

Development of 1 kWh (300 Ah) class lithium-ion battery

M. Majima^{a,*}, K. Hanafusa^a, Y. Oka^a, G. Tanaka^a, H. Yoshida^b, E. Yagasaki^b, T. Tada^b

^a Osaka R&D Laboratories, Sumitomo Electric Industries, Ltd., 1-1-3 Shimaya, Konohana-ku, Osaka 554, Japan

^b Technical Research Center, The Kansai Electric Power Company, 3-11-20 Nakoji, Amagasaki, Hyogo 611, Japan

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Abstract

A large-capacity lithium-ion battery of 1 kWh (300 Ah) class was fabricated by using LiCoO₂ and natural graphite as the cathode and anode materials, respectively, and LiPF₆ as the electrolyte to develop industrially usable batteries for energy source. Our battery delivered an energy density of 60 Wh/kg (133 Wh/l) with weight and volume of a container included with a cycle life of 245 cycles, which was longer compared with that of our former battery using LiBF₄ as the electrolyte [5,6]. These improvements were achieved by changing the following factors: (i) use of LiPF₆ as the electrolyte; (ii) optimizing the mixing ratio of the solvent (EC/DEC); (iii) employing a plate spring for the buffer of electrode expansion and shrinkage; (iv) minimizing residual moisture. © 1997 Elsevier Science S.A.

Keywords: Capacity; Lithium-ion batteries; Cathodes; Anodes; Electrolytes

1. Introduction

A rechargeable lithium-ion battery has high performances such as higher voltage and energy density compared with other battery types [1]. Extensive studies recently have been conducted on a lithium-ion battery using carbon material as the anode [2–4]. This battery has the advantageous characteristics of long cycle life and excellent safety, compared with a battery using lithium metal. Small-size lithium-ion batteries with a capacity of around 1 Ah have already been commercially available. Development of large-capacity lithium-ion batteries are also expected for electric power storage purposes.

Although our previous cell achieved an energy density of 58 Wh/kg or 111 Wh/l using LiBF₄ as the electrolyte and the same electrode system, it had the drawback of a short cycle life of about 60 cycles [5,6]. We investigated various factors affecting the battery life using a single-cell system. The composition of the electrolyte and the setup of the battery were found to be extremely important. Based on these findings, a large-capacity battery consisting of LiCoO₂ and natural graphite as the electrodes and LiPF₆ as the electrolyte was fabricated for further examination. This paper describes the results of the newly designed battery.

2. Experimental

2.1. Battery fabrication

A cathode was made from a mixture of LiCoO₂ (84 wt.%), electro-conductive materials (8 wt.%) and a binder (8 wt.%). A solvent, *n*-methyl-2-pyrrolidone, was added to the mixture for pasting. This paste was applied to both sides of a 20 μm thick aluminium collector, resulting in a cathode sheet of 200 μm in thickness. The cathode was cut into a square shape with a size of 170 mm × 170 mm. The anode was made from a mixture of natural graphite (84 wt.%) and a binder (16 wt.%). The anode was fabricated in the same way as the cathode except that copper was used as the collector material. The large-capacity battery consisted of 659 coupled electrodes connected in parallel. Aluminium and copper bars of 2 mm diameter were used as the anode and cathode connecting bars, respectively. Porous polypropylene films of 25 μm thick were employed as separators. These cells were installed in a titanium container which plate thickness was 4 mm and total weight was 8.3 kg. Titanium plate spring of 0.5 mm thick was used to prohibit the dropping of active materials from the electrode surface due to the expansion or shrinkage during charge and discharge cycling. An electrolyte of 1 M LiPF₆ in a mixed solvent of ethylene carbonate/diethyl carbonate (EC/DEC) was poured into the container. It impregnated the separators and electrodes under reduced pressure.

* Corresponding author



Fig. 1 Photograph of the fabricated battery.

Table 1
Specification of the fabricated battery

Active material	LiCoO ₂ (cathode) Natural graphite (anode)
Collector	Al (cathode) Cu (anode)
Electrode size	170 mm × 170 mm
Number of cells	659 cells
Electrolyte	1 M LiPF ₆ in EC/DEC (7:3)
Battery size	184 mm × 187 mm × 248 mm
Battery volume	8.53 l
Battery weight	18.4 kg
Titanium container	4 mm (thickness), 8.3 kg (weight)
Rated capacity	343 Ah
Average discharge voltage	3.5 V

The fabricated battery is shown in Fig. 1, and its specifications are listed in Table 1.

2.2. Charge/discharge tests

The battery was charged and discharged at a current density of 0.15 mA/cm² for 8 h, and the voltage was limited to the range of 3.0–4.3 V. However, the value of the eighth cycle at 0.2 mA/cm², which is about 30% larger than that of usual current density, was employed for 9 h to estimate the maximum capacity of the battery. We defined the cycle life as when the end point of the charge voltage reached 4.3 V. In these tests, the charge and discharge cycles were conducted at steady current. This type of battery life estimation method is more strict than that of usual ones in which charge and discharge is repeated till the pre-determined cut-off voltage. Nevertheless, it is possible to compare the results obtained by the two methods. All measurements were performed at 25 °C. The current at charge and discharge in the present work can be expressed as 0.1 C.

3. Results and discussion

It was demonstrated through the tests using small-capacity cells that LiBF₄ is more reactive to the lithium-intercalated graphite anode than LiPF₆, resulting in the formation of inactive LiF on the electrode surface [7]. Therefore, it is difficult to expect a long cycle life of the battery with the LiBF₄ electrolyte. Based on the results on the small-capacity cells, the following changes were made on the large-capacity battery:

1. The electrolyte was changed from LiBF₄ to LiPF₆.
2. The ratio of EC/DEC was optimized.
3. The plate spring was installed to adjust expansion and shrinkage of electrodes during the charge/discharge reactions.
4. Residual moisture was minimized.

The test results will be detailed in a separate paper in the near future [8]. Fig. 2 shows the effect of the ratio of EC/DEC on the battery life, which was obtained with a small coin cell. It is clear from this figure that the greater is the EC ratio, the longer is the battery life. However, there must be a critical EC mixing ratio, above which solvent viscosity becomes too high to operate at lower temperatures. The longest cycle data was achieved when its ratio was around 7:3. Fig. 3 shows the charge/discharge curves for the eighth cycle. As is clear in this figure, the battery gives an average discharge voltage of 3.5 V, output power of 126 W, and energy

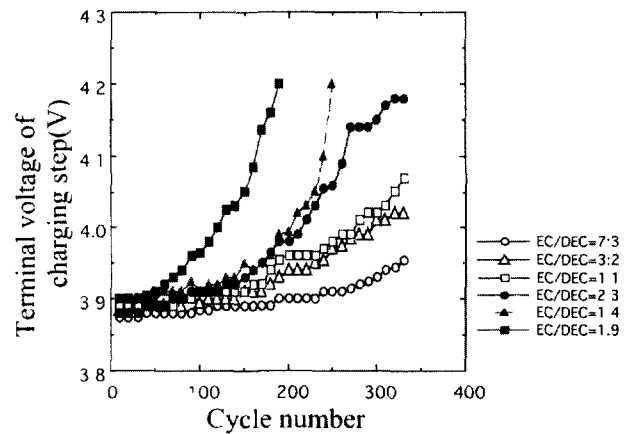


Fig. 2. Effect of the EC/DEC ratio on the battery life

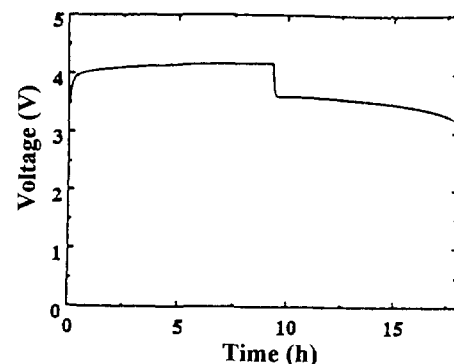


Fig. 3. Charge/discharge curves during the eighth cycle.

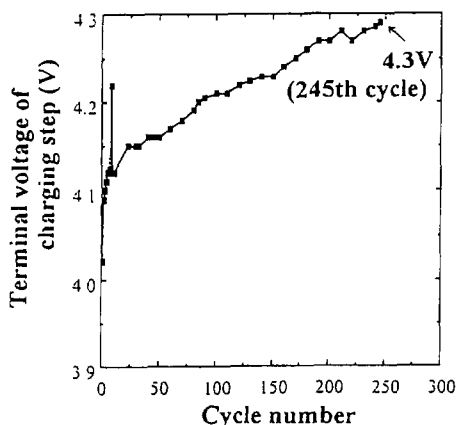


Fig. 4. Variation of the terminal voltage of each charging step.

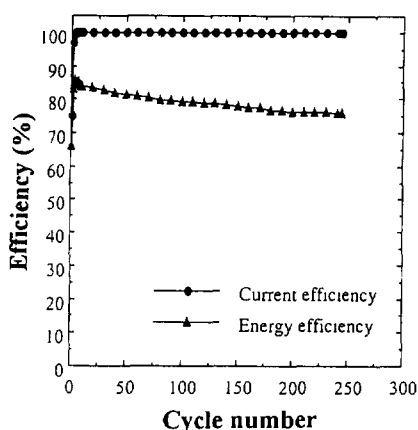


Fig. 5. Variation of the efficiency with the change in cycle number.

of 1134 Wh. It also delivers the energy density of 60 Wh/kg and 133 Wh/l. The voltage at the beginning of discharge using a large-scale cell was smaller due to the greater internal resistance compared with usual small coin cells. Fig. 4 illustrates the variation of the terminal voltage of each charging step obtained with the large battery, so the end voltage with cycling in this figure was found to be somewhat different from that in Fig. 2. There is no difficulty to understand the tendency of cycle life of the battery. By decreasing residual moisture from 200 to 100 ppm, 150 mV lowering of the terminal voltage of charging step was detected. By using plate spring, battery life is greatly increased. We have already achieved a battery life as long as 245 cycles. Fig. 5 shows the variation of current efficiency as well as energy efficiency with the change in cycle number. This figure clearly shows that current efficiency stays at 99.9% throughout the cycle number tested. On the other hand, energy efficiency, initially around 85%, tends to deteriorate gradually. This tendency can be explained by the increase in internal resistance of the battery with the cycle number. Fig. 6 illustrates the variation of the cell resistance as a function of the change in cycle

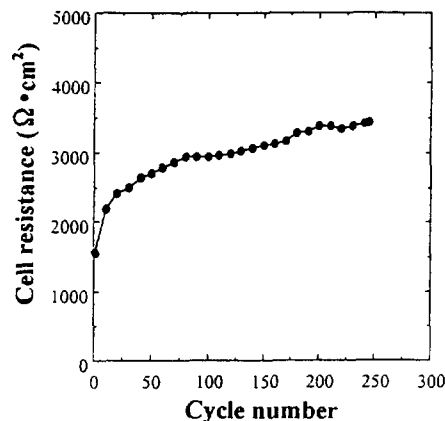


Fig. 6. Variation of cell resistance with the change in cycle number

number. This cell resistance shows 7 to 10 times higher than that obtained with a small-size single cell of 0.3 Ah, which was used in a laboratory test. As is clear in this figure, the cell resistance increases with cycle number. We performed chemical analysis and observation of X-ray diffraction of the electrode surface after the charge/discharge tests. We also found some deposits on the separators with a scanning electron microscope. These findings will be detailed in a separate paper [8].

4. Summary

A test battery of 1 k Wh (300 Ah) class of lithium-ion cell was fabricated based on the findings obtained by use of single-unit cells. Through this work, 60 Wh/kg and 133 Wh/l of energy density and cycle life of 245 cycles were achieved. A further extension of battery life can be expected by the employment of a charging step performed under constant current and voltage.

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