FLOWING ELECTROLYTE BATTERIES. TEST METHODS AND RESULTS

PAUL C. BUTLER and CARL E. ROBINSON

Sandia National Laboratories, Division 2525, P.O. Box 5800, Albuquerque, NM 87185 (U.S.A.)

Introduction

Prototype zinc/bromine, zinc/ferricyanide, and iron/chromium redox flowing electrolyte cells and batteries have been tested at Sandia National Laboratories since 1980 in order to evaluate development program progress. These units have been subjected to baseline tests to determine stable operating conditions, a factorial test matrix to evaluate the sensitivity of electrochemical efficiency to changes in operating conditions, and life cycle tests. In some cases, stable baseline performance was not obtained and, therefore, the other test modes were not performed. Also, some batteries failed prior to completion of the factorial test matrix. In three cases, however, the entire test regime was implemented and completed; these batteries are still on life cycle test.

Most of this work has concentrated on the Exxon Research and Engineering Company zinc/bromine technology. Zinc–bromine batteries from Gould/Energy Research Corporation and GEL have also been evaluated. Electrically, these batteries have ranged in size from 12 to 30 V and 500 W h to 6 kW h, at about the $C/3$ rate. Variables in the factorial test regimes have been charge and discharge rate, amount of zinc loading and, in some cases, temperature. Coulombic, voltaic, and energy efficiencies were the response variables. Data obtained in these tests have been reduced, and significant main effects and interactions have been calculated. Statistically significant battery performance prediction equations have also been derived.

This paper will review the test methods used to evaluate these batteries. The factorial test matrix and its results will be described. Other necessary aspects of prototype testing, such as operation and maintenance issues, will be discussed.

Test facilities

Sandia utilizes a computer-controlled test facility. A Hewlett-Packard 1000 mini-computer serves as the master computer for test control and data reduction tasks. It is interfaced to Hewlett-Packard 80 series personal computers which control individual tests, perform data acquisition, and transmit data to the master computer. All computer software was developed in-house during a four-year period. A Sandia-designed, computer-controlled relay interface with hardware disconnect circuits is used to select charge or discharge and closed or open circuit operation. Commercially available power supplies and loads are used for charging and discharging a wide variety and sizes of cells and batteries.

Test methods

Six different flowing electrolyte units have been evaluated in recent years [1] representing two technologies and three developers. These cells and batteries are described in Table 1. Two Exxon zinc/bromine batteries, which were initially tested in 1982, continue. A GEL zinc/bromine battery was delivered to Sandia in late 1984 and first tested in December. One of two Lockheed zinc/ferricyanide cells placed on test in 1983 continued, while the other failed and was replaced by a new cell during 1984. The evaluation process consisted of electrical cycling under various test regimes, chemical analysis of electrolyte during operation, and mechanical analysis of system components.

TABLE 1

Flow batteries tested at Sandia since 1982

SNL ID no.	Type	Developer	Start test	Mean discharge voltage	Capacity (A h)
301	Zinc/bromine	Exxon	10/82	12	40 at *C*/3
300	Zinc/bromine	Exxon	10/82	30	40 at *C*/3
394	Zinc/bromine	GEL	12/84	25	130 at *C*/4
344	Zinc/ferricyanide	Lockheed	09/83	1.6	3.5 at *C*/2
345	Zinc/ferricyanide	Lockheed	09/83	1.6	3.5 at *C*/2
380	Zinc/ferricyanide	Lockheed	04/84	1.6	3.5 at *C*/2

The electrical cycle test regime consisted of baseline, parametric, and qualified life testing. Baseline tests were used to duplicate developer test conditions to verify proper battery operation and capacity. Open circuit capacity losses were measured in some cases. Once stable operation was assured, a parametric cycle test plan was implemented. The effect on efficiency and general operation was determined. After completion of these tests, a qualified life cycle test regime was begun. Cells and batteries were operated using baseline cycles until the average energy efficiency over five cycles dropped to below 40%. Failure analysis was then performed.

A typical electrical cycle for zinc flow batteries consisted of a timed, constant current charge to deposit a specified amount of zinc (theoretically).

TABLE 2

Flow battery baseline test regimes

SNL ID no.	Electrode area (cm^2)	Charge current density ($mA\ cm^{-2}$)	Discharge current density ($mA\ cm^{-2}$)	Charge time (h)	Zinc loading ($mA\ h\ cm^{-2}$)	Discharge cutoff voltage
301	600	20	20	3	60	8
300	600	20	20	3	60	20
394	1936	10	10	6	62	17
344	60	35	35	2	70	1.4
345	60	35	35	2	70	1.4
380	60	35	35	2	70	1.4

Batteries were charged, put on a one- to five-minute wait under open circuit conditions, then discharged under constant current. Discharge was terminated at a predetermined cutoff voltage. At that point the battery was either recycled or a complete discharge was performed, which forced the battery to zero volts. It was necessary periodically to completely strip the zinc deposit off the substrate to insure uniform zinc deposition on subsequent cycles. Baseline cycle parameters for all units are described in Table 2.

To better evaluate the performance of prototype batteries, a parametric plan was developed based on published guidelines [2]. Four factors were selected that were expected to affect battery performance: (i) charge rate; (ii) discharge rate; (iii) maximum state-of-charge for each cycle; (iv) ambient temperature.

High and low levels of each factor were chosen depending upon the individual battery design limitations. This test plan leads to 16 unique cycle types; *i.e.*, different combinations of each of the four factors in the high and low situations. Five replicates of each of the 16 cycle types were planned in order to obtain statistically valid data. In most cases, it was not possible to experimentally implement the temperature test. In that situation, with only three factors, eight unique cycle types result.

Several chemical analyses were performed during electrical testing. Electrolyte pH, bromine concentration, ferricyanide concentration, and other species were determined. Specific gravity and viscosity were also determined on some electrolytes. The results of these analyses were used to monitor chemical changes during electrical testing. These results also guided electrolyte maintenance activities by indicating when the concentration of certain species required adjustment.

The mechanical integrity of these systems was also evaluated. Problems with plumbing components, electrolyte pumps, thermal management systems, and cell stack leaks were encountered, resolved and documented. Preventive maintenance activities were also carried out and documented.

Average efficiency values for all tests are summarized in Table 3. These values represent averages over the life of each unit. Test regimes for each cell

TABLE 3

Flow battery data summary

SNL ID no.	Mean coulombic efficiency (%)	Mean voltaic efficiency (%)	Mean energy efficiency (%)	No. of cycles	Status
301	87.7 ± 0.3	78.1 ± 0.2	68.5 ± 0.3	1196	on test
300	68.4 ± 0.6	68.1 ± 0.4	46.6 ± 0.6	652	on test
394	82 ± 2	82 ± 1	67 ± 2	145	on test
344	75 ± 2	86.8 ± 0.3	65 ± 2	93	failed
345	83 ± 1	77.7 ± 0.3	64.6 ± 1	246	failed
380	82 ± 2	83.3 ± 0.3	68 ± 2	406	failed

or battery were different, involving various charge and discharge rates, zinc loading, and temperature. Thus, individual test regimes must be considered when interpreting these data.

Test results

Exxon zinc/bromine batteries — 500 W h battery #301

This battery has been under evaluation for 2.5 years and is presently on a life-cycle testing regime. It has completed the four-factor test matrix. Specific values of the factors used in these tests are given in Table 4.

TABLE 4

Factorial test plan for Exxon and GEL batteries

Factors	Exxon #301		GEL #394	
	Low	High	Low	High
Temperature (°C)	20	40	–	–
Charge rate (A)	11.7	17.4	10	30
Discharge rate (A)	11.7	17.4	10	30
Zinc loading (mA h cm^{-2})	35	60	46	77

The results of these tests have been used to derive a performance prediction equation, main effects, and two-factor interactions. The prediction equation is:

$$\text{Efficiency (\%)} = b_0 + b_1x_A + b_2x_B + b_3x_C + b_4x_D + b_5x_Ax_B + b_6x_Ax_C + \\ + b_7x_Ax_D + b_8x_Bx_C + b_9x_Bx_D + b_{10}x_Cx_D.$$

The x variables are defined by:

$$x_A = \frac{T-30}{10};\ x_B = \frac{C-14.5}{2.8};\ x_C = \frac{D-14.5}{2.8};\ x_D = \frac{Z-47.5}{12.5};$$

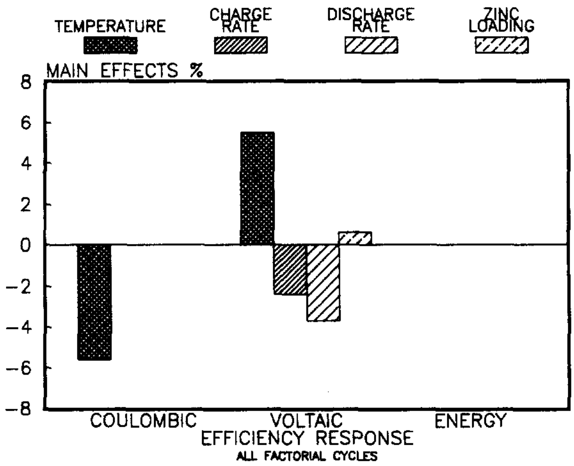

Fig. 1. Exxon battery #301 Zn/Br_2 factorial analysis significant at the 99% level F test.

where T = Battery temperature (°C); C = Charge rate (A); discharge rate (A); Z = Zinc loading (mA h cm^{-2}). Values of the b coefficients are listed in Table 5.

The main effects of this battery for coulombic, voltaic and energy efficiency are plotted in Fig. 1. Similar data for another zinc/bromine battery are also plotted later for comparison. The factor having the largest effect is temperature, in a negative sense for coulombic efficiency and in a positive sense for voltaic efficiency. The net effect (energy efficiency) is very minor.

A qualified life cycle test will be continuing until the failure criteria are satisfied.

Exxon 1.2 kW h battery #300

This battery has been under test for 1.5 years and is being life-cycled. It has completed a three-factor test matrix. Temperature was not evaluated as a factor for this battery. Because of an unavoidable one-year idle period, which resulted in a drop in all efficiencies, overall performance of this unit has been inferior to that of battery #301. The relative values of the main effects are similar to those for battery #301.

GEL zinc/bromine battery #394

The three-factor test matrix was recently completed for this battery. Temperature was not used as a variable in these tests. The factors are given in Table 4. The prediction equation is:

$$\text{Efficiency (\%)} = b_0 + b_1x_A + b_2x_B + b_3x_C + b_4x_Ax_B + b_5x_Ax_C + b_6x_Bx_C + \\ + b_7x_Ax_Bx_C\,.$$

The x variables are defined by:

TABLE 5

Factorial test prediction equation coefficients

Battery	Efficiency variable	b Coefficients										
		b_0	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	b_9	b_{10}
Exxon #301	Coulombic	86.3	−2.8	0.60	0.22	0	0.33	0.44	−0.24	0.06	0	0.19
	Voltaic	80.9	2.8	−1.2	−1.9	0.31	0.19	0.25	−0.18	0.19	−0.03	−0.01
	Energy	69.2	0.14	−0.38	1.4	0.23	0.48	0.63	−0.67	0.19	−0.10	0.13
GEL #394	Coulombic	83.4	−0.46	1.6	−6.6	0	−0.42	1.0	0.24			
	Voltaic	83.2	−2.7	−3.6	0.47	0.075	0.065	0.21	−0.24			
	Energy	69.3	−2.7	−1.6	−5.1	0.05	−0.14	1.2	−0.025			

$$x_A = \frac{C-20}{5} \qquad x_B = \frac{D-20}{5} \qquad x_C = \frac{Z-62}{15.5}$$

where:
C = Charge rate (A); D = Discharge rate (A); Z = Zinc loading (mA h cm^{-2}). The b coefficients are listed in Table 5. In this case, it is composed of main effect terms, two-factor interaction terms, and a statistically significant three-factor interaction term.

The factor effects on efficiencies are markedly different for this zinc/bromine battery design. They are illustrated in Fig. 2. In this case, zinc loading had the largest effect on efficiency. This test is continuing to evaluate life cycle capability.

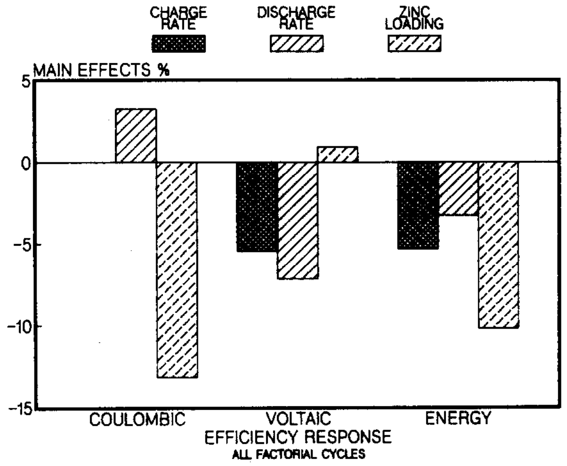

Fig. 2. GEL battery #394 Zn/Br_2 factorial analysis significant at the 99% level F test.

Lockheed zinc/ferricyanide cells #380

This technology is in an earlier stage of development than are the zinc/bromine systems. Numerous cell design and fundamental technology problems were encountered in baseline tests of these cells. Issues regarding cell case integrity, zinc electrode plating uniformity and reproducibility, and electrolyte species concentration balance were determined. Because these problems prevented stable performance, a factorial test matrix was not performed. The results of these tests are being used to guide the development of this technology.

Conclusion

This paper has described the methodology used to evaluate flowing electrolyte batteries at Sandia. A three- or four-factor statistical test matrix has been discussed, along with resulting performance prediction equations and the identity of the most important operating variables. The use of carefully planned factorial test matrices results in well-defined equations which describe battery performance. These tests should be applied to technologies in the early stages of development because of their inherent lack of reproducibility. Nevertheless, this method provides valuable battery design and performance information for experimental battery systems.

Acknowledgement

This work is supported by the U.S. Department of Energy under contract DE-AC04-76DP00789.

References

1 P. C. Butler, D. W. Miller, C. E. Robinson and G. P. Rodriguez, A review of flow battery testing at Sandia, *Proc. 19th Intersoc. Energy Conv. Eng. Conf., San Francisco, CA, 1984*, p. 863.
2 S. L. Basin and W. C. Spindler, Using statistically designed experiments in development of advanced battery systems, *EPRI EM-1346*, Electric Power Research Institute, 1980.