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Design and characteristics of large-scale lithium ion battery

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Abstract

Adequate cell design, especially concerning energy density and cycle life, is important for the development of large-scale lithium ion batteries. In this study, we were able to survey the expansion and shrinkage of the layer-built electrodes of a prismatic cell during charge and discharge tests. Natural graphite and mesophase carbon micro beads (MCMB) were used as anode active material for the comparison purpose. Based on the findings of this study, a plate spring and lightweight battery case were designed. In addition, an improved large-scale battery employing these parts was manufactured for further examination.

Keywords: Lithium; Cell design; Large scale; Cathode; Anode

1. Introduction

We have been developing large capacity lithium-ion batteries for electric power storage [1,2]. In a lithium-ion battery, electrodes repeatedly expand and contract during the charge and discharge cycles. X-ray diffraction shows a maximum 1% expansion for cathode-active materials, $LiCoO_2$ [3], and a maximum of 10% expansion for anode-active materials, natural graphite [4]. For the battery, in which $LiCoO_2$ and natural graphite are used as active materials, the effects of expansion and contraction of electrodes are extremely important, since periodical charge and discharge are essential for this type of battery. Binders and separators, both indispensable components of real batteries, may play an important role in buffering and, absorbing electrode displacement. Kitoh et al. [5] examined the expansion and contraction behavior of electrodes used in a single cell small-sized battery. Unfortunately, none of the findings has been reported for laminate electrodes, which highlights the necessity of this type of work. Therefore, the following measurements were conducted using a bag type battery to understand the required strength of the battery case: (1) displacement of the laminate electrodes under a constant weight load and (2) the pressure caused by a constant displacement.

In this study, MCMB, which was recognized as a useful electrode material, was also examined to make the battery compact. This material may be useful to achieve a high energy density. Furthermore, the displacement of a plate spring was examined based on the findings obtained for the expansion and contraction behavior of the laminate electrodes to exploit a reformed type of plate spring.

2. Experimental methods

Fig. 1 shows the test battery used. A bag type vessel made of aluminum foil (15 μm thick) and polyethylene laminate was used to cover the whole battery. In addition, a fluoride resin plate was used as an enclosure to protect both the side of the electrode and the bottom of the electrode laminates. The upper part of the electrode laminates was covered using a movable fluoride resin plate (3 mm thick). Also a movable stainless steel (10 mm thick) was placed onto the movable fluoride resin plate to deliver a delicate change of load or displacement to the measuring device. Table 1 shows the details of the battery tested. Square electrodes (10 cm) were used. Two hundred and forty cells, i.e., a total of 120 laminates, each consisting of an anode, a separator and a cathode, were formed. These were installed in an aluminum–polyethylene laminate bag. The open end of the bag was sealed using a heat-sealer. The capacity of this middle-sized battery was 173 Wh.

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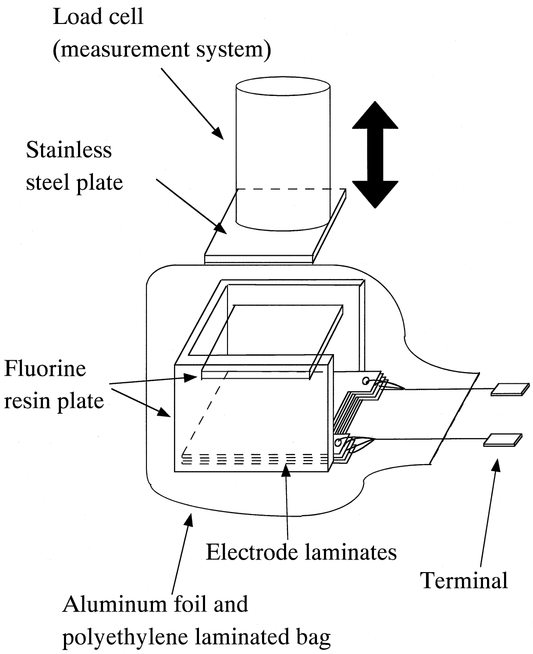

Fig. 1. Schematic illustration of test battery.

2.1. Test 1

A weight of 30 kg was placed onto the stainless steel box. The displacement of the electrodes was measured using a micro-gauge during charge and discharge cycles.

2.2. Test 2

The initial load was set at 30 kg (0.3 kg/cm^2). The pressure generated in the battery was measured with load cell during charge and discharge cycles.

3. Result and discussion

Fig. 2 shows the results obtained from Test 1. The expansion phenomenon during charge conditions was observed with the both cells using natural graphite and MCMB, and in addition, contraction occurred during the discharge step. The displacement shown by natural graphite was almost 3 times greater than that of MCMB.

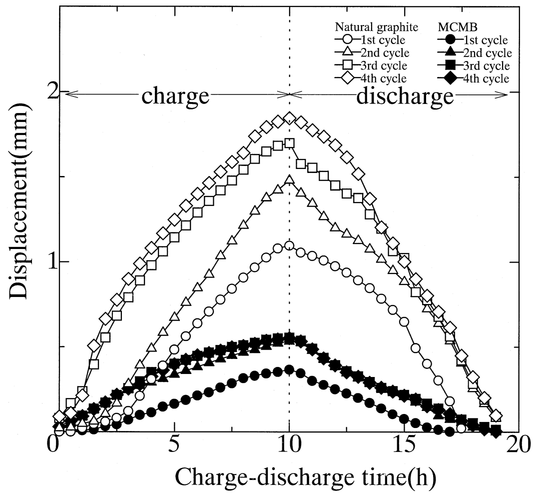

Fig. 2. Change in displacement of natural graphite and MCMB electrode with cycle number.

Fig. 3 presents the change in maximum displacement observed at the end of the charge step in charge–discharge cycle. With both anode-active materials, expansion tends to converge to respective constant values. Using MCMB, a second cycle was adequate to achieve a stable state of 0.55 mm, while it took 4 or 5 cycles to achieve stable state of 1.84 mm using natural graphite.

Fig. 4 depicts the results from Test two. When natural graphite was used as an anode active material, a load of 505 kg was generated, while only 161 kg was generated using MCMB.

From these findings from Test 1, the maximum displacement generated per unit cell using natural graphite

Table 1
Constitution of the bag-type battery

Active material	$LiCoO_2$ (cathode)
	Natural graphite (anode)
Electrolyte	1M $LiPF_6$ in EC:DEC(7:3)
Collector	Al (cathode)
	Cu (anode)
Electrode size	100 mm × 100 mm
Number of electrodes laminated sheets	120 sheets (240 cells)
Separator	Fine porous film made of polypropylene
Capasity	48 Ah(173 Wh)
Energy density	166.3 Wh/l (volume basis)
	78.6 Wh/kg (weight basis)
Battery case	Aluminum and polyethylene foil laminated bag
Current density	0.2 mA/cm^2

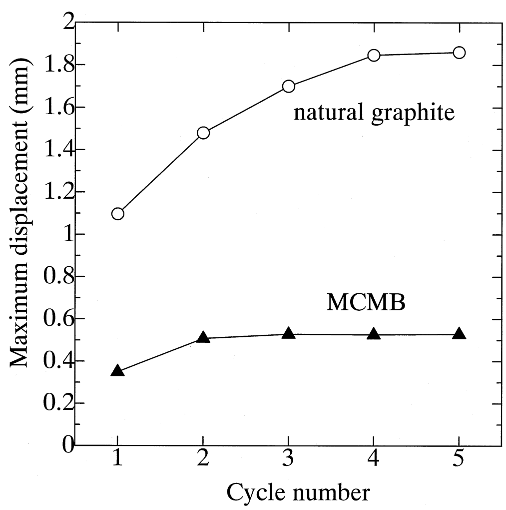

Fig. 3. Change in maximum displacement for a natural graphite or MCMB electrode with cycle number.

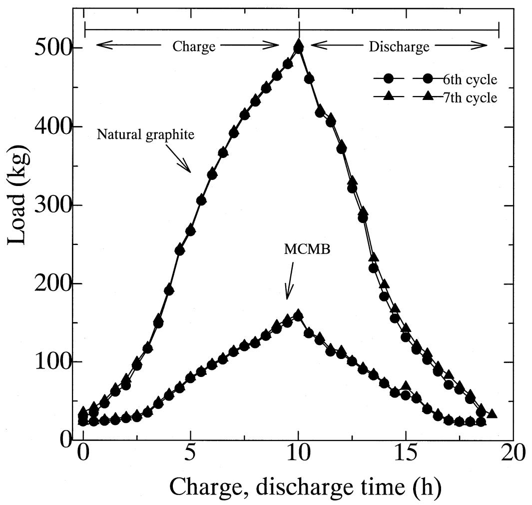

Fig. 4. Determination of load generated on a natural graphite or MCMB electrode for large-sized battery.

was calculated as 7.69 μm, while it was 2.29 μm using MCMB. Since the total thickness of both anode and cathode active material is about 170 μm, the actual expansion detected is less than 10% of the actual thickness of the electrodes.

However, the load on the electrode was 5.05 kg/cm^2 for natural graphite, while it was only 1.61 kg/cm^2 for MCMB, since the area of electrodes used in Test 2 was 100 cm^2. Based on the findings of this study, a plate spring and lightweight battery case were designed.

3.1. Design of plate spring and a lightweight battery case

Around 700 laminates in total, each consisting of a 20-cm square electrode, were used to construct a large scale battery. Based on the findings obtained by the expansion and contraction measurements mentioned above, a novel type of plate spring and lightweight battery case was designed and constructed. Fig. 5 schematically illustrates the inside of the battery.

3.1.1. Design of plate spring

The plate spring was mainly constructed of titanium metal. For simplicity, a disk plate fixed at periphery having an equally distributed load was employed for the calculation. Bending of the pressing plate employed for pressing the laminated electrodes was calculated from the following equation [6]:

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

where ω_{max} is the maximum bending, P is the applied force per unit area, a is the pitch of the plate spring, E is the elastic constant and h denotes the thickness of the plate spring. A Poissons ratio of 0.3 was used. Titanium plate of 3 mm thickness was used as the pressing plate. When $P = 5$ kg/cm^2 to incorporate a larger safety factor into the equation, a value of $\omega_{max} = 2.92$ mm was obtained.

Using 3 mm titanium plate and allowing ω_{max} to be less than 0.1 mm and $P_{max} = 10$ kg/cm^2, the pitch of plate 2 a should be smaller than 72.4 mm. Since the electrode size was 20 cm square, at least 3 points were supported, i.e., a wave number of 3 was regarded as adequate. The thickness of the plate spring and the wave number that satisfied $\omega_{max} = 0.1$ mm were calculated. Calculation was performed by a finite element method using a MSC-NASTRAN software of USA, assuming the friction between a plate spring and a pressing plate is negligibly small. In these calculations, the value of the elastic constant of Titanium of 10850 kg/mm^2, and the wave shape of the sine curve were taken. Fig. 6 depicts the results obtained. Using 0.5 mm thick titanium plate springs, periodic bends can be expected by setting the wave crests at both sides of the pressing plate. It is anticipated that the maximum bend approaches a target value of 0.1 mm when a total of 6 positions are supported with the wave crests of the pressing plates. The contraction of the plate spring caused extension in both directions. In Fig. 7, Type 1 shows the calculation obtained by assuming the use of a 5 mm initial wave height of the plate spring and a 5 kg/cm^2 load, and Type 2 corresponds to $P = 10$ kg/cm^2 and a 10 mm initial wave height of the plate spring. By setting the wave crests at the end of the plate spring to 2 mm from the inner part of the pressing plate for type 1 and type 2, a maximum bending of 0.05 mm was achieved.

3.2. Lightweight battery case

For the development of low-cost battery case of light weight, aluminum was primarily tested. Plate I shows the

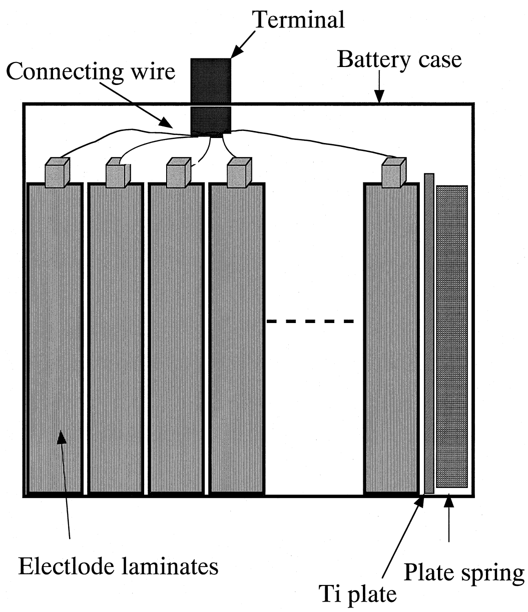

Fig. 5. Schematic illustration of the cross-section of 400 Ah class large-scale battery.

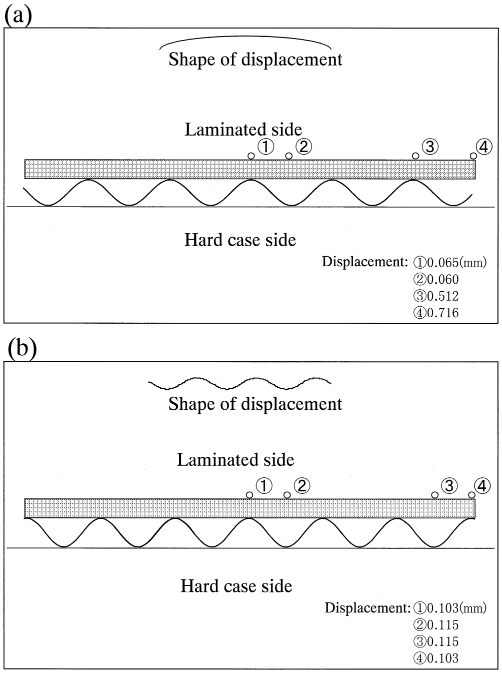

Fig. 6. Simulations of plate spring design (1).

external appearance of a trial hard case. An aluminum plate of 4 mm thickness was used to avoid any warp or displacement caused by the use of 20 cm^2 electrodes.

3.2.1. The thickness of Al plate

The thickness of the Al plate was calculated using the above equation [6]. In this calculation, an elastic constant of Al of 7000 kg/mm^2 was used. P_{max} was measured at

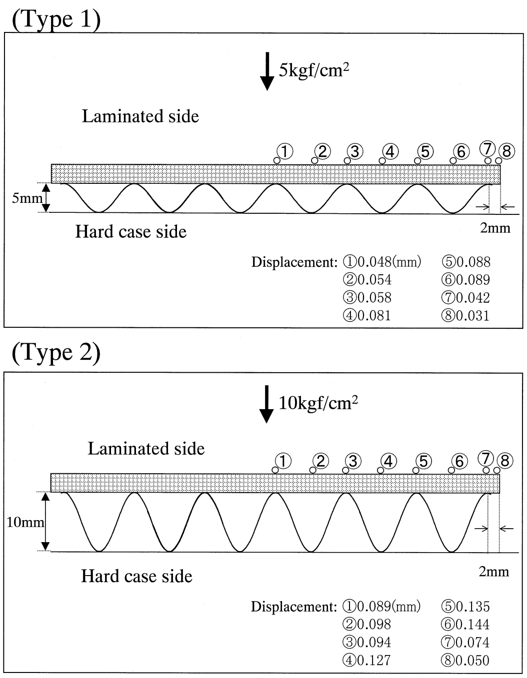

Fig. 7. Simulations of plate spring design (2).

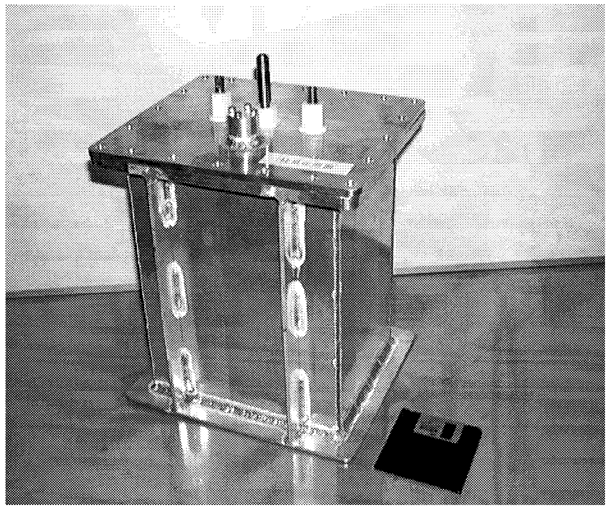

Plate I. Photograph of large scale battery.

1.6 kg/cm^2, and a value of $h = 3.4$ mm was obtained. However, P was calculated by assuming $h = 4$ mm, and a value of 2.6 kg/cm^2 was obtained. Therefore, the safety factor under these conditions was 1.63. To increase the safety factor, two ribs were attached on each side of the laminate. Accurate calculations of the improved strength after attaching the ribs was not carried out. However, this improved hard case must be sufficiently safe, since the increase in the vertical surface area from the loading direction is surrender to that experienced by H shaped steel.

An improved large-scale battery employing these parts was built, to carry out further examinations. The characteristics of the fabricated battery will be discussed in a separate report.

4. Conclusions

(1) Experimental work was done using a laminate type battery, in which $LiCoO_2$ was used as the cathode active material while natural graphite or MCMB was used for the anode, to measure the expansion and contraction characteristics of large-sized lithium ion batteries. When MCMB was employed, both displacement and load were less than those of natural graphite.

(2) Based on the findings obtained through the experiments on expansion and contraction, a plate spring and a lightweight battery case were designed.

(3) A maximum load of 5.0 kg/cm^2 was determined using natural graphite, while it was only 1.6 kg/cm^2 using MCMB. Use of MCMB allowed a reduction in the plate thickness used for the hard case. This result suggests the possibility of an increase in energy density of the battery. This factor is particularly important for a large-scale battery.

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