

Research for Lithium-Ion Battery with Li-ion Pre-Doped Negative Electrode

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Abstract: The lithium-ion battery has excellent performance and characteristics as compared with other secondary batteries. Small lithium-ion batteries are used in portable devices, mobile devices, digital cameras, etc., while large lithium-ion batteries are used in commercial devices, plug-in hybrids, electric vehicles, etc., and recently MaaS (Mobility as a Service) is expected to be applied. In addition, a large-capacity secondary battery such as a lithium-ion battery is also desired in a coordinated operation (Battery Energy Storage System) with an electric power system. With much demand for batteries expected in the future, development to increase the battery capacity of lithium-ion batteries is being promoted.

Key words: lithium-ion battery, lithium metal powder, li-ion pre-doping, intercalation, negative electrode slurry

1. Introduction

It is essential that the positive and negative electrodes that make up the lithium-ion battery have an intercalation reaction through the electrolyte. As the electrolytic solution, an organic electrolytic solution such as ethylene carbonate (EC) in which about 1 mol of a lithium salt such as LiPF₆ is dissolved is used. Actually, an electrolytic solution in which a highly dissociative LiPF₆ salt is dissolved in a mixed solution of ethylene carbonate having a high dielectric constant and dialkyl carbonate having a low clay is used. Since the material composition of the positive electrode material and the negative electrode material is a layered structure, these electrode materials have a function of inserting and extracting lithium ions. In particular, during charging, lithium ions are released from the positive electrode into the

electrolytic solution and occluded (doped) in the negative electrode. By efficiently doping the negative electrode with lithium ions, it is possible to expect an increase in battery capacity and terminal voltage as a battery cell. The purpose of this research is to obtain some knowledge that pre-doping lithium ions to the negative electrode of a lithium-ion battery leads to an increase in battery capacity.

2. Charge and Discharge Reactions at Positive and Negative Electrodes of Lithium-Ion Battery

Fig. 1 shows a schematic diagram of a lithium-ion battery. Both ends of the battery are composed of a positive electrode and a negative electrode. Each of the electrodes is immersed in an organic electrolytic solution, so that positive and negative electrodes are responsible for the exchange of lithium ions between the electrodes. Lithium ion (Li⁺) becomes a positively charged cation when the lithium atom (Li) emits an electron (e⁻), and becomes an important charged carrier that controls the function of the battery. During charging, lithium ions move in the electrolytic solution

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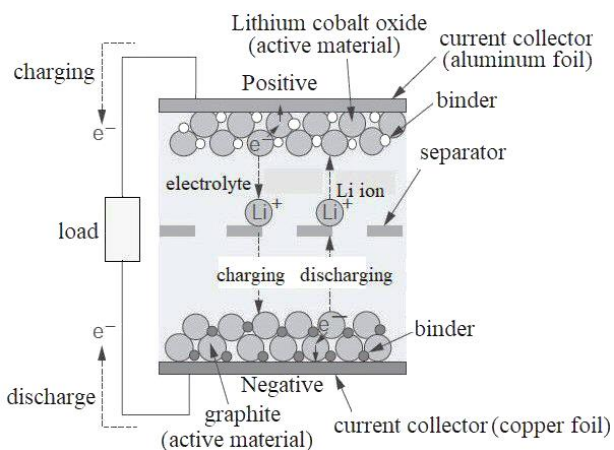


Fig. 1 Schematic diagram of lithium-ion battery

from the positive electrode to the negative electrode, and during discharging, they move from the negative electrode to the positive electrode. Electrons are exchanged between the electrodes with the movement of lithium ions, and a current flows between the electrodes through an external circuit. That is, during charging, lithium ions flow in the electrolytic solution from the positive electrode to the negative electrode, and at the same time, electrons flow from the positive electrode to the negative electrode through the power source of the external circuit. The amount of electrons flowing can be controlled by changing the magnitude of the power (voltage \times current) of the power supply. On the other hand, during discharge, lithium ions flow from the negative electrode to the positive electrode, and at the same time, electrons flow from the negative electrode to the positive electrode through the electrical load (resistance, etc.) of the external circuit.

As a standard configuration example, when lithium cobalt oxide is used for the positive electrode material and carbon is used for the negative electrode material, the reaction equations during charge and discharge are expressed as follows. A reaction in which a lithium atom (Li) loses an electron (e^-) and becomes a lithium ion (Li^+) is called an oxidation reaction, and conversely, a reaction in which a lithium ion obtains an electron and returns to lithium is called a reduction reaction.

For charging: (Li ions are released)
 Positive electrode reaction: $Li \rightarrow Li^+ + e^-$
 Negative electrode reaction: $Li^+ + 6C + e^- \rightarrow LiC_6$
 (Li ions are occluded)
 Overall reaction: $Li + 6C \rightarrow LiC_6$

Extracted lithium ions from lithium cobalt oxide pass through the electrolytic solution and enter the carbon to be occluded. This process is the lithium ion doping itself. By doping with more lithium ions, the intercalation reaction at the positive and negative electrodes is promoted. The positive electrode obtains the electrons that have passed through the external circuit and lithium cobalt oxide is produced.

For discharging:
 Positive electrode reaction: $Li^+ + e^- \rightarrow Li$
 Negative electrode reaction: $LiC_6 \rightarrow Li^+ + 6C + e^-$
 Overall reaction: $LiC_6 \rightarrow Li + 6C$

Lithium ions are extracted from carbon, which is an inert substance, and released into the electrolytic solution. Lithium ions pass through the electrolytic solution and enter the layered structure of cobalt oxide (CoO_2), which is the positive electrode active material. At the positive electrode, cobalt oxide is combined with electrons that have passed through an external circuit, so that lithium cobalt oxide ($LiCoO_2$) is produced.

3. Trial Manufacture of Lithium Ion Battery by Li-Ion Pre-doping

A lithium-ion battery using lithium cobalt oxide as a positive electrode material and carbon as a negative electrode material is manufactured by pre-doping lithium ion into the negative electrode material. Specifically, a negative electrode sheet containing lithium metal powder is manufactured in the process of manufacturing a slurry using the negative electrode active material. The lithium ion battery manufactured in this manner is called a lithium pre-doped lithium ion battery (abbreviated as Lithium pre-doped LIB). The structure of the positive and negative electrode sheets is shown in Fig. 2. The size of the positive electrode is

400 mm long \times 78 mm wide, and the size of the negative electrode is 290 mm long \times 78 mm wide. The tabbed lead frame is spot-welded to each current collector. Table 1 shows the mixing ratio of the active material in the positive and negative electrode slurries. The mixing ratio of Li metal powder in the negative electrode slurry was determined to be 0.05 g and 0.1 g [2].

The positive and negative electrode sheets are manufactured by the slurry manufacturing method that has been implemented in our laboratory. The lithium metal powder used in the prototype was approximately 10 $\mu\text{m}\phi$ in size and had a purity of 99.5% (Fig. 3). Regarding the timing of mixing the lithium metal powder, one mixing time of the mixer is 15 minutes, so after mixing 20 times continuously, the mixing container is put in the argon gas atmosphere of the vacuum glove box. After the lithium metal powder is

Table 1 Mixing ratio of positive and negative electrode active materials.

(a) Positive electrode active material

Component	Weight (g)
LiCoO ₂	31
Conductive carbon	1
PVDF (Binder)	0.75
NMP (Electrode liquid)	10

(b) Negative electrode active material

Component	Weight (g)
Graphite	22.5
Conductive carbon	0.5
PVDF (Binder)	2
NMP (Electrode liquid)	26.57
Li metal powder	0.05 or 0.1

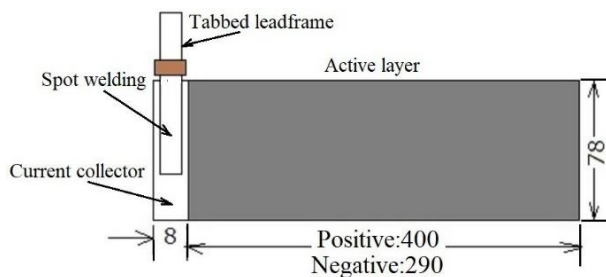
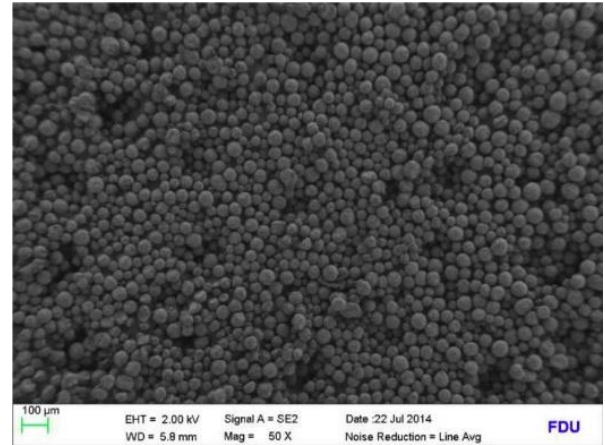


Fig. 2 Composition of positive and negative electrode sheets.



(a) Lithium metal powder container with argon gas purge



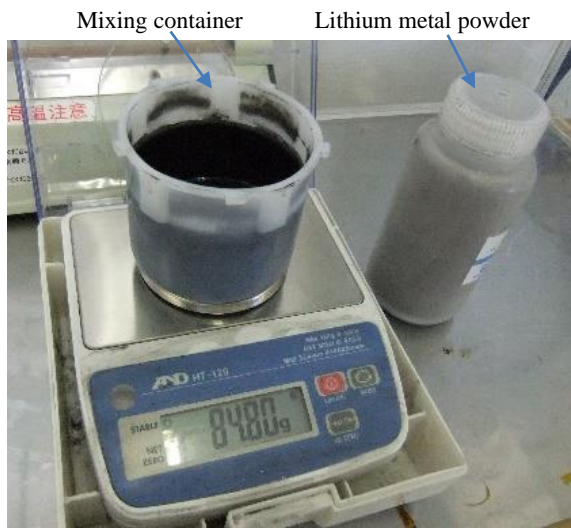
(b) SEM photo image

Fig. 3 Composition of positive and negative electrode sheets.

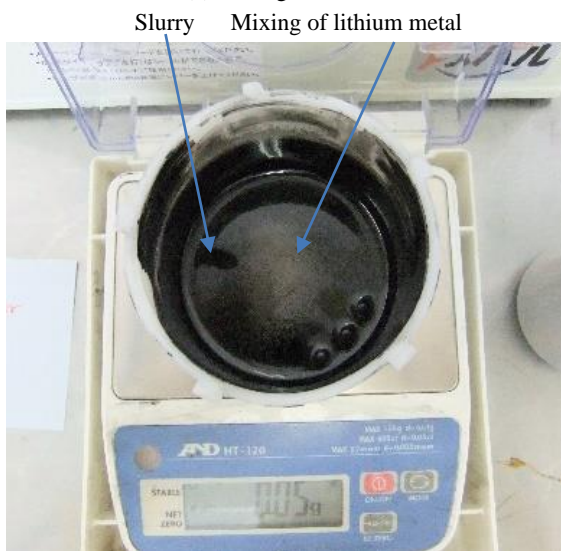
weighed in the vacuum glove box and mixed with the slurry in the mixing container, the slurry is sufficiently mixed using a stirring stick. Finally, after the mixing container was taken out from the vacuum glove box, the slurry was mixed only once with the mixer to complete the negative electrode slurry (Fig. 4). The prepared negative electrode slurry is coated on both sides of a copper foil as a current collector and baked (100°C, 4 hours) to complete a negative electrode sheet.

The total thickness of the fabricated positive and negative electrode sheets was measured (Table 2). An almost uniform active layer thickness was obtained. Finally, the lead frame with tabs is spot-welded to the positive and negative electrode sheets, and then the electrode body is manufactured by the winding method. Next, the electrode body was set with a pouch type aluminum laminate cell, the laminate cell was folded and the electrode body was sealed, and then the electrolyte (22 mL) was injected into the laminate cell

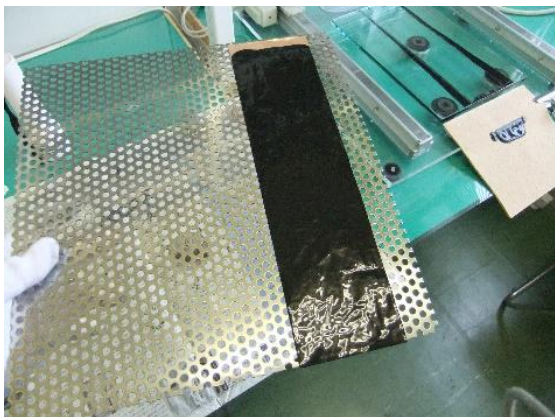
in the vacuum glove box to form a battery cell. Finally, the battery cell is finished (Fig. 5).



(a) Mixing container



(b) Lithium metal powder

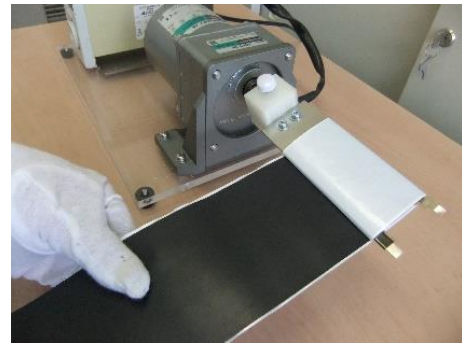


(c) Slurry coating

Fig. 4 Mixing lithium metal powder into negative electrode slurry.



(a) Positive and negative electrode sheet



(b) Winding process



(c) Electrode body on to pouch cell



(d) Electrolyte injection by graduated cylinder



(e) Completed battery cell

Fig. 5 Battery cell assembly flow.

Table 2 Total thickness of positive and negative electrode sheets.

(a) Positive electrode double coated sheet

		Unit: μm			
Positive	Al foil		16		average
Total thickness	A	132	131	136	133
	B	138	138	134	137

(b) Negative electrode double coated sheet

		Unit: μm			
Negative	Cu foil		9		average
Total thickness	C	179	173	175	176
	D	181	176	170	176

4. Charge and Discharge Evaluation of Prototype Battery Cell

Lithium metal powder was mixed into the negative electrode slurry to pre-dope the negative electrode with lithium ions. Charge and discharge evaluations were compared between this prototype battery cell (lithium pre-doped LIB) and an undoped battery (blank LIB) manufactured under the same conditions. Initial charging was performed by the CCCV method with the setting of voltage 4.2 V and charging current 300mA. The discharge evaluation was performed with the current set to 300 mA and 400 mA and the discharge

end voltage set to 2.8 V. Fig. 6 shows the test results of the discharge characteristics when the discharge current was 300 mA. Comparing the battery capacities of both, the estimated value of Lithium pre-doped LIB is obtained for $3 \text{ h} \times 300 \text{ mA} = 900 \text{ mAh}$ when the average time to discharge is 180 minutes, and in the case of blank LIB, the value of $2.5 \text{ h} \times 300 \text{ mA} = 750 \text{ mAh}$ is estimated. Under the conditions of this experiment, it was confirmed that the battery capacity was increased by about 1.2 times by pre-doping the negative electrode with lithium ions. The terminal voltage of Lithium pre-doped LIB seems to be higher than that of blank LIB. About this experimental tendency, further experimental validation will be required. Similar comparison results are obtained when the discharge current is 400 mA. Regarding the initial charging characteristics, no significant difference was observed between the lithium pre-doped LIB and the blank LIB in both the charging voltage and the charging current with time.

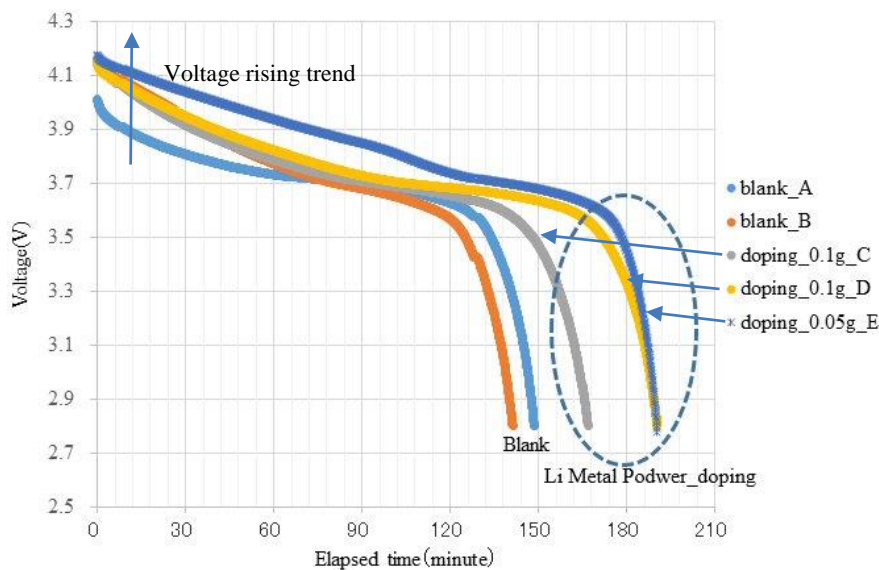


Fig. 6 Comparative evaluation of discharge capacity.

5. Conclusion

About the reason for increase the battery capacity by pre-doping lithium metal powder by mixing the negative electrode flurry, in addition to the transfer of

lithium ions from the original positive electrode into the electrolyte solution and occlusion in the negative electrode during the charging process, it is speculated that it is due to the effect of pre-doping in which the

lithium ions are forcibly occluded in the negative electrode.

In the trial production of this study, the amount of the lithium metal powder mixed was set to 0.05 g and 0.1 g based on our trial experience of pre-doping of the lithium ion capacitor. However, no difference was found between the amounts of 0.05 g and 0.1 g. This is because when the mixed amount was 0.1 g or more, abnormalities such as viscosity and heat generation of the slurry were observed when the slurry was mixed. Lithium metal reacts with moisture in the air and instantly deteriorates, so it is essential to handle and assemble lithium metal powder in a vacuum glove box. For this reason, proficiency is required to prepare the slurry and to manufacture the cell.

However, reproducibility was confirmed in the battery capacity evaluation results, and it was confirmed that pre-doping of lithium ions in the negative electrode leads to an increase in battery capacity. Therefore, we were able to obtain one valuable finding for future research progress.

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