

# Development of long life lithium ion battery for power storage

Masatoshi Majima<sup>a,\*</sup>, Satoshi Ujiie<sup>b</sup>, Eriko Yagasaki<sup>b</sup>,  
Keiji Koyama<sup>a</sup>, Shinji Inazawa<sup>a</sup>

<sup>a</sup>Osaka R&D Laboratory, Sumitomo Electric Industries Ltd., 1-1-3 Shimaya Konohana-ku, Osaka 554-0024, Japan

<sup>b</sup>Technical Research Center, The Kansai Electric Power Company Inc., 3-11-20 Nakoji, Amagasaki, Hyogo 661-0974, Japan

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## Abstract

With the aim of developing lithium ion batteries with a long life and high efficiency for power storage, we experimentally evaluated combinations of cathode and anode active materials, in which batteries are able to obtain over 4000 cycles or 10 years of life. An acceleration method was evaluated using coin cells. We found that changing the current density was effective for evaluating battery life, since the logarithm of the cycle life showed a linear relationship to current density. Based on the current density increasing method, various combinations of cathode and anode active materials were tested. The cell system of  $\text{LiCoO}_2/\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  clearly showed a long life of about 4000 cycles. The energy density of the cell using the  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  anode is obviously smaller than that using a graphite anode, the cell with  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  anode was thought to have some merit especially in the large-scale-layer-built type battery by the applicability of the Al anode collector and a light weight battery case. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium ion battery; Power storage;  $\text{LiCoO}_2$ ;  $\text{LiMn}_2\text{O}_4$ ;  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$

## 1. Introduction

In previous papers [1–3], the authors reported studies performed for the development of a 1 kWh class lithium ion battery for power storage, using  $\text{LiCoO}_2$  and natural graphite as cathode and anode active materials, respectively, with 1 M  $\text{LiPF}_6$  dissolved in ethylene carbonate/diethyl carbonate (EC/DEC) as an electrolyte. In those studies, the construction of the batteries was based on the results of fundamental research using a coin cell or large-scale single cell done to elucidate the problems encountered when batteries were dismantled after the previous model reached to the battery life. A total of 543 cycles were achieved, exceeding the initial target of 500 cycles. It was also found that factors such as uniform impregnation of the electrolyte into the electrode laminates and maintenance of uniform conditions of laminates by the control of expansion and contraction during charge and discharge, respectively, were very important for the long life of large-scale lithium ion batteries.

The purpose of the present study is to develop 1 kWh class lithium ion batteries of long life, 4000 cycles, and high

efficiency. Through a comprehensive survey of electrode active materials presently available in the market, test batteries using  $\text{LiCoO}_2$  and  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  or PCG (artificial graphite) as the cathode and anode active materials, respectively, with 1 M  $\text{LiPF}_6$  dissolved in EC/DEC as an electrolyte, were constructed. Acceleration tests were done to determine the battery life, and it was found that  $\text{LiCoO}_2/\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  as well as  $\text{LiCoO}_2/\text{PCG}$  are promising batteries of long life. In regard to this, the expansion and contraction of the battery accompanied with the charge and discharge, respectively, were measured. It was found that  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  is superior as a light battery in terms of a low degree of expansion and contraction, whereas  $\text{LiCoO}_2/\text{PCG}$  is excellent for high energy density.

## 2. Test procedures

### 2.1. Preparation of electrodes

#### 2.1.1. Cathode

After a comprehensive survey and fundamental testing of various cathode active materials, including  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$  and their derivatives,  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$  and  $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$  were chosen for their availability in the

\* Corresponding author. Fax: +81-6-6466-1274.

E-mail address: majima-masatoshi@sei.co.jp (M. Majima).

market and superiority of characteristics.  $\text{LiCoO}_2$  with a mean particle size of  $6.5 \mu\text{m}$  (Nippon Kagaku Ind., Japan) and  $\text{LiMn}_2\text{O}_4$  (or its derivatives from Tosoh Corporation, Japan or Nikki Chemical Co. Ltd., Japan) were used as the cathode active materials, and carbon black with a mean particle size of about  $0.6 \mu\text{m}$  (Lonza, Switzerland) was used as a conductive agent. On the other hand, PVdF powder (Aujimont, Italy) was used as a binder, and *n*-methyl-2-pyrrolidone was used as a solvent to prepare electrode paste.

The cathode active material, conductive agent, binder, and solvent were mixed at a weight ratio of 10:1:1:5.5 under a high purity nitrogen atmosphere for about 1 h. The paste obtained was spread over an aluminum foil about  $20 \mu\text{m}$  thick with a doctor blade using an electrode-coating machine (Sank, Japan). The paste was applied so that the weight after drying of the electrode would become  $0.02\text{--}0.03 \text{ g/cm}^2$  unless otherwise indicated. The machine was designed to pass the paste applied to the foil by doctor blading through a dry atmosphere at  $150^\circ\text{C}$  for about 2 min. In this process (primary drying), most of the solvent was eliminated by evaporation. After the passage through the drying furnace, the electrode was wound, stored in an incubator, and the residual solvent and moisture were removed by vacuum drying at  $150^\circ\text{C}$  for 4 days (secondary drying). After secondary drying, the electrode was compressed with a roll presser (Sank, Japan) to reduce its effective thickness to 80% of the active material layer. After the electrode was cut to predetermined size, it was dried under normal pressure at  $150^\circ\text{C}$  for 4 days (tertiary drying) and then was used to prepare a battery.

### 2.1.2. Anode

Among various anode active materials examined, the following three materials were chosen as suitable:  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  with a mean particle size of  $7.0 \mu\text{m}$  (Toho Titanium Co. Ltd., Japan), PCG with a mean particle size of  $10.0 \mu\text{m}$  (Osaka Gas Co. Ltd., Japan) and natural graphite with a mean particle size of  $12.0 \mu\text{m}$  (The Kansai Coke and Chemicals, Japan). PVdF powder (Aujimont, Italy) was used as a binder, and special grade *n*-methyl-2-pyrrolidone was used as a solvent to prepare paste.  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ , carbon black, binder, and solvent were mixed at a weight ratio of 10:1:1:5.5. PCG or natural graphite, binder, and solvent were mixed at a weight ratio of 10:2:10. They were kneaded in a high purity nitrogen atmosphere for about 1 h. The paste obtained was spread over a copper foil of  $20 \mu\text{m}$  thick by doctor blading using an electrode-coating machine (Sank, Japan). The paste was applied so that the weight after drying of the electrode would be  $0.02 \text{ g/cm}^2$  using  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ , and  $0.01 \text{ g/cm}^2$  using PCG or Natural graphite unless otherwise indicated. The electrode was dried and cut similar to the cathode and the electrode was compressed to a thickness of about 80% at  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ , and 60% at PCG of that of the active material layer excluding the thickness of the metal foil.

### 2.1.3. Preparation of electrode laminates

The cathode, separator, and anode were layered in this order, and the terminals of every 20 cathode–anode pairs were bound with rivets. They were further layered to the predetermined number of electrodes, and electrode laminates were obtained. The entire process of layering of electrodes was performed in a dry box containing an atmosphere of 100% argon.

### 2.2. Electrolyte

The electrolyte was prepared by dissolving 1 M  $\text{LiPF}_6$  (Mitsubishi Chemical, Japan) in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), and 1 M  $\text{LiPF}_6$  (Sumitomo Seika Chemicals Co. Ltd., Japan) with a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The mixture of EC and DEC was prepared at a volume ratio of 7:3 unless otherwise indicated. After infusion of the electrolyte, the pressure was reduced to 400 Torr using a pump, and impregnation of the electrolyte was done for 144 h.

### 2.3. Preparation of coin batteries

For the selection of active materials for the electrode and the acceleration tests of battery life, coin batteries were used. The case of the coin battery consisted of an aluminum lid serving as the cathode, a stainless steel (SUS 304) case serving as the anode, a nickel spacer, and a polyethylene gasket to insulate the lid from the case. A hole of 1 mm in diameter was made in the center of the cathode by removing the active material, and aluminum foil was connected to the lid at this site using a spot welder. The electrode was designed to have an area of  $1 \text{ cm}^2$  except for the hole in the center. The anode was prepared by spot welding the nickel spacer to the case material and, then, connecting a copper foil with the nickel spacer. The anode also had an area of  $1 \text{ cm}^2$ . A polypropylene separator, which was slightly larger than the cathode or anode and  $25 \mu\text{m}$  thick, was inserted between the cathode and anode, and about 0.2 cc of an electrolyte was infused. All procedures were carried out in a dry box containing argon, in which the moisture was controlled at 0.01 ppm or less. After infusion of the electrolyte, the pressure inside the side box attached to the dry box was reduced to 660 Torr, and electrolyte impregnation was performed for 5 min. The battery case was covered with the lid and sealed with a caulking machine.

### 2.4. Preparation of single cell

Using  $\text{LiCoO}_2$  or  $\text{LiMn}_2\text{O}_4$  (or its derivatives) as cathode active material and natural graphite, PCG, or  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  as anode active material, single-cells were fabricated as shown in Table 1 for evaluation of battery life. For acceleration cycle test of the battery, single cells with a structure shown in Fig. 1 were evaluated. The cathode and anode, which were cut to a predetermined size and placed on each side of the

Table 1  
Composition of test cell

Cell number	Cathode	Anode	Electrolyte (electrolysis 1 M LiPF <sub>6</sub> )
①	LiCoO <sub>2</sub>	Li <sub>4/3</sub> Ti <sub>5/3</sub> O <sub>4</sub>	EC:DEC/7:3
②	LiCoO <sub>2</sub>	PCG	EC:DEC/7:3
③	LiCr <sub>0.1</sub> Mn <sub>1.9</sub> O <sub>4</sub>	Natural graphite	EC:DMC/3:7
④	LiCr <sub>0.1</sub> Mn <sub>1.9</sub> O <sub>4</sub>	PCG	EC:DMC/3:7
⑤	LiCr <sub>0.1</sub> Mn <sub>1.9</sub> O <sub>4</sub>	Li <sub>4/3</sub> Ti <sub>5/3</sub> O <sub>4</sub>	EC:DMC/3:7

separator, were sandwiched with fluorine resin plates with a thickness of 3 mm and furthermore with SUS 304 plates with a thickness of 10 mm, and these layers were bound with bolts. The number of bolts used varied with the size of the electrodes, but the bolts were tightened with a torque wrench so that a pressure of about 3 kg/cm<sup>2</sup> would be applied to the electrodes. This unit was placed in an SUS 304 case with an interior wall coated with fluorine resin. Then, a predetermined volume of electrolyte was infused into the dry box, the lid was closed by interposing an o-ring (Viton), the pressure of the interior was reduced to 660 Torr through the orifice of the safety valve in the lid, and this state was maintained for a predetermined period. The period of decompression was carried out for 144 h. After impregnation, the lid was opened, the surplus electrolyte was removed, and the cathode and anode were connected to the terminals attached to the lid.

### 2.5. Cycle test of batteries

Coin cells and single cells were assessed using an HJ series charge–discharge apparatus (Hokuto Denko, Japan). Unless otherwise indicated, the batteries were charged at a constant current for a predetermined time, discharged to the lower limit voltage at the same current density, and this cycle was repeated. The test materials are listed in Table 2.

Table 2  
List of active materials used for cycle test

Active material	Experimental capacity at 0.2C (mAh/g)	Theoretical capacity (mAh/g)	Initial cyclability
Li <sub>x</sub> CoO <sub>2</sub>	125	137 (X = 0.5)	Excellent
Li <sub>x</sub> Mn <sub>2</sub> O <sub>4</sub>	120	148 (X = 1.0)	Not good
Li <sub>x</sub> Cr <sub>0.1</sub> Mn <sub>1.9</sub> O <sub>4</sub>	110	140 (X = 0.95)	Good
Natural graphite	330	372	Good
PCG	320	372	Excellent
Li <sub>4/3+x</sub> Ti <sub>5/3</sub> O <sub>4</sub>	150	175 (X = 1.0)	Excellent

### 2.6. Fabrication of a 50 Ah class battery and a method for contraction–expansion measurement

50 Ah class batteries were fabricated for the contraction–expansion measurement test. Fig. 2 schematically illustrates the structure of the test battery. The cathode, separator, and anode were layered in this order in a dry box filled with an argon gas, and the laminates were inserted into a flexible Al-based laminate pack. A predetermined volume of the electrolyte was infused into the battery case, the electrodes were impregnated with the electrolyte under low-pressure, and the battery pack was heat-sealed. The aluminum collector on the cathode side and the copper collector on the anode side were connected to copper external terminals via wires coated with fluoride resin. The appearance of the battery was basically the same as that of the previous study [3]. Table 3 lists the constitution of the test batteries.

Evaluation of the contraction–expansion measurement of 50 Ah class battery was made using a BS2500 series charge–discharge apparatus (Keisokuki Center Ltd., Japan). The battery was charged at a current density of 0.2 mA/cm<sup>2</sup> for 10 h under a constant current (CC), and discharged at the same current density to a predetermined lower voltage, and this cycle was repeated.

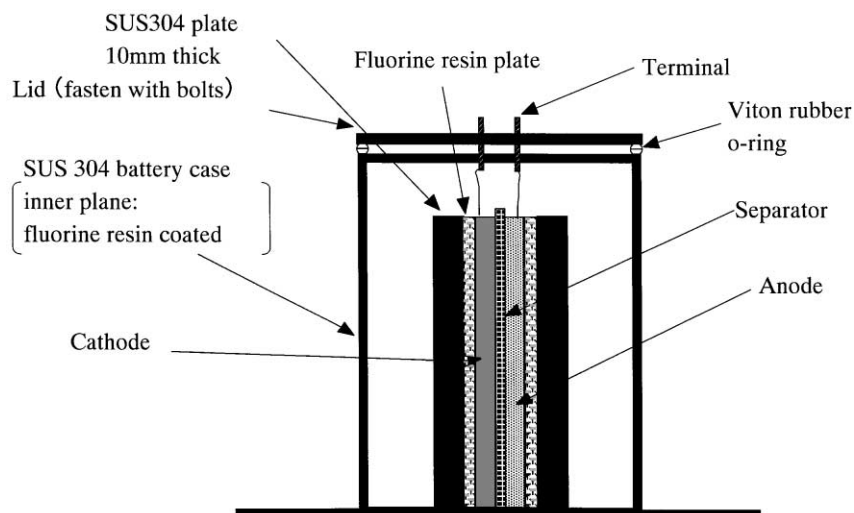


Fig. 1. Schematic illustration of the single cell system.

Table 3  
Constitution of the 50 Ah class bag-type battery

Battery type	LiCoO <sub>2</sub> /Li <sub>4/3</sub> Ti <sub>5/3</sub> O <sub>4</sub>	LiCoO <sub>2</sub> /PCG
Electrolyte	1 M LiPF <sub>6</sub> in EC:DEC/7:3	1 M LiPF <sub>6</sub> in EC:DEC/7:3
Collector	Al/Al	Al/Cu
Separator	Fine porous film made of polypropylene	Fine porous film made of polypropylene
Electrode size	100 mm × 100 mm	100 mm × 100 mm
Number of electrodes	120 sheets (240 cells)	120 sheets (240 cells)
Battery case	Aluminum and polyethylene foil laminated bag	Aluminum and polyethylene foil laminated bag
Current density	0.2 mA/cm <sup>2</sup>	0.2 mA/cm <sup>2</sup>

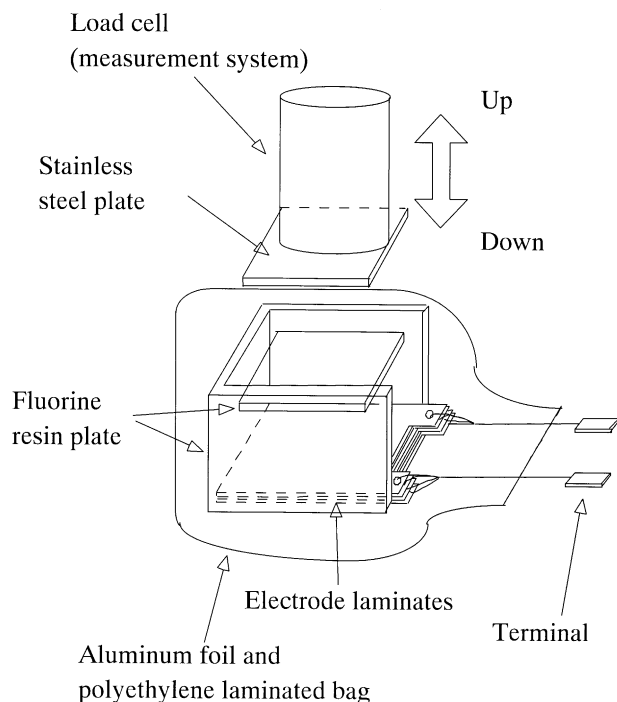


Fig. 2. Schematic illustration of the 50 Ah class battery for contraction and expansion measurement.

In Test 1, which consists of the first to fifth cycles, a weight of 30 kgf was placed on to the stainless steel plate. The change in expansion and contraction of the electrode was measured using a micro-gauge during charge and discharge cycles. By contrast, in Test 2, consisting of the sixth to seventh cycles, the initial load was set at 30 kg (0.3 kg/cm<sup>2</sup>). The pressure generated in the battery was measured with load cell during charge and discharge cycles.

### 3. Results and discussion

#### 3.1. Acceleration test for battery evaluation

Assuming one cycle consists of 8 h charge and 8 h discharge and target is 4000 cycles, it takes 7.3 years for the evaluation when current density is set at 0.2 mA/cm<sup>2</sup> (1/8C, DOC 70%). Therefore, it is necessary to apply a suitable acceleration method for practical evaluation. The

applicability of the acceleration test method, based on current density increase, was examined. To examine the applicability of this method, LiCoO<sub>2</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> and LiMn<sub>2</sub>O<sub>4</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> test batteries were used.

Current densities were changed in the range of 0.4–1.6 mA/cm<sup>2</sup>. If we apply 1.6 mA/cm<sup>2</sup>, we can shorten the evaluation period approximately to 11 months.

Fig. 3 shows the results of acceleration tests for the LiCoO<sub>2</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> battery. At current densities at 1.6, 1.4 and 1.2 mA/cm<sup>2</sup>, the batteries reached their life in short duration. Evaluation tests at other current densities are still going on. Defining battery life as the number of cycles at which charge end voltage reaches 4.0 V, the relationship between battery life and current densities of 1.4, 0.8, and 0.4 mA/cm<sup>2</sup> were determined by the extrapolation technique. As can be seen in Fig. 4, a linear relationship was observed between the logarithm of battery life and current density, indicating easy application of this acceleration method for the evaluation of battery life. Assuming 8 h each of charge–discharge, the current density was kept at 0.2 mA/cm<sup>2</sup>. Under these conditions, battery life can be simply estimated as 50,000 cycles. But real battery life might be shorter than estimated value of 50,000 cycles because there are many other deterioration factors in the long-term test like moisture contamination as what we call shelf life. In this regard, researchers [4–6] reported that the LiCoO<sub>2</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> battery is characteristic of a very long life electrodes couple, and the results obtained in the present study qualitatively support this.

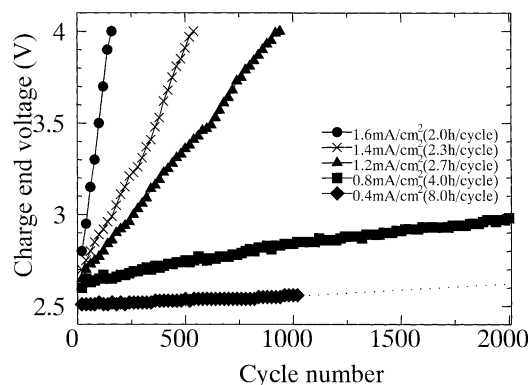


Fig. 3. Acceleration test of LiCoO<sub>2</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> coin cell done by changing current density.

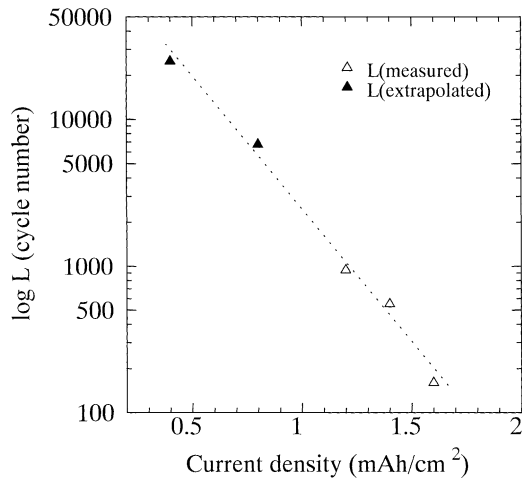


Fig. 4. Cycle life estimation made for LiCoO<sub>2</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> coin cell.

Fig. 5 depicts the cycle dependency of the LiMn<sub>2</sub>O<sub>4</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> cell determined at different current densities. The value of charge end voltage determined at 1.6 mA/cm<sup>2</sup> was high. This is attributed to the conductivity of LiMn<sub>2</sub>O<sub>4</sub> which is lower than that of LiCoO<sub>2</sub>.

A method of evaluating battery life by changing current density is suitable for battery systems using active materials of high electron conductivity. The appropriateness of this acceleration method was experimentally confirmed with the LiCoO<sub>2</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> cell.

3.2. Acceleration evaluation of single cells using long life electrode active materials

LiCoO<sub>2</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub>, LiCr<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> and other types of cells listed in Table 1 were subjected to charge at a constant 0.6 mA/cm<sup>2</sup> (DOC 70%), then discharged at the same current density until the potential reached 1 V. This cycle was repeated. With batteries in which the anode was natural graphite, discharge was done until 3 V at the same

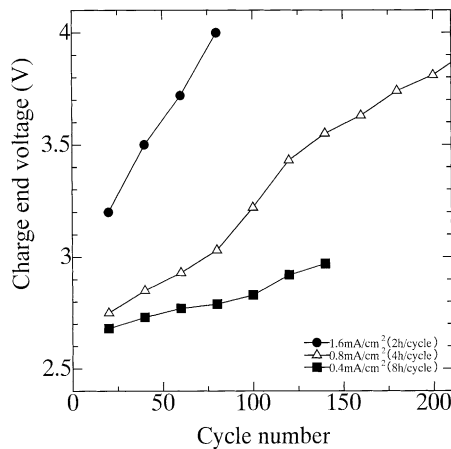


Fig. 5. Acceleration test with LiMn<sub>2</sub>O<sub>4</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> coin cell done by changing current density.

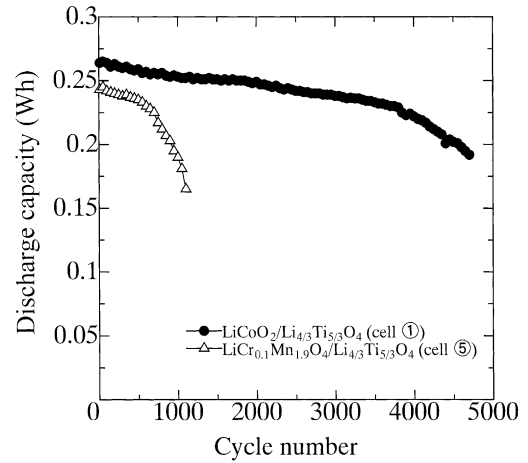


Fig. 6. Effect of high rate charge on cycle life of single cell (Part I).

current density. The electrolyte used in all cells was 1 M LiPF<sub>6</sub> dissolved in EC:DEC at a volume ratio of 7:3.

Fig. 6 shows the experimental results with the batteries of LiCoO<sub>2</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> and LiCr<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub>/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub>, which are referred to as cell ① and ⑤, respectively, in Table 1. Cell ① has already shown a life of over 4000 cycles and was still working soundly. We can expect a life longer than 5000 cycles. The life of cell ⑤ was less than 1200 cycles. However, it is more important to improve the characteristics of cathode active materials.

Fig. 7 shows the experimental results obtained with the cells of LiCoO<sub>2</sub>/PCG, Cr<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub>/natural graphite and LiCr<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub>/PCG, which are referred to as cell ②, ③ and ④, respectively, in Table 1. Cell ③ and ④ clearly had shorter life than 1000 cycles, however, the expected life of cell ② is almost 3000 cycles.

From these experimental results, we can summarize the cyclability order of cathode and anode active materials; cathode: LiCoO<sub>2</sub> > LiCr<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub>, and anode: Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> > PCG > natural graphite.

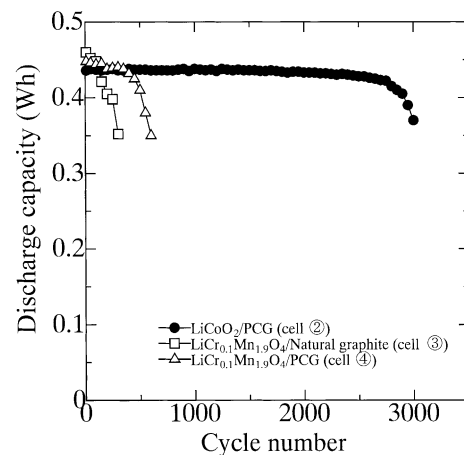


Fig. 7. Effect of high rate charge on cycle life of single cell (Part II).

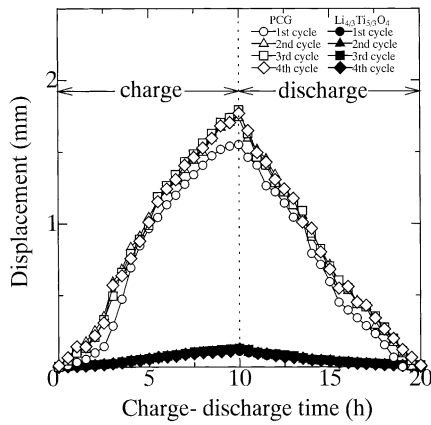


Fig. 8. Change in displacement of PCG or  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  electrodes with cycle number.

### 3.3. Contraction–expansion-measurement of the 50 Ah class battery and design of a battery case

Fig. 8 shows the results of Test 1. The expansion phenomenon during charge conditions was observed and contraction occurred during the discharge step. The maximum displacement shown by  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  was negligibly small in comparison with PCG.

Fig. 9 depicts the results of Test 2. When PCG was used as an anode, a maximum load of 480 kgf was generated and this value is close to the datum of natural graphite, which was reported by the anthers researcher, as shown in Table 4. This finding is attributable to the similarity between PCG and natural graphite in the degree of graphatization and shape of the powder. In contrast, only 55 kgf was generated using  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  and most of the load would be caused by  $\text{LiCoO}_2$  taking into account that  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  is a no strain system [4].

For the development of a lightweight battery case, the appropriate thickness of the case based on aluminum was calculated using the following equation [7]:

$$\omega_{\max} = 0.171 \frac{Pa^4}{Eh^3} \quad (1)$$

where  $\omega_{\max}$  is the maximum bending,  $P$  the applied force per unit area,  $a$  denotes the width of the battery case,  $E$  the

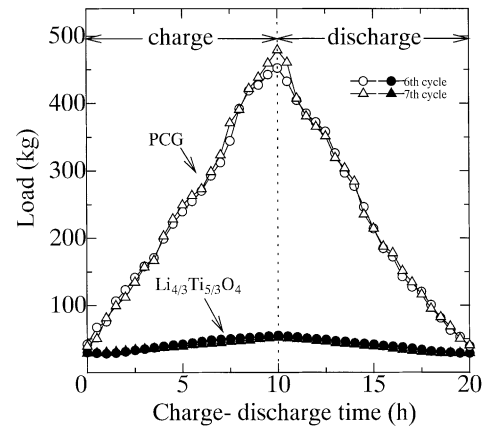


Fig. 9. Change in load generated on a PCG or  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  electrodes for large-sized battery.

Table 4  
Comparison of maximum pressure

Cell type	Maximum pressure (kgf/cm <sup>2</sup> )
LiCoO <sub>2</sub> /PCG	4.80
LiCoO <sub>2</sub> / $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$	0.55
LiCoO <sub>2</sub> /natural graphite	5.05 [3]
LiCoO <sub>2</sub> /MCMCB	1.61 [3]

elastic constant and  $h$  denotes the thickness of the battery case. In this calculation, Poisson's ratio of 0.3 and an elastic constant of Al of 7000 kg/mm<sup>2</sup> were used. Under the condition of  $\omega_{\max} < 0.1$  mm,  $h = 4.00$  mm (LiCoO<sub>2</sub>/PCG cell) and  $h = 0.97$  mm (LiCoO<sub>2</sub>/ $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  cell) were obtained.

### 3.4. Comparison of energy density for a large-scale prismatic cell

From the results of the accelerating test, a long cycle life of the LiCoO<sub>2</sub>/PCG cell and LiCoO<sub>2</sub>/ $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  cell were obtained. We estimated the energy density of the 350 Ah class large-scale prismatic batteries. In Table 5, the weight of the battery case was referred to the calculation value of 3.3. The energy capacity of the LiCoO<sub>2</sub>/PCG cell was 1.5 times that of the LiCoO<sub>2</sub>/ $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  cell. An Al collector can

Table 5  
Energy density of 350 Ah class lithium ion battery

Battery type	LiCoO <sub>2</sub> / $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$	LiCoO <sub>2</sub> /PCG
Active material with binder and conductive agent (kg)	3.36(+)/2.76(-)	3.36(+)/1.31(-)
Collector (kg)	0.38(Al)/0.38(Al)	0.38(Al)/1.11(Cu)
Battery case (kg)	1.35(Al base)	5.38 (Al base)
Plate spring or other parts (kg)	1.60	1.75
Electrode size	200 mm × 200 mm	200 mm × 200 mm
Number of electrodes	175 sheets (350 cells)	175 sheets (350 cells)
Average discharge voltage (V)	2.4	3.6
Capacity (Wh)	840	1260
Energy density (Wh/kg)	85.5	94.8
Energy density (Wh/l)	137.0	200.0

be used, when  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  is used for an anode, because  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  shows a potential of 1.5 V versus Li. Also, a lightweight battery case can be applied for the  $\text{LiCoO}_2/\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  cell, because of its small maximum pressure. There is no distinct difference in energy density on a weight basis between  $\text{LiCoO}_2/\text{PCG}$  and  $\text{LiCoO}_2/\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ , as clearly shown by the estimation of the 350 Ah class large-scale prismatic batteries.

#### 4. Conclusions

1. From the acceleration evaluation at the current density of  $0.6 \text{ mA/cm}^2$  (DOC 70%) of single cells using long life electrode active materials, a life of over 4500 cycles in the  $\text{LiCoO}_2/\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  cell and over 2800 cycles in the  $\text{LiCoO}_2/\text{PCG}$  cell was confirmed.
2. Based on the cycling experimental results, we can summarize the cyclability order of cathode and anode active materials as follows: cathode,  $\text{LiCoO}_2 > \text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ ; anode,  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4 > \text{PCG} > \text{natural graphite}$ .
3. From the contraction–expansion measurement of 50 Ah class batteries, a maximum pressure of  $0.55 \text{ kg/cm}^2$  for  $\text{LiCoO}_2/\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  and of  $4.80 \text{ kg/cm}^2$  for  $\text{LiCoO}_2/\text{PCG}$  was obtained.
4. There is no distinct difference in energy density on a weight basis between  $\text{LiCoO}_2/\text{PCG}$  and  $\text{LiCoO}_2/\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ , as clearly shown by the estimation of the 350 Ah class large-scale prismatic batteries.

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