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High-capacity thick cathode with a porous aluminum current collector for lithium secondary batteries

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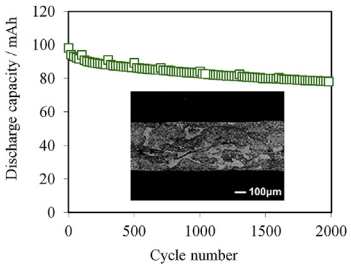
HIGHLIGHTS

- A thick $LiFePO_4$ cathode with a porous current collector has been developed.
- 8.4 m Ah cm^{-2} has been realized for the $LiFePO_4$ cathode with 400 μm thickness.
- Good rate capability (discharge capacity ratio of 1.0C/0.2C = 0.980) was obtained.
- 80% of the initial capacity was retained at 2000th cycle.

GRAPHICAL ABSTRACT



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ABSTRACT

A high-capacity thick cathode has been studied as one of ways to improve the energy density of lithium secondary batteries. In this study, the $LiFePO_4$ cathode with a capacity per unit area of 8.4 m Ah cm^{-2} corresponding to four times the capacity of conventional cathodes has been developed using a three-dimensional porous aluminum current collector called "FUSPOROUS". This unique current collector enables the smooth transfer of electrons and Li^+-ions through the thick cathode, resulting in a good rate capability (discharge capacity ratio of 1.0 C/0.2 C = 0.980) and a high charge-discharge cycle performance (80% of the initial capacity at 2000th cycle) even though the electrode thickness is 400 μm. To take practical advantage of the developed thick cathode, conceptual designs for a 10-Ah class cell were also carried out using graphite and lithium-metal anodes.

1. Introduction

Recently, the lithium secondary battery has a higher energy density compared to other secondary batteries. Therefore, the lithium secondary battery, especially the lithium ion battery, has been used for various applications, such as portable devices, electric vehicles (xEV), smart grids, and energy storage system (ESS). However, the electric power consumption of portable devices is increasing due to the multifunction applications of such devices. In addition, electric vehicles do not have an adequate cruising range. Therefore, a higher energy density lithium secondary battery has been strongly demanded.

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In order to improve the energy density of the lithium secondary battery, high capacity anode and cathode materials are necessary. Lithium metal and its alloys have been investigated as promising candidates for high-capacity electrodes [1–15]. On the other hand, candidates for a high-capacity cathode are currently limited [16–18]. In order to use a high-capacity anode, such as the lithium metal anode, the cathode capacity per unit area should be improved by using new materials or a thick electrode. Conventionally, an aluminum foil, which is electrochemically stable in a high potential environment, is used as the cathode current collector for lithium secondary batteries [19–23]. The thickness of the aluminum foil is generally from 10 to 30 μm. The cathode is prepared by coating a slurry containing the active material, conductive material, binder, and dispersing medium on the aluminum foil followed by drying and pressing processes. The thickness of the coated cathode is usually at most 150 μm. In order to increase the energy density of the lithium secondary battery, the combination of thick cathodes and thin high capacity anodes is a practical solution. The thicker cathode provides a higher capacity per unit area [24,25]. A schematic illustration of the thick electrode is shown in Fig. 1.

However, the thick cathode has many problems. Many cracks, dropouts, and exfoliations are caused by the volume change in the coated layer during charge and discharge. In addition, the ohmic resistance increases with the increasing thickness of the electrode due to the low electronic conductivity of the composite matrix.

FUSPOROUS®, which has been developed by UACJ Co., Ltd., is a porous aluminum. It has a three-dimensional open porous structure. When a cathode material mixture is filled into the pores of the FUSPOROUS®, the cathode material is tightly held in the three-dimensional current collector, resulting in an increase in the cathode material amount per unit area [26–29].

In this study, an improvement in the energy density has been investigated by increasing the amount of cathode material. This thick electrode may decrease the cost due to reducing the number of components in the cell. The possibility of a high-capacity thick cathode with a porous aluminum current collector for lithium secondary batteries is described.

2. Experimental

The amount of active material per unit area was controlled by changing the amount of the filled slurry and thickness of the porous aluminum current collector. The thickness was adjusted by the pressing process. The slurry consisted of carbon-coated lithium iron phosphate (LFP) powder as the cathode material, acetylene black, sodium carboxymethyl cellulose, and polymethylacrylate binder at the weight ratio of 100: 6.8: 2: 3. Sodium carboxymethyl cellulose was used as a dispersant and a binder. The viscosity of the slurry was adjusted by adding the proper amount of water. The prepared slurry was filled into the pores of the porous aluminum current collector under vacuum. The electrode was then dried and pressed to obtain the proper density. The electrode was next formed with a 20-mm diameter. An aluminum foil was welded to the current tab. On the other hand, the conventional composite electrode was prepared using the same slurry. The specifications of the prepared cathodes are summarized in Table 1.

Cross sections of porous aluminum current collector and prepared electrodes were observed by a scanning electron microscope (SEM) (JEOL JSM-5310LV). From the SEM images, their microstructures were confirmed, and the thicknesses of the electrodes were estimated.

The basic electrochemical properties of the thick cathodes with a porous aluminum current collector were evaluated by a half-cell test. In order to compare this thick electrode with a conventional cathode, a half-cell test was also conducted using the standard composite electrode. The cathode with a 20-mm diameter was used as the working electrode, lithium metal foil as the counter electrode and the reference electrode, and 1.3 mol dm^{-3} lithium hexafluorophosphate dissolved in a mixed solvent of ethylene carbonate, ethyl methyl carbonate, and dimethyl carbonate with the volume ratio of 2:5:3 as the electrolyte. Each electrochemical property was measured by a battery test system (Toyo system TOSCAT-3100). The working electrode was charged to 4.2 V vs. Li/Li^+ and then kept at 4.2 V vs. Li/Li^+ until the charging current decreased to less than 0.05 C, then discharged to 2.0 V vs. Li/Li^+ at various currents at 25 °C. A 0.1 C charge and a 0.1 C discharge were carried out for the first cycle. As the activation cycles, a 0.2 C charge-discharge cycle was then carried out for four cycles. The fifth and the sixth discharge tests were conducted at 0.2 C and 1.0 C with a 0.5 C charge, respectively, as an evaluation of the discharge rate performance. In addition, the 0.5 C charge - 0.5 C discharge cycle performance was also evaluated. Electrochemical impedance spectroscopy (EIS) of the cells with LFP1 and LFP3 was then measured by a Solartron SI 1280 at the 0% state of charge (SOC), 50% SOC, and 100%SOC, and the measuring potential was fixed at each SOC. The scanning range was from 20 kHz to 0.01 Hz.

In order to evaluate the battery performance with these cathodes, full cells were constructed using these cathodes and graphite anodes. The specifications of the test cells are shown in Table 2. A cell with the thick cathode (LFP2) could not be assembled due to peeling off of the coated layer. The evaluation of the test cells was carried out using the conventional thin cathode (LFP1) and the thick cathode with porous aluminum as the current collector.

The slurry of the anode material mixture was coated on a copper foil with a 10-μm thickness. The anode slurry was prepared by the mixing of graphite as the anode material, sodium carboxymethyl cellulose and polystyrene-butadiene as the binder in the ratio of 98:1:1 and adding water for viscosity adjustment. They were then

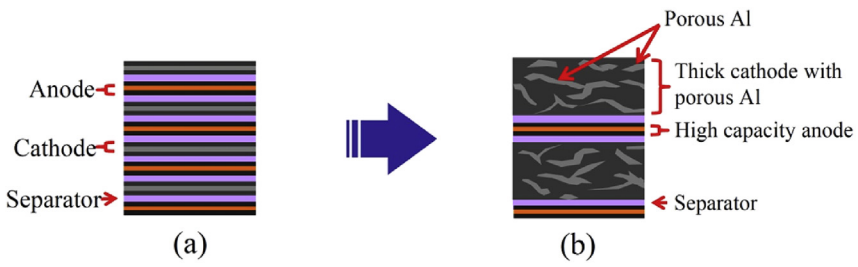

Fig. 1. Schematic structure of two kinds of lithium secondary batteries, (a) Conventional battery which consists of thin cathodes and thin anodes, (b) High energy density battery which consists of thick cathodes and thin anodes with high capacity.