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Large-scale development of lithium batteries for electric vehicles and electric power storage applications

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Abstract

In Japan there was a dramatic increase in the production of lithium secondary batteries which reached a value of 210 billion yen in 1997. There are signs that this trend is increasing. These lithium batteries are presently used as small portable power sources. For these uses there has been a broadening in the research and development of lithium batteries. At the same time, advances in the research of large type lithium batteries for electric vehicles and dispersed-type electric power storage systems have been conducted on a grand scale by Japanese universities, government research laboratories and private companies. The level of activity in the research and development of lithium batteries in Japan is apparent by the state of related patent applications and number of papers presented at meetings held in Japan. LIBES is at the center of the research and development into large-type lithium batteries in Japan. Hitachi, and Shin-Kobe Electric Machinery, as members of LIBES, are carrying out the research and development of large-type lithium batteries for electric-power storage. In FY1997, the 250 W h cells, made of 10 wt.% silver–graphite anodes and spinel-type manganese oxide cathodes, which were connected together and stacked in a series of eight to make a 2 kW h module, produced desirable results and showed the prospects for good safety.

Keywords: Lithium batteries; Electric-power storage; Graphite anode; Manganese oxide cathode

1. Introduction

The production of lithium secondary batteries in Japan has rapidly increased in recent years. Most of these lithium batteries have been used as the power source of portable equipment such as portable telephones, notebook-size personal computers, etc. It is expected that the increasing demand for these uses will last for at least ten more years.

On the other hand, it is forecasted that large-scale lithium batteries will be used as power sources for electric vehicles and electric power-storage systems in the near future [1]. More than ten private companies in Japan are now developing lithium batteries for these applications. Most of these companies are members of LIBES (Lithium Battery Energy Storage Technology Research Association). LIBES has been entrusted with the promotion of a national project named 'Dispersed-Type Battery Energy Storage Technology' in the New Sunshine Program of the AIST (Agency of Industrial Science and Technology) of MITI (Ministry of International Trade and Industry) under a 10-year contract with NEDO (New Energy and Industrial Technology Development Organization) since FY1992, and has been developing lithium batteries for electric vehicles and stationary power-storage systems in this project [2,3].

The reason for the increasing demand, the production of batteries and application for patents are discussed, and the current technology status of the Hitachi/Shin-Kobe team is described in this paper.

2. Uses and background

The present and near-future uses and the background behind the uses of lithium batteries in Japan are summarized in Table 1.

There are two reasons for the promotion of research and development of large-scale lithium batteries, the protection of the environment and the saving of fossil fuels.

3. Production of batteries

Fig. 1 shows the quantity and value of primary cells and secondary batteries in Japan in 1997. About 6.3 billion cells and batteries with a value of about 800 billion yen

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Table 1
Uses and background of lithium batteries

Uses	Background
(1) Portable equipment	The desire for a more convenient life
· Telephones	Technological progress of semiconductor, liquid crystal and other electronic parts
· Personal computers	
· Audio instruments	
(2) Electric vehicles	Protection of environment
(3) Load leveling systems	Saving of fossil fuels
(4) Electric power storage for solar cells, wind power station, etc.	

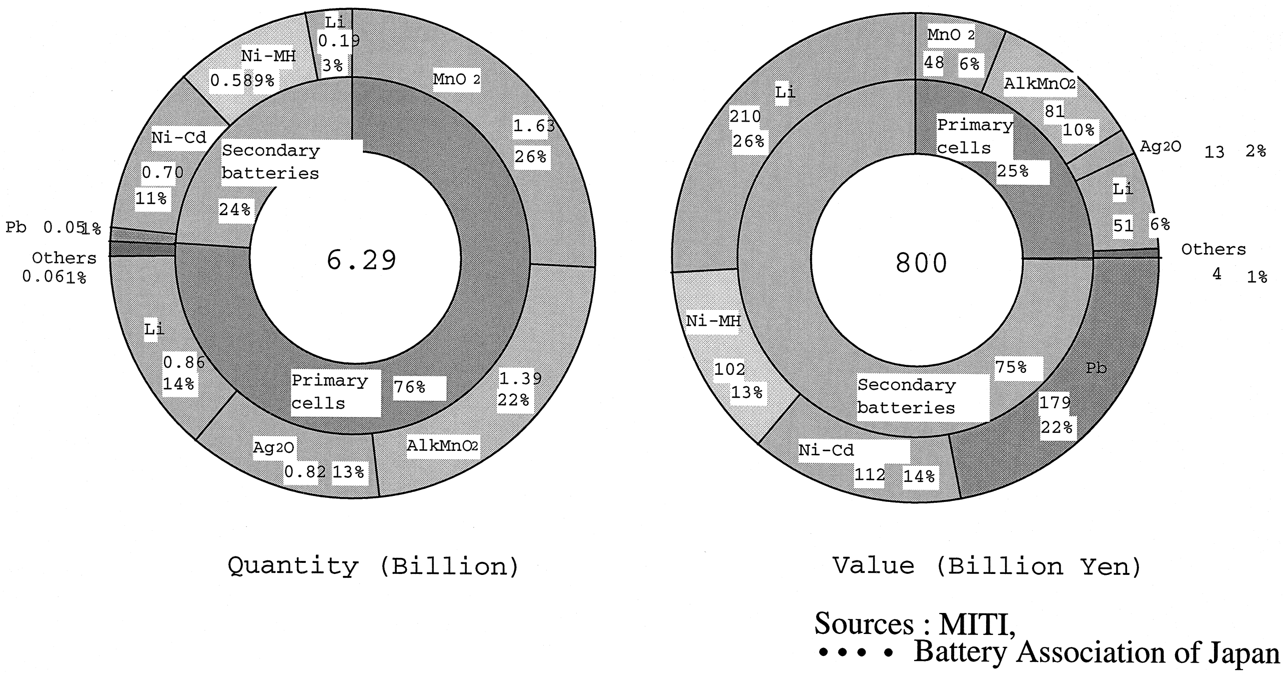

Fig. 1. Quantity and value of primary cells and secondary batteries in Japan.

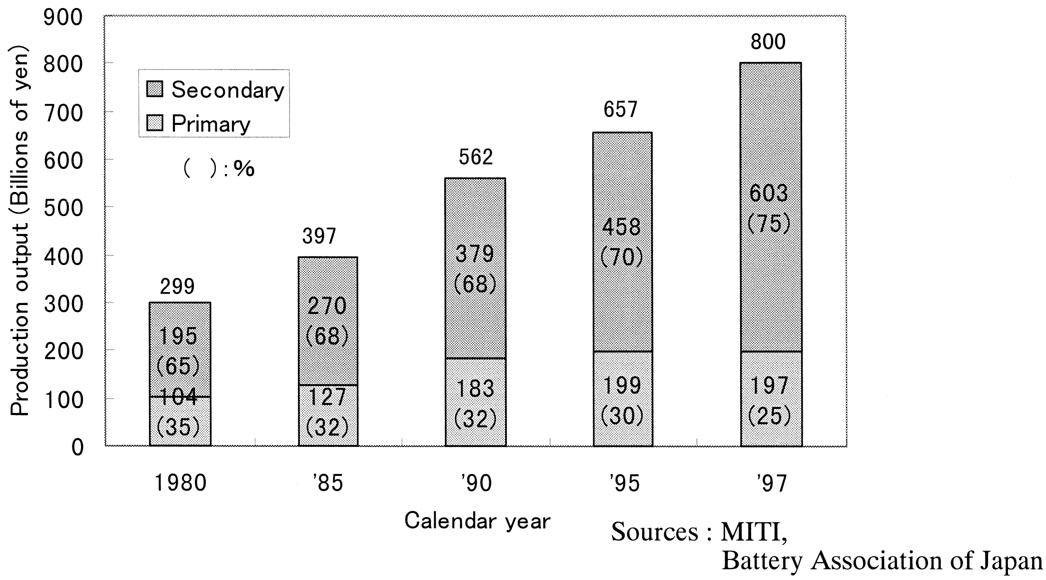

Fig. 2. Trends in production value of primary cells and secondary batteries in Japan.

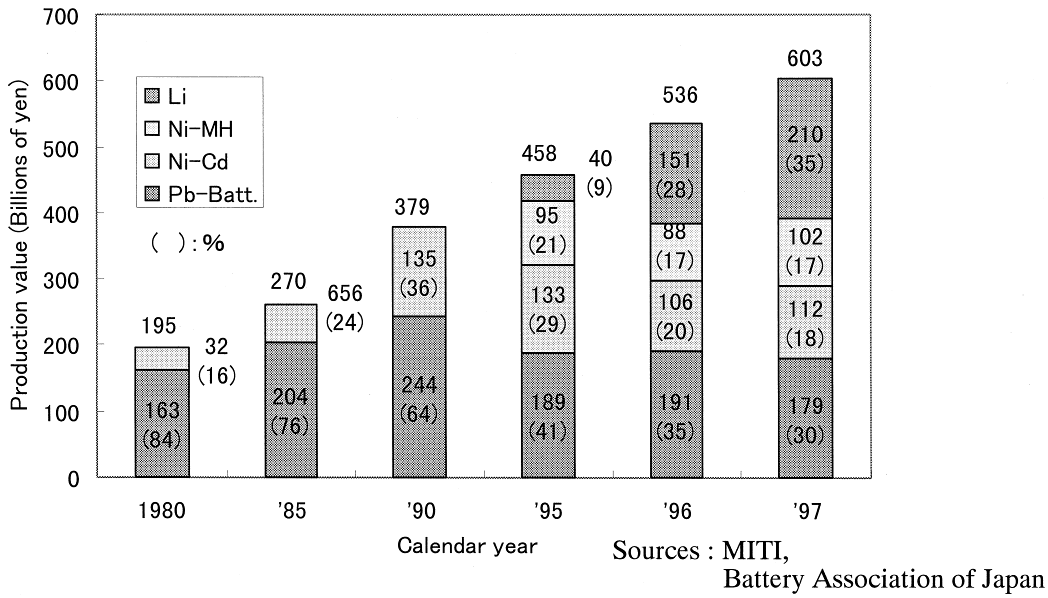

Fig. 3. Trends in production output for each type of secondary battery in Japan.

were produced in Japan. The value of lithium secondary batteries was 26% of the total electrochemical cells and batteries.

Fig. 2 shows the trend in the production value of primary cells and secondary batteries. The value of primary cells has nearly doubled in 17 years, but has not recently increased. On the other hand, the rapid increase in rechargeable batteries is very evident for this figure.

Fig. 3 shows the trends in the production value of different types of secondary batteries. The appearance of

Table 2
Recent meetings related to chemical cells and batteries in Japan

Meeting	Electrochem. Soc. Japan, 1997 autumn meeting	The 38th Battery Meeting
Sponsor	Electrochem. Soc. of Japan	Committee of Battery Technology (Electrochem. Soc. of Japan)
Date	10–11 Sept. 1997	11–13 Nov. 1997
Location	Tokyo	Osaka
Total number of papers presented	452	233
Number of papers presented relating to chemical cells and batteries	82	228
(1) Primary cells	–	3 (1%)
(2) Secondary batteries	54 (66%)	152 (67%)
(3) Fuel cells	28 (34%)	71 (31%)
(4) Other items	–	2 (1%)

Table 3
Papers presented relating to secondary batteries

Meeting	Electrochem. Soc. Japan, 1997 autumn meeting		The 38th Battery Meeting	
Total	54	66%	152	67%
(1) Pb	–	–	5	3%
(2) Ni–Cd,Ni–MH	9	17%	19	12%
(3) Li	45	83%	124	82%
Cathode	(17)	(38%)	(51)	(41%)
Anode: carbon	(9)	(20%)	(30)	(24%)
Anode: Li metal, alloy, oxide	(3)	(6%)	(6)	(5%)
Electrolyte: liquid	(8)	(18%)	(10)	(8%)
Electrolyte: solid (cont. polymer)	(4)	(9%)	(16)	(13%)
Characteristics, measuring procedure	(3)	(6%)	(10)	(8%)
Other items	(1)	(2%)	(1)	(1%)
(4) Other batteries	–	–	4	3%

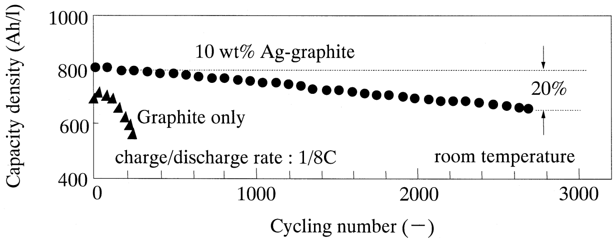

Fig. 4. Decrease in capacity density of 10 wt.% Ag–graphite anode.

nickel metal–hydride batteries in 1993 and lithium batteries in 1995 can be seen. The production output figure for lithium batteries has increased every year since them. In 1997 the figure was 35% of the total production output for secondary batteries, surpassing the 30% figure for lead–acid batteries.

4. Activities of research and development of lithium batteries in Japan

The Japanese battery industry has been supported by many universities, government research laboratories and companies making electrode materials, electrolytes, separators, cans, parts for safety, measuring instruments, production machines, etc. Especially, these involved companies have had high level technologies and have strongly contributed to the promotion of lithium battery technology in Japan.

In Japan, good technical communication among universities, government research laboratories and industries is one reason why the research and development of lithium batteries can be actively pursued in Japan. Table 2 shows recent meetings related to chemical cells and batteries held in Japan. Three hundred and ten papers related to cells and batteries were presented at two meetings held in the autumn of 1997. About two-thirds of the papers concerned secondary batteries.

Table 3 shows the number of papers related to secondary batteries that were presented at two meetings. Over 80% of the papers presented were related to lithium batteries.

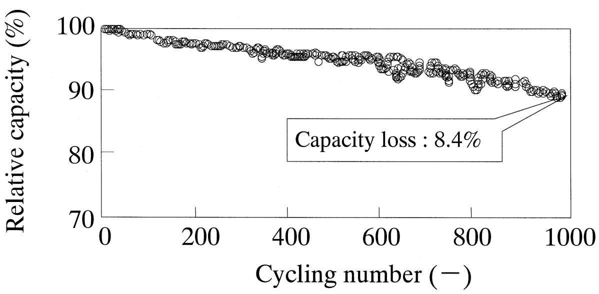

Fig. 5. Decrease in capacity of spinel-type manganese oxide cathode.

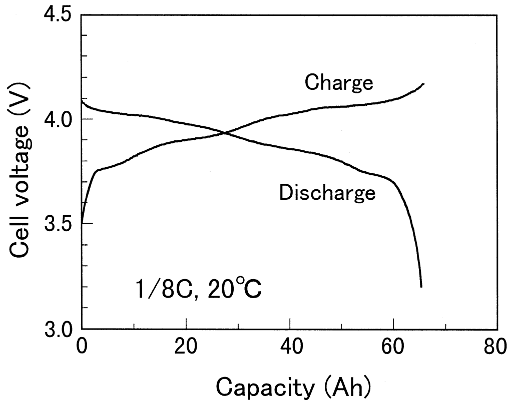

Fig. 6. Charge and discharge curves of a 250 W h cell.

Table 4 shows the number of laid-open publications, namely unexamined but opened patent applications and the number of applicants concerning lithium batteries in 1997. There were 1154 laid open to public inspection and 127 applicants. With the Japanese system, if patent applications are written in due form, almost all of them are made public after about a year and half. The figure of 127 companies in the table shows that Japan is extremely active in the development of this industry.

5. The status of Hitachi / Shin-Kobe

The efforts of Hitachi / Shin-Kobe have been directed toward developing large scale lithium ion batteries for the dispersed electric-power-storage system with support of MITI [4].

The development targets are displayed in Table 5. The aim is to develop a 2 kW h class module by the end of FY2001 which is judged to be economical, safe and can be recycled. In FY1997, we underwent the trial production of 250 W h cells which were connected in a series of eight to form a 2 kW h module and then measured its efficiency. This is outlined below.

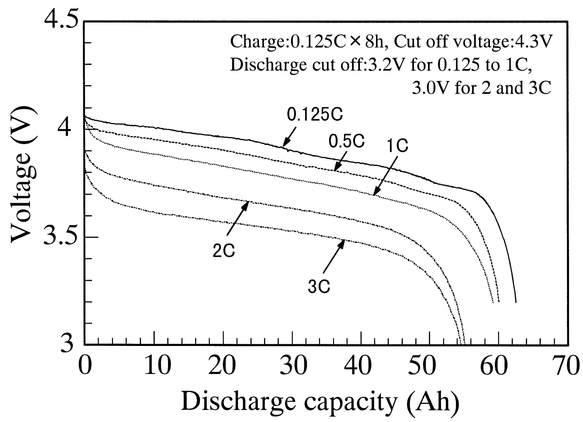

Fig. 7. Discharge rate characteristics of a 250 W h cell.

Table 4
Number of applicants with number of laid open publications (1997)

Applicants	Number of laid open publications							Total
	1–5	6–10	11–20	21–30	31–50	51–100	101–150	
Private companies								
Japan	91	16	5	7	3	3	2	127
Other countries	13	–	–	–	–	–	–	13
Private/universities/government research laboratories	12	–	–	–	–	–	–	12
Total number of laid open publications: 1154								
Total number of applicants: 152								

Table 5
Targets of the lithium secondary batteries for electric power storage applications

Item	Target value
Energy capacity	2 kW h class (module)
Energy density	
(W h/kg)	120
(W h/l)	240
Life cycle (cycle)	3500
Energy efficiency (%)	90

Table 6
Specifications of a 250-W h cell

Active material (+/−)	$LiMn_2O_4$/Ag–graphite
Dimensions (mm)	163 (*W*)×43 (*D*)×150 (*H*)
Weight (kg)	2.4
Average voltage (V)	3.8
Rated capacity (A h)	66

5.1. Anode

Graphite was used for the anode. Sliver was precipitated on the surface of the graphite [5]. An anode using this composite material has shown desirable results such as (1) higher capacity as the result of increasing insertion sites and (2) longer life as a consequence of enhanced electric conductivity. The influence of the charge/discharge cycles on capacity density is shown in Fig. 4. Only a 20% decrease in capacity was observed after 2800 charge/discharge cycles.

5.2. Cathode

Manganese oxides have been used for the cathodic active materials, because they are not very expensive and are safer compared to cobalt oxides and nickel oxides [6]. However, the manganese oxide cathode has a couple of weak points which include a not very long cycle life and a slightly low capacity density.

These problems have been solved by using a spinel-type manganese oxide containing lithium atoms in part of the manganese sites of the manganese oxide crystal. Fig. 5 shows the performance of the cathode using a lithium-containing spinel-type manganese oxide as the active material. The decrease in capacity is only 8.4% even after 1000 charge/discharge cycles.

5.3. 250 W h cell

Table 6 shows the specifications of a 250 W h cell. The 250 W h cells which used the anode and the cathode described above were operated and evaluated. The charge and discharge curves of a cell at 20°C and 1/8 C is shown in Fig. 6. A capacity of 65 A h was obtained.

The discharge rate characteristics are displayed in Fig. 7. Eighty-five percent of the capacity was obtained for a 3-C discharge rate compared to the 0.125-C discharge rate.

A photograph of a cell is shown in Fig. 8. The measurements in Fig. 6 reveal that the cell's energy density reached 105 W h/kg and 239 W h/l.

Table 8
Specifications of a 2-kW h module

Cell arrangement	8 cells in series
Dimensions (mm)	167 (*W*)×373 (*D*)×188 (*H*)
Weight (kg)	21.0
Average voltage (V)	30.4
Rated capacity (A h)	66

Table 7
Abuse tests for 250-W h cells

Tests	Conditions	Results
Overcharge	Continous charge at 1/8 C	Venting, no fire, no rupture
External short circuit	Short circuit resistance: 10 m Ω	Venting, white smoke, no fire, no rupture
Nail penetration	Nail diameter: 5 mm	Venting, white smoke, no fire, no rupture
Crush	Carbon steel rod 9 mm in diameter	Venting, white smoke, no fire, no rupture

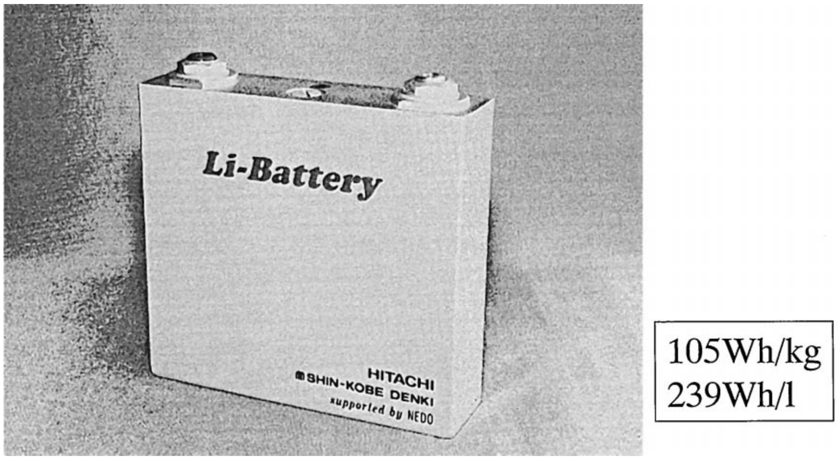

Fig. 8. Photograph of a 250 W h cell.

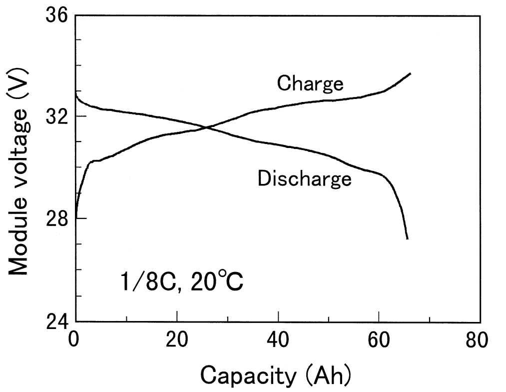

Fig. 9. Charge and discharge curves of a 2 kW h module.

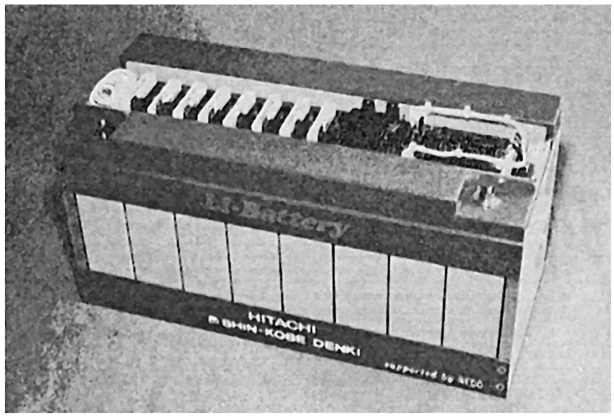

Fig. 10. Photograph of a 2 kW h module.

Abuse tests were carried out on this cell. The test items, conditions and results can be seen in Table 7. During these tests, white smoke was emitted; however, the cell did not blow up or catch fire.

It seems that the cell is safer as a result of using manganese oxide.

5.4. 2 kW h module

Table 8 shows the specifications of the 2 kW h module made by stacking and connecting eight 250 W h cells together. Fig. 9 displays the charge and discharge curve and Fig. 10 is a photograph of the module. The cell controller is in the center of the top part.

The discharge capacity of 65 A h and the average voltage of 31 V were observed under the operating conditions shown in Fig. 9. The energy densities of this module are 96 W h/kg and 178 W h/l.

5.5. Future prospects

Hitachi and Shin-Kobe intend to do research in the following areas:

1. Even more improvements in energy density
2. Improvements and clarification of safety aspects
3. Consideration of economical demand

Acknowledgements

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