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Development of lithium secondary batteries for electric vehicles and home-use load leveling systems

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Abstract

The Lithium Battery Energy Storage Technology Research Association (LIBES) has been conducting R&D on large-scale lithium secondary batteries for use in electric vehicles and home-use load leveling systems as part of the New Sunshine Program by the Agency of Industrial Science and Technology (AIST) of the Ministry of International Trade and Industry (MITI) under a contract with the New Energy and Industrial Technology Development Organization (NEDO) since FY 1992. The R&D by LIBES, which is in Phase 2, has developed several hundred Wh class prototype cells of 4 types and 2 or 3 kWh class modules of each type connecting those cells in series. At the same time, LIBES member companies are conducting studies on supporting technologies for the above R&D, on the evaluation test, and on next-generation lithium secondary battery technology development. Here we describe the current results and status of LIBES's R&D as well as those technological aspects. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium secondary batteries; Electric vehicles; Load leveling systems

1. Introduction

The results of LIBES's R&D in the Phase 1 stage (FY 1992–1994) and a summary of the results of the first interim evaluation in 1995 for the 10 Wh class cells are shown in the 'Development of 10 Wh class lithium secondary cells in the New Sunshine Program' presented by Aragane et al. (LIBES) [1] in the IMLB 8 (Table 1). The evaluation results showed that discharge capacity, specific energy and energy density of all the 8 battery types have potential for use in electric vehicles and home-use load leveling systems. However, the needs of breakthrough for the cycle life of the Lithium Polymer Battery in the Long Life Type Batteries (Stationary Type) and Lithium Metal Battery in the High Energy Density Type Batteries (EV-application type) were suggested due to their insufficient cycle life at that period (FY 1998), as shown in Table 1.

Based on the results of the 1st interim evaluation in FY 1996, the work share in LIBES was changed as follows; 4 companies for scaling up cells and development of battery modules, 2 companies for the supporting technology study, 3 companies for the study on next-generation battery technology, Central Research Institute of Electric Power Industry (CRIEPI) for performance evaluation tests and Nippon Telegraph and Telephone (NTT) for safety tests. The current work share in LIBES is shown in Table 2.

2. Features of several hundreds Wh class cells under development

Four types of several hundreds Wh class cells, each 2 for EV application and stationary use, have been developed until FY 1997. Performance and safety tests of the 4 types of 2 or 3 kWh class modules connected those types of cells in series are scheduled in 1998. The R&D framework of these 4 cells is described below.

2.1. Stationary type battery A

On the basis of improving energy density and cycle life, $LiNi_{0.7}Co_{0.3}O_2$ which is prepared by substituting a part of Ni of $LiNiO_2$ with Co is the chosen cathode. A graphite-coke hybrid is the anode chosen in order to mitigate the rapid potential rise at the end of discharge and to improve cycle life. The battery shape is cylindrical.

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Table 1
Results of the first interim evaluation for 10 Wh class cells

Type	Cell chemistry	10 Wh class results			
		Discharge capacity (Wh)	Specific energy (Wh/kg)	Energy density (Wh/l)	Cycle life[a] (cycle)
Long life type (stationary type)	Li $Co_{0.3}Ni_{0.7}O_2$/graph.	12.1	111	255	> 700
	$LiNiO_2$/Ag-graph.	11.8	123	277	> 700
	$LiNi_{0.7}Co_{0.3}O_2$/graph. + coke	10.8	101	235	> 550[b]
	Lithium polymer electrolyte	2.6	28	57	10
High-energy density type (EV-application type)	$LiCo_{0.98}Mg_{0.01}Ni_{0.01}O_2$/graph.	11.3	126	251	> 300
	$LiMn_{1.8}Co_{0.2}O_4$/graph.	14.7	123	263	> 300
	$LiMn_2O_4$(Cu)/Li metal	13.5	132	240	41
	$LiNi_{0.97}B_{0.03}O_2$/carbon	10.6	139	256	> 300

[a]Revised in March 1998.
[b]In progress.

Table 2
Work share in LIBES

Development of Battery Module	Stationary type	Sanyo Electric
		Hitachi/Shin-Kobe Electric Machinery
	EV-application type	Japan Storage Battery/Mitsubishi Electric
		Matsushita Battery
	Supporting battery technology	Osaka Gas
		Toshiba
Development of next-generation battery technology	Lithium polymer battery	Yuasa
	Lithium metal battery	Denso
	Nonflammable electrolyte	Mitsubishi Chemicals
Total system study	System analysis and performance test	CRIEPI
	Safety test	NTT

Table 3
Cell design and performances of several hundreds Wh class prototype cells

Type	Cell design	Discharge capacity (Wh)	Specific energy (Wh/kg)	Energy density (Wh/l)	LIBES member company
Stationary Type A	Cathode: $LiNi_{0.7}Co_{0.3}O_2$	270	120	240	Sanyo Electric
	Anode: graphite-coke hybrid				
	Electrolyte: $LiPF_6$/EC + DEC				
	Cell structure: Cylindrical				
Stationary Type B	Cathode: $LiMn_2O_4$	210	100	230	Hitachi and Shin-Kobe Electric Machinery
	Anode: Ag-dispersed graphite	250	105	239	
	Electrolyte: $LiPF_6$/EC + DMC		108	226	
	Cell structure: Prismatic				
EV-application Type A	Cathode: $LiCo_{0.98}Mg_{0.01}Ni_{0.01}O_2$	360	129	288	Japan Storage Battery and Mitsubishi Electric
	Anode: graphite	400	140	310	
	Electrolyte: $LiPF_6$/EC + DMC + DEC				
	Cell structure: Elliptical cylindrical				
EV-application Type B	Cathode: $LiMn_2O_4$	340	107	251	Matsushita Battery
	Anode: graphite	370	117	275	
	Electrolyte: $LiPF_6$/EC + EMC				
	Cell structure: Cylindrical				

2.2. Stationary type battery B

$LiMn_2O_4$ is the cathode chosen due to its anticipated cost reduction capabilities. Ag-dispersed graphite is the anode chosen in order to improve life cycle. The battery shape is prismatic.

2.3. EV-application type battery A

Aiming at conductivity improvement, $LiCo_{0.98}Mg_{0.01}$-$Ni_{0.01}O_2$, prepared by substituting a part of Co of $LiCoO_2$ with a small amount of Mg and Ni, is currently the chosen cathode. $LiNi_{1-x}Co_xO_2$ is under investigation, aiming at further improvement of energy density. Graphite is the chosen anode. The battery shape is elliptical cylindrical.

2.4. EV-application type battery B

$LiMn_2O_4$ is the cathode chosen due to its anticipated cost reduction capabilities. Graphite is the chosen anode. Battery shape is cylindrical.

3. Results

Scaling up of cells and performance improvement have been carried out by trial and error. Discharge capacity, specific energy and energy density of the 4 types of several hundreds Wh class prototype cells are shown in Table 3. Cycle life test has been initiated.

10 Wh class cells, which have the same cell chemistry as Stationary Type A, retained 86% of their initial capacity after 1,250 cycles under 70% DOD and had long life, as shown in Fig. 1.

As a result of the cathode test using a half cell, Stationary Type B cell retained 92% of its initial capacity after 1000 cycles under full discharge, and in the anode test using a half cell, the cell retained 80% of its initial capacity after 2700 cycles under full discharge and also had long life.

The prototype 360 Wh class cell, which has the same cell chemistry as EV-application Type A cell, retained 80% of its initial capacity after 450 cycles as shown in Fig. 2.

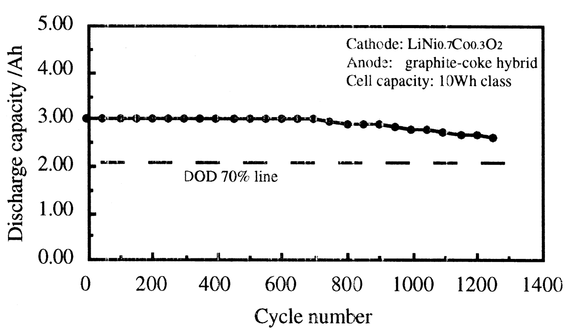

Fig. 1. Cycle performance of 10 Wh class cell (Stationary Type A).

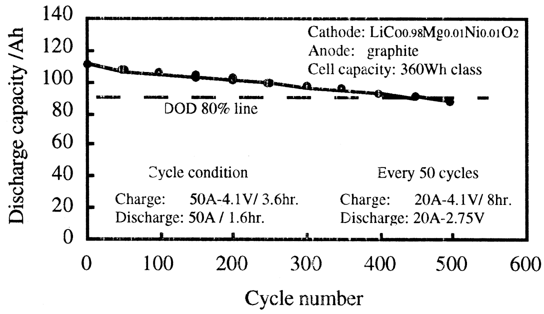

Fig. 2. Cycle performance of 360 Wh class cell (EV-application Type A).

The results of high-rate discharge tests revealed that Stationary Type B cell and EV-application Type A cell have a specific power (DOD 75%) of 500 W/kg.

The nail penetration as an internal short-circuit test, the crush test, the overcharging test and the short-circuit test were conducted on 270 Wh class cells that have the same cell chemistry as EV-application Type B cell. As a result, neither fire nor explosion was observed as shown in Table 4.

These results show that the safety of large-scale cells with $LiMn_2O_4$ cathode is maintained.

Based on the development of large-scale cells as described above, LIBES fabricated 2 or 3 kWh class battery modules for each 4 types of battery systems. These battery modules consist of 8 cells connected in series.

For example, in the case of EV application battery A, a specific energy of 132 Wh/kg and an energy density of 218 Wh/l were obtained.

In developing of the 4 types of large-scale cells and in supporting studies for the development, improvement of battery materials such as cathode active materials, anode active materials and electrolytes is under way. The results obtained thus far are summarized below.

3.1. Cathode active materials

LIBES is trying to find ways and means of using $LiNiO_2$ and $LiMn_2O_4$ instead of $LiCoO_2$ which is mainly used in small electronic equipment, for reasons of natural resource conservation and cost reduction.

$LiNi_{1-x}Co_xO_2$ is attractive from the viewpoints of increment capacity, cycle life improvement and cost performance.

Table 4
Results of safety tests of the cell (EV-application Type B)

Test item	Cell capacity (Wh)	Results
Nail penetration	270	· no fire
Crush		· no explosion
Overcharge		· venting with smoke
Short-circuit		

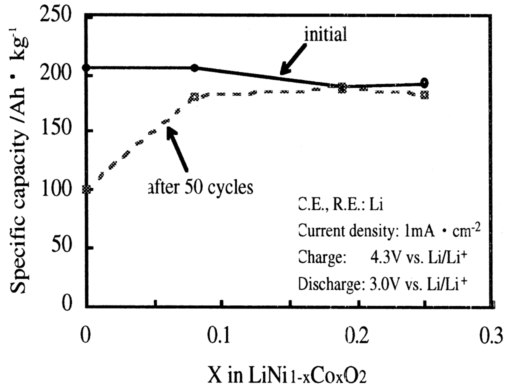

Fig. 3. Relationship between Co concentration and discharge capacity of $LiNi_{1-x}Co_xO_2$.

Researchers of Toshiba studied systematically the relationship of Co concentration (x value) with discharge capacity and thermal stability in the $LiNi_{1-x}Co_xO_2$ cathode, the results of which are shown in Figs. 3 and 4, respectively.

The initial discharge capacity of approximately 200 Ah/kg in $LiNiO_2$ without Co was the highest and it decreased as Co concentration increased. Although the discharge capacity of $LiNiO_2$ without Co was 100 Ah/kg due to the cycle deterioration after 50 cycles, it was found that a peak discharge capacity of 175–190 Ah/kg was obtained when Co concentration was between 8–25%. The prediction based on thermal stability data shows that the exothermic peak temperature of $LiNiO_2$ is approximately 211°C and it increases as the concentration of Co increases; for instance, it increases to approximately 218°C when Co concentration is 23% and to 225°C at a Co concentration of 36%. Based on the above data, a Co concentration from 10 to 30% will be practical. For $LiNi_{1-x}Co_xO_2$, Sanyo Electric and Mitsubishi Electric are studying independently, and their study results on the effect of Co concentration on specific capacity show almost the same tendency qualitatively. In addition, the effect of addition of third element addition is under study.

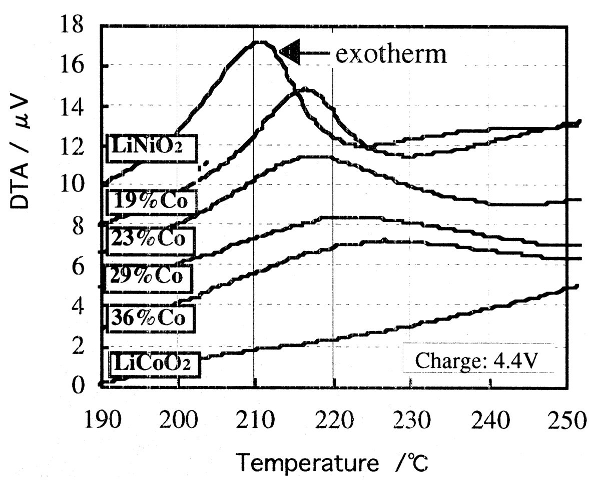

Fig. 4. Relationship between Co concentration and thermal stability of $LiNi_{1-x}Co_xO_2$.

$LiMn_2O_4$ is attractive from the viewpoint of material cost. As mentioned above, as regards cycle life, life of more than 1000 cycles was obtained by the half-cell test. Several breakthroughs will be required in order to improve high temperature storage stability. As shown in Fig. 5, researchers of Matsushita Battery found that the amount of Mn dissolved in the electrolyte decreases as the synthesis temperature of $LiMn_2O_4$ increases. However, decrease in discharge capacity was observed at temperatures higher than 950°C.

3.2. Anode active materials

Currently, as regards cathode materials for large-scale cells, the development of anode materials is pursued with focus on graphite materials. In Stationary Type A, the material is graphite-coke hybrid, a mixture of graphite and coke, in order to extend the cycle life. In the Stationary Type B, Ag-dispersed graphite was used for the same purpose.

Osaka Gas achieved a specific capacity of 340–350 Ah/kg with boron-catalyzed artificial graphite, which is near the theoretical value (372 Ah/kg). The aim of our study is to realize a value higher than the theoretical value by doping Li ions not only in the graphite layer but also in the cavities. Studies on the applicability of hard-carbon, as well as graphite are underway.

3.3. Organic electrolyte material

The organic electrolyte material is $LiPF_6$, which, as a solute, is dissolved in co-solvents of EC and chained carbonates. In the future, basic studies focusing on the applicability such as lithium imide will be conducted.

Besides the R&D on battery scaling up and module fabrication, LIBES has been conducting.

(i) R&D on dendrite suppression technology, aiming at the applicability of lithium metal anode, (ii) studies on nonflammable electrolytes aiming at improvement of

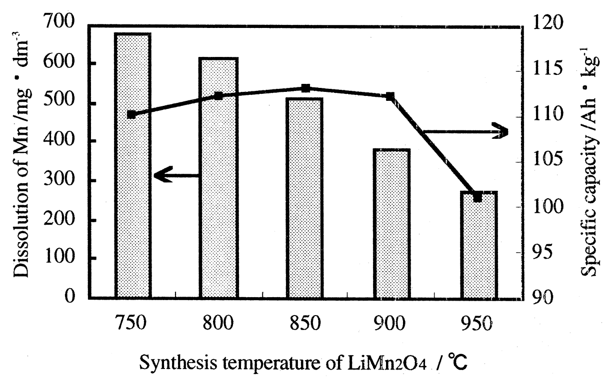

Fig. 5. Relationship of Mn dissolution in the electrolyte and specific capacity with synthesis temperature of $LiMn_2O_4$.

safety, and (iii) studies on solid polymer electrolytes, the results of these R&D are promising for the commercialization of advanced lithium secondary batteries in the 21st century.

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References

[1] J. Aragane, K. Matsui, H. Andoh, S. Suzuki, H. Fukuda, H. Ikeya, K. Kitaba, R. Ishikawa, J. Power Sources 68 (1997) 13–18.