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Performance of large-scale secondary lithium batteries for electric vehicles and home-use load-leveling systems

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Abstract

The results of performance tests of the battery modules and single cells developed as part of the Japanese national project for energy storage are reported. Two types of 2 kWh-class modules for stationary use have almost attained the target of initial performance, but the cycle lives are still about 1000 cycles. Similarly, two types of 3 kWh-class modules for EV application have achieved the targets of 150 Wh/kg and 400 W/kg. The energy density of each single cell exceeded the target by about 20%, but in the case of the single cells of cylindrical shape, the target could not be achieved because of dead space in the modules. Cell performance under severe conditions of −20 °C or continuous discharge at 1.0*C* were suitable for practical use. The influence of the dynamic stress on cycle performance is shown to be slight, but the subject of energy storage at high temperature is pointed out in the case of the cells containing Mn oxide cathode.

Keywords: Lithium ion batteries; Performance test; Electric power storage; Electric vehicle

1. Introduction

The Japanese national project "Dispersed-Type Battery Energy Storage Technology" promoted by Ministry of Economy, Trade and Industry (METI) was started in financial year (FY) 1992 and research and development was completed in FY 2001. The objective is the efficient operation of electric power network systems, taking into consideration energy conservation and global environment protection. The target is load leveling, on the demand side, of several 10 kWh-class energy storage systems using lithium secondary batteries with high energy density and energy efficiency [1–3].

In this project, four types of batteries were scaled up to 300–500 Wh and were fabricated into 2–3 kWh-class modules through two interim evaluations. They are divided into two applications, stationary application (home-use load-leveling system) and electric vehicle (EV) application. CRIEPI has been conducting the performance test of these batteries as an impartial and common evaluator from the user's standpoint since 1997. Battery modules and large cells developed in the final stage were tested to evaluate their fulfillment of the target. In this paper, these test results are described.

2. Tested items and conditions

The targets of the modules for both stationary and EV applications are shown in Tables 1 and 2, respectively. The battery capacity, specific energy, energy density and energy efficiency are obtained from the capacity test. The charge conditions were in accordance with the developer's recommended procedure within 8 h. Basically they were regulated by the rated capacities in the stationary module and by the voltages of the single cells between 4.1 and 4.2 V in the EV modules. The discharge condition was 8 h rate for the stationary module and 5 h rate for the EV module, which were regulated by the voltages of the single cells between 3.2 and 2.7 V.

The life cycle tests were performed at 70% DOD for the stationary module and at 80% DOD for the EV module, and capacity tests were carried out every 50 cycles. Since a long life of 3500 cycles is required for the cells for stationary use, an accelerated aging test was carried out for the single cells fabricated in FY 2000 under suitable charging–discharging rate conditions [4]. Specific peak power (W/kg) was obtained by two testing methods, i.e. *I–V* performance by the constant current method and the constant pulse power method proposed by CRIEPI [5].

Thermal performance test, constant current discharge series and standing test (self-discharge) were performed

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Table 1
Performance of stationary modules

Item	Target	A (Ni–Co)	B (Mn)
Battery capacity (kWh)	2	2.3	2.5
Specific energy (Wh/kg)	120	128	122
Energy density (Wh/l)	240	197 (285)	255 (295)
Energy efficiency (%)	90	98	96
Cycle life (cycles)	3500	No test (900)[a]	Now testing[a] (1200)[a]

Single cell result is within parenthesis.
[a] FY 2000-prototype.

Table 2
Performance of EV modules

Item	Target	C (Ni–Co)	D (Mn)
Battery capacity (kWh)	3	3.8	4.1
Specific energy (Wh/kg)	150	150	155
Energy density (Wh/l)	300	252 (341)	244 (376)
Specific power (W/kg)	400	490	440
Energy efficiency (%)	85	97	96
Cycle life (cycles)	1000	570[a] (800)[a]	580[a] (750)[a]

Single cell result is within parenthesis.
[a] FY 2000-prototype.

for reference. Moreover, the calendar life test and the dynamic stress test were also carried out.

3. Specifications of tested batteries

The four types of battery modules subjected to performance tests are shown in Fig. 1. Type A for stationary use was fabricated by Sanyo Electric in FY 2000. Its component cell shape is cylindrical and the cell system consists of a $LiNi_{0.7}Co_{0.3}O_2$/graphite and hard carbon hybrid. Type B for stationary use was fabricated by Hitachi and Shin–Kobe Electric Machinery in FY 2001. Its component cell shape is prismatic and the cell system consists of Li-rich $LiMn_2O_4$/Ag-dispersed graphite. Type C for EV application was fabricated by Japan Storage Battery and Mitsubishi Electric in FY 2001. Its component cell shape is an elliptical cylinder and the cell system consists of $LiNi_{1-x-y}Co_xMn_yO_2$/multi-layered graphite. Type D for EV application was fabricated by Matsushita Battery. Its component cell shape is cylindrical and the cell system consists of $LiMn_2O_4$ with a trace amount of Cr/graphite. $LiPF_6$ in ethylene carbonate based solvent was used with all types of cell systems. Performance tests were carried out at 25 °C and three modules, excepting type B were cooled with a fan.

All four types of modules consist of eight series-connected single cells and are compactly packaged. A battery management system (BMS), which controls the SOC level of the single cells and outputs the signals for charging and discharging operations, is incorporated in each module.

4. Results and discussion

4.1. Core performance tests for stationary modules

The core performances of the stationary modules are shown in Table 1. Their battery capacities, specific energies and energy efficiencies achieved the target of the project. In particular, the energy efficiencies, which contained the power consumption for BMS operations but did not contain the electricity for the blower for cooling, are markedly higher than other batteries such as lead acid batteries and

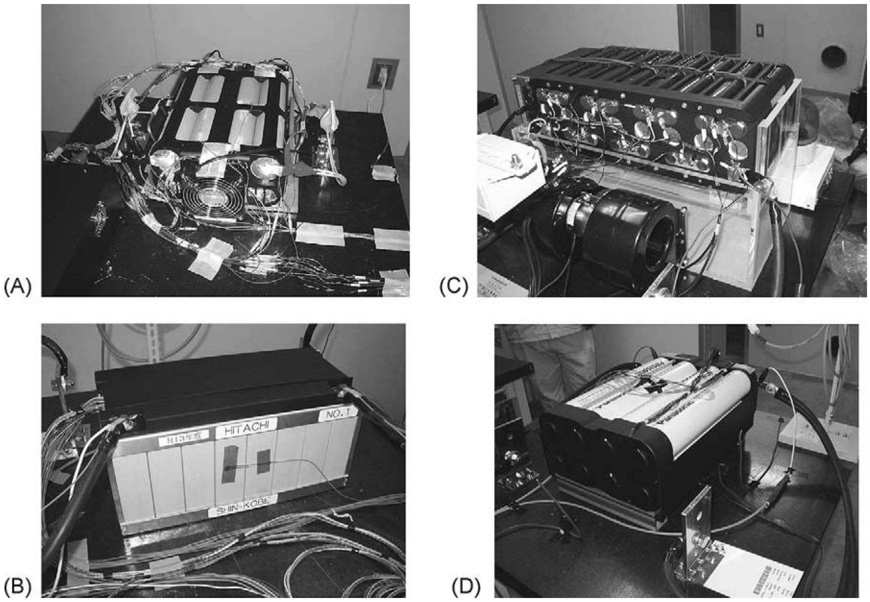

Fig. 1. Battery modules used in performance tests: (A) Ni–Co system of stationary type; (B) Mn system of stationary type; (C) Ni–Co system of EV application type; (D) Mn system of EV application type.

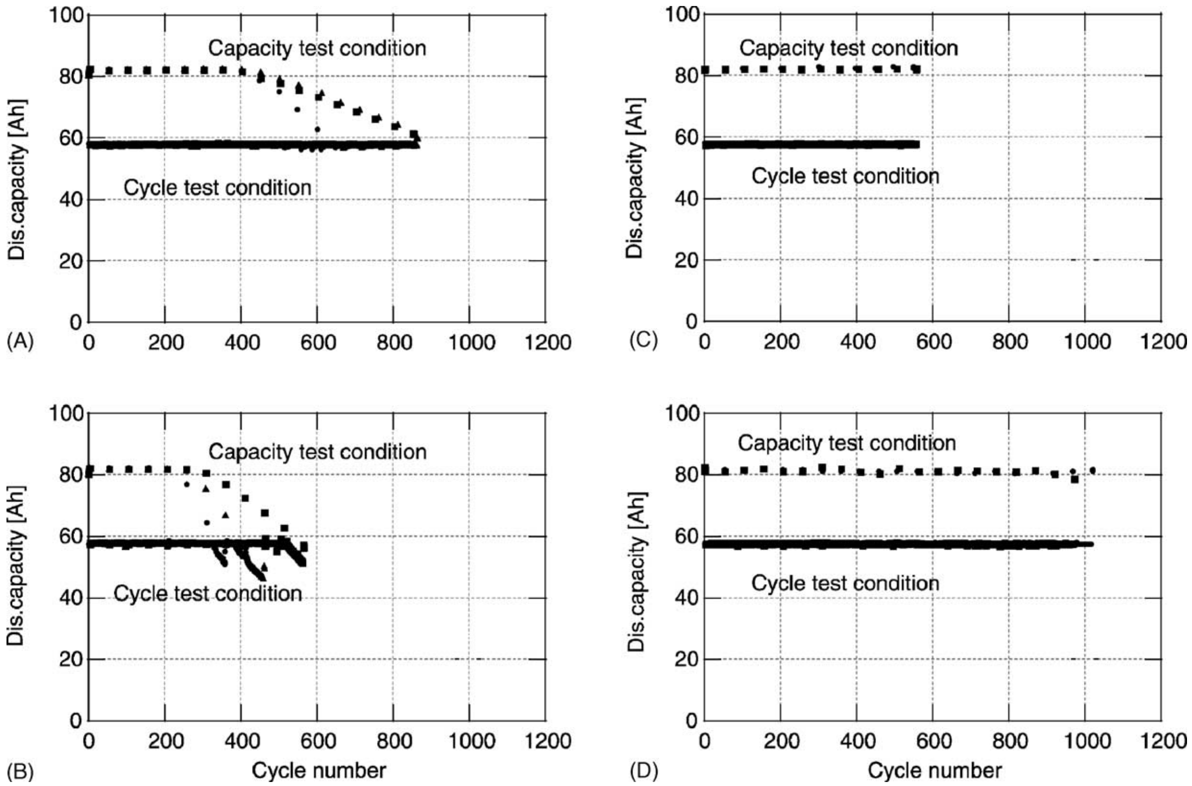

Fig. 2. Cycle performances of single cells of Ni–Co system fabricated in FY 2000: (A) standard condition (0.125 C) of EC:DEC electrolyte; (B) accelerated condition (0.25 C) of EC:DEC electrolyte; (C) standard condition (0.125 C) of EC:EMC electrolyte; (D) accelerated condition (0.25 C) of EC:EMC electrolyte.

nickel metal hydride systems. This suggests that lithium secondary batteries are promising for use in energy storage systems. In the case of type B, the energy density fulfilled the target of 240 Wh/l. On the other hand, in the case of type A, energy density was 82% of the target because dead space was included in the module. The energy densities of component cells of these two types of modules did not much differ greatly.

The cycle performance of the single cells of type A fabricated in FY 2000 is shown in Fig. 2. Results for both EC:DEC electrolyte and EC:EMC electrolyte are shown. In the case of EC:DEC electrolyte, cycle life was 900 cycles under the standard condition and 550 cycles under the accelerated condition. In the case of EC:EMC electrolyte, the operations were continued for 1000 cycles under the accelerated condition but capacity fading was not observed The cycle life is expected to be over 2000 cycles, as estimated from the charge end voltage. The electrolytes were found to have much influence on the reversibility and cycle performance as reported by Ein-Eli et al. [6]. The species of the solvents and their ratio need to be optimized in order to prolong the cycle lives of the cell [7]. The cycle performance

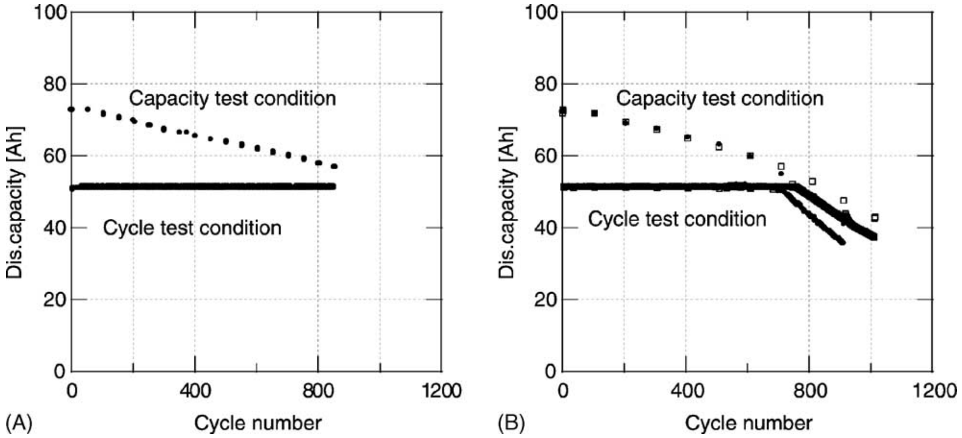

Fig. 3. Cycle performances of single cells of Mn system fabricated in FY 2000: (A) standard condition (0.125 C); (B) accelerated condition (0.33 C).

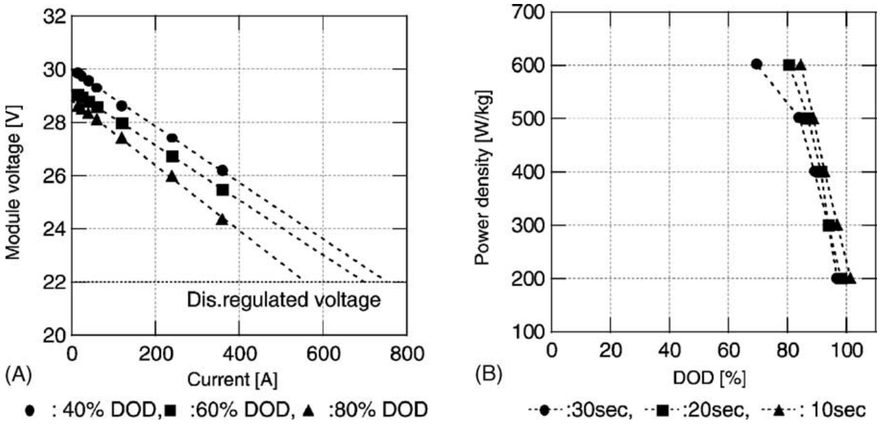

Fig. 4. Power capabilities of Ni–Co system module for EV application: (A) *I–V* performance and (B) constant power pulse method.

of the single cells of type B fabricated in FY 2000 is shown in Fig. 3. Eight hundred cycles were obtained under the accelerated condition and 1200 cycles were estimated from the tendency of capacity decrease under the standard condition. In the case of half-cell tests for both the cathode and the anode, 3500 cycles were obtained in the type B cell. A small type A cell of 10 Wh class showed a life of over 2000 cycles. Therefore, the target is expected to be achieved in the near future.

4.2. Core performance tests for EV modules

The core performances of the EV modules are shown in Table 2. The tendency of obtained results was similar to that in the case of stationary modules. In both types C and D, the specific energy satisfied the high target level of 150 Wh/kg. A high specific power of over 400 W/kg was obtained at 80% DOD for 30 s. Power capabilities of the type C module determined by both the *I–V* performance test and the constant power pulse method are shown in Fig. 4. In the case of the *I–V* performance test, the power density was calculated to be 489 W/kg at 80% DOD for 30 s. On the other hand, the value obtained directly under the same conditions was 520 W/kg by the constant power pulse method. The differences between the values obtained by the two testing methods, were within 20%. The value estimated from *I–V* performance is considered to be affected by the voltage profiles and their regulated discharge voltages.

The cycle performances of types C and D modules and single cells were insufficient. As a reference, the influence of the dynamic stress on cycle performance was examined for two 0.8 kWh-class modules of type C fabricated in FY 1999. The specific energy of these modules was 124 Wh/kg. Cycle lives under both constant current discharge and dynamic stress were over 1000 cycles as shown in Fig. 5, and little difference of cycle performances between two discharge loads was detected [8].

4.3. Other performance tests

4.3.1. Thermal performance test

Thermal performance tests were carried out after holding the modules for over 12 h at a fixed temperature after charging at 25 °C. Thermal performances of two types of single cells for EV application are shown in Fig. 6. The value of discharge energy at each temperature was normalized, with 100% being on the one at 25 °C. These performances were suitable for a practical use since over 70% of the energy could be discharged even at −20 °C. In general, the discharge energy increases with operating temperature. The

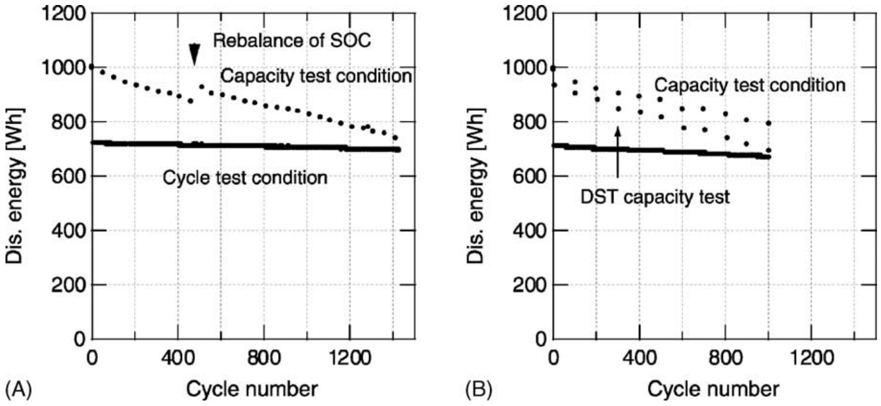

Fig. 5. Cycle performances of 0.8 kWh-class modules of Ni–Co system fabricated in FY 1999: (A) constant current discharge; (B) dynamic stress.

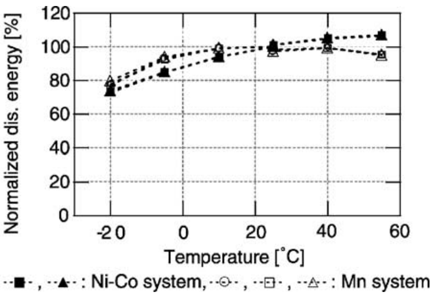

Fig. 6. Thermal performance of the single cells for EV application normalized with 100% being the discharge energy at 25 °C.

reason for the lack of an increase at higher temperatures in the Mn system is considered to be the effects of the test experience of the schedule from lower temperature.

4.3.2. Constant discharge test series

Discharge profiles of stationary modules of the Mn system with constant current discharge between 0.125 and 1.0 C are shown in Fig. 7. The discharge energy of over 90% was obtained even at 1.0 C. The surface temperature of the module in this test was the highest among all performance tests including power capability tests. The temperature at the center of the middle component cell increased to almost 50 °C at the end of discharge at 1.0 C. The supporting loads for stationary use are much smaller than 1 C, so the system with this module will be operable without forced cooling.

4.3.3. Standing test and calendar life test

Capacities of the single cells decreased by about 3–15% from the fully charged state over a period of 30 days at 25 °C. This capacity loss can be recovered by a few repetitions of cycling. This level is almost the same as that of a commercialized small cell [9].

In the calendar life test, there was a tendency for cell degradation to be promoted upon storage at high temperature and high SOC. The test result for type C indicated that its performance was good and the rate of fading capacity was about 4% per 1000 h at 55 °C with the cell in the fully charged state. In the cases of types B and D cells containing a Mn oxide cathode, the performance at a high temperature of 55 °C was insufficient for practical use. However, the change in the microstructure of the carbon anode and the substitution of a trace amount of another element for Mn oxide in the cathode were found to contribute to the improvement of calendar life at high temperatures.

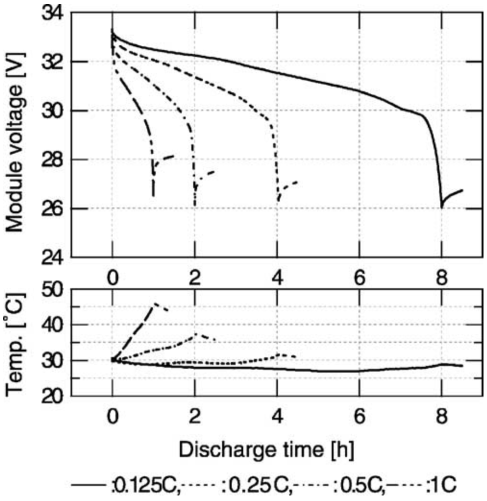

Fig. 7. Discharge profiles of stationary module of Mn system obtained from constant discharge tests between 0.125 and 1.0 C.

5. Conclusions

Performances and characteristics of four types of modules developed as part of the Japanese national project were clarified. Core performances of battery capacity, specific energy and energy efficiency fulfilled the target. The energy density of each single cell exceeded the target by about 20%, but in the case of the single cells of cylindrical shape, the target could not be achieved because of dead space in the modules. Cycle lives of the single cells for stationary use were at the 1000 cycle level, and it will be necessary to improve the manufacturing process and technology of large cells. Performances under severe conditions such as −20 °C and a continuous high discharge rate at 1 C were sufficient for practical use. For EV application, the influence of dynamic stress on cycle performance was shown to be a slight, but the issue of energy storage at high temperatures was pointed out in the case of the cells containing Mn oxide cathode.

For practical applications, further research and development will be necessary to resolve the remaining issues described above and various other aspects such as battery economy and safety. The practical use of battery energy storage technology is expected to play an important role in reducing environmental burden and in enabling the effective utilization of renewable energy.

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