

Application of porous polymer to composite electrodes with inorganic solid electrolytes

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Abstract

The electrochemical performances of composite positive electrodes including polymer materials have been investigated in lithium secondary cells with inorganic solid electrolytes. The polymer added to the electrode generally tends to enlarge the electrode impedance because of its insulating nature. Comparison of charge and discharge characteristics between some composite electrodes in this study revealed that the texture of polymer-coated on the surface of the active materials had a dominant influence on their electrochemical performance. It was found that porous polymer would be promising for the composite electrodes with high performance.

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1. Introduction

A rapid growth of an information technology society has brought a magnificent improvement on the performances of various electronic devices. High-performance secondary cells have been playing an important role since they have been used as the power sources especially for smaller and lighter portable electronic devices including cellular phones. As lithium-ion cells have the highest energy density when compared with other secondary cells, their market and output have been increasing dramatically. However, there also exists a strong demand for improvement of their safety performance because they use flammable organic liquid electrolytes. Thus lithium-ion cells using nonflammable inorganic solid electrolytes have attracted considerable attention as an alternative.

The ionic conductivity of inorganic solid electrolytes has been significantly improved, for example, those of $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ [1] and thio-LISICON $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ [2] were of the order of 10^{-3} S/cm. As the inorganic solid electrolytes have generally been obtained as powder materials, they have low molding ability leading

to difficulty in processing and establishing sheet-like cell components. It brought a concept of the composite solid electrolytes with polymer materials that would work as a binder [3]. This concept was also applied to produce composite electrodes though their electrochemical performances were too low for the practical use [4].

In this study, a polymer material was coated on the surface of a positive active material in order to discuss and improve the electrochemical performance of composite electrodes. $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ and poly-vinylidene fluoride (PVdF) were used as a positive active material and a polymer material, respectively. The effect of textural feature of the added polymer on the electrode performances is discussed.

2. Experimental

2.1. Synthesis of solid electrolytes

Solid electrolyte ($\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$) was prepared according to the procedure reported [2]. Li_2S , GeS_2 , and P_2S_5 were mixed with a mortar and a pestle with a weight ratio of 39:18:43 in an argon-filled glove box. The mixture was sealed in an evacuated quartz tube, inside of which was coated with pyrolytic carbon, and heated at 700°C for 8 h followed by cooling slowly to room temperature.

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The synthesized $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ was subjected to the following tests after grinding.

2.2. Preparation of positive active materials coated with polymer materials

A PVdF solution with a concentration of 1 wt.% was prepared by dissolving PVdF in *N*-methyl-2-pyrrolidone (NMP). $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ used as a positive active material was immersed in the PVdF solution. After drying, $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ coated with non-porous PVdF was thus prepared. Also, the $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ after immersion in the PVdF solution was introduced to an extraction process to make the PVdF coating porous [5]. After drying, $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ coated with porous PVdF was obtained. Thus two kinds of the active materials, i.e. $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ coated with porous PVdF and a non-porous one, were obtained.

Furthermore, in order to evaluate the effect of the amount of coating porous polymer, PVdF solutions with different concentrations were prepared and used in the immersion and the following extraction processes. Various $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ coated with different amounts of porous PVdF were thus prepared in the same manner.

2.3. Preparation of composite positive electrodes and measurement of their electrochemical performance with polymer-coated active materials

Positive active materials of $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ coated with PVdF, porous or non-porous, solid electrolytes of $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ and electrical conductive materials of acetylene black were mixed with a weight ratio of 60:40:1 with a mortar and a pestle to produce a positive electrode mixture. A solid electrolyte layer made of 180 mg of $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$, 200 mg of this positive mixture and 450 mg of a metallic indium sheet as a negative electrode were pressed to be a three-layer pellet with 16 mm in a diameter. This pellet was sealed in a coin-type case made of stainless steel to produce a test cell. The negative electrode had larger capacity in charge than the positive electrode in the test cells.

Also a positive mixture was prepared using $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ without PVdF coating. The same weight ratio for the positive mixture was used here since the amount of PVdF coated was negligible. A reference cell was then manufactured with the positive mixture in the same manner described above.

Each test cell was charged to 3.5 V, or with the amount of charge of 17 mAh where the number of Li^+ ions de-intercalated from $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ was 0.65, and discharged to 2.5 V at a current density of $95 \mu\text{A}/\text{cm}^2$ at 25°C . This charge and discharge was repeated ten times to evaluate the cycle performance of the cells. Also, the impedance of the cells was measured after the 3rd discharge at 25°C by ac impedance method with an electrochemical interface (Solartron 1286) connected to a frequency response analyzer (Solartron 1260) applying 10 mV (ac) in a frequency range from 10^6 to 10^{-2} Hz.

3. Results and discussion

The first charge and discharge characteristics of the test cells with various composite positive electrodes are shown in Fig. 1(a) and (b), respectively. The cell with $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ coated with non-porous PVdF showed larger polarization on charge than that of the reference cell, leading to a smaller amount of charge passed, while that with porous polymer showed a comparable polarization to the reference cell. Also, the cell with non-porous polymer showed much smaller discharge capacity than the other two.

Fig. 2 shows the change in the discharge capacity of the test cells. The discharge capacity of the cell with the material coated with porous PVdF had been kept almost constant during 10 cycles. This result showed that the effect of porous PVdF coating had been maintained on cycling. The discharge capacities at the first cycle were small for the cells with the materials coated with porous polymer and non-coated one because they were not fully charged by terminating with the a charge of 17 mAh. After the second cycle, they were fully charged to be terminated at 3.5 V.

Fig. 3 shows the impedance plots of the test cells at discharged state after three cycles. The cell with $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ coated with non-porous PVdF exhibited higher impedance than that with porous one as well as that of the reference cell.

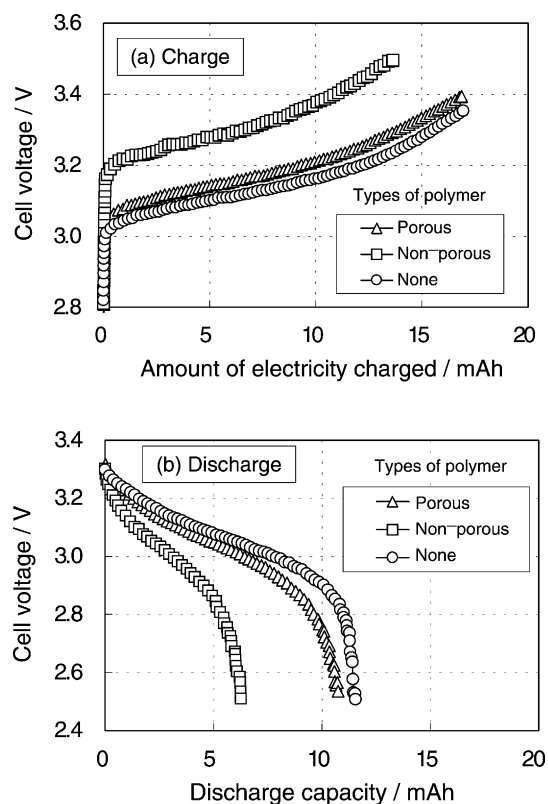


Fig. 1. Effect of porous polymer-coated on positive active materials on initial charge (a) and discharge (b) characteristics of $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2/\text{In}$ cells at $95 \mu\text{A}/\text{cm}^2$ at 25°C .

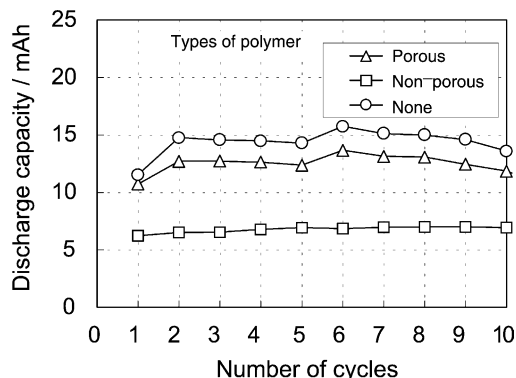


Fig. 2. Change in the discharge capacity of $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2/\text{In}$ cells with polymer-coated positive active materials. Charge and discharge were carried out between 3.5 and 2.5 V at $95 \mu\text{A}/\text{cm}^2$ at 25°C .

These results suggested that the non-porous PVdF coated on $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ would prohibit the transfer of Li^+ ions and lead to lower electrochemical performance. When the PVdF coating was porous, the contact between $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ and the solid electrolytes could be maintained through the pores to allow higher transfer of Li^+ ions.

Table 1 represents a relationship between the concentrations of PVdF solutions and the amount of PVdF coated on $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$. The amount of PVdF coated was increased with an increase in the concentrations of PVdF solutions. These values were almost the same for both porous and non-porous PVdF.

The first charge and discharge characteristics of cells with $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ coated with various amounts of PVdF are shown in Fig. 4(a) and (b), respectively. An increase in the concentration of PVdF solutions, that is the amount of PVdF coated, increased the polarization on charge and decreased the amount of charge passed and the discharge capacity. However, it was remarkable that the cell with $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ coated with porous PVdF showed better performance than that with non-porous PVdF even though the

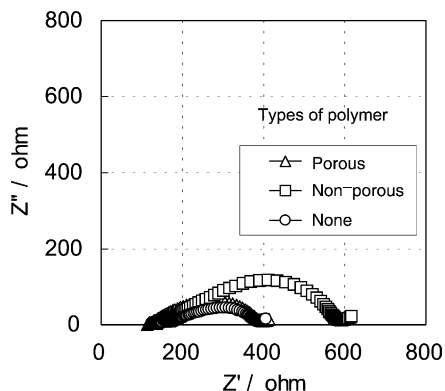


Fig. 3. Impedance plot of $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2/\text{In}$ cells with polymer-coated positive active materials. Impedance was measured after three cycles. Charge and discharge were carried out between 3.5 and 2.5 V at $95 \mu\text{A}/\text{cm}^2$ at 25°C .

Table 1

Comparison of the concentrations of PVdF solutions and the amount of PVdF coated on $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$

Concentration of PVdF solutions (wt.%)	Amount of PVdF coated (wt.%)
1	0.22
3	0.74
5	1.49

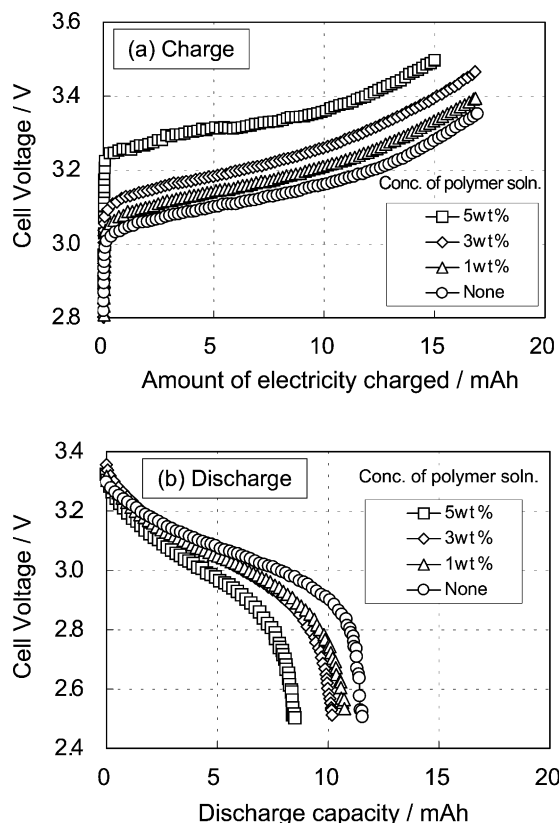


Fig. 4. Effect of amount of porous polymer-coated on the positive active materials on initial charge (a) and discharge (b) characteristics of $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2/\text{In}$ cells at $95 \mu\text{A}/\text{cm}^2$ at 25°C .

amount of the former was larger than the latter. Consequently, porous polymer would give higher molding ability for the composite electrodes because larger amount of polymer would be effectively added without lowering the electrode performance.

As a conclusion, the porous PVdF coated on $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ has been effective for composite electrodes since it would allow higher transfer of Li^+ ions and lead to higher molding ability.

4. Conclusions

In order to improve the electrochemical performance of the composite electrodes with polymer materials for lithium secondary cells with inorganic solid electrolytes, a porous

polymer has been proposed. When the PVdF coated on $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ was non-porous, the composite electrodes showed lower electrochemical performance and an increase in impedance. On the other hand, when it was porous, the composite electrodes showed comparable performance to that without PVdF coating. It was found that porous PVdF was effective to allow higher transfer of Li^+ ions through the pores since the electrode performance was not so much deteriorated in spite of the addition of insulating polymer.

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