

Development of lithium batteries for energy storage and EV applications

N. Terada*, T. Yanagi, S. Arai, M. Yoshikawa, K. Ohta, N. Nakajima, A. Yanai, N. Arai

Lithium Battery Energy Storage Technology Research Association (LIBES), Toshima-ku, Tokyo, 170-0013, Japan

Abstract

The results of the Japanese national project of R&D on large-size lithium rechargeable batteries by Lithium Battery Energy Storage Technology Research Association (LIBES), as of fiscal year (FY) 2000 are reviewed. Based on the results of 10 Wh-class cell development in Phase I, the program of Phase II aims at further improvement of the performance of large-size cells and battery modules, and the formulation of roadmaps toward worldwide dissemination of large-size lithium secondary batteries. In addition to the above R&D programs, a new target was presented particularly for the near-term practical application of several kWh-class battery modules in FY 1998.

For the large-size battery modules, two types of 2 and 3 kWh-class battery modules have been developed for stationary device and electric vehicle applications, respectively. The battery modules for both types have achieved most of the targets other than cycle life. Currently, further improvements in the cycle life of the cells themselves are being pursued. For this purpose, the materials for cathodes and anodes, the shapes and structures for batteries and the methods for cell connection are being re-investigated.

The development of middle-size battery systems for mini-size electric vehicles (EVs), as well as for demand-side stationary device applications is under way. These battery systems have been fabricated and their fundamental performance confirmed. They are now being subjected to field tests. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium secondary battery; Battery energy storage; Electric vehicles; Active materials

1. Introduction

Since its invention by a Japanese company in 1991, the lithium ion battery has attracted much attention both of consumers and companies of different kinds because of its performance potential, growing markets and rapid increases in production. Lithium ion batteries have so far been used for portable electronic devices such as cellular phones camcorders and portable computers. The size of the commercially available battery is limited to 10 Wh, while some larger ones are in pre-pilot evaluation.

Although large-size lithium ion batteries have all so many advantages over other types of secondary batteries, they are not yet on the market on a commercial scale. This is due to reasons, which include difficulties in processing and safety issues. However, the demands for large scale battery energy storage are increasing for reasons of saving energy and environment protection, i.e. development of electric vehicle (EV) and HEV, load-leveling of electric power, and supplementary systems for solar and wind power.

Although much work is being conducted on the fundamental and applied aspects round the world, Japan is still the

leading country in both production and R&D of the lithium battery. For R&D of large-size lithium batteries, Japan is very active and a national project has been carried out. In this paper, the results of the on-going Japanese national project will be reviewed.

Since fiscal year (FY) 1992, Lithium Battery Energy Storage Technology Research Association (LIBES) has been conducting R&D on rechargeable lithium battery technology for both EVs and stationary battery energy storage systems [1,2]. Battery energy storage technology was one of the promising candidates for the efficient operation of electric power network systems. New Energy and Industrial Technology Development Organization (NEDO) entrusted LIBES with the R&D, named “dispersed-type battery energy storage technology” as part of the New Sunshine Program promoted by Ministry of International Trade and Industry (MITI). In January of 2001, MITI was reorganized to become the Ministry of Economy, Trade and Industry (METI).

The schedule of the project is shown in Table 1. Phase I of the project ran from FY 1992 through FY 1996. The R&D of phase I focused on basic battery technologies including cathode/anode materials, electrolytes, and so on, in order to fabricate 10 Wh-class cells [3,4]. Based on the results of the interim evaluation in FY 1996, the first amendment of the basic plan was carried out. Phase II of the project starting in

* Corresponding author. Tel.: +81-395-511-021; fax+81-359-511-025.
E-mail address: teradan@libes.dcc.co.jp (N. Terada).

Table 1
R&D schedule and subjects of the “development of disperse battery energy storage technology”

Fiscal year (FY)	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001
Schedule	← Phase 1 →					← Phase 2 →				
					Interim evaluation 1st amendment of R&D plan		Check and review of large-scale cells and battery modules	2nd amendment of R&D plan	Pre-final evaluation	Final evaluation
Subjects of R&D										
Development of high performance battery	<ul style="list-style-type: none"> Material research R&D of high performance cell (10 Wh-class) 					<ul style="list-style-type: none"> Scaling up of cells Fabrication of modules Improvement of reliability 				
Total system study	<ul style="list-style-type: none"> Market entry scenario System design 					<ul style="list-style-type: none"> Performance tests Cost analysis Safety tests Recycling <p>Middle-size battery development for early commercialization</p>				

FY 1997, was focused on the scaling up of four types of cells up to several hundred Wh, and the fabrication of modules.

The review to determine which battery systems of the several hundred Wh-class prototype cells and which of the 2–3 kWh-class modules were to be continued further was implemented by NEDO in FY 1998. As a result of this, the development of four types of battery technologies was selected to be continued further [5,6].

In FY 1999, a new target for near-term practical applications using middle-size battery modules was added in a second amendment of the basic plan. Fundamental research in novel materials and next generation battery technology has been carried out in parallel with the development of battery modules [7]. The historical development of battery energy storage technology in the Japanese national project was described in reference [8]. Lithium battery technology has good potential for contributing to global environmental protection and for saving fossil resources in addition to improving local air pollution and the load factor of electricity demand.

2. Work share in LIBES

Table 2 shows the work share in LIBES. LIBES has promoted R&D through “a competition and cooperation for the task” among the members. The scaling up and the enhancement of safety and reliability of cells and battery modules have been conducted step by step through improvement in the properties of cathodes, anodes, and electrolytes by materials research. The manufacturing process is also important. Middle-size battery systems have been fabricated and tested to study the factors governing applicability, such as control and protection characteristics, to accelerate the near-term practical use of the lithium secondary battery. Battery safety technology and carbon material synthetic technology have been developed for the purpose of supporting the R&D.

At the same time, forward-looking research also has been carried out to realize next generation battery technologies.

Table 2
Work share in LIBES

Development of battery module: large-size and middle-size	Stationary type EV-application type Technology support	Hitachi/Shin-Kobe Japan storage battery/Mitsubishi electric Osaka gas Toshiba
Development of next-generation battery	Lithium polymer battery Lithium metal battery Nonflammable electrolyte	Yuasa Denso Mitsubishi chemical
Study of total system	System analysis and performance test Safety test	CRIEPI NTT

2.1. Development of battery modules

Fig. 1 shows photographs of typical prototype modules with their main specifications. The features of the battery modules are as follows [2].

1. Stationary type

1.1. Stationary type A

$\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ is chosen as the cathode active material for its good capacity and cycle life. Graphite/hard carbon hybrid is selected as the anode active material to improve cycle life. The cell shape is cylindrical [9,10].

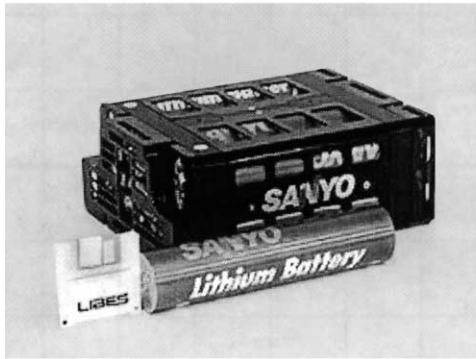
1.2. Stationary type B

For the cathode Li-rich manganese spinel (LiMn_2O_4) is chosen for its good cycleability. Manganese oxide is an abundant and less expensive metal. Graphite dispersed with Ag is used as an anode active material because of its good cycleability. The cell shape is prismatic [11,12].

2. EV application type

2.1. EV application type A

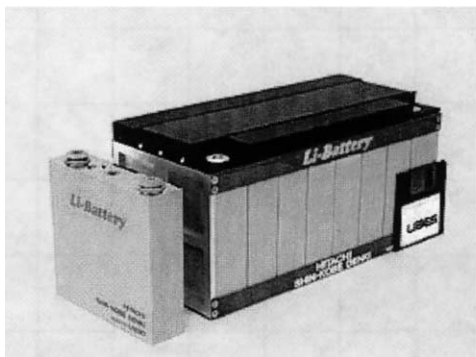
A cathode active material of $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ system is investigated to improve electrochemical characteristics and thermal stability and to examine its mass production potential. The negative electrode has a multi-layered structure of carbon materials. The cell shape is elliptic cylindrical [13,14].



Specification of a large-size single cell and 2kWh-class battery module (Stationary Type A: Ni-Co System)

Item	250Wh class cell	2kWh class module
Battery system	Stationary Type A	
positive electrode / negative electrode	$\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ Graphite/hard carbon hybrid	
Component of module	cylindrical	8 cells in series
Dimensions (mm)	$\phi 64 \times L312$	$W265 \times L328 \times H135$
Weight (kg)	2.19	18.1
Voltage (V)	3.5	28.
Capacity (Ah)	80	80

Specification of a large-size single cell and 2kWh-class battery module (Stationary Type B: Mn System)

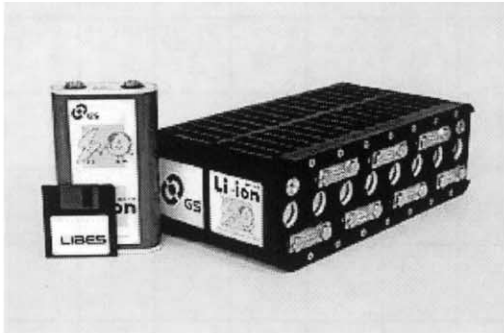


Item	250Wh class cell	2kWh class module
Battery system	Stationary Type B	
positive electrode / negative electrode	Li-rich LiMn_2O_4 Ag-dispersed Graphite	
Component of module	Prismatic	8 cells in series
Dimensions (mm)	$W160 \times 41 \times L155$	$W164 \times L349 \times H171$
Weight (kg)	2.41	20.8
Voltage (V)	3.9	31.2.
Capacity (Ah)	75	75

(a)

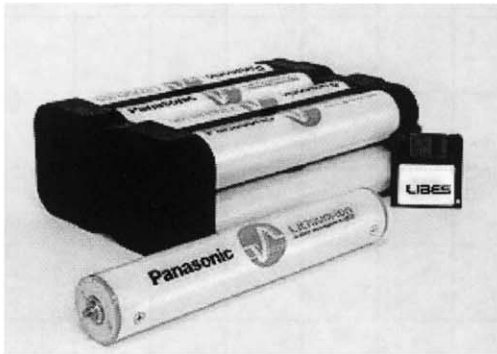
Fig. 1. (a) Photograph and specifications of 2 kWh-class modules for stationary application develop by LIBES, (b) Photographs and specifications of 3 kWh-class modules for electric vehicle application developed by LIBES.

Specification of a large-size single cell and 3kWh-class battery module (EV Application Type A: Ni-Co System)



Item	400Wh class cell	3kWh class module
Battery system	EV Application Type A	
positive electrode / negative electrode	LiNi _{1-x-y} Co _x Mn _y O ₂ Multi-layered Graphite	
Component of module	Elliptical Cylindrical	8 cells in series
Dimensions (mm)	W130*T50*L210	W265*L328*H135
Weight (kg)	2.7	24.4
Voltage (V)	3.65	28.8
Capacity (Ah)	122	122

Specification of a large-size single cell and 3kWh-class battery module (EV Application Type B: Mn System)



Item	400Wh class cell	3kWh class module*1)
Battery system	EV Application Type B	
positive electrode / negative electrode	LiMn ₂ O ₄ Graphite	
Component of module	Cylindrical	8 cells in series
Dimensions (mm)	φ 65*L410	W280*L420*H140W*1)
Weight (kg)	3.34	29*1)
Voltage (V)	3.8	30.4*1)
Capacity (Ah)	123	110*1)

*1) FY1998-prototype module

(b)

Fig. 1. (Continued).

2.2. EV application type B

As a cathode active material, LiMn₂O₄ is chosen from the standpoint of its cost reduction capabilities. Graphite is chosen as an anode active material. The cell shape is cylindrical [15].

2.2. Battery systems for near-term practical use

Battery module developers in LIBES have developed middle-size batteries aiming at near-term practical applications [7].

2.3. Supporting technology

In order to support the R&D of the modules, synthetic carbon material technology and battery safety technology have been developed.

1. Carbon materials

The role given to the carbon material developer is to produce carbon anode materials with higher specific capacity, and to steadily supply a sufficient amount of high performance carbon material to battery manufacturing members.

2. Battery safety technology

The objective of this technology is to analyze the mechanism of the behavior of lithium battery under abused conditions.

2.4. Next generation battery technology

1. Solid polymer electrolyte battery technology

The dry polymer used in lithium secondary battery is being prospected to improve battery safety and flexibility in cell design. For example, bipolar electrodes could be stacked to enhance specific energy.

2. Lithium metal anode battery technology

The lithium metal anode has poor cycleability in spite of its high capacity. The suppression of dendritic growth of lithium metal would lead to secondary cells with very high specific energy.

3. Nonflammable electrolyte

A nonflammable solvent is expected to prevent the cell from venting with fire. This technology could drastically decrease safety problems and extend the application of lithium battery with high reliability, although new environmental problems, which might be caused the emission of harmful chemicals, should be carefully examined before this development could be adopted.

2.5. Study on total systems

This subject involves the analysis and evaluation of required performance, optimum capacity, environmental safety, cost-effectiveness, and efficient utilization of resources such as recycling.

1. System analysis and performance tests

An investigation was carried out to develop strategies for introducing lithium secondary battery systems and to propose methods for testing battery performance. Tests of the prototype battery modules have been carried out to evaluate their fundamental performance.

2. Safety tests

Safety evaluation tests of prototype cells without safety devices were carried out to monitor the phenomena under abuse conditions. These data supply

information to improve cell safety. An investigation of procedures of safety tests for large-size lithium battery modules has been carried out aiming at establishing fundamental test methods.

3. Status of R&D in battery technology

The performance of 2 and 3 kWh-class modules at the end of FY 2000 is summarized in Tables 3 and 4.

3.1. Battery module

The battery modules of each type consist of eight cells connected in series.

1. Stationary type

1.1. Stationary type A

To achieve higher energy density, components of the 250 Wh-class single cell have been improved. The improvement also includes optimizing the cell design by making the cell case more compact. The specifications of a large-size single cell are shown in Fig. 1. Table 3 shows preliminary test results of a 2 Wh-class battery module. As is shown, the energy density of a single cell increased by 4% in FY 2000 compared to that in FY 1999.

1.2. Stationary type B

Single cells of 250 Wh-class and battery modules have been developed with Ag-dispersed graphite negative electrodes and Li-rich LiMn_2O_4 positive electrodes. The improvement includes decreasing the weight of the single cell and module, the optimizing the electrodes design by improving the active material of the negative electrode and the current collectors. The specification of a large-size single cell is shown in Fig. 1. Table 3 shows the preliminary test results of a 2 Wh-class battery module. A capacity increase of 15% was achieved in FY 2000 compared with the same size battery module fabricated in FY 1999. Cycle life test is still going on.

2. EV application type

2.1. EV application type A

Table 3

Status of R&D (preliminary test results) of large-size battery modules for stationary application

	Target	Nickel–cobalt (type A) ^a	Manganese (type B) ^b
Discharge capacity (kWh)	2	2.28	2.34
Specific energy (Wh/kg)	120	126	112
Energy density (Wh/l)	240	194	239
Energy efficiency (%)	90	96	95.6
Cycle life (cycle) ^c	3500	~780 ^d	~930 ^e

^a Battery shape: cylindrical.

^b Battery shape: prismatic.

^c Life cycle criteria; 70% of nominal capacity.

^d FY 1998-prototype module: one cell was changed at 325 cycles.

^e FY 1998-prototype module: charging was changed from CC method to CC + CV method at 845 cycle.

Table 4
Status of R&D (preliminary test results) of large-size battery modules for EV application

	Target	Nickel–cobalt (type A) ^a	Manganese (type B) ^b
Discharge capacity (kWh)	3	3.55	3.17 ^c
Specific energy (Wh/kg)	150	146	130 ^d
Energy density (Wh/l)	300	271	235 ^d
Specific power (W/kg)	400	783 ^e	416 ^c
Energy efficiency (%)	85	96	96.6 ^c
Cycle life (cycle) ^f	1000	~620 ^e	~460 ^e

^a Battery shape: elliptical cylindrical.

^b Battery shape: prismatic.

^c FY 1998-prototype module.

^d The value calculated for a module based on that of a single cell.

^e FY 1999-prototype module.

^f Life cycle criteria; 80% of nominal capacity.

A prototype 400 Wh-class cell was designed and fabricated. To improve the charge/discharge characteristics of batteries, mechanical characteristics of $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ particles for the positive electrode were optimized. A specific energy of 164 Wh/kg, and an energy density of 332 Wh/l were attained for the 400 Wh-class. A prototype 3 kWh-class battery module equipped with a cell sensor (CS) was manufactured. Performance tests were carried out to confirm the improvement. Specific energy and energy density as a module reached 146 Wh/kg and 271 Wh/l respectively as shown in Table 4. A cooling system was optimized by computer simulation in order to lengthen the life of the battery module.

2.1. EV application type B

The cathode active material based on LiMn_2O_4 was optimized in its composition in order to achieve the final energy density goal. A new prototype cell was fabricated using, the negative electrode optimized by minimum irreversible capacity carbon a lightweight case and other components. The prototype cell showed a specific energy of 140 Wh/kg, an energy density of 346 Wh/l, and a specific power of 465W/kg. The cycle life test for the modified FY 2000 specification cell was started.

3.2. Fundamental technology; latest topics in progress

In order to achieve the targets of the project, the improvement of battery materials such as cathode active materials, anode active materials and electrolytes has been continued.

3.2.1. Positive electrodes

Ni–Co system cathodes were investigated by substituting of the Ni in LiNiO_2 with Co and/or other metals. Fig. 2 shows the specific capacities of the ternary metal oxide system of Ni–Co–Mn [16]. This ternary oxide cathode could show good thermal stability characteristics. The cells with Ni–Co–Mn system cathode stood at various temperatures for 200 days in a calendar life test as shown in Fig. 3. The largest capacity fading of ca. 20% occurred for a cell

after standing at 55°C, the highest temperature of the testing conditions.

The durability of the cell capacity of a manganese spinel positive electrode was examined. The capacity fading was larger after storage at high temperature compared with that of a LiCoO_2 or a LiNiO_2 cell. Fig. 4 shows the storage characteristics of the cell with a manganese spinel positive electrode at different states of charge (SOC) [17]. It was recognized that the capacity fading of the positive electrode was small in the range above 40% SOC; on the other hand, it had a maximum value near 20% SOC.

By analysis of crystal structure before and after storage, it was clarified that the capacity fading of the low SOC cell after high temperature storage was caused by a crystal structure change of the LiMn_2O_4 . It was found that the substitution of heterogeneous metal element into Mn-site of LiMn_2O_4 could improve the crystal change.

3.2.2. Negative electrodes

Stationary type batteries require a long-term service life of 10 years corresponding to about 3500 cycles. The anode plays an important role in the cycle life retention of batteries.

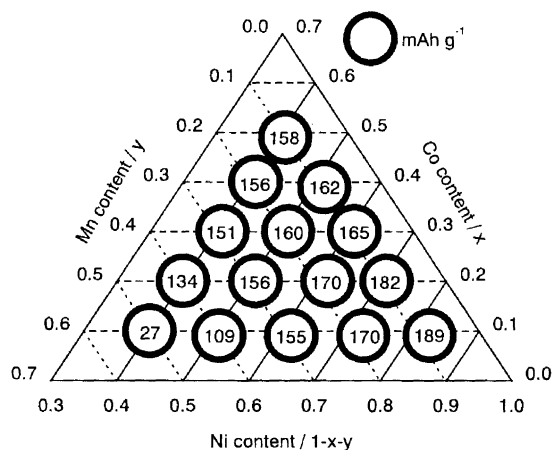


Fig. 2. Plots of the discharge capacity for $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ systems positive active materials; charge: 1 mA cm^{-2} to 4.3 V vs. Li/Li^+ at 25°C; discharge: 1 mA cm^{-2} to 3.0 V vs. Li/Li^+ at 25°C.

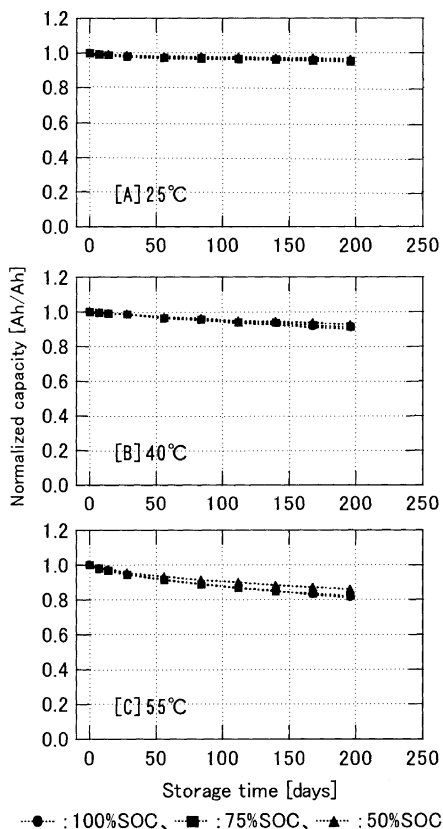


Fig. 3. Normalized discharge capacity of 3rd cycle after storage in calendar life test (Ni-Co-Mn system positive electrodes).

Sanyo found that the mixture of graphite with coke carbon in the anode showed a better life performance than that of graphite anode alone. The 10 Wh-class cell with a negative electrode of graphite/coke hybrid carbon fabricated in FY 1996 had been cycled to about 2300 cycles as shown in Fig. 5 [18]. Post analysis of the cycled cell using NMR suggested that inactive lithium was accumulated in the decomposition products of electrolyte on the negative electrode during

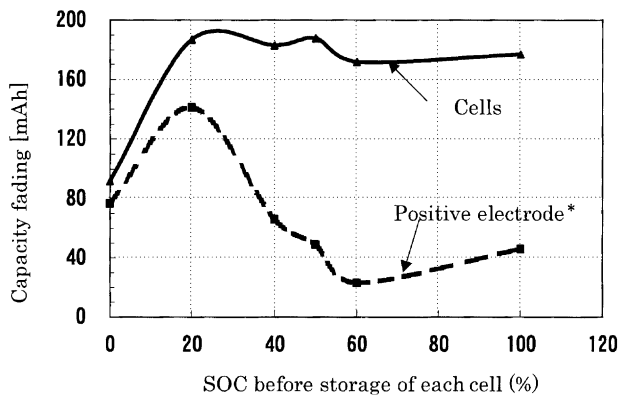


Fig. 4. Storage characteristics of secondary lithium cells with manganese spinel positive electrode at different SOC; (*) positive electrode: The values were determined by capacity test using the cathode of decomposed cells after storage at different SOC.

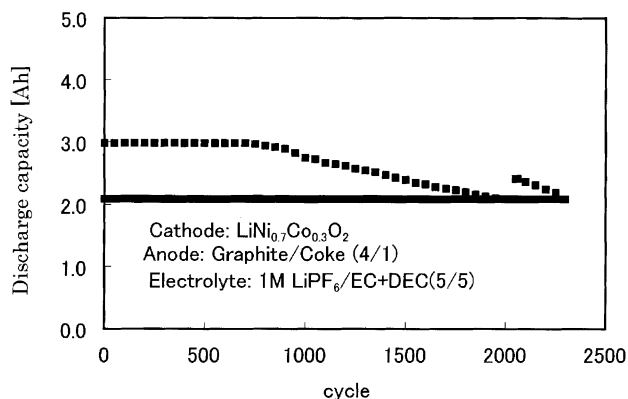


Fig. 5. Cycle performance of 10 Wh-class cell (charge/discharge: 0.4 C rate).

cycling. Recently it was found that the graphite/hard carbon hybrid carbon had a high discharge capacity of 371 Ah/kg almost as large as the theoretical value of LiC_6 . Concerning the cell using the graphite/hard carbon hybrid anode, a better cycle performance than that using the graphite/coke hybrid anode was reported [19]. The cycle performance of 2 Wh-class cell using a graphite/hard carbon hybrid electrode showed a deterioration rate of the discharge capacity of 0.00334% per cycle.

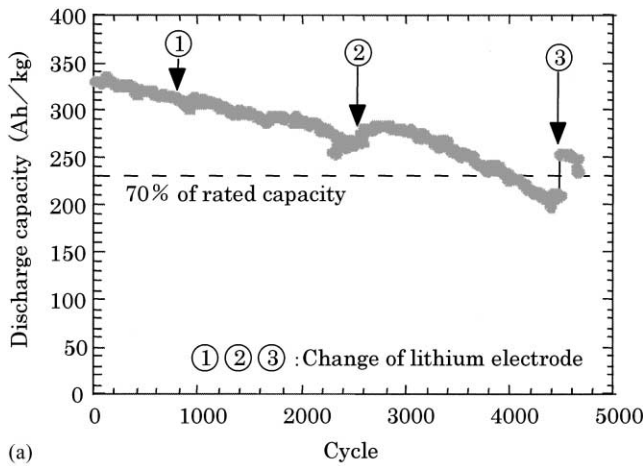
Hitachi Ltd., and Sin-Kobe Electric Machinery Co. Ltd., the co-working group for the stationary type B (manganese system), revealed an excellent behavior of the Ag-dispersed massive graphite [20]. Fig. 6a shows the cyclability of the Ag-dispersed graphite anode in a half-cell. A dispersed massive graphite has a large discharge capacity and has a small irreversible capacity based on a side reaction. A cycle life of about 4000 cycles was achieved. In addition to anode capability, Li-rich LiMn_2O_4 spinel cathode achieved about 3500 cycles at 70% DOD in a half-cell as shown in Fig. 6b [21,22].

A multi-layered graphite anode was proposed by Japan Storage Battery Co. Ltd., to improve the electrical contact between the active material layers and the current collector foil [14].

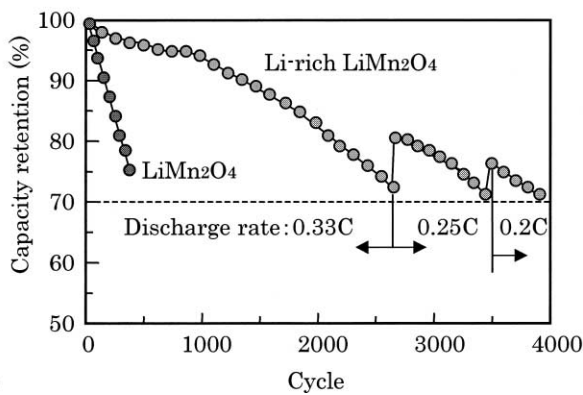
Osaka Gas Co. Ltd. produced a hard carbon that had higher capacity than the value of 372 Ah/kg based on the composition of LiC_6 . They made an intensive study of the effect of an oxidation-treatment of the carbon on its anode performance [23]. The effect of the oxidizing treatment in air with phosphorous pentoxide (P_2O_5) on the electrochemical performance of the hard carbon was examined. Fig. 7 shows charge/discharge curves for P_2O_5 -doped hard carbons. Their capacity apparently depends on the amount of P_2O_5 . It seemed that the optimum P_2O_5 content was ca. 5%. They also examined the effect of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ -dopant [24].

3.2.3. Electrolytes

A large-scale battery system employs lithium hexafluorophosphate (LiPF_6) as a solute. The solvent is a carbonate mixture based on ethylene carbonate (EC), diethyl carbonate



(a)



(b)

Fig. 6. (a) Cycle life of 10% Ag-dispersed graphite in a half-cell (counter electrode is lithium metal); (b) cycle life of Li-rich LiMn_2O_4 electrode.

(DEC), ethyl–methyl carbonate (EMC), and so on. The electrolyte solution of each battery system was selected carefully considering the interaction between the electrolytes and the cathode/anode couples as an alternative to LiPF_6 -based electrolytes, the possibility of other electrolyte systems has been investigated in the next generation battery technology research.

Yuasa has been investigating solid polymer electrolytes based on a cross-linked random copolymer of ethylene oxide (EO) and propylene oxide (PO). The ionic conductivity of a

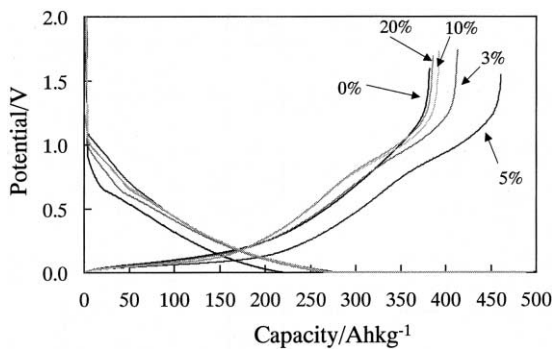


Fig. 7. Charge/discharge curves of hard carbon prepared from P_2O_5 -doped precursors.

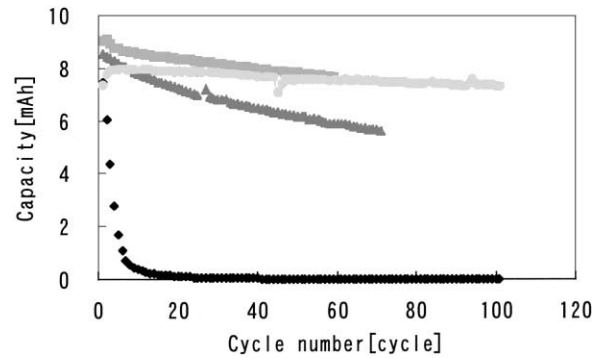


Fig. 8. Cycle ability of Li/LiCoO_2 cell using polymer electrolytes. Electrolytes: (◆) LiBF_4 (EO/Li=20/1), (■) $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (EO/Li=20/1), (△) $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$ (EO/Li=20/1), (○) $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (EO/Li=10/1). Constant current, 1mA; voltage range between 4.1 and 3.0 V temperature at 60°C ; effective electrode area 15.84 cm^2 .

typical solid polymer electrolyte was about 10^{-4} S/cm at 60°C . Fig. 8 shows the cycle capability of the solid electrolyte in Li/LiCoO_2 cells [25]. The content and species of salt affected the cycleability [26]. Cycle tests are continuing after more than 400 cycles in a cell of $\text{Li/solid electrolyte/LiCoO}_2$.

Denso Co. has been investigating a lithium metal technology. The insufficient coulombic efficiency of lithium anode resulted in poor cycle characteristics of the system. A new type of electrolyte involving $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ (LiBETI: lithium bis-ethyl sulfonic imide) and cyclic ether compounds was applied to this system. It is suggested that lithium cyclic efficiencies have a relationship with the charge transfer resistance in various electrolytes [27]. They assembled a 10 Wh-class cell using the LiBETI-based electrolyte (0.9 M LiBETI + 0.1 M $\text{LiPF}_6/\text{EC} + \text{THP} + \text{DOX}$ (40:30:30)), and tested the cycleability. Over 350 cycles of the 10 Wh-class cell (120 Wh/kg, 242 Wh/l) were as shown in Fig. 9.

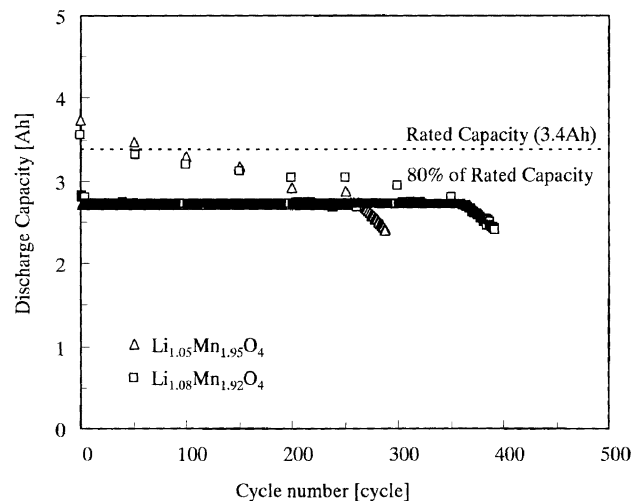


Fig. 9. Cycle performance of 10 Wh-class $\text{LiLi}_2\text{Mn}_3\text{O}_2$ cells. Charging rate: $1/14.5\text{ C}$, discharging rate $1/4\text{ C}$; electrolyte 0.9 M LiBETI + 0.1 M $\text{LiPF}_6/\text{EC} + \text{THP} + \text{DOX}$ (40:30:30).

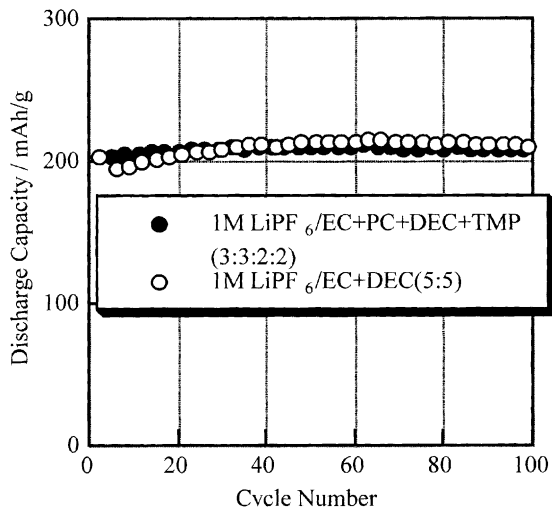


Fig. 10. Cycling performance of Li/hard carbon coin cell with different electrolytes. Current: 0.2 mA cm^{-2} , cutoff: 0–1.5 V.

Mitsubishi Chemical Co. supplied the LiBETI-based electrolyte mentioned above [28]. They also have been developing nonflammable electrolytes that have sufficient electrochemical properties [29].

TMP (trimethyl phosphate)-based electrolytes with LiPF_6 solute were investigated. The stability of nonflammable electrolytes in a cell depend on the structure of the carbon anode materials. Fig. 10 shows the cycling performance of Li/hard carbon coin cells with $\text{LiPF}_6/\text{EC} + \text{PC} + \text{DEC} + \text{TMP}$ (3:3:2:2) and $\text{LiPF}_6/\text{EC} + \text{DEC}$ (5:5) electrolytes. A good cycling performance in the nonflammable electrolyte cell similar to that in the conventional electrolytes cell was observed.

3.2.4. Module technology

A battery module is assembled with eight cells in series connection. A battery management system (BMS) has the function of rebalancing the cell capacities in a module. In the case of stationary type B, the cell voltages in the module at the end of discharge were distributed within about a 50 mV

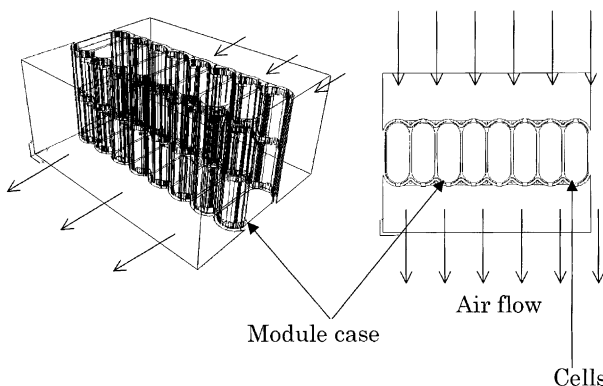


Fig. 11. Images of cooling simulation for electric vehicle application type A.

range [12]. This means that a rebalancing function of the BMS between the cell capacities worked well.

It is very important to manage the thermal characteristics of the module during charge and discharge [14]. The modules were designed considering an air-cooling system using the thermal simulation program shown in Fig. 11.

4. Scope for the battery technology

4.1. Near-term practical application

The development of middle-size batteries for near-term practical applications were added to one of the objectives in the basic plan of the project as a part of the amendment following the check and review in FY 1998. LIBES has been conducting R&D aiming at the eventual application of a middle-scale battery module in compact energy storage devices, commuter cars, electric scooters and so on.

R&D items aiming at the eventual application of middle-scale battery modules are as follows.

1. A 300–500 Wh-class battery systems and for lighting systems and for dispersed load-leveling.
2. A 1.5 kWh-class battery system for a mini load-leveling apparatus (named Mini LL) which is supplying electric power to home electric equipment during daytime.
3. A 13 kWh-class battery system for a small electric car.
4. A 1.5 kWh-class battery system for an electric scooter.

Fig. 12 shows some of models for the middle-size battery system.

4.1.1. Operation of a mini-scale load-leveling device (Mini LL)

The Central Research Institute of the Electric Power Industry (CRIEPI) has been carrying out operational tests of a mini-scale load-leveling device (Mini LL) that was manufactured by Hitachi. The Mini LL system composed of eight middle-sized modules with eight manganese type cells for stationary use has a 3 kVA-class converter/inverter system. At ambient temperature the AC input and output energy were examined. The battery energy storage efficiency (DC/DC: including peripheral circuits) was also measured to confirm the operation of the voltage-equalizing circuit.

4.1.2. Operational tests using EV application type batteries

Before installation on EVs, a Ni–Co type battery module composed of seven cells in series connection and a manganese type battery module with four cells in series connection were examined for initial performance, such as capacity and peak power. A constant current method and a DST (dynamic stress test) 120 method were adopted for the capacity test.

Measurement systems were set up to obtain operating data for mini-size EVs. The systems were installed in a mini-size one-passenger electric vehicle and in an electric scooter.



(A)



(B)



(C)

Fig. 12. Some models of middle-size battery systems for near-term practical use: (A) Mini load-leveling device (stationary type); (B) mini electric vehicle (EV) (EV application type); (C) electric scooter-ES-X2 with on-board monitoring device (EV application type).

Operational tests of the measurement systems were performed using separate VRLA type batteries with controller. The battery packs of Ni–Co type batteries and manganese type batteries were installed in the mini-size electric vehicle

and the electric scooter, respectively, to begin the driving tests.

4.2. Battery testing method

No standard testing method of the electric performance of large-size lithium secondary battery has yet been completely established. The fundamental performance tests such as battery capacity, power density and cycle life have been performed to evaluate the progress of R&D of the modules [30]. Battery tests that were focused on simulating practical use have been started aiming at further improvement. Mitsubishi Electric Co. carried out DST that simulated a modified practical driving pattern using small cells at various temperatures.

LIBES has also been conducting safety tests. Nippon Telegraph and Telephone Co. (NTT) has proposed various methods for safety testing in order to develop practically safe batteries based on the idea authorized by the Industry Technology Council of Japan as shown in Table 5. Safety tests were carried out of prototype large-size cell which were fabricated in FY 1998, without safety devices such as thermal fuse. Forced discharge tests caused no apparent change in the four types of cells. But results showed that the cells sometimes smoked, ignited and even reacted explosively during certain abuse condition. Based upon these data, several improvements of large-size cell safety have made steady progress.

Fig. 13 shows an approach concept to clarify relationships between battery characteristics and battery safety issues proposed by Toshiba Corporation [31,32]. In order to establish the technology for the safety of large-size lithium secondary batteries, it is essential to analyze quantitatively the mechanism of unsafe phenomena taking place in abuse tests, such as the nail-penetrating test.

As one of results, the thermal stability of Ni oxide cathodes was improved up to about 250°C by substituting certain amount of aluminum for Ni.

4.3. Socio-economic aspects of the lithium secondary battery system

CRIEPI has carried out an investigation based on the socio-economic aspects of the battery technology under cooperation with other members of LIBES.

Fig. 14 shows a cost estimate of the battery. The target cost level/kWh of battery for a 20 kWh-class stationary application was set from a calculation of the difference between the consumer electricity rates in daytime and in nighttime. In the case of a 45 kWh-class EV application, the target cost level was calculated from the difference between the cost of electricity at the nighttime when charging the EV batteries and the cost of gasoline required for running a conventional internal combustion engine vehicle for the same range in Japan. The calculated target costs were from about 43,000 to 35,000 Yen/kWh. On the other hand the estimated battery cost

Table 5
Safety test conditions for the battery developed by LIBES

Test conditions (for cell)	
Nail penetration	A fully charged cell is penetrated with a metallic nail. Nail diameter: 2.5–10 mm.
Crush	Crush the center of a fully charged cell by using a metal rod of 10–20 mm in diameter until the cell is deformed to 1/2 of the initial dimension or the drastic reduction of OCV is observed.
Overcharge	A fully discharged cell is to be charged at a constant current for the time corresponds to 250% of nominal capacity.
Overdischarge	A fully charged cell is to be discharged at a constant current for the time corresponds to 250% of nominal capacity.
External short circuit	A fully charged cell is short-circuited. The external short resistance is 1 mΩ or less.
Test conditions (for module)	
Insulation	DC voltage of 500 V is applied between the battery electrode and the ground for 10 min.
Earthquake tolerance	Vibration of 1.0g acceleration are applied in the vertical direction for 10 s. (Stationary type only)
Vibration	Vibration tests simulating driving conditions are performed. (EV application type only)
Monitoring of consequences in the event of accidental damages	The toughest test item, selected from various tests for cells, is applied to one cell located at the center of the module. The consequences of damage to the cell on other cells in the module are examined.
Water immersion	Entire module battery is immersed in salt water (sea water composition) in the case of EV application type or in tap water in the case of stationary type for 8 h.
Fire-exposure	A charged cell is exposed to the hottest region of an 8 feet diameter flame produced using a diesel fuel (JP-4) for 10 min. (EV application type only)

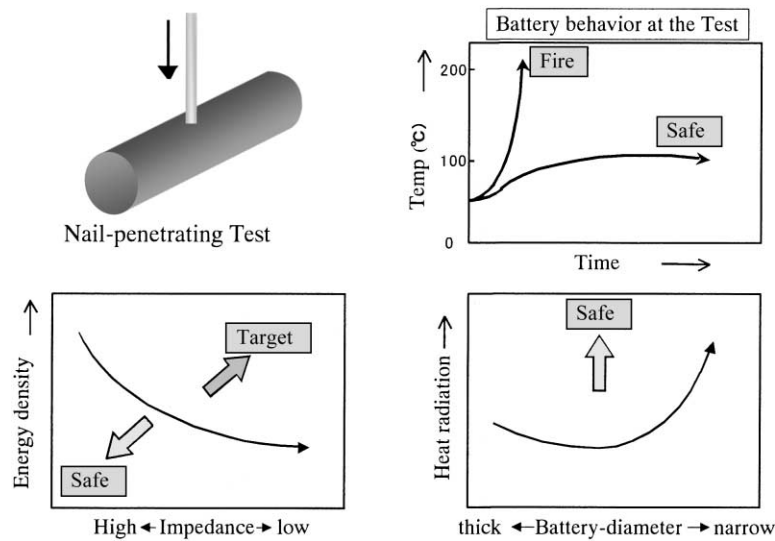


Fig. 13. Schematic concept to approach the battery performance and abuse criteria condition.

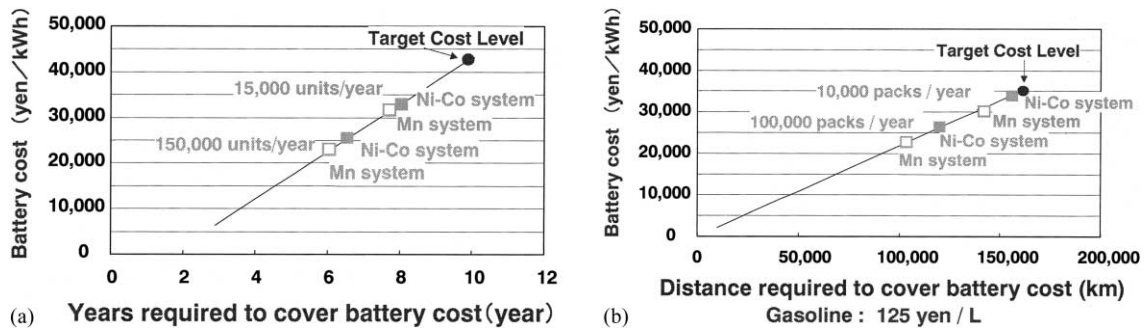


Fig. 14. Cost estimation/kWh of battery in the future, for 20 kWh-class load-leveling apparatus for home use, and for 45 kWh-class electric vehicles in Japan. (a) For 20 kWh-class load-leveling apparatus; (b) for 45 kWh-class electric vehicle.

under mass production in the future will be around 30,000 Yen/kWh based on the above assumptions.

The other aspect of the great importance is the environmental burden through out the life cycle of the battery. In this connection the recycling processes and disposal procedures after the battery's service life were investigated. A preliminary life cycle inventory was under taken [33].

These investigations define the future prospects for the practical use of lithium ion batteries [34].

5. Conclusion

Lithium battery technologies for energy storage have been steadily developed. Final objectives for the stationary type battery module included electrical performances such as a discharge capacity of 2 kWh, a specific energy of 120 Wh/kg, an energy density of 240 Wh/l, a charge/discharge efficiency of 90%, and a cycle life of 3500 cycles. Testing of the modules manufactured in FY 2001 will achieve most of the objectives except the cycle life. In order to prove the prospect of the target cycle life of 3500 cycles, the cycle test will be conducted after FY 2001. Therefore the cycle life of the stationary type modules will be estimated by an accelerated cycle test and other methods within FY 2001.

In the case of EV application type batteries, the fundamental performance will satisfy the final target levels of the module such as a discharge capacity of 2 kWh, a specific energy of 150 Wh/kg, an energy density of 300 Wh/l, charge/discharge efficiency of 85%, and a cycle life of 1000 cycles in FY 2001.

Middle-size battery modules have satisfied the fundamental requirements of application models. Middle-size battery systems will be assembled and tested in FY 2001. For practical applications R&D will be continued to seek further improvement taking in to account various aspects of battery economy and safety.

These results will be reflected in the stage next of R&D and in practical commercialization. The practical usage of the battery technology in the near future is expected to play an important role in reducing the environmental burden caused by fossil fuel consumption, and in enabling the effective utilization of renewable energy.

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