

## PERFORMANCE TESTING OF 10 kW-CLASS ADVANCED BATTERIES FOR ELECTRIC ENERGY STORAGE SYSTEMS IN JAPAN

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### Summary

The results of the performance testing of 10 kW-class advanced batteries — Na-S, Zn-Cl<sub>2</sub>, Zn-Br<sub>2</sub> and redox-flow type batteries — are summarized. Energy efficiency and capacity at three discharge rates are presented in addition to energy density, self-discharge rate, estimated short circuit current, etc. It was evident that the performance of the advanced batteries was adequate to achieve the project goals for electrical energy storage. Further improvements are needed in the areas of self-discharge, electric insulation, and auxiliary systems. Based on continued technical progress, there is reasonable expectation that pilot plants of 1 MW (8 MW h) will be constructed and demonstrated in the next phase of the project.

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### Introduction

Modern a.c. power systems, *e.g.*, oil fired plants, nuclear power plants, have been developed for technical and economical reasons as primary power sources in response to instantaneous electrical load. Electric utilities have two types of a.c. power generating plant — base load plant, and peaking or cycling equipment — to meet fluctuating energy demand in a cost-effective manner. Base load plants are designed to operate for 24 hours each day throughout the year at constant power and to generate low cost electrical power despite the high capital costs. Peaking or cycling equipment is used to meet daily demand peaks. Such equipment is, typically, a low-efficiency,

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fossil-fuel steam plant with gas turbine driven generators. While daily or yearly load variation has been increasing owing to the development of new industries and widely-used air-conditioners, the cost and availability of fossil and distillate fuels are becoming serious problems. In Japan, a typical daily load curve has a 40% midnight factor (ratio of minimum power to peak power), and a typical annual load curve has a 60% load factor (ratio of average power to peak power). These problems could be solved or greatly mitigated if, to cope with fluctuating demand, energy storage systems were used in collaboration with base load plants. If electrical energy was stored at off-peak periods and released at peak periods using energy storage systems, e.g., pumped hydro-electric- and advanced battery systems, etc., the energy output would be controlled according to demand and the load factor would be improved. Consequently, load leveling has become an attractive method from an energy-saving point of view, and the substitution of oil by atomic or other prime-energy sources is expected to become increasingly important. The potential of pumped hydro-electricity appears to be limited due to siting problems, energy density, capital cost, etc. Also, other advanced energy storage systems using compressed air, superconductors, etc., have serious problems yet to be solved. A great deal of attention is therefore being given to advanced secondary batteries as being the most versatile method of storing energy for electric utility systems. The advanced battery shows promise in respect of operative feasibility, flexibility of size and location, rapid response, environmental aspects and economic benefits. These advantages have resulted in active research into, and development of, the advanced battery and energy storage utility.

In Japan, *The Development of an Advanced Battery Electric Power Storage System* was initiated as a national research program within the *Moonlight Project* of 1980 [1, 2]. This project was established by the Agency of Industrial Science and Technology (AIST), the Ministry of International Trade and Industry (MITI), through the national research institutes, and the New Energy Development Organization (NEDO). In this project, high performance advanced batteries and the application of technology to energy storage systems have been studied and developed. Based on this research, a 1 MW (8 MW h) electrical energy storage system will be constructed and tested for the feasibility of its practical application by about 1990 (Fig. 1). The specific performance targets in the 1 MW system are summarized in Table 1. The first phase of the work has been to build and test the 1 kW (8 kW h) modules. The first interim performance test of the 1 kW class batteries — Na-S, Zn-Cl<sub>2</sub>, Zn-Br<sub>2</sub>, and the redox-flow type (Cr-Fe) battery — was carried out in 1983 at our Institute. The characteristics of the advanced batteries were discussed and problems to be solved were clarified [3]. The performance was then improved by developing the electrode and electrolyte materials and scaling up the batteries to the 10 kW class; this improvement was undertaken by the five contractors — Yuasa Battery Co., Ltd. and NGK Spark Plug Co., Ltd (Na-S), Furukawa Electric Co., Ltd. (Zn-Cl<sub>2</sub>), Meidensha Electric Mfg. Co., Ltd. (Zn-Br<sub>2</sub>), and Mitsui



concepts of the advanced battery not previously considered have been studied at our Institute [4 - 14].

In the next phase of the project, a 1 MW class advanced battery system pilot plant will be constructed from the same type of electrodes and/or unit cells as for the 10 kW class batteries. It was considered that the time was therefore ripe to evaluate the 10 kW class advanced batteries with regard to performance goals, and to review the problems still to be solved. The second interim performance test for 10 kW class advanced batteries was carried out at our Institute between September and December, 1986. The results are detailed in this report.

## Experimental

The 10 kW (80 kW h) advanced batteries were tested as detailed below; the battery specifications are summarized in Table 2.

TABLE 2  
Specifications for 10 kW class advanced batteries

| Battery                                | Na-S   | Zn-Cl <sub>2</sub>          | Zn-Br <sub>2</sub>                | Redox-flow type                      |
|--|--|-----------------------------|-----------------------------------|--------------------------------------|
| Dimensions (m <sup>3</sup> )           | 1.60 × 1.25<br>× 1.96                                | 1.39 × 1.95<br>× 2.26       | 1.37 × 1.59<br>× 1.67             | 4.02 × 4.00<br>× 1.51                |
| Weight (kg)                            | 2465   | 3138                        | 2915                              | 12820                                |
| Unit cell                              |  |                             |                                   |                                      |
| Area (cm <sup>2</sup> )                | 495  | 2800                        | 1600                              | 6000                                 |
| Current density (mA cm <sup>-2</sup> ) | 50.5   | 22.0                        | 13.0                              | 30.8                                 |
| Voltage (V)                            | 1.8  | 1.95                        | 1.67                              | 0.9                                  |
| Capacity (A h/8 HR)                    | 200  | 495                         | 166                               | 1480                                 |
| Total numbers                          | 280  | 96                          | 288                               | 60                                   |
| Configuration*                         | (7s × 10p)<br>× 4s                                   | (24s × 2p)<br>× 2p          | (24s × 3p)<br>× 4p                | 30s × 2p                             |
| Open circuit voltage (V)               | 58.0   | 50.9                        | 43.8                              | 62.0                                 |
| Charging power (kW)                    | 15.0   | 14.9                        | 12.7                              | 12.8                                 |
| Discharging power (kW)                 |  |                             |                                   |                                      |
| 8 HR                                   | 12.5   | 11.6                        | 10.0                              | 10.0                                 |
| 6 HR                                   | 16.0   | 14.5                        | 13.0                              | 12.8                                 |
| 4 HR                                   | 22.5   | 20.0                        | 19.0                              | 17.4                                 |
| Contractor                             | Yuasa Battery Co., Ltd. and NGK Spark Plug Co., Ltd. | Furukawa Electric Co., Ltd. | Meidensha Electric Mfg. Co., Ltd. | Mitsui Eng. & Shipbuilding Co., Ltd. |

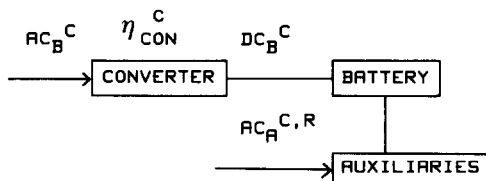
\*s and p denote that the cells are connected in series and parallel, respectively.

(i) Capacity, energy efficiency and energy density

Energy efficiency and capacity were determined at three discharge rates: 8, 6 and 4 h rate (HR) after 8 HR charge. In the second interim evaluation test, the energy efficiency was defined according to Fig. 2 and eqns. (1)

1. DURING CHARGE (INCLUDING REST TIME)

$$AC_O^C = AC_B^C + AC_A^{C,R}$$



2. DURING DISCHARGE

$$AC_O^D = AC_B^D - AC_A^D$$

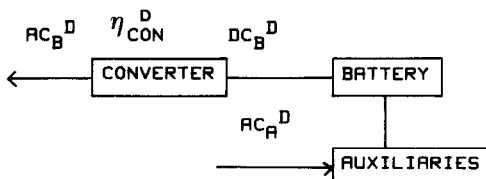


Fig. 2. Energy flow of advanced battery energy storage system.  $AC_O^C$  = overall(O) input of a.c. energy;  $AC_B^C$ ,  $DC_B^C$ ,  $AC_A^C$  = input energy to converter, battery, and auxiliaries, respectively, during charge. Similarly,  $AC_O^D$ ,  $AC_B^D$ ,  $DC_B^D$ , and  $AC_A^D$  refer to the corresponding energy during discharge.  $\eta_{CON}^{C,D}$  = efficiency of a.c. - d.c. converter during charge (C) and discharge (D).

and (2). A one-way efficiency of 0.95 for the a.c. - d.c. power converter was used in the following calculations.

(a) Battery efficiency,  $\eta_B$  (d.c./d.c. efficiency), which is calculated from the charged d.c. energy ( $DC_B^C$ ) and discharged d.c. energy ( $DC_B^D$ ) of the batteries.

$$\eta_B = \frac{DC_B^D}{DC_B^C} \quad (1)$$

(b) Overall energy efficiency,  $\eta_O$  (a.c./a.c. efficiency), which is determined from the energy consumed by the auxiliaries ( $AC_A^D$ ,  $AC_A^C$ ) and the round-trip efficiency of the a.c. - d.c. converter ( $\eta_{CON}^C$ ,  $\eta_{CON}^D$ ) at charge and discharge, in addition to the stored and extracted energy of the batteries.

$$\eta_O = \frac{AC_O^D}{AC_O^C} = \frac{DC_B^D \eta_{CON}^D - AC_A^D}{\frac{DC_B^C}{\eta_{CON}^C} + AC_A^C} \quad (2)$$

$$\left[ \begin{array}{l} AC_O^D = AC_B^D - AC_A^D, \quad AC_B^D = DC_B^D \eta_{CON}^D \\ AC_O^D: \text{AC output energy from the overall} \\ \quad \text{system during discharge.} \\ AC_O^C = AC_B^C + AC_A^C, \quad AC_B^C = DC_B^C / \eta_{CON}^C \\ AC_O^C: \text{AC input energy to the overall} \\ \quad \text{system during charge.} \end{array} \right]$$

In practice, eqn. (2) is valid, because the energy efficiency should be considered as the overall energy storage system. Retained capacity, average current, and energy density were also measured at 8, 6 and 4 HR discharge.

### (ii) Cycle life test

Energy efficiency and capacity were observed in relation to charge/discharge cycles at the 8 HR from a reliability point of view.

### (iii) Self-discharge rate

To determine the reliability and feasibility of maintenance, the self-discharge rate was found by measuring the capacity after setting aside the fully charged batteries for 24 and 168 h. The electrolytes of the flow type batteries — Zn-Cl<sub>2</sub>, Zn-Br<sub>2</sub> and the redox-flow type battery — were removed from the cell stacks for this test. Because the 8 HR discharge of the batteries could be started within a few minutes, the stand-by state during which the battery was inoperative for a prolonged period, *e.g.*, more than one day, was defined. Thus, the active materials' self-discharge was greatly reduced for these batteries. The decreasing ratios of energy efficiency,  $\Delta\eta_O$ ,  $\Delta\eta_B$  were determined by comparing the capacity, after setting aside for 24 and 168 h, with that of a standard 8 HR cycle. The value  $\Delta\eta_O$  includes, and  $\Delta\eta_B$  excludes, the energy consumed by the auxiliaries. The energy required to keep the batteries in a stand-by state at the operating temperature was also determined; this was called the stand-by energy.

### (iv) The starting and stopping time

The time required to start and stop the operation of the batteries was determined to clarify the feasibility of the operation. It was observed from, and to, the waiting period during which the cell stacks were filled with the electrolyte at the operating temperature. The time observed here must be several minutes shorter than that based on the stand-by condition. Self-discharge must be much improved in advance of practical application, therefore the starting and stopping time was observed based on this waiting condition. Also the transition time from the charge mode to discharge at 10 kW was measured.

### (v) Transient response properties for load variations

The rise and fall times of the battery system were measured at 8 HR charge and 8, 6, and 4 HR discharge.

*(vi) Internal resistance*

An a.c. impedance method and a d.c. current step method were adopted to determine the internal resistance of the batteries after removal of the cables from the batteries and the charge/discharge equipment. The initial short circuit battery current was also determined by our method [4, 5].

*(vii) Voltage-current characteristics*

A  $V-I$  scan was run on the batteries at 6 states, *i.e.*, the initial, middle, and final stages of the 8 HR charge and discharge. The depths of charge (or discharge) of these stages were 0.5/8, 4/8 and 7.5/8, respectively. The voltage was recorded after 3 min at each current setting. The polarization characteristics of the batteries are discussed.

In addition to the above items, the electrical insulation and the compliance with environmental standards were examined. Table 3 details the accessories of the 10 kW class advanced batteries. Detailed testing conditions are summarized in Table 4. The battery testing facilities were computerized and had a capability for 24-hour-a-day operation. Cycle tests were conducted using the charge/discharge equipment and the microcom-

TABLE 3

The auxiliaries of the 10 kW advanced batteries

|                  | Na-S                                      | Zn-Cl <sub>2</sub>        | Zn-Br <sub>2</sub>        | Redox-flow type      |
|------------------|---|---------------------------|---------------------------|----------------------|
| Heater           | 0 - 3 <sup>a</sup><br>(PID <sup>b</sup> ) |                           |                           | 0 - 14<br>(ON - OFF) |
| Fan              | 0 - 0.2<br>(const.)                       |                           |                           |                      |
| Refrigerator     |   | 0.75<br>(ON - OFF)        | 0.05 - 0.14<br>(ON - OFF) |                      |
| Pump             |   |                           |                           |                      |
| 1. Cooling water |   |                           | 0.04 - 0.13<br>(ON - OFF) |                      |
| 2. Electrolyte   |   | 0.08 - 0.2<br>(Inverter)  | 0.25 - 0.75<br>(const.)   | 0 - 0.4<br>(const.)  |
| 3. Gas           |   | 0.1<br>(ON - OFF)         |                           |                      |
| UV lamp          |   | 0.04 - 0.08<br>(ON - OFF) |                           |                      |
| Rebalancing      |   |                           |                           | 0.12<br>(ON - OFF)   |

<sup>a</sup>Numerical values refer to the electric power (kW) consumed by the auxiliaries.

<sup>b</sup>Methods of controlling the auxiliaries' power are shown in parentheses.

TABLE 4

Testing conditions for the 10 kW class advanced batteries

| Items  | Na-S    | Zn-Cl <sub>2</sub> | Zn-Br <sub>2</sub> | Redox-flow type |
|--|---------|--------------------|--------------------|-----------------|
| <b>1. Energy efficiency</b>  |         |                    |                    |                 |
| <b>Charge</b>  |         |                    |                    |                 |
| Power (kW)   | 15.0    | 14.9               | 12.7               | 12.8            |
| Duration (h)   | 8       | 8                  | 8                  | 8               |
| <b>Discharge</b>   |         |                    |                    |                 |
| Power (kW)   | 8 HR    | 12.5               | 11.6               | 10.0            |
| (c.o.v.*, V)   |         | (12.5)             | (24.0)             | (24.0)          |
|  | 6 HR    | 16.0               | 14.5               | 13.0            |
|  |         | (16.0)             | (24.0)             | (24.0)          |
|  | 4 HR    | 22.5               | 20.0               | 19.0            |
|  |         | (22.5)             | (24.0)             | (24.0)          |
| <b>2. Rate of self-discharge; standing time (h): 24 and 168</b>  |         |                    |                    |                 |
| <b>3. Life cycle; energy efficiency in relation to 8 HR cycles</b>   |         |                    |                    |                 |
| <b>4. Internal resistance</b>  |         |                    |                    |                 |
| a.c. impedance method: input voltage = 10 mV, 0.01 Hz-20 kHz   |         |                    |                    |                 |
| d.c. current step method: input voltage = 5 - 100 mV   |         |                    |                    |                 |
| <b>5. V-I characteristics; voltage after 3 min duration of rated current</b>   |         |                    |                    |                 |
| during charge (A)  | 0 - 300 | 0 - 500            | 0 - 500            | 0 - 400         |
| during discharge (A)   | 0 - 600 | 0 - 600            | 0 - 500            | 0 - 600         |
| <b>6. Starting and stopping time; time for starting 8 HR operation from cooled down and stand-by state, and for stopping to stand-by state</b> |         |                    |                    |                 |
| <b>7. Electrical insulation; d.c. 3000 V (1 min) between an electrode and container</b>  |         |                    |                    |                 |

\*Cut-off voltage.

puter. The computer automatically monitored battery voltage, current, and temperature, and served as a controller and data acquisition device. Ampere hours and watt hours were integrated over the sampling interval. Other testing equipment was designed and constructed in advance of the second interim performance test.

## Results and discussion

The evaluation testing results are summarized in this section. Detailed results will be published elsewhere [15 - 17].

### (i) Capacity, energy efficiency and energy density

Figures 3 and 4 show the charge and discharge curves at 8, 6, and 4 HR. The discharge capacity of the batteries exceeded the target of 8 h at



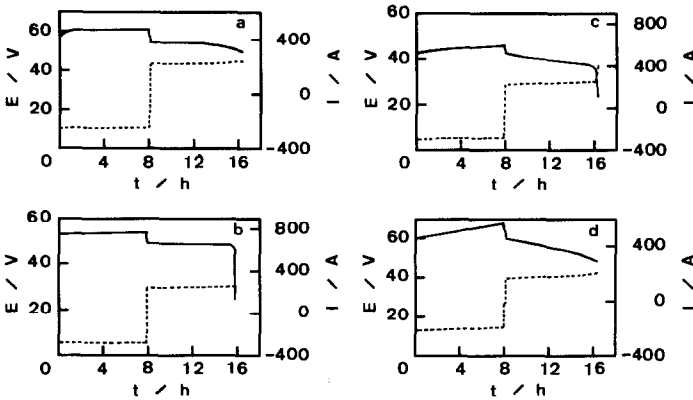


Fig. 3. Charge and discharge curves at 8 HR discharge. —, Voltage; ---, current. Curves a, b, c, and d refer to Na-S, Zn-Cl<sub>2</sub>, Zn-Br<sub>2</sub>, and redox-flow type battery, respectively.

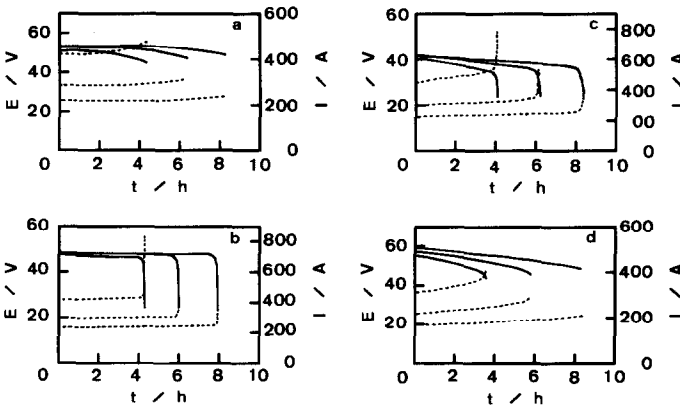


Fig. 4. Discharge curves at the rated discharge. Symbols are as in Fig. 3.

the nominal power. The battery efficiency ( $\eta_B$ ) and overall efficiency ( $\eta_O$ ) are summarized for three discharge rates in Tables 5 and 6. The overall efficiency at 8 HR was observed as 77.1, 65.7, 71.1, and 69.4% for Na-S, Zn-Cl<sub>2</sub>, Zn-Br<sub>2</sub>, and the redox-flow type battery, respectively. As shown in Table 7, the 10 kW battery efficiency was much improved in comparison with those of the 1 kW class batteries in spite of the scale-up [3]. The battery efficiency and overall efficiency are expected to attain the goal of 80 and 70%, respectively.

The overall efficiency was determined for one cycle,  $\eta_O$ , excluding the energy consumed by the auxiliaries during rest time after discharge. The rest time clearly depends on the operation cycle. For practical purposes, the energy efficiency should be given as a daily,  $\eta_{O,D}$ , and weekly operation,  $\eta_{O,W}$ . The efficiencies of  $\eta_{O,D}$  and  $\eta_{O,W}$  were estimated for the appropriate

TABLE 5

Energy efficiency and capacity of 10 kW class Na-S and Zn-Cl<sub>2</sub> batteries at three discharge rates

| Mode                    | Na-S    |         |         | Zn-Cl <sub>2</sub> |         |         |
|-------------------------|---------|---------|---------|--------------------|---------|---------|
|                         | 8       | 6       | 4       | 8                  | 6       | 4       |
| Discharge rate (HR)     | 8       | 6       | 4       | 8                  | 6       | 4       |
| Charge                  |         |         |         |                    |         |         |
| duration (h)            | 7.998   | 7.993   | 7.990   | 8.000              | 8.000   | 8.000   |
| energy (kW h)           |         |         |         |                    |         |         |
| battery                 | 119.902 | 119.831 | 119.793 | 119.197            | 119.185 | 119.178 |
| aux.*                   | 2.973   | 1.195   | 0.930   | 4.893              | 5.708   | 5.157   |
| Rest after charge       |         |         |         |                    |         |         |
| energy (kW h) aux.*     | 0.013   | 0.026   | 0.011   | 0.041              | 0.011   | 0.028   |
| Discharge               |         |         |         |                    |         |         |
| duration (h)            | 8.442   | 6.466   | 4.399   | 8.018              | 6.059   | 4.324   |
| energy (kW h)           |         |         |         |                    |         |         |
| battery                 | 105.516 | 103.476 | 99.031  | 92.964             | 87.813  | 86.452  |
| aux.*                   | 0.590   | 0.499   | 0.561   | 1.573              | 2.728   | 1.234   |
| Rest after discharge    |         |         |         |                    |         |         |
| energy (kW h) aux.*     | 0.000   | 0.000   | 0.000   | 1.595              | 2.278   | 2.896   |
| Efficiency              |         |         |         |                    |         |         |
| $\eta_B$ (%)            | 88.00   | 86.35   | 82.67   | 77.99              | 73.68   | 72.54   |
| $\eta_O$ (%)            | 77.13   | 76.79   | 73.61   | 65.71              | 60.47   | 60.58   |
| Energy density          |         |         |         |                    |         |         |
| (kW h m <sup>-2</sup> ) | 52.46   | 51.49   | 49.24   | 33.72              | 31.39   | 31.44   |
| (kW h m <sup>-3</sup> ) | 26.77   | 26.27   | 25.12   | 14.92              | 13.89   | 13.91   |
| (W h kg <sup>-1</sup> ) | 42.57   | 41.78   | 39.95   | 29.12              | 27.11   | 27.16   |

\* Auxiliaries.

operation schedules, as shown in Table 8. Small differences were observed between the three kinds of energy efficiencies for the Zn-Cl<sub>2</sub> and Zn-Br<sub>2</sub> batteries because of the small amount of stand-by energy. However, for Na-S and the redox-flow type battery, the daily and weekly efficiencies were remarkably less than the efficiency of a single cycle,  $\eta_O$ , because of the large stand-by energy. The energy per footprint area, volume, and weight, was calculated for the capacity at the 8 HR discharge as shown in Tables 5 and 6. The Na-S battery showed the highest values of all the energy densities in the four types of battery. By contrast, all the forms of energy density of the redox-flow type battery were smaller by an order of magnitude than those of the other three batteries because of the large quantity of redox solution — 8 m<sup>3</sup>. The capacity of the redox-flow type battery decreased as the discharge rate increased. This is possibly because the electrolyte circulating pump was underpowered.

TABLE 6

Energy efficiency and capacity of 10 kW class Zn-Br<sub>2</sub> and redox-flow type batteries at various discharges

| Mode                    | Zn-Br <sub>2</sub> |         |         | Redox-flow type |         |         |
|-------------------------|--------------------|---------|---------|-----------------|---------|---------|
|                         | 8                  | 6       | 4       | 8               | 6       | 4       |
| Discharge rate (HR)     | 8                  | 6       | 4       | 8               | 6       | 4       |
| Charge                  |                    |         |         |                 |         |         |
| duration (h)            | 8.002              | 8.002   | 8.002   | 8.002           | 8.002   | 8.002   |
| energy (kW h)           |                    |         |         |                 |         |         |
| battery                 | 101.555            | 101.457 | 101.498 | 102.099         | 102.082 | 102.087 |
| aux.*                   | 1.910              | 1.903   | 1.907   | 2.714           | 2.663   | 2.918   |
| Rest after charge       |                    |         |         |                 |         |         |
| energy (kW h) aux.*     | 0.015              | 0.011   | 0.011   | 0.047           | 0.028   | 0.033   |
| Discharge               |                    |         |         |                 |         |         |
| duration (h)            | 8.373              | 6.147   | 4.093   | 8.348           | 5.739   | 3.564   |
| energy (kW)             |                    |         |         |                 |         |         |
| battery                 | 83.645             | 79.854  | 77.739  | 83.475          | 73.458  | 62.022  |
| aux.                    | 2.011              | 1.559   | 1.510   | 2.811           | 1.912   | 1.211   |
| Rest after discharge    |                    |         |         |                 |         |         |
| energy (kW h) aux.*     | 0.087              | 0.058   | 0.087   | 0.000           | 0.000   | 0.000   |
| Efficiency              |                    |         |         |                 |         |         |
| $\eta_B$ (%)            | 82.36              | 78.71   | 76.59   | 81.76           | 71.96   | 60.75   |
| $\eta_O$ (%)            | 71.11              | 68.31   | 66.46   | 69.39           | 61.62   | 52.27   |
| Energy density          |                    |         |         |                 |         |         |
| (kW h m <sup>-2</sup> ) | 37.48              | 35.95   | 35.00   | 5.016           | 4.449   | 3.782   |
| (kW h m <sup>-3</sup> ) | 22.45              | 21.52   | 20.95   | 3.322           | 2.947   | 2.504   |
| (W h kg <sup>-1</sup> ) | 28.00              | 26.86   | 26.15   | 6.292           | 5.581   | 4.743   |

\*Auxiliaries.

TABLE 7

Comparison of battery efficiency in the first ( $\eta_{B,1st}$ ) and second ( $\eta_{B,2nd}$ ) interim evaluation tests

|                    | Na-S | Zn-Cl <sub>2</sub> | Zn-Br <sub>2</sub> | Redox-flow type |
|--------------------|------|--------------------|--------------------|-----------------|
| $\eta_{B,1st}$ (%) | 85.9 | 71.1               | 80.1               | 76.7            |
| $\eta_{B,2nd}$ (%) | 88.0 | 78.0               | 82.4               | 81.8            |

### (ii) Cycle life characteristics

Cycle life tests were continued to attain the goal of 1500 cycles. The battery,  $\eta_B$ , and overall  $\eta_O$ , energy efficiencies for 10 kW class advanced batteries are shown in relation to cycle number from October 1986 to September 1987 in Table 9 and Figs. 5 and 6. The battery and the overall efficiencies were almost maintained at the initial level, and little performance deterioration was observed for the four types of advanced batteries. The

TABLE 8

Overall energy efficiency for the single cycle  $\eta_O$ , daily cycle  $\eta_{O,D}$  and weekly cycle  $\eta_{O,w}$  of 10 kW class advanced batteries

|                       | Na-S | Zn-Cl <sub>2</sub> | Zn-Br <sub>2</sub> | Redox-flow type |
|-----------------------|------|--------------------|--------------------|-----------------|
| $\eta_O$ (%)          | 77.1 | 65.7               | 71.1               | 69.4            |
| $\eta_{O,D}^*$ (%)    | 75.7 | 65.1               | 70.7               | 67.7            |
| $\eta_{O,w}^{**}$ (%) | 71.4 | 64.3               | 70.7               | 63.2            |

\*Calculated for the schedule: 1 day = charge (8 h) + rest (2 h) + discharge (8 h) + rest (6 h).

\*\*Calculated for the schedule: 1 week = 5 days' operation + 2 days' rest.

TABLE 9

The battery efficiency ( $\eta_B$ ) and overall efficiency ( $\eta_O$ ) of 10 kW class advanced batteries in the second cycle life test (as at the end of September 1987)

|                    | Na-S | Zn-Cl <sub>2</sub> | Zn-Br <sub>2</sub> | Redox-flow type |
|--------------------|------|--------------------|--------------------|-----------------|
| Initial efficiency |      |                    |                    |                 |
| $\eta_B$ (%)       | 85.7 | 78.1               | 79.7               | 78.6            |
| $\eta_O$ (%)       | 77.0 | 66.2               | 68.4               | 66.1            |
| Current status*    |      |                    |                    |                 |
| No. of cycles      | 380  | 268                | 257                | 257             |
| $\eta_B$ (%)       | 83.0 | 76.6               | 78.5               | 78.1            |
| $\eta_O$ (%)       | 74.8 | 64.6               | 67.2               | 66.1            |

\* In progress.

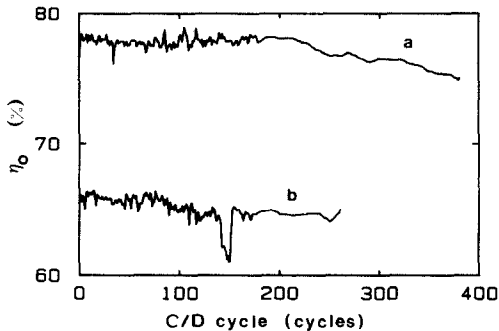


Fig. 5. C/D cycle dependence of overall energy efficiency,  $\eta_O$ , from October 1986 to September 1987. Symbols are as in Fig. 3. After 170th cycle, average values for each 10 cycles are plotted.

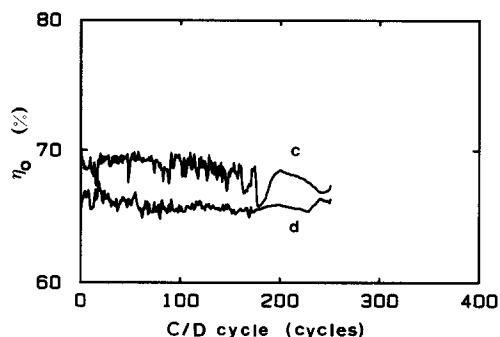


Fig. 6. C/D cycle dependence of overall energy efficiency,  $\eta_0$ , from October 1986 to September 1987. Symbols are as in Fig. 3. After 170th cycle, average values for each 10 cycles are plotted.

TABLE 10

The battery efficiency ( $\eta_B$ ) of 1 kW class advanced batteries in the first cycle life test (as at the end of September 1987)

|                                     | Na-S | Zn-Cl <sub>2</sub> | Zn-Br <sub>2</sub> | Redox-flow type |
|-------------------------------------|------|--------------------|--------------------|-----------------|
| Initial efficiency,<br>$\eta_B$ (%) | 85.9 | 71.1               | 80.1               | 76.7            |
| Current status*                     |      |                    |                    |                 |
| No. of cycles                       | 1059 | 655                | 597                | 859             |
| $\eta_B$ (%)                        | 68.4 | 72.4               | 75.0               | 65.8            |

\*In progress.

results of the first interim life cycle test are given in Table 10. All the 1 kW class version batteries have attained 500 cycles and retained a battery efficiency of some 70%.

### (iii) Self-discharge rate

The goals for  $\Delta\eta_0$  and  $\Delta\eta_B$  were set at 5% of the 8 HR capacity after standing for one week. By removing the electrolyte from the cell stacks for the flow type batteries, the rate was dependent on the stand-by energy and/or the remaining electrolyte in the cell stacks. The decreasing ratios of capacity and battery efficiency,  $\eta_B$ , for the four batteries were rather low, as shown in Tables 11 and 12, by comparison with ordinary Pb-acid batteries. The stand-by energy was larger for the Na-S (19.4 kW h/day) and the redox-flow type battery (20.1 kW h/day) than for the Zn-Cl<sub>2</sub> (0.7 kW h/day) and the Zn-Br<sub>2</sub> battery (0.0 kW h/day). Therefore, the decreasing ratio of the overall efficiency,  $\Delta\eta_0$ , including energy consumed by the auxiliaries, was very large for these batteries. The Na-S and the redox-flow type batteries are suitable for daily operation for load leveling purposes.

TABLE 11

Rate of self-discharge of 10 kW class Na-S and Zn-Cl<sub>2</sub> batteries

|  | Na-S    |         | Zn-Cl <sub>2</sub> |         |
|--|---------|---------|--------------------|---------|
| Standing time (h)                                | 24      | 168     | 24                 | 168     |
| Charge energy (kW h)                             |         |         |                    |         |
| battery  | 119.918 | 119.929 | 119.183            | 119.167 |
| aux.*  | 4.703   | 4.654   | 4.551              | 4.955   |
| Rest after charge                                |         |         |                    |         |
| energy (kW h) aux.*                              | 17.999  | 136.096 | 0.117              | 4.738   |
| Discharge energy (kW h)                          |         |         |                    |         |
| battery  | 105.402 | 105.410 | 89.832             | 88.941  |
| aux.*  | 0.601   | 0.589   | 1.694              | 1.681   |
| Rest after discharge                             |         |         |                    |         |
| energy (kW h) aux.*                              | 0.000   | 0.000   | 1.9122             | 2.362   |
| Battery efficiency                               |         |         |                    |         |
| $\eta_B$ (%)                                     | 87.90   | 87.89   | 75.37              | 74.64   |
| Overall efficiency                               |         |         |                    |         |
| $\eta_O$ (%)                                     | 66.83   | 37.29   | 63.35              | 60.23   |
| Decreasing rate of capacity (% h <sup>-1</sup> ) | 0.00    | 0.00    | 0.15               | 0.03    |
| Decreasing ratio of $\eta_B$ (%)                 | 0.11    | 0.12    | 3.36               | 4.30    |
| Decreasing ratio of $\eta_O$ (%)                 | 13.35   | 51.66   | 3.59               | 8.34    |
| Stand-by energy (kW h h <sup>-1</sup> )          | 0.750   | 0.810   | 0.0049             | 0.0282  |

\*Auxiliaries.

However, these batteries should not be used for urgent power sources which must be retained at the operating temperature thereby consuming the stand-by energy. By contrast, Zn-Cl<sub>2</sub> and Zn-Br<sub>2</sub> batteries are applicable, even in this instance.

*(iv) Starting and stopping time*

The times necessary to start and stop the operation, and also to switch from charge to discharge, were measured. The starting and stopping times at the operating temperature were observed to be within 1 s for Na-S, Zn-Br<sub>2</sub> and the redox-flow type battery and about 2 min for the Zn-Cl<sub>2</sub> battery. It was confirmed that the advanced battery system is started and stopped in a much shorter time than that of a hydroelectric power plant (several min). Since Na-S and redox-flow type batteries are operated at 350 °C and 35 - 40 °C, respectively, a warming-up period from the cooled state is necessary. The time was noted as 87.5 and 24.9 h for the Na-S and the redox-flow type battery, respectively. The switching from charge to discharge was quickly accomplished for all the batteries except Zn-Cl<sub>2</sub>, whose reservoir of solvated chlorine must be cooled just before charge.

TABLE 12

Rate of self-discharge of 10 kW class Zn-Br<sub>2</sub> and redox-flow type batteries

|  | Zn-Br <sub>2</sub> |         | Redox-flow type |         |
|--|--------------------|---------|-----------------|---------|
| Standing time (h)                                | 24                 | 168     | 24              | 168     |
| Charge energy (kW h)                             |                    |         |                 |         |
| battery  | 101.574            | 101.545 | 102.072         | 102.058 |
| aux.*  | 1.943              | 1.900   | 2.717           | 2.893   |
| Rest after charge                                |                    |         |                 |         |
| energy (kW h) aux.*                              | 0.080              | 0.043   | 20.764          | 140.764 |
| Discharge energy (kW h)                          |                    |         |                 |         |
| battery  | 77.945             | 77.428  | 78.691          | 78.973  |
| aux.*  | 1.852              | 1.819   | 2.664           | 2.680   |
| Rest after discharge                             |                    |         |                 |         |
| energy (kW h) aux.*                              | 0.051              | 0.051   | 0.000           | 0.000   |
| Efficiency                                       |                    |         |                 |         |
| $\eta_B$ (%)                                     | 76.74              | 76.25   | 77.09           | 77.38   |
| $\eta_O$ (%)                                     | 66.24              | 65.88   | 55.06           | 28.81   |
| Decreasing rate of capacity (% h <sup>-1</sup> ) | 0.283              | 0.044   | 0.239           | 0.0321  |
| Decreasing ratio of $\eta_B$ (%)                 | 6.82               | 7.42    | 5.71            | 4.83    |
| Decreasing ratio of $\eta_O$ (%)                 | 6.85               | 7.35    | 20.65           | 58.48   |
| Stand-by energy (kW h h <sup>-1</sup> )          | 0.0034             | 0.00025 | 0.865           | 0.838   |

\* Auxiliaries.

The time for the Zn-Cl<sub>2</sub> battery should be reduced by automating the bulb switching for controlling the Cl<sub>2</sub> gas pressure and optimising the refrigeration. The stopping time was observed to be within 1 s for all the advanced batteries.

(v) *Transient response properties for load variation [15]*

The rise and fall times of the battery systems (battery and C/D cyler) were observed as being within 20 and 1 ms, respectively, as shown in Fig. 7 and Table 13. The response time is determined by the impedance characteristics of the overall systems. It was independent of battery type and state of charge, because the impedances of the overall battery systems were not affected by the batteries, but by the cyler and cable, etc. The results indicate that the battery systems respond quickly to irregular and large load fluctuations.

(vi) *Internal resistance*

The resistance was measured and the initial short circuit current estimated, as shown in Table 14. The impedance characteristics of the 10 kW class module batteries were much different from those of unit cells [16],

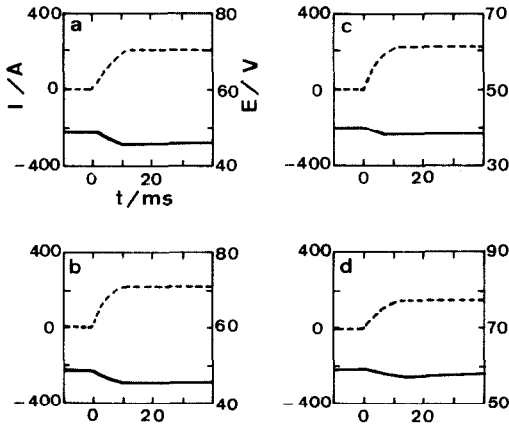


Fig. 7. Transient characteristics (rising) of the 10 kW class advanced batteries at 8 HR charge. Symbols are as in Fig. 3.

TABLE 13

Apparent response time of the 10 kW class batteries

| Measurement point |                   | Response time <sup>a</sup> (ms) |                    |                    |            |         |
|-------------------|-------------------|---------------------------------|--------------------|--------------------|------------|---------|
|                   |                   | Na-S                            | Zn-Cl <sub>2</sub> | Zn-Br <sub>2</sub> | Redox-flow | Pb-acid |
| 8 HR charge       | rise <sup>b</sup> | 14                              | 8                  | 19                 | 13         | 18      |
|                   | fall <sup>c</sup> | 0.4                             | 0.4                | 0.4                | 0.4        | 0.2     |
| 8 HR discharge    | rise              | 10                              | 7                  | 7                  | 9          | 11      |
|                   | fall              | 1                               | 1                  | 2                  | 1          | 0.5     |
| 6 HR discharge    | rise              | 10                              | 6                  | 7                  | 10         |         |
|                   | fall              | 0.7                             | 2                  | 3                  | 0.5        |         |
| 4 HR discharge    | rise              | 10                              | 6                  | 8                  | 8          |         |
|                   | fall              | 0.8                             | 2                  | 2                  | 0.8        |         |

<sup>a</sup>Time for the current to change from 10 to 90% of rated values and containing that of the C/D equipment.

<sup>b,c</sup>Rise and fall times were measured, respectively, at the start and finish of rated charge or discharge.

and scarcely depended on states of charge. This is probably because the capacitance of the plate electrodes parallel to each other and the inductance of the terminal and manifold between the unit cells are dominant in the internal resistance of the batteries.

(vii) *Voltage-current characteristics [17]*

The results showed that the polarization characteristics of the batteries were essentially linear over a wide current range for both charge and dis-



TABLE 14

Internal resistance and short circuit current of 10 kW class advanced batteries

|                                      | Na-S | Zn-Cl <sub>2</sub> | Zn-Br <sub>2</sub> | Redox-flow type |
|--------------------------------------|------|--------------------|--------------------|-----------------|
| <b>Internal resistance</b>           |      |                    |                    |                 |
| a.c. method (mΩ)                     | 14   | 12                 | 12                 | 17              |
| d.c. method (mΩ)                     | 13   | 11                 | 12                 | 16              |
| <b>Initial short circuit current</b> |      |                    |                    |                 |
| a.c. method (A)                      | 4100 | 4200               | 3500               | 3500            |
| d.c. method (A)                      | 4400 | 4600               | 3500               | 3700            |

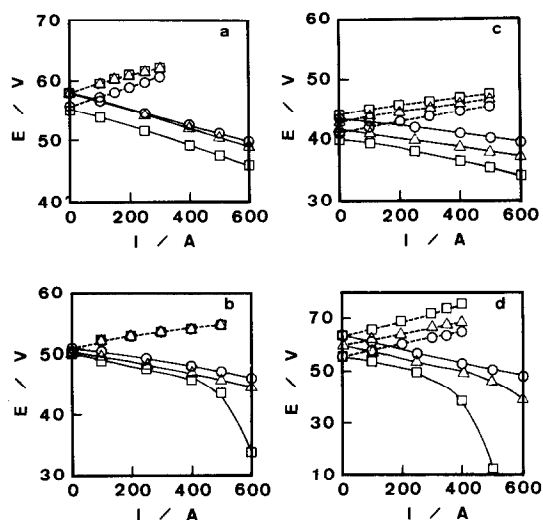


Fig. 8. Voltage-current curves of the 10 kW class advanced batteries. Curves a, b, c, and d are as in Fig. 3. Symbols  $\circ$ ,  $\triangle$ , and  $\square$  refer to the initial (0.5/8), middle (4/8) and final (7.5/8) stages of the 8 HR charge and discharge, respectively. (The depth of charge or discharge of the stages are shown in parentheses.) - - -, charge; —, discharge.

charge, indicating a predominantly ohmic impedance of about 10 mΩ (Fig. 8). The values were consistent with those observed in Section (vi). It was also verified that the advanced batteries were amenable to high rate discharges up to 600 A and charges of 300 - 500 A.

The electrical insulation between an electrode and cell container was tested after removing the cables of auxiliaries and sensors, because these elements were not optimized at this stage. The results showed that improvements in insulation are still necessary for the overall battery systems. Concentrations of poisonous gases, such as SO<sub>2</sub> (Na-S), Cl<sub>2</sub> (Zn-Cl<sub>2</sub>), Br<sub>2</sub> (Zn-Br<sub>2</sub>) and HCl (redox-flow type), were monitored both inside and outside the testing rooms over the testing period. No gas contents above the environmental standards of Japan were detected. No safety problems were

TABLE 15

Characteristics and problems of the 10 kW class advanced batteries

| Battery            | Advantage  | Problem  |
|--------------------|--|--|
| Na-S               | <ol style="list-style-type: none"> <li>1. Very high energy efficiency (<math>\eta_O = 77.1\%</math>)</li> <li>2. No self-discharge</li> <li>3. Remarkably high energy density (<math>52.5 \text{ kW m}^{-2}</math>, <math>26.8 \text{ kW h m}^{-3}</math>, <math>42.6 \text{ W h kg}^{-1}</math>)</li> </ol> | <ol style="list-style-type: none"> <li>1. Large stand-by energy (<math>19.4 \text{ kW h day}^{-1}</math>)</li> <li>2. Temperature control system necessary</li> <li>3. Reliability and high cost of solid electrolyte</li> </ol>   |
| Zn-Cl <sub>2</sub> | <ol style="list-style-type: none"> <li>1. Stable voltage during charge and discharge</li> <li>2. Little stand-by energy (<math>0.7 \text{ kW h day}^{-1}</math>)</li> </ol>  | <ol style="list-style-type: none"> <li>1. Rather low energy efficiency (<math>65.7\%</math>)</li> <li>2. Complex solvation technique for efficient operation</li> <li>3. High auxiliaries' power</li> <li>4. Low energy density</li> <li>5. Dendritic zinc deposition</li> </ol>   |
| Zn-Br <sub>2</sub> | <ol style="list-style-type: none"> <li>1. High energy efficiency (<math>\eta_O = 71.1\%</math>)</li> <li>2. Little stand-by energy (<math>0.0 \text{ kW h day}^{-1}</math>)</li> <li>3. Temperature control is unnecessary</li> <li>4. Low cost electrode</li> </ol>   | <ol style="list-style-type: none"> <li>1. High self-discharge rate (<math>\Delta\eta_B = 7.4\% \text{ week}^{-1}</math>)</li> <li>2. Dendritic zinc deposition</li> </ol>  |
| Redox-flow type    | <ol style="list-style-type: none"> <li>1. Long operational life is expected because active materials neither deposit nor dissolve</li> </ol>   | <ol style="list-style-type: none"> <li>1. Low energy density (<math>5 \text{ kW h m}^{-2}</math>, <math>3.3 \text{ kW h m}^{-3}</math>, <math>6.3 \text{ W h kg}^{-1}</math>)</li> <li>2. Large stand-by energy (<math>20.1 \text{ kW h day}^{-1}</math>)</li> <li>3. Temperature control system necessary (<math>40 \text{ }^\circ\text{C}</math>)</li> </ol> |

encountered with these batteries, but halogen gas scrubbing systems were occasionally needed to cope with minor halogen gas releases from the Zn-Cl<sub>2</sub> and Zn-Br<sub>2</sub> batteries. Finally, the current status, and the problems to be overcome in respect of the 10 kW class advanced batteries are summarized in Table 15. The reliability, safety, and economic assessments of the total battery systems should be established in advance of practical applications; these are outside the scope of this investigation.

## Conclusion

It is evident that the performance of the four 10 kW class advanced batteries developed in Japan is sufficient to achieve the project goals —

energy efficiency, cycle life,  $I$ - $V$  characteristics, fast response, etc. However, improvements are needed in the areas of self-discharge, electrical insulation, and auxiliary systems via engineering and manufacturing process developments in the future. Based on continued technical progress, it is reasonable to expect that pilot plants of 1 MW/8 MW h will be constructed and demonstrated in the final phase of this project.

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