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Development of 10 Wh class lithium secondary cells in the 'New Sunshine Program'

J. Aragane *, K. Matsui, H. Andoh, S. Suzuki, H. Fukuda, H. Ikeya, K. Kitaba, R. Ishikawa

Lithium Battery Energy Storage Technology Research Association (LIBES), Ikebukuro FN building, 3-9-10, Higashi-Ikebukuro, Toshima-ku, Tokyo 170, Japan

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Abstract

The LIBES member companies have developed 10 Wh class lithium secondary cells in 1996. Through the Phase 1, the member companies developed elementary technologies and reflected these into a 10 Wh class cell. The 10 Wh class cells have substantially fulfilled the targets of the first interim evaluation for capacity, energy density and specific energy. Some of these cells have not satisfied the targets of cycle life, therefore, it was obvious that the cycleability should be set at 3500 cycles for the long life type and at 500 cycles for the high energy density type, respectively. It appeared that the solid polymer electrolyte type 10 Wh cell implied the importance of the interface control between active materials and solid polymer electrolyte and improved ionic conductivity, and that the lithium metal system needs to restrain the lithium reaction with electrolyte. The incompleteness of cycle life seems to come from the selection of the active materials, the capacity balance of the materials and the volume of the electrolyte involved. Further R&D on cell design and material development are necessary in the cell system for the final targets in 2001. © 1997 Elsevier Science S.A.

Keywords: Lithium secondary cells; Energy storage; Lithium; Cobalt oxide; Nickel oxide; Manganese oxide; Lithium metal; Solid polymer electrolytes

1. Introduction

The Lithium Battery Energy Storage Technology Research Association (LIBES) conducts research and development on the project 'Dispersed Battery Energy Storage Technology' in the New Sunshine Program by the Agency of Industrial Science and Technology (AIST), Ministry of International Trade and Industry (MITI). This work is being carried out based on the contract with New Energy and Industrial Technology Development Organization (NEDO).

The purpose, working structure and plans of this project were previously reported [1]. This project has two activities (long life type, high energy density type) for the advanced batteries development and two activities (carbon material, electrolyte material) for the battery material development. According to the schedule and targets, the LIBES member companies have conducted R&D of elementary technology on lithium rechargeable cells through the Phase 1. Table 1 shows the schedule and numerical targets on the different cell types. The targets have been amended to new ones, e.g. 150 Wh/kg, 300 Wh/l and 1000 cycles in 3 kWh mobile batteries for EV applications.

Table 1
Project's schedules and targets

				'92	'93 '94	'95	'96 '97	'98	'99 2000	'01
R&D items					Phase I elemetary technologies		Phase II scale-up cells & battery		Phase III improvemet of reliability	
High-performance advanced batteries	Long life type		Specific energy (Wh/kg)		100	The 1st Interim evaluation	110	The 2nd Interim evaluation	120	The final evaluation
			Energy density (Wh/l)		200		220		240	
			Cycle life (cycle)		700		1500		3500	
			Energy conversion efficiency(%)		—		>80		>90	
			Cell capacity		10Wh class		100Whclass		100sWh class	
			Module battery capacity		—		kWhclass		20kWh class	
	High energy density type		Specific density (Wh/kg)		120		150		180	
			Energy density (Wh/l)		240		300		360	
			Cycle life (cycle)		300		400		500	
			Energy conversion efficiency(%)		—		>75		>85	
			Cell capacity		10Wh class		100Wh class		100sWh class	
			Module battery capacity		—		kWh class		30kWhclass	
	Battery material	Carbon materials for anode	Long life type	Capacity (mAh/g)	300		340		370	
			High energy density type	Capacity (mAh/g)	340		370		400	
		Organic electrolyte	Potencial Window (V)		0 ~ 4.3		0 ~ 4.5		0 ~ 4.5	
			Conductivity (mS/cm)	r.t.	≧6		≧8		≧8	
				-20℃	≧2		≧3		≧3	
			Boiling point (℃)		≧70		≧100		≧100	
Total system	(1) Introduction method of dispursed battery energy storage systems				Evaluation of effects of introduction		Investigation on infra structure		Method of introduction	
	(2) Common technologies such as module-battery technology and cycle life evaluation technology				Several Wh class module battery		Test of kWh class module battery		Test of 20 ~ 30kWh class battery system	

* Corresponding author.

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Table 2
Features of 10 Wh class cells

	Member company	10 Wh class cell features			
		Cell structure	Cathode	Anode	Electrolyte
Long life type	Mitsubishi Electric	Folding type	$LiCo_{0.3}Ni_{0.7}O_2$	Graphitized MCMB	$LiClO_4$/EC + DME
	Hitachi	Prismatic	$LiNiO_2$	Ag-dispersed graphite	$LiPF_6$/EC + DMC
	Sanyo	Cylindrical	$LiCo_{0.3}Ni_{0.7}O_2$	Natural graphite + cokes	$LiPF_6$/EC + DEC
	Yuasa	Prismatic	$LiCo_{0.95}B_{0.05}O_2$	Natural graphite	Solid polymer (B)
High energy density type	Japan Storage Battery	Prismatic	$LiMg_{0.01}Ni_{0.01}Co_{0.98}O_2$	Graphite	$LiPF_6$/EC + DME + DEC
	Matsushita Battery	Cylindrical	$LiMn_{1.8}Co_{0.2}O_4$	Ga + carbon	$LiPF_6$/EC + EMC
	Nippondenso	Cylindrical	Cu added $LiMn_2O_4$	Ca dispersed Li metal	$LiPF_6$/EC + DME
	Toshiba	Prismatic	$LiNi_{0.97}B_{0.03}O_2$	Hard carbon	$LiPF_6$/EC + EMC

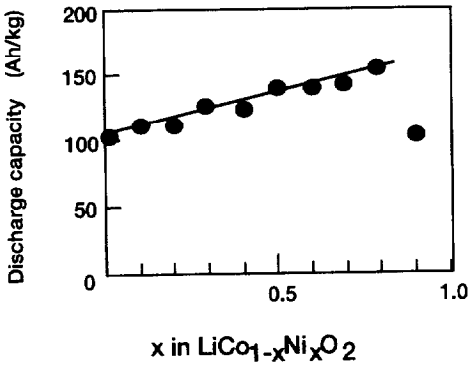

Fig. 1. Effect of nickel substitution in $LiCo_{1-x}Ni_xO_2$.

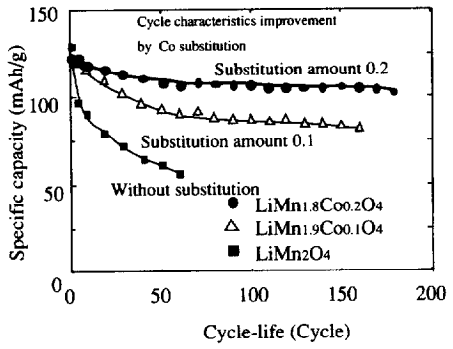

Fig. 2. Effect of cobalt substitution in $LiMn_2O_4$.

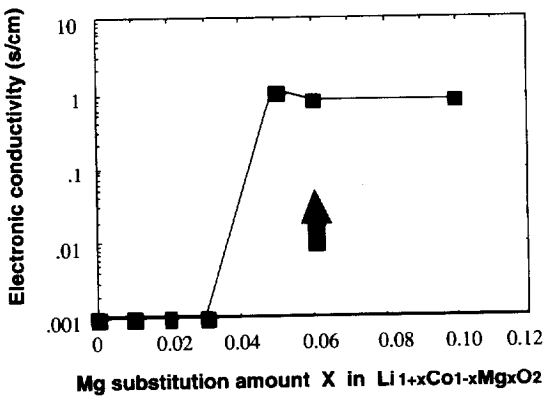

Fig. 3. Improvement of the electronic conductivity by magnesium substitution in $LiCoO_2$ electrode.

2. Cell characteristics

The member companies have already manufactured 10 Wh class cells and are now testing these cells for their cycle lives as a result of Phase 1. Through the Phase 1, the member companies developed elementary technologies and reflected the technologies into a 10 Wh class cell. As a result, the cells have company-dependent characteristics. In this context, a precise comprehension of each cell performance needs for an ensuing step, analyzing the elementary technologies employed. Table 2 shows the elementary technologies, in particular the materials which each company has employed into the 10 Wh class cell.

These 10 Wh class cells have employed the following technologies: cathode; anode; electrolyte, and electrode structure.

2.1. Cathode

Substitution by foreign elements was studied to provide a cell with structural stability and substantial improved cycleability, together with increased capacity. This method was applied to $LiCoO_2$, $LiMn_2O_4$ and $LiNiO_2$ materials. Fig. 1 shows that $x = 0.8$ in $LiCo_{1-x}NiO_2$ system gives the highest discharge capacity, the relation being dependent on the manufacturing process. Fig. 2 shows the effect of cobalt substitution in $LiMn_2O_4$. Fig. 3 shows that the addition of magnesium was effective for enhancing the electron conductivity. The substitution effect of nickel, borium, cobalt and magnesium in each of the active material was experimentally confirmed in preliminary tests, however, it is important to reconfirm the results in the 10 Wh class cells.

2.2. Anode

Silver-dispersed composite anode material was developed. As shown in Fig. 4, silver is dispersed on the graphitic carbon material. Silver is supposed to be alloyed with lithium in charging, therefore the overall capacity could be enhanced together with the capacity of graphite. This type of anode have some advantages such as high electronic conductivity,

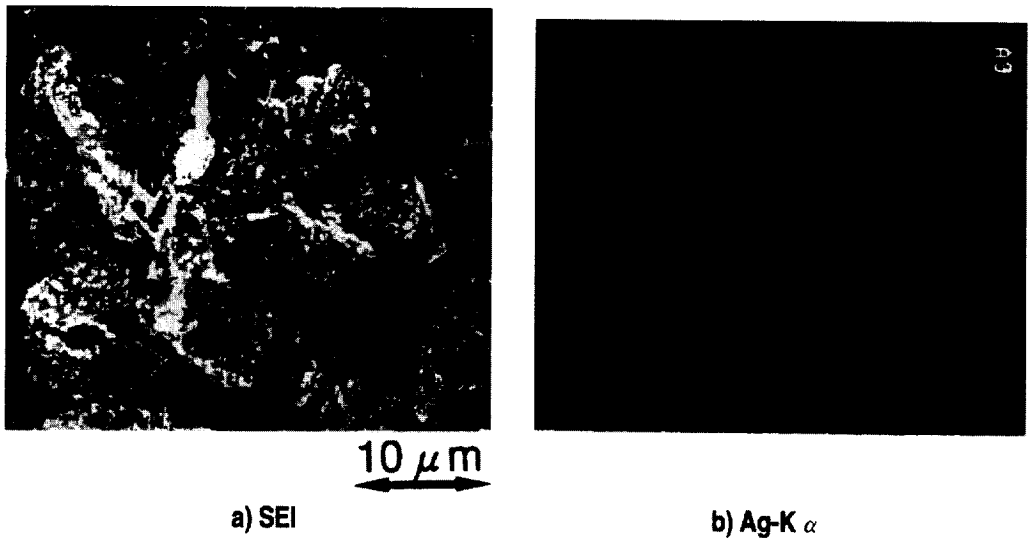

Fig. 4. SEM and X-ray mapping of silver-dispersed graphite composite anode: (a) SEI, and (b) Ag Kα.

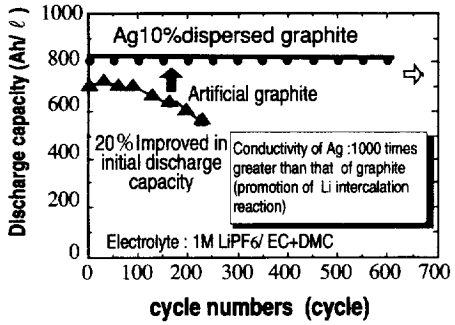

Fig. 5. Cycle performance of silver-dispersed graphite composite anode.

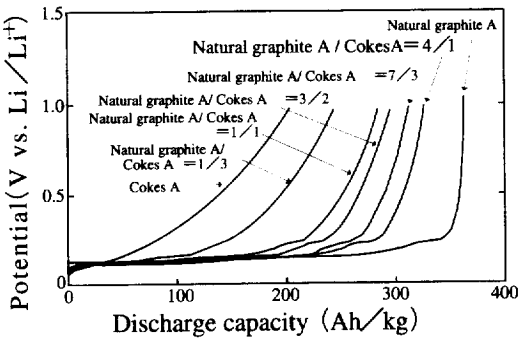

Fig. 6. Hybrid effect of natural graphite and cokes; electrolyte: $LiPF_6$/EC+DEC/cm^2; charge/discharge current density: 0.25 mA.

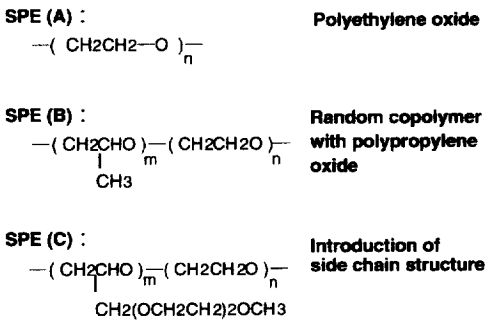

Fig. 7. Improvement of the ionic conductivity by synthesising of new polymers.

high capacity and increased heat transfer. Fig. 5 shows the cycle performance of capacity of the silver-dispersed graphite. The high and stable discharge capacity (800 Ah/l, 330 Ah/kg) was obtained. In addition, the carbon material maker proposed a new model for a reaction of carbon with lithium ion for the lithium rechargeable battery. The reaction involves doping of lithium ions in the amorphous part of the carbon materials and an intercalation in a graphitic layer. They developed new carbon materials based on the model, and the high capacity was experimentally confirmed in a coin-size cell.

In addition, focused on an improvement of performance of graphite materials, a mixing effect (hybrid effect) was studied. Generally, graphitic material has a stable charge/discharge performance, however, it has a rapid voltage change in the vicinity of the discharge cut-off voltage. To improve this voltage characteristics, coke is mixed with graphite. Fig. 6 shows the mixing effect of natural graphite and coke. The natural graphite–coke mixed anode (mixed ratio: 4/1) showed the best trade-off performance between the discharge capacity and the voltage change at a discharge end. The moderate slope of the voltage leads to an easy control of voltages in module battery.

2.3. Electrolyte

New technologies were only applied to a solid polymer type (SPE) 10 Wh class cell. The ionic conductivity was focused and some structural modifications were conducted on a poly(ethylene oxide) material. Fig. 7 shows the molecular structure which were tested for polymer electrolyte. As a result, it was found that the random copolymer is superior to the other structures on the point of ionic conductivity. Fig. 8 shows that SPE(B), random copolymer with poly(propylene oxide), had a conductivity value of 2.3×10^{-4} S/cm (60 °C). Thermal stability tests also show that SPE(B) had good thermal stability.

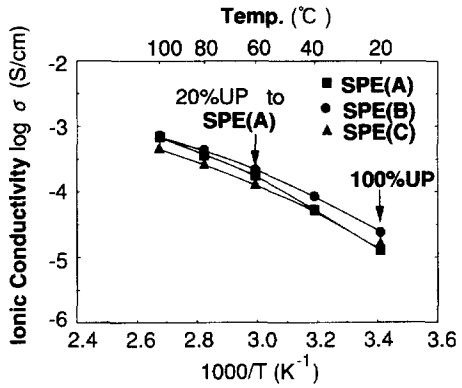

Fig. 8. Improvement of the ionic conductivity by examining the polymer structure.

2.4. Electrode structure

Several designs were proposed in this project, see Table 2. In addition to the typical structures such as prismatic and cylindrical types, a folding-type electrode structure has been developed. Fig. 9 shows the folding-type electrode structure for the 10 Wh class cells. This structure has a better temperature distribution than other structures because of the current collectors which are formed at each end of the electrode in a stack structure. This advantage is suitable for large scale batteries without accumulating heat in charge/discharge processes. Involving the electrode structure, one should pay attention to the cell design that needs much consideration on heat evolution using thermal simulation and experimental tests.

3. Results and discussion

The member companies have manufactured 10 Wh class cells and tested their energy density, specific energy, and cycle life. The cells have been evaluated whether or not they satisfy the target values as shown in Table 1. The target of specific energy (Phase 1, 10 Wh class cell) is 100 Wh/kg for a long life type cell, and 120 Wh/kg for a high energy density type. Table 3 shows the results of the 10 Wh class cells. In the cells where an SPE was used in the long life type and lithium metal was used as the anode material in a high energy density type, the performances could not be satisfactory. In the former, it was considered that both the control of interface between the polymer and active materials and the improvement of ionic conductivity of the polymer were necessary to obtain a better cell performance. In the lithium metal anode system, since the consumption of the lithium metal was reported, a restriction of the lithium–electrolyte reaction was considered to be of great significance. MITI has judged that these two systems needs further elementary development before scaling-up of the cell.

On the other hand, other companies' 10 Wh cells fulfilled the targets of the capacity, the energy density and specific energy. As shown in Table 3, however, it was not expected that some cells will satisfy the targets of cycle life. This has come from the selection of active materials, the capacity balance of the active materials and the volume of the electrolyte. For example, Matsushita Battery Industrial has rebuilt refined cells whose capacity balance has been adjusted by increasing the cathode capacity; they obtained a better cycle performance until 50 cycles. Further R&D on cell design and material development will be necessary in all of the cell systems in order to obtain the final targets in 2001.

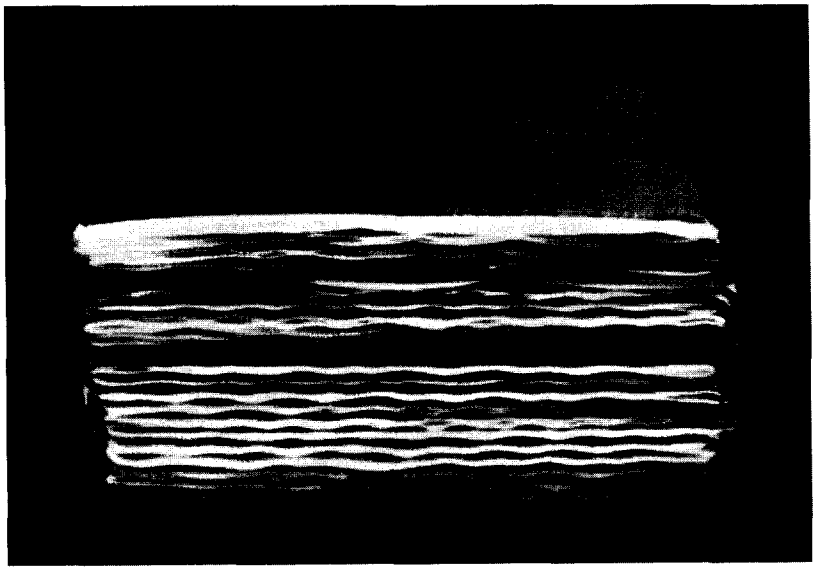

Fig. 9. Structure of a folding-type 10 Wh class cell: $LiCo_{1-x}Ni_xO_2$, graphitized MCMB and organic electrolyte; $W \times D \times H \times = 51 \times 47 \times 19$.

Table 3
Results of 10 Wh class cells

	Member company	10 Wh class cell results					Remarks	Cycle life projection
		Discharge capacity (Wh)	Specific energy (Wh/kg)	Energy density (Wh/ℓ)	Cycle life (cycles)	Projected cycle life (cycles)		
Long life type	Mitsubishi Electric	12.1	111	255	230	~1000	Presumed to fulfill the targets	Projected cycle life was estimated from the change in the end voltage in charging
	Hitachi	11.8	123	277	153	~700	Presumed to fulfill the targets	Projected cycle life was estimated from the change in the end voltage in charging
	Sanyo	10.8	101	235	96	>700	Presumed to fulfill the targets	Projected cycle life was estimated from the cycle life of small size cells
	Yuasa	2.6	28	57	10		10 Wh not attained	Test cell were stopped at 10 cycles due to performance loss
High energy density type	Japan Storage Battery	11.3	126	251	200	>300	Presumed to fulfill the targets	Projected cycle life was estimated from the accelerated cycle life tests
	Matsushita Battery	14.7	123	263	170	150	Cycle life not promising	Observed the separated of the Ga layer from the carbon layer
	Nippon Denso	13.5	132	240	41		Cycle life not promising	Difficult to estimate the cycle life
	Toshiba	10.6	139	256	200	>300	Presumed to fulfill the targets using MCF	(MCF was used instead of hard carbon)

From the above-mentioned reason, not only numerical satisfaction, but also a fulfillment of the elementary technologies noted here and potential for a scale-up of the cells (Phase 2: fiscal year 1996–1998, 100 Wh class) in each member company are of great significance. Therefore, it is supposed that it needs some deliberate considerations to complete the evaluation with regard to cycleability. In addition, technical comparison of the cells is of no significance in an academic point of view because they are absolutely at a different stage of developing energy storage use lithium cells. Each company is expected to pursue their tasks on their own systems for their own aims in Phase 2.

Acknowledgements

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[1] T. Hazama, M. Miyabayashi, H. Andoh, R. Ishikawa, S. Furuta, H. Ishihara and J. Shonaka, *J. Power Sources, 54* (1995) 306.