, of the role the polybromide plays is that it absorbs bromine on charge and releases it on discharge. No thought was given to the availability of the bromide ions in the polybromide for electrochemical reaction.

We performed calculations regarding the bromide ion concentration swing in the positive electrolyte during charge. These involve removal via electrode reaction and flux through the separators to the positive electrolyte due to diffusion and migration. What these calculations indicate is that the flux of bromide ions through the separator cannot fully support the charge reaction, and that the bromide ion concentration should go to zero prior to the full charge. Laboratory testing has contradicted these conclusions; full charges have been achievable without complete bromide ion depletion.

In order to explain what we observed in the laboratory, we had to include the bromide ions in the polybromide as being available for the reaction. Thus, these would have to be replaced by chloride ions to maintain the electrical neutrality. At end of charge, the polybromide would be essentially the chloride salt of the quaternary ammonium ion (Q^+Cl^-) plus complexed bromine.

The possibility of this occurring was quite easy to verify. We prepared the chloride salt of the compound, dissolved it in water, and added bromine. A polyhalide phase formed resembling the bromide analog, thus confirming our hypothesis.

The impact of this is twofold: (1) the electrolyte cost will be lowered. Not as much bromide will be required in the aqueous phase, allowing us to use zinc chloride (which is one fifth the cost of zinc bromide in \$/lb mole) to provide the zinc ions. This could amount to a savings of ~\$1/kWh. (2) The positive electrolyte storage volume will be reduced, since approximately one fourth of the bromide ions will be

stored in the polybromide phase at start of charge. This will result in an increased footprint (kWh/ft^2) for the battery (higher energy density); the magnitude of this increase has not been estimated at this time.

2. Transference Numbers in Aqueous Zinc Bromide

The transference number of zinc in zinc bromide solutions exhibits peculiar behavior in that it becomes negative in concentrated solutions. This is of significance in that it shows the high degree of ion association in zinc halide electrolytes. Measurements of transference numbers for zinc bromide electrolytes were performed in conjunction with activity coefficient measurements. Details of the work are included in Appendix E; however, the scope and results of the investigation are described briefly below.

The potentials of concentration cells with liquid junction

were measured and combined with previously published measurements of the activity coefficients of aqueous zinc bromide to yield values of the cation and anion transference numbers.

The ranges of temperature and molality chosen for this study were 0°C to 36°C and 0.5 mol.kg^{-1} to 4.0 mol.kg^{-1} ; (m_2-m_1) was maintained at 0.5 mol.kg^{-1} .

For a finite difference Δm in the molality of the two cell compartments of cell (1) the integral cation transference number $\bar{t}_+$ equals $(2FE/3RT)/\Delta \ln m \pm$.

For molalities greater than 1.0 mol.kg^{-1} , t_+ may be taken as the arithmetic mean of the values at the molalities m_1 and m_2 of the two cell compartments, with an error less than 0.004 in the transference number.

The results of the calculations of t_+ are shown in Figure 23, where the transference number t_+ is plotted versus the molality of zinc bromide. To avoid overlap, the curve for each temperature has been displaced by 0.100 from the curve for the next lower temperature. The circles show the values obtained for cell (2), while the triangles represent values computed from the cell potentials for cell (3).

The transference number t_+ rapidly decreases with increasing molality and becomes negative between 2.5 and 3.0 mol.kg⁻¹. The negative cation transference numbers in concentrated solutions of zinc bromide are consistent with the formation of zinc bromide anionic complexes of the type $\text{ZnBr}_n^{(2-n)}$.

These measurements, to reiterate, were performed on zinc-bromide electrolytes, since they were easily obtainable while measuring activity coefficients for that binary electrolyte. As previously discussed, the battery electrolyte has additional, supporting electrolytes. Appendix A presents a multi-component transport study performed for specifying the design electrolyte composition. The above results of the study on zinc bromide-only, while somewhat academic, do serve to illustrate the strong ion association properties of zinc in zinc halide electrolytes.

FIGURE 23
TRANSFERENCE NUMBERS OF AQUEOUS ZINC BROMIDE
AT VARIOUS TEMPERATURES

6. COST STUDY OF AN 80kwh MODULE

A. INTRODUCTION

The design of an 80kWh stand-alone module has been the most emphasized phase of this program; all the other activities, construction, testing and optimization, have their basis in the design of the battery hardware. A limited cost study has been performed along with the design, to place constraints on selection of the materials of construction, their configuration and their manufacturing techniques, constraints arising from the requirement of building a cost-effective battery. The cost study was limited to purchased materials and components in compliance with the established cost guidelines, as explained below, and yielded a total of \$54/kWh.

The standardized costing methodology (SCM, Ref.5) specifies a semi-mature manufacturing technology. This would not be true of a facility producing 80kWh modules, since we do not foresee this module size being of any commercial interest for utility energy storage. The 80kWh module is of interest only as an intermediate step in hardware scaleup; performing a complete manufacturability study for it would be an unwise expenditure of resources, and the resulting factory costs would be misleading. Rather, we may decide on a module capacity of 1-2 MWh to achieve economies of scale and to improve the overall reliability of the battery. This cost study did, however, preserve the spirit of the SCM.

Manufacturability considerations were given to the design of every component, even though the manufacturing costs were not calculated. High volume, automated, and thus low cost techniques including injection molding for the electrode frames, grid spacers, and end plates, clicker punch press cutting of separators, and induction-heat sealing of electrodes into frames were not only envisioned but also actually employed in prototype part production. Off-the-shelf components, such as the plumbing and the static mixing column, were specified wherever possible. And finally, eventual suppliers were contacted early on to

provide the lead times required for any special items, such as the electrolyte solution, pumps, electrodes and the bromine complexing agent, to become standard, off-the-shelf items. We have established the feasibility of large volume, low cost manufacturability for every major component of the battery module. The battery manufacturing facility would thus be essentially an assembly plant for the purchased materials and components.

The cost study is presented in two sections, first a summary and discussion of the costs for the battery module, followed by a section containing the specific cost information for each component.

B. COST SUMMARY

The total estimated cost of purchased materials and components for an 80kWh module, based on the bipolar submodule design, is \$54/kWh (1979 dollars). This is for an annual production rate of 2500 MWh, as specified by the SCM. The three largest cost components (see Table 9) are the polybromide (\$9/kWh, 16% of total), the electrodes (\$10/kWh, 18% of total), and the module structure (\$9/kWh, 16% of total). Two other major contributors to the total cost are the electrolyte (\$4/kWh, 7% of total) and the electrolyte plumbing (\$5/kWh, 8% of total). The other eleven items comprise the remaining 35% of the total cost.

The cost data generally represent firm pricing of the components projected to the high volumes specified for the required annual production rate.

In the following section, the cost details will be presented component by component, appropriately referenced for source information where possible.

TABLE 9

80 kWh MODULE
PURCHASED MATERIALS AND COMPONENTS
-COST SUMMARY-

<u>ITEM</u>	<u>\$/kWh</u>	<u>PERCENT OF TOTAL COST</u>
Electrolyte	3.62	7
Polybromide	8.71	16
Electrodes	9.75	18
Separators	1.39	2
Frames	2.52	5
Grids	1.63	3
End Plates	2.00	4
Plumbing	4.57	8
Pumps	2.56	5
Bus Bars	1.00	2
Positive Electrolyte Tank	2.19	4
Negative Electrolyte Tank	0.90	2
Polybromide Tank	0.46	1
Mixer	3.13	6
Heat Exchanger	0.81	1
Containment	8.63	16
TOTAL	\$53.87/kWh	100

C. 80KWH MODULE PURCHASED MATERIALS AND COMPONENTS COST

The module component costs are individually discussed here in \$/kWh. All figures are anticipated high-volume prices from the vendors to be utilized upon commercialization. Many of the figures include expected technology advances due to volume production.

a. Electrolyte: The positive and negative sides of the electrolyte system each require 94 gallons of the following composition:

2M ZnBr_2
3M KCl
1M ZnCl_2

Each 80kWh module will require 304.04 pounds of ZnBr_2 costing \$0.67 per pound (Ref.6) at volume quantities. This results in \$203.71 per module or \$2.55/kWh.

The module will also require 138.8 pounds of KCl costing \$0.40 (Ref.7) per pound at volume quantities. This results in \$55.52 per module or \$0.69/kWh.

To complete the electrolyte solution 72.16 pounds of ZnCl_2 are required, costing \$0.425 (Ref.8) per pound at volume quantities. This results in \$30.67 per module or \$0.38/kWh.

The total electrolyte cost is \$289.90 or \$3.62/kWh.

b. Polybromide: Bromine storage is accomplished by a bromine complexing agent to which residual bromine is added. The module requires 359.33 lbs. of the compound combined with 183.98 pounds of bromine. The compound is volume priced at \$1.80 per pound (proprietary source) so the cost per module is \$646.80 or \$8.08/kWh. The bromine is volume priced at \$0.27 per pound (Ref.6) so the cost per module is \$49.67 or \$0.62/kWh. These combine to a total polybromide cost of \$696.47 per module or \$8.71/kWh.

c. Electrodes: The bipolar design utilizes a carbon electrode. There are 260 of these per 80kWh module. The estimated price per electrode is \$3.00 (proprietary source) bringing the electrode cost to \$9.75/kWh.

d. Separator: The DARAMIC® microporous separators are placed between each electrode pair and also act as end plate gaskets. There are 270 pieces per module with a price of \$0.16 per square foot (Ref.9) with each separator utilizing 2.5 sq.ft. Each piece also requires a secondary punching operation performed on an automated feed press at a cost of \$0.012 per piece (Ref.10). The total cost per piece is \$0.172 resulting in a module separator cost of \$1.39/kWh.

e. Cell Electrode Frames: An injection molded polypropylene frame is used for each electrode. There are 260 frames per module at a piece price of \$0.775 which translates into a cost of \$2.52/kWh (Ref.11).

f. Cell Spacer Grids: On either side of the carbon electrode, an injection molded polypropylene grid spaces it from the separator. The grids on the positive and negative sides, while of different design, are similarly priced at \$0.26 apiece. There are 250 positive and 250 negative grids resulting in a total cost of \$1.63/kWh (Ref.11).

g. Cell End Plates: There are 2 end plates per cell, thus 20 per 80kWh module. These parts are presently machined from block polypropylene but will be injection molded in commercialization. The \$8.00 piece price (Ref.11) reflects anticipated molding cost. This results in a cost of \$2.00/kWh.

h. Electrolyte Flow System Plumbing: The two independent electrolyte flow loops are constructed from commercially available extruded polypropylene pipe and injection molded polypropylene fittings. These parts are joined by heat welding. The various components and their costs are presented in Table 10.

TABLE 10

80kWh MODULE
PLUMBING PARTS LIST

<u>ITEM</u>	<u>NO. REQUIRED</u>	<u>PRICE/EACH</u>	<u>TOTAL PRICE</u>
1" pipe	20 ft.	8.60/20 ft.	\$ 8.60
2" pipe	60 ft.	16.60/20 ft.	49.80
2" elbows-90°	24	1.08	25.90
2" elbows-45°	2	1.08	2.16
2" tees	24	1.23	27.13
2" flanges	12	1.77	21.28
2" valves	2	15.43	30.86
2" flange gaskets	6	1.67	10.00
1"-2" adapter	20	1.61	32.27
1½"-2" adapter	2	1.71	3.42
1½" pipe nipple	1	1.19	1.19
1" elbows-90;	47	9.57	26.79
1" unions	48	2.45	117.52
½"-1" adapter	2	0.68	1.36
½" union	2	3.27	6.54

\$365.83

Price per kWh = $\$365.83/80 = \$4.57/\text{kWh}$.

Note: All items schedule 80 polypropylene.

i. **Electrolyte Pumps:** The module requires three magnetically coupled pumps for the negative electrolyte, positive electrolyte and polybromide systems. While pumping against similar head pressures, the electrolyte pumps handle higher volumes than the polybromide pump. The electrolyte pumps are priced at \$87.20 each (Ref.13) resulting in a combined price of \$2.18/kWh. The polybromide pump at \$30 apiece adds an additional \$0.375/kWh bringing the total pump cost to \$2.56/kWh. This pricing is based on specially designed and fabricated pumps that will have reached a mature state of development.

j. **Bus Bars:** The bipolar cells will produce 40A current and require a total of 30 feet of conductor per 80kWh module. Conductor prices for this current are \$2.40/ft (Ref.14). This has been adjusted to \$1.00/kWh to allow for termination connector costs.

k. Positive Electrolyte Tank: The positive electrolyte tank, which also acts as a settler to separate the polybromide phase after mixing, will be rotationally molded out of polypropylene. This will result in a piece price of \$95.00 (Ref.15). The polypropylene fiber mesh inserted in the tank to filter the polybromide out of solution will cost \$80.00 resulting in a total price of \$175.00 per module of \$2.19/kWh.

l. Negative Electrolyte Tank: The negative electrolyte tank is rotationally molded out of polypropylene and is totally enclosed. The price per tank is \$72.00 (Ref.15) resulting in a cost of \$0.90/kWh.

m. Polybromide Tank: The polybromide storage tank will also be a rotationally molded polypropylene vessel. The price for this tank is \$37.00 (Ref.15) resulting in a cost of \$0.46/kWh.

n. Electrolyte/Polybromide Mixer: The static mixer core used to combine the positive electrolyte and the polybromide will be an in-line unit with titanium cores and a polypropylene shell. The total cost of each mixer will be \$250.00 (Ref.16) for a cost of \$3.13/kWh.

o. Heat Exchanger: The heat exchanger is a titanium coil which is to be immersed in the negative electrolyte tank. There is one piece per module at a price of \$65.00 each (Ref.17). The resulting cost is \$0.81/kWh. An auxiliary system for controlling the flow of process cooling water is required, but it lies outside the scope of this study.

p. Module support structure: The submodules, tanks, pumps and plumbing are supported on a polypropylene skid by a steel support structure. The estimated cost for these is \$690 per module (Ref.18), or \$8.63/kWh; the steel support structure alone accounts for 70% of this total.

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APPENDIX A

**MULTICOMPONENT TRANSPORT
IN THE
ZINC-BROMINE BATTERY**

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A theoretical and experimental study of the ionic transport processes occurring in the zinc-bromine battery has been performed, to assist in selecting the optimum electrolyte composition and quantity for the battery design.

In designing a battery, an important goal is to provide sufficient electrode reactants to achieve the desired storage capacity. If all the reactants in the battery are available for the electrode reactions, the calculation becomes one of simple stoichiometry. Because of mass transport or other kinetic limitations, however, full utilization of the reactants is not generally feasible. Excess reactants must thus be provided, which, depending on their cost, can add significantly to the size and cost of the battery. These considerations apply equally to the zinc-bromine battery.

During charge of a zinc-bromine battery, zinc ions are reduced to zinc metal at the negative electrodes, and bromide ions are oxidized to bromine at the positives. We have found that excess electrolyte must be provided for the battery to achieve its design charge capacity. Otherwise, one of the electrodes (usually the negative) becomes highly polarized prior to end-of-charge because of reactant depletion. Closer examination of this depletion effect has uncovered two important facts.

First, the excursion in electrode polarization occurs when either the zinc or bromide ion concentration falls below 0.5 molar (the depletion concentration). Second, and somewhat surprising, is that, while zinc ion depletion is occurring at the negatives, its concentration in the positive electrolyte can be several molar, and greater than at start of charge. This concentration difference exists across the microporous separator, whose presence is required to limit the transport rate of bromine from the positive electrodes to the negatives, and thus limit the self-discharge rate. This phenomenon of zinc ion accumulation in the positive electrolyte prompted us to study, in more detail, the ionic transport processes occurring in the battery.

The objective of the study was to determine an electrolyte composition

and volume which provides sufficient ions for a charge to design capacity without depletion, balanced with the requirement for as high a utilization as possible to minimize its cost. The approach employed was a combination of experimentation using a laboratory cell system and a theoretical model based on the fundamental equation for multi-component transport in concentrated electrolyte solutions, each of which will be described next.

The experimental work was performed on a 32Wh cell system assembled for this testing; Figure 1 is a diagram of the setup. The cell, containing one negative electrode, one positive, and one separator, was connected to electrolyte circulation loops for both negative and positive electrolyte flow. The electrolyte volumes in the reservoirs were kept suitably small, to maintain a proper ratio of volume to cell capacity and thus insure a realistic degree of electrolyte utilization. Bromine storage was via complexation in a polybromide phase external to the cell stack (not shown in Figure 1). The experiments consisted of charging the cell at a constant current density ($40\text{mA}/\text{cm}^2$, the design value) to full capacity, i.e. $200\text{mAh}/\text{cm}^2$, while sampling both electrolytes for quantitative analysis at start of charge and every hour to end of charge. The specie concentrations were determined and plotted versus time into charge, for comparison with the predictions of the theoretical model.

The basis of the theoretical model is the multicomponent diffusion equation for concentrated electrolytes (Figure 2). This relates the flux of ions, expressed as velocity differences on the right-hand side of the equation, to the driving force, i.e. the gradient of electrochemical potential, on the left-hand side. The diffusion coefficient characterizes the interactions of the species present in the solution. Specie velocities can be converted to molar fluxes by multiplying by the specie molar concentrations. When applied to the physical system at hand, this equation can be used to predict what the specie fluxes will be.

In the present case, the transport equation is applied to the electrolyte solution in the microporous separator, in which the driving forces for transport are manifest. That is, the electrolyte solution on either side of the separator is well mixed and thus of uniform composition.

However, concentration differences can and do exist between the negative and positive electrolytes, giving rise to concentration gradients across the separator. A resistive potential gradient also exists across the separator during passage of current. It is these gradients which provide the driving forces for ionic transport, and which, when summed, comprise the gradient of electrochemical potential.

The gradient of electrochemical potential is defined in Figure 3, equation 1. As stated above, it is the sum of concentration and potential gradients, plus a correction term for activity coefficients, which was neglected here for simplicity. Justification for this will come later. A second and more obvious simplification was to reduce the equations to one dimension "x", that normal to the plane of the separator. This is a good assumption when the current distribution in the cell is uniform, which was the case here. A combination of the transport equation and the definition of the electrochemical potential gradient yields, upon rearrangement, the key equation for the model (Figure 3, equation 3), which directly relates the specie fluxes to the concentration and potential gradients. Equation 3 can be applied to each specie present in the electrolyte. However, there are one less independent equations than there are species present; the final relationship is provided by the Gibbs-Duhem equation (equation 4). In the flux equations, the potential gradient must first be guessed, as will be described later on, but the concentration gradients are always known, as will be discussed next.

The composition of the electrolyte is known at start of charge. Additionally it is uniform, positive to negative, so no concentration gradients exist. From that point on into charge, the composition of both electrolytes is computed at regular intervals (15 minutes) by solving the transport equations and using the newly calculated fluxes to "update" the compositions from the previous time interval via mass balance calculations (Figure 4). That is, each specie concentration change over the time interval is the sum of the flux term (gain or loss, depending on direction) and an electrode reaction term (for zinc at the negative and bromide at the positive). This sequence is used to step the composition through time. It is a straightforward procedure, but it does require knowledge of which

species are actually present in the electrolyte for accurate solution of the flux equations.

Zinc ions form strong complexes with halide ions in zinc halide electrolytes; Figure 5 depicts the various combinations possible. Instead of just three species, i.e. zinc, chloride and bromide, up to fourteen additional complex species can exist. Their concentrations are determined by the equilibrium constants for the various complexation reactions and the nominal composition of the electrolyte solution. This complexation phenomenon makes rigorous solution of the transport equations virtually impossible. The problem is not the large number of species (and thus equations), because a high speed digital computer is ideal for such work. Rather, it is the lack of complete equilibrium constant information, the generation of which could easily comprise a multi-year effort. To circumvent this problem, some simplifying assumptions were made which, it was hoped, would be validated by the experimental data.

The complexation process was reduced, for the purposes of the model, to one of extremes (Figure 6). That is, all zinc and chloride ions available were assumed to form tetra-chloro zincate, which was believed to be the strongest complex. If the chloride were in excess, it and the bromide would remain as simple ions. If zinc were in excess, it would form, with bromide, tetra-bromozincate to completion. Whichever was in excess would then remain as the simple ion (zinc or bromide). The potassium ions and water molecules were assumed to be un-complexed throughout. Transport equations were then written for each of the resulting species, for numerical solution by the computer.

The computer program comprised a series of nested iteration loops (Figure 7). The innermost loop involved a Gauss-Seidel iteration to convergence for solution of the coupled, linear, transport equations, based on the known concentrations (and these known concentration gradients through the separator) and an assumed potential gradient across the separator.

Upon convergence, the ionic fluxes were summed to calculate the total current density through the separator for comparison with the specified

current density. Iteration proceeded in this next outer loop, using the potential gradient as the adjustable parameter, until current density compliance was achieved. The specie fluxes were then used to adjust the electrolyte concentrations for the time interval at hand. The newly calculated concentrations were then used back in the innermost loop to re-solve the flux equations for the next time interval. This last, outtermost loop served to step the program through time to provide the concentration profiles required. These predicted profiles were then compared with the actual data for validation of the model.

The first experimental cycle was performed using the up-till-then preferred electrolyte solution, 2.5M zinc bromide and 3M potassium chloride. The data and predicted profiles are presented in Figures 8A-D. Two problems were encountered with this electrolyte formulation.

First, zinc ion depletion occurred in the negative electrolyte prior to the end of the scheduled five hour charge (Figure 8A), which precluded the attainment of design capacity by 15%. It was observed that, just after four hours of charge, the cell voltage began to rise exponentially as the result of negative electrode polarization; charging was secured when the cell voltage exceeded 2.2V. Second, bromide ion utilization was only 45% (see Figure 8B), which is too low for economic practicality. The good news, however, was that the model adequately predicted the concentration profiles, and helped explain the transport phenomena observed.

The behavior of zinc ion, i.e. its accumulation on the positive side concurrent with its depletion on the negative, is attributable to the anionic migration of the tetra-halo zincate species from the negative to the positive side during charge. The nearly constant zinc ion concentration on the positive side near end of charge indicates a balance of the migration term with diffusion of free zinc ions back to the negative side, owing to the concentration gradient which has built up.

Based on this explanation, it was clear that excess zinc ions would be needed to achieve a full charge. Zinc chloride addition was preferred over zinc bromide because the chloride salt is one fifth the cost of the bromide

salt per mole. The optimal composition of the electrolyte was yet to be determined, and this is where the model paid for itself.

Numerous computer-simulated battery charges were performed, with a variety of electrolyte combinations, in a trial and error process to determine favorable combinations. These took only seconds to perform on the computer, while the same number of actual laboratory runs would have taken weeks. As a final result, the most favorable electrolyte specification was as follows:

Composition

2M ZnBr_2 /1M ZnCl_2 /3M KCl

Volume

5 ℓ /kWh for each the negative and positive electrolyte

This formulation was tested in a second charge of the test cell; the results were very encouraging (Figures 9A-D). The full five hour charge was achieved without zinc ion depletion (Figure 9A). Bromide ion utilization was up as well (to 55%), but still not as high as desired; the practical maximum for this is probably 70%. And the accuracy of the model is even better than for the first run.

The above specification has, because of its favorable performance, been chosen for the electrolyte. Some "fine tuning" will obviously take place as the system design matures, particularly in the direction of increasing the bromide ion utilization, to lower the installed cost of the battery.

FIGURE 1

MULTICOMPONENT DIFFUSION IN CONCENTRATED SOLUTIONS

$$C_i \nabla \mu_i = RT \sum_j \frac{C_i C_j}{C_T \mathcal{D}_{ij}} (V_j - V_i)$$

μ_i Electrochemical Potential
 V_i Velocity
 $\mathcal{D}_{ij}$ Diffusion Coefficient

Flux of Species i : $N_i = C_i V_i$

Substituting:

$$C_i \nabla \mu_i = RT \sum_j \frac{C_i N_j - C_j N_i}{C_T \mathcal{D}_{ij}} \quad (1)$$

GOULD ➡

FIGURE 2

THE GRADIENT OF ELECTROCHEMICAL POTENTIAL:

$$\nabla \mathcal{H}_i = RT \nabla \ln C_i + z_i F \nabla \phi + RT \nabla \left(\ln f_i - \frac{z_i}{z_n} \ln f_n \right) \quad (2)$$

Combining (1) and (2), Rearrange, Neglect Activity Coefficients, Reduce to One Dimension:

$$N_i \left(\frac{1}{C_T} \sum_{j \neq i} \frac{C_j}{D_{ij}} \right) - \frac{C_i}{C_T} \sum_{j \neq i} \frac{N_j}{D_{ij}} = - \frac{dC_i}{dx} - \frac{C_i z_i F}{RT} \frac{d\phi}{dx} \quad (3)$$

Gibbs-Duhem:

$$\sum_{i=1}^n C_i \nabla \mathcal{H}_i = 0 = \sum_{i=1}^n RT \frac{(C_i N_j - C_j N_i)}{C_T D_{ij}} \quad (4)$$

GOULD →

FIGURE 3

CONCENTRATION GRADIENTS:

$$\frac{dC_i}{dx} = \frac{C_i^p - C_i^n}{L} ; \text{Known}$$

MASS BALANCE:

$$Vn \frac{dC_i^n}{dt} = -N_i A + \frac{IS_i}{n} ;$$

Where $\sum S_i M_i \rightarrow ne$

$$\left. \begin{array}{l} \text{eg: } \text{Zn} - \text{Zn}^{+2} \longrightarrow 2e \\ \text{for } \text{Zn}^{+2} ; S_i = -1 \quad n=2 \end{array} \right) Vn \frac{dC_{\text{Zn}}^n}{dt} = -N_{\text{Zn}} A + \frac{I(-1)}{(2)}$$

GOULD →

FIGURE 4

WHICH SPECIES ARE PRESENT?

ELECTROLYTE: $\text{ZnBr}_2 + \text{KCl}$

COMPLEXATION:

VALENCE SPECIES

+2	Zn					
+1	ZnCl	ZnBr				
0	ZnCl_2	ZnClBr	ZnBr_2			
-1	ZnCl_3	ZnCl_2Br	ZnClBr_2	ZnBr_3		
-2	ZnCl_4	ZnCl_3Br	ZnCl_2Br_2	ZnClBr_3	ZnBr_4	

GOULD ➔

FIGURE 5

COMPLEXATION ASSUMED

GOULD ➔

FIGURE 6

COMPUTATIONAL FLOW CHART

FIGURE 7

ZINC ION BEHAVIOR, CYCLE 1
(2.5M ZnBr_2 , 3M KCl)

FIGURE 8

BROMIDE ION BEHAVIOR, CYCLE1
(2.5M ZnBr₂, 3M KCl)

GOULD →

FIGURE 9

POTASSIUM ION BEHAVIOR, CYCLE 1
(2.5M ZnBr_2 , 3M KCl)

FIGURE 10

GOULD →

A-17

FIGURE 11

GOULD →

SPECIES TRANSPORT DURING CHARGE

FIGURE 12

A-19

FIGURE 13

BROMIDE ION BEHAVIOR, CYCLE 2
(2M ZnBr_2 , 1M ZnCl_2 , 3M KCl)

GOULD →

FIGURE 14

POTASSIUM ION BEHAVIOR, CYCLE 2
(2M ZnBr_2 , 1M ZnCl_2 , 3M KCl)

GOULD →

FIGURE 15

CHLORIDE ION BEHAVIOR, CYCLE 2 (2M ZnBr_2 , 1M ZnCl_2 , 3M KCl)

FIGURE 16

APPENDIX B

CYCLE TEST CELL DATABASE

PREPARATIONS

PREPARATION NUMBER

PREPARATION 1. H_2SO_4 ETCH
2. RUTHENIZED STD. PROCEDURE
ETC.

COMPONENTS

COMPONENTS

TYPE CODE

TYPE 1. TITANIUM (POROUS)
2. $2\text{MZNBR}_2/4\text{MKCL}$
ETC.

CELL

CELL NUMBER
STARTING DATE
CHARGE CURRENT
ETC.

CELL PARTS

PART NUMBER
PART
PART TYPE CODE
PREPARATION NUMBER

CYCLE

CYCLE NUMBER
CYCLE DATE
VOLTAIC EFFICIENCY
COULOMBIC EFFICIENCY
ENERGY EFFICIENCY

MAINTENANCE

CYCLE NUMBER
PH
BROMINE CONCENTRATION
ETC.

RELIABILITY

CYCLE NUMBER
FAILURE CODE
FAILURE TIME
ETC.

APPENDIX - C

DETERMINATION OF ZONYL FSN BY THE COLORIMETRIC

COBALT THIOCYANATE METHOD

A sensitive method for the determination of polyethylene oxide derivatives (ZONYL FSN) results from their complex formation with cobalt thiocyanate followed by measurements of the absorbance of the blue complex. The complex formed between the non ionic surfactant (ZONYL FSN) and cobalt thiocyanate is extractable into chloroform and has absorption maxima at 620 nm and at 318.5 nm with the absorptivity being sixfold greater at the lower wavelength.

Apparatus

- Spectrophotometer, suitable for use at 318.0 nm and at 620 nm and equipped with 1 and 5 cm cells.
- Separatory funnels, equipped with Teflon stopcocks.

CAUTION!

All glassware must be clean and free of surfactants. Wash all glassware initially with an ionic-type detergent, rinse well with water, then 5% alcoholic hydrochloric acid solution; follow with additional water and methanol rinses. Segregate this glassware and use only for this purpose.

Reagents

ZONYL FSN, from DuPont

Chloroform, spectral grade

Sodium chloride, reagent grade

Cobaltous nitrate, reagent grade

Ammonium thiocyanate, reagent grade

Ammonium cobalt thiocyanate reagent

Prepare by dissolving 15g of $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, 100g of NH_4SCN , and 80g of NaCl in 500 ml of distilled or deionized water.

Ammonium hydroxide, reagent grade

Ammonium Chloride, reagent grade

pH10 Buffer solution. Dissolve 70g of NH_4Cl in 570 ml of ammonium hydroxide and dilute with deionized water to 1 liter. Transfer to a polyethylene bottle.

ZONYL FSN, Standard solution. Dissolve 1.000g of ZONYL FSN in deionized water and dilute to 1 liter. 1ml of this standard solution contains 1mg of ZONYL FSN.

Procedure

- 1) Take a sample of electrolyte containing an appropriate amount of ZONYL FSN (anywhere from 1 to 20 mg). Place the sample in a 250 ml separatory funnel.
- 2) Add an equal volume of pH 10 buffer to the solution above. Shake well until zinc is dissolved. Let the solution cool to room temperature.
- 3) Add 10 ml of Chloroform; shake for 1 to 2 minutes vigorously, using occasion venting. Allow the layers to separate.
- 4) Withdraw the lower, chloroform, phase into a 125 ml separatory funnel, being careful not to transfer any droplets of water.
- 5) Add to the chloroform layer 10ml. of ammonium cobaltothiocyanate reagent, 2.5g of NaCl, and shake vigorously for 1-2 minutes. Let stand for 5 minutes.
- 6) Drain a portion of the lower chloroform layer in a spectrophotometer cell. Read the absorbance at 620 nm or 318 nm. Correct for the absorbance of a reagent blank.
- 7) Determine the ZONYL FSN content in the sample by comparing to a calibration curve.

Preparation of Calibration Curve

- 1) Transfer into 250 ml separatory funnels 2,4,6,8 and 10 ml of the ZONYL FSN standard solution. Adjust the volume to 25 ml with deionized or distilled water.
- 2) Proceed with steps (2) to (6) of the procedure.
- 3) Plot the calibration curve. (Absorbance vs. mg ZONYL FSN).

Calculations

Calculate the non ionic surfactant concentration from the corrected absorbance as follows:

$$\text{ZONYL FSN, ppm} = \frac{\text{mg ZONYL FSN from calibration curve} \times 1000}{\text{sample volume (ml)} \times \text{sample density (g/ml)}}$$

APPENDIX D

BROMINE STORAGE MODEL

Notation:

OR	amount of organic complexing agent	mole
R	by-pass rate	l/sec
F	feed rate from reservoir	l/sec
TF	total flow rate through battery	l/sec
C1	inlet bromine concentration to battery	g/l
C2	outlet bromine concentration from battery	g/l
C3	outlet bromine concentration from settler	g/l
V	volume of battery (positive side)	l
t	time	sec
X _o	initial bromine/organic ratio	--
X	bromine/organic ratio	--
I	operating current	Amp
I _o	equivalent operating current (converted from operating current to production or consumption rate of bromine)	g/sec
K1, K2, K3	constants	
a, b	constants obtained from regression for relating equilibrium aqueous phase bromine concentration to polybromide bromination level (see Figure D-2).

$$(R+F)C_1 + I_o - (R+F)C_2 = V \frac{dC_2}{dt} \quad \text{EQ(1)}$$

$$(R+F)C_1 = R * C_2 + F * C_3 \quad \text{EQ(2)}$$

$$C_3 = a * e^{bX(t)} \quad \text{EQ(3)}$$

$$X(t) = X_o + \left(\frac{I_o}{160 * OR} \right) t \quad \text{EQ(4)}$$

EQ(1) & EQ(2) are obtained from material balance of bromine on System 1 & System 2 as shown above. EQ(3) relates the equilibrium bromine concentration in the electrolyte to the bromine/organic ratio of the oil phase. EQ(4) relates the bromine/organic ratio to time.

Substitute EQ(2) into EQ(1)

$$F(C_3 - C_2) + I_o = V \frac{dC_2}{dt} \quad \text{EQ(5)}$$

Substitute EQ(4) into EQ(3)

$$C_3 = a * e^{bX_o} * e^{\left(\frac{bI_o}{160 * OR} \right) t} \quad \text{EQ(6)}$$

Substitute EQ(6) into EQ(5)

$$F(a * e^{bX_o} * e^{(\frac{bI_o}{160 * OR})t} - C_2) + I_o = V \frac{dC_2}{dt} \quad \text{EQ(6)}$$

or

$$\frac{dC_2}{dt} + (\frac{F}{V})C_2 = (\frac{F * a}{V} * e^{bX_o})e^{(\frac{bI_o}{160 * OR})t} + \frac{I_o}{V} \quad \text{EQ(7)}$$

let

$$K_1 = \frac{F}{V}$$

$$K_2 = \frac{F * a * e^{bX_o}}{V}$$

$$K_3 = \frac{bI_o}{160 * OR}$$

then EQ(7) becomes

$$\frac{dC_2}{dt} + K_1 * C_2 = K_2 * e^{K_3 t} + \frac{I_o}{V} \quad \text{EQ(8)}$$

$$\text{I.C. } t = 0, \quad C_2 = C_1 = C_3$$

$$= a * e^{bX_o}$$

$$= \frac{K_2}{K_1}$$

Solve EQ(8) with the initial condition

then

$$C_2 = (\frac{K_2}{K_1 + K_3})(e^{K_3 t} - e^{-K_1 t}) + (\frac{K_2}{K_1})e^{-K_1 t} + (\frac{I_o}{V * K_1})(1.0 - e^{-K_1 t}) \quad \text{EQ(9)}$$

$$C_3 = a * e^{bX_o} * e^{K_3 t} \quad \text{EQ(10)}$$

Once C2, C3 have been determined, then

$$C_1 = (R * C_2 + F * C_3) / (R + F) \quad \text{EQ(11)}$$

FIGURE D-2
EQUILIBRIUM PARTITION PROPERTIES BETWEEN
AQUEOUS AND POLYBROMIDE PHASES (LAB DATA)

APPENDIX E

PHYSICAL CHEMISTRY OF THE ZINC-BROMINE BATTERY II. TRANSFERENCE NUMBERS OF AQUEOUS ZINC BROMIDE

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ABSTRACT

The zinc-bromine battery is under development by Gould Inc. for use in bulk energy storage. In the design and optimization of this system it is important to know the transport behavior of zinc during cycling. The cation transference number of zinc in concentrated halide solutions is negative, and this peculiarity can substantially influence the operation of zinc-halogen cells. In this study the transference number of zinc was measured in the electrolyte of the zinc-bromine battery, as a function of temperature and electrolyte composition. The results are interpreted in terms of complex ion formation, and the importance of the results in the design of the zinc-bromine battery is discussed.

In recent years considerable interest has been expressed in the secondary zinc-bromine battery for bulk energy storage and vehicular propulsion (1-7). In the design and optimization of any new battery system, a large amount of physicochemical and electrochemical data must be collected. This is particularly true of the zinc-bromine system, in which unique problems arise owing to the high solubility of bromine in concentrated bromide solutions. We have undertaken a systematic study of the physical chemistry of the zinc-bromine battery, including chemical, thermal, and electrochemical aspects. This paper is the second of a series in which measurements of fundamental properties of the zinc-bromine system will be reported.

During cycling of a zinc-bromine battery large changes in zinc bromide concentration occur, and solution effects play an important role in determining several properties of interest. The first paper in this series (8), denoted by I hereafter, reported activity coefficients of aqueous zinc bromide derived from measurements of potentials of the cell without liquid junction,

The activity coefficients are useful in predicting the temperature and concentration dependence of the open-circuit potential, in calculations of thermal properties (9), and in electrochemical modeling studies (10).

In the present work the potentials of the concentration cells with liquid junction

were measured and combined with the results of I to yield values of the cation and anion transference numbers. These quantities should be useful in understanding the concentration changes which occur in the positive and negative electrolytes during cycling of the zinc-bromine battery.

Practical considerations dictate the ranges of temperature and composition over which properties of zinc bromide solutions are required. Zinc-bromine batteries for bulk energy storage will undoubtedly operate above ambient temperature because of electrical inefficiency of the charge-discharge cycles. Economics demands that the volume of electrolyte be minimized to reduce storage tank costs, so the concentration of zinc bromide in the discharged battery must be high. The ranges of temperature and molality chosen for this study were 0°C to 35.9°C and 0.5 mol·kg⁻¹ to 4.0 mol·kg⁻¹.

EXPERIMENTAL

Zinc bromide was obtained from the Dow Chemical Company as a 60 wt.% aqueous solution with specific gravity 1.894 at 25°C. This material was stirred overnight with powdered zinc, then stirred with activated charcoal and filtered. Analysis of the purified material by atomic absorption spectroscopy at Gould Laboratories and the manufacturer's analysis are shown in Table I. Small additions of hydrobromic acid gave a stock solution in which the zinc:bromide ratio was 1:2 within experimental error of ±0.08 percent, and from which no precipitate formed upon dilution.

Silver, silver bromide electrodes were of the thermal-electrolytic type, prepared by the procedure of Bates (11). Bias potentials among these electrodes were less than 0.010 mV. Zinc amalgam electrodes were made from 0.99999 purity zinc rods sealed with epoxy resin in Pyrex glass tubes (12).

Two types of Pyrex glass cells were studied for use in the measurements. The first type, which is rather complicated to construct and to use, was modeled after the cell of MacInnes. (13) A much simpler 2-compartment cell was constructed from two vertical 20 mm I.D. Pyrex tubes joined by a length of 6 mm I.D. tubing extending from the bottom of one compartment to a position near the top of the second compartment. A stopcock with a Teflon plug in the middle of the vertical part of the connecting tube was used to form the liquid junction.

Results using the two types of cells were identical within the experimental error of about 0.008 mV, and the simple cell was used in all of the measurements reported here.

Separate solutions of zinc bromide were prepared for each experiment by addition of a weighed amount of water to a weighed amount of stock solution. The stock solution was analyzed gravimetrically by precipitation of silver bromide and volumetrically by differential titration with ferrocyanide for zinc. Immediately before use solutions were thoroughly purged with nitrogen; the cell was filled and the electrodes were inserted in the cell compartments inside a nitrogen-filled glove bag. Cells were immersed in a water bath whose temperature was maintained within $\pm 0.02^\circ\text{C}$ and read to $\pm 0.01^\circ\text{C}$ with a series of ASTM calibrated mercury-in-glass thermometers. The measuring instrument was a Guildline model 9577 $7\frac{1}{2}$ -digit voltmeter, which was read to 0.001 mV.

The reproducibility of the electrodes was studied in I. Originally measurements had been planned over the range of 0°C to 50°C , but exposure to 50°C caused a lowering of the potential of about 1 mV when the cells were returned to room temperature. Restriction of the highest temperature to 35.9°C eliminated the hysteresis problem.

RESULTS AND DISCUSSION

The results for cell [2] with silver, silver chloride electrodes are given in Table II. The molality range extends from $0.5 \text{ mol}\cdot\text{kg}^{-1}$ to $4.0 \text{ mol}\cdot\text{kg}^{-1}$, and the difference between the molalities m_1 and m_2 of the cell compartments was always $0.5 \text{ mol}\cdot\text{kg}^{-1}$. Results for cell [3] at the extremes and the middle of the molality range are presented in Table III. The measurements with zinc amalgam electrodes were performed primarily to check the reliability of the silver, silver chloride electrode results. The analysis of measurements on both cells requires a relation between the observed potential and the transference numbers of the ions.

The expression for the potential difference dE between the electrodes of cell [2] for an infinitesimal molality difference dm in the two cell compartments is

$$dE = (3RT/2F)t_+d\ln m_{\pm} \quad [4]$$

where R is the gas constant, T is the absolute temperature, F is Faraday's constant, t_+ is the cation transference number, and $\gamma_{\pm}$ is the mean activity coefficient of the ions. For a finite difference Δm in the molality of the two compartments we define the integral cation transference number $\bar{t}_+$ by

$$\bar{t}_+ = (2FE/3RT)/\Delta\ln m_{\pm} \quad [5]$$

To calculate a value of $\bar{t}_+$ from the observed cell potential E requires either the potential of the corresponding cell without liquid junction or, equivalently, the ratio of the activity coefficients in the two cell compartments.

Figure 1 shows the results obtained for $\ln \gamma_+$ from cell [1] in I. From these activity coefficients and the cell potentials of Table II, the integral transference number $\bar{t}_+$ were calculated using Equation [5]. An examination of the concentration dependence of $\bar{t}_+$ shows that, within experimental error, $\bar{t}_+$ is equal to t_+ at the geometric mean of the molalities of the two cell compartments. For molalities greater than $1.0 \text{ mol} \cdot \text{kg}^{-1}$ $\bar{t}_+$ may be taken as t_+ at the arithmetic mean of the two molalities, with an error of less than 0.004 in the transference number.

The results of the calculations of t_+ are shown in Figure 2, where the transference number t_+ is plotted versus the molality of zinc bromide. Because the temperature dependence of t_+ is small, to avoid overlap the curve for each temperature has been displaced downward by 0.100 from the curve for the next lower temperature. Thus, each tick mark on the ordinate represents the same value of 0.400. The circles show the values obtained for cell [2], while the triangles represent values computed from the cell potentials for cell [3]; ~~Table III~~, the equation corresponding to Eq. [5] for the anion transference number, and the relation

$$t_+ + t_- = 1 \quad [6]$$

The square shown on the curve for 22.9 C shows the value of 0.404 calculated from the equivalent conductances of the ions at infinite dilution (14) at 25°C.

The transference number t_+ rapidly decreases with increasing molality and becomes negative between 2.5 and 3.0 $\text{mol} \cdot \text{kg}^{-1}$. Figure 2 shows that at 25°C the molality dependence of t_+ for zinc chloride [15] and iodide [16] is similar to that for the bromide. The negative cation transference numbers in concentrated solutions of the zinc halides are consistent with the formation of anionic complexes of the type $\text{ZnX}_n^{(2-n)-}$, where $n > 2$. Evidence for the predominance of the species ZnX_4^{2-} comes from isopiestic vapor pressure measurements (17) and, more directly, from Raman studies of aqueous solutions of the chloride (18, 19), bromide (19, 20) and iodide (18, 21).

Suppose the assumption is made that in concentrated aqueous zinc bromide the complexation reaction

goes nearly to completion. Then an analysis of the processes which lead to Gibbs energy changes in cell [2] shows that the apparent

cation transference number t_+ (app) is actually the difference in the transference numbers of the zinc and tetrabromozincate ions,

$$t_+ (\text{app}) = t_{\text{Zn}^{2+}} - t_{\text{ZnBr}_4^{2-}} \quad [8]$$

This relation was noted by Robinson and Stokes (22). For ZnI_2 solutions Eq. [8] gives zinc ion transference numbers which diminish with increasing molality and reach about 0.22 at $10 \text{ mol} \cdot \text{kg}^{-1}$. This behavior seems plausible on the basis of the behavior of similar 2-2 electrolytes such as zinc, magnesium and cadmium sulfates. A more quantitative approach to complexation equilibrium in zinc bromide solutions will not be attempted here.

The application of the results for transference numbers of zinc bromide to the operation of the zinc-bromine battery is not straightforward, but some insight can be gained by considering a simplified case. For a battery with a microporous separator and an electrolyte containing only concentrated aqueous zinc bromide, the cell reaction at the beginning of discharge can be written

where t_1 and t_2 are the transference numbers of Zn^{2+} and ZnBr_4^{2-} , respectively; and "pos" and "neg" refer to the positive and negative electrolytes. The concentration of bromine is assumed to be on the order of 10^{-2} mol/l , so that the fraction of current carried by the Br_3^- ion is negligible. Reaction [9] shows the tendency of ion migration to increase the concentration of zinc bromide (or "zinc tetrabromozincate") in the negative electrolyte. After an appreciable concentration gradient of zinc species has built up, diffusion across the separator will oppose the effect of migration and tend to equalize the zinc concentrations in the two electrolytes. On charge the direction of ion migration will be reversed, and the negative electrolyte will be depleted of the zinc species required for deposition of the metal.

As we have seen, the simplified cell reaction [9] with $t_2 > t_1$ predicts zinc migration away from the electrode at which it is deposited on charge. Does this imply the possibility of incomplete zinc utilization because of mass transfer limitations near the end of charge? In a practical battery containing only zinc bromide as the electrolyte the solute concentration will decrease on charge to a concentration where the apparent cation transference number is no longer negative. Then both migration and diffusion will favor movement of soluble zinc species toward the zinc electrode, and severe mass transfer limitations are unlikely. However, the addition of a supporting electrolyte can alter these conclusions. In particular, addition of a high concentration of a halide-containing electrolyte

assures that nearly all of the soluble zinc species will be bound up in anionic complexes which migrate away from the zinc electrode during charge. Experimental measurements are now in progress in our laboratory to assess the influence of ion transport on the operation of zinc-bromine cells with and without supporting electrolytes.

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TABLE I. ANALYSIS OF ZINC BROMIDE

<u>Impurity</u>	<u>Concentration, *ppm</u>	<u>Concentration, **ppm</u>
Ca	12	ND
Mg	23	ND
Na	10	ND
Sn	ND	<1
Cd	3	3
Si	4	ND
Cu	5	1
Fe	2	1
Pb	ND	1
Mn	ND	<1

* Analysis by Dow Chemical Company

** Analysis at Gould Laboratories

ND Not Determined

TABLE II. EXPERIMENTAL POTENTIALS OF CELL [2]

$m_1/\text{mol}\cdot\text{kg}^{-1}$	$m_2/\text{mol}\cdot\text{kg}^{-1}$	E/mV						
		0.00°C	5.50°C	11.00°C	17.00°C	22.90°C	29.40°C	35.90°C
4.000	3.500	-0.902	-0.921	-0.959	-1.004	-1.037	-1.070	-1.093
3.500	3.000	-0.414	-0.432	-0.459	-0.475	-0.497	-0.527	-0.557
3.000	2.500	0.237	0.209	0.169	0.130	0.082	0.038	-0.004
2.500	2.000	0.974	0.938	0.895	0.840	0.787	0.723	0.666
2.000	1.500	2.026	1.993	1.954	1.917	1.848	1.774	1.698
1.500	1.000	4.298	4.227	4.138	4.038	3.921	3.794	3.656
1.000	0.500	8.584	8.683	8.725	8.707	8.658	8.556	8.438

TABLE III. EXPERIMENTAL POTENTIALS OF CELL [3]

$m_1/\text{mol}\cdot\text{kg}^{-1}$	$m_2/\text{mol}\cdot\text{kg}^{-1}$	E/mV						
		0.00°C	5.50°C	11.00°C	17.00°C	22.90°C	29.40°C	35.90°C
4.000	3.500	8.275	8.331	8.394	8.461	8.518	8.573	8.631
2.500	2.000	8.557	8.558	8.557	8.557	8.551	8.560	8.554
1.000	0.500	21.885	21.809	21.644	21.394	21.081	20.652	20.168

FIGURE 1
LOGARITHM OF THE MEAN ACTIVITY COEFFICIENT
OF AQUEOUS ZINC BROMIDE AT VARIOUS TEMPERATURES

FIGURE 2
 TRANSFERENCE NUMBERS OF AQUEOUS ZINC BROMIDE
 AT VARIOUS TEMPERATURES

FIGURE 3
TRANSFERENCE NUMBERS OF AQUEOUS ZINC HALIDES AT 25°C