



Short communication

Electrochemical performance of all-solid-state lithium secondary batteries improved by the coating of $\text{Li}_2\text{O}-\text{TiO}_2$ films on LiCoO_2 electrode

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ARTICLE INFO

Article history:

Received 16 May 2009

Received in revised form 16 July 2009

Accepted 18 July 2009

Available online 28 July 2009

Keywords:

All-solid-state battery

Lithium battery

Solid electrolyte

Surface coating

ABSTRACT

All-solid-state lithium secondary batteries using LiCoO_2 particles coated with amorphous $\text{Li}_2\text{O}-\text{TiO}_2$ films as an active material and $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass-ceramics as a solid electrolyte were fabricated; the electrochemical performance of the batteries was investigated. The interfacial resistance between LiCoO_2 and solid electrolyte was decreased by the coating of $\text{Li}_2\text{O}-\text{TiO}_2$ films on LiCoO_2 particles. The rate capability of the batteries using the LiCoO_2 coated with $\text{Li}_2\text{Ti}_2\text{O}_5$ ($\text{Li}_2\text{O}\cdot 2\text{TiO}_2$) film was improved because of the decrease of the interfacial resistance of the batteries. The cycle performance of the all-solid-state batteries under a high cutoff voltage of 4.6 V vs. Li was highly improved by using LiCoO_2 coated with $\text{Li}_2\text{Ti}_2\text{O}_5$ film. The oxide coatings are effective in suppressing the resistance increase between LiCoO_2 and the solid electrolyte during cycling. The battery with the LiCoO_2 coated with $\text{Li}_2\text{Ti}_2\text{O}_5$ film showed a large initial discharge capacity of 130 mAh/g and good capacity retention without resistance increase after 50 cycles at the current density of 0.13 mA/cm².

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1. Introduction

All-solid-state lithium secondary batteries have been researched and developed as highly safe secondary batteries. In particular, all-solid-state batteries using inorganic solid electrolytes without flammable components are desirable batteries which can resolve the safety issues. In addition, all-solid-state batteries usually exhibit long cycle performance. Thin film batteries have been reported to show excellent long-cycling performances (over 50,000 times) at room temperature [1–3]. For bulk-type all-solid-state batteries, which have large energy density because of the use of composite electrodes with a powder mixture of active material and electrolyte, we reported that the batteries In/LiCoO_2 using $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass-ceramic solid electrolytes were reversibly charged and discharged for more than 500 cycles [4].

Although all-solid-state batteries using inorganic solid electrolytes show good cycle performance, there are some issues to be resolved for practical application of all-solid-state batteries. For example, the operation under a high current density of more than several mA/cm² is difficult for all-solid-state lithium secondary batteries. In order to apply to a large scale power source for hybrid electric vehicles and electric vehicles, a high power operation of the batteries is required. The increase of energy density and the further improvement of cycle performance are also desired.

In order to improve a rate capability of all-solid-state batteries, a decrease of total resistances of all-solid-state batteries is very important because all-solid-state batteries are affected by large current–resistance drop in the operation at a high current density. Highly conductive lithium-ion solid electrolytes have been developed to decrease the resistance of solid electrolyte layer of all-solid-state batteries; high lithium-ion conductivities of more than 10^{-3} S/cm at room temperature have been achieved in sulfide solid electrolytes [5–9]. Among them, $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass-ceramics are most promising solid electrolytes because of their wide electrochemical window. The design of composite electrodes of active materials and solid electrolytes is also important. The use of suitable conductive additives and the optimization of the composite ratio of active materials and solid electrolytes have been carried out; the charge and discharge under a high current density more than 1 mA/cm² were achieved in the bulk-type all-solid-state cells [10,11]. Moreover, there is a large interfacial resistance between LiCoO_2 and the sulfide solid electrolyte; the improvement of the interface is required. Modification of interface between LiCoO_2 electrode and the sulfide electrolyte by the coatings of oxide thin films has been reported to decrease the interfacial resistance. Ohta et al. first reported that the coatings of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiNbO_3 , and LiTaO_3 on LiCoO_2 particles by spray coating brought about excellent rate capability in the all-solid-state batteries using crystalline $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (thio-LISICON) as a solid electrolyte [12–14]. We also reported that the coatings of Li_2SiO_3 and SiO_2 by a simple sol–gel technique were effective in a decrease of the interfacial resistance of all-solid-state batteries using $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass-ceramic

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solid electrolytes; as a result, the electrochemical performance was improved [15–17]. The results of the study for the Li_2O – SiO_2 coatings on LiCoO_2 particles indicated that the lithium-ion conductivity of coating materials is important for good electrochemical performance. The electrochemical performance of the batteries is affected by the type of coating materials which influences the properties such as lithium-ion and electron conductivities. However, the coatings except amorphous Li_2O – SiO_2 films have not been studied in the all-solid-state batteries using Li_2S – P_2S_5 solid electrolytes. The influence of metal-ions in metal oxide coatings has not been clarified yet.

In this study, amorphous Li_2O – TiO_2 films were used as coating materials by changing metal oxide from silicate to titanate which is a common transition metal oxide. This substitution was performed in order to examine what kinds of materials are suitable in all-solid-state batteries using Li_2S – P_2S_5 glass-ceramic solid electrolytes. The Li_2O – TiO_2 films at two different compositions of 33 mol.% Li_2O ($\text{Li}_2\text{Ti}_2\text{O}_5$) and 0 mol.% Li_2O (TiO_2) were used as coating materials in order to study the influence of lithium-ion conductivity in the coating films. Moreover, the electrochemical performances such as rate capability and cyclability of the all-solid-state cells using Li_2S – P_2S_5 solid electrolytes and LiCoO_2 coated with titanate films were compared with those of the cells using LiCoO_2 coated with silicate films.

2. Experimental

Amorphous films of Li_2O – TiO_2 with the Li_2O contents of 33 mol.% ($\text{Li}_2\text{Ti}_2\text{O}_5$) and 0 mol.% (TiO_2) were selected as coating materials. The coating layers of $\text{Li}_2\text{Ti}_2\text{O}_5$ and TiO_2 on LiCoO_2 particles were formed using the sol–gel method. The $\text{Li}_2\text{Ti}_2\text{O}_5$ sols were prepared from ethanol (10 mL, 99.5%; Wako), lithium ethoxide (LiOEt , 1 mmol, 1 M solution in ethanol; Aldrich), titanium tetra-*iso*-propoxide [$\text{Ti}(\text{O}-i\text{-Pr})_4$, 1 mmol, 95%; Wako], and acetyl acetone (1 mmol, 99%, Wako). The TiO_2 sols were also prepared from ethanol (10 mL), $\text{Ti}(\text{O}-i\text{-Pr})_4$ (1 mmol), and acetyl acetone (1 mmol). The sols of $\text{Li}_2\text{Ti}_2\text{O}_5$ and TiO_2 were mixed with LiCoO_2 particles (Toda Kogyo; Brunauer–Emmett–Teller BET surface area of $0.12 \text{ m}^2/\text{g}$). After drying at room temperature, the mixture was heated at 350°C for 30 min. The weight ratio of the coating materials $\text{Li}_2\text{Ti}_2\text{O}_5$ and TiO_2 to the LiCoO_2 particles was 0.1/100. Average thickness of coating materials was *ca.* 2 nm, which was estimated from the BET surface area of LiCoO_2 , the weight ratio of the coating materials to LiCoO_2 , and the density of the coating materials.

The $80\text{Li}_2\text{S}$ – $20\text{P}_2\text{S}_5$ (mol.%) glass-ceramic for solid electrolytes was prepared using mechanical milling and subsequent heat treatment. For the preparation of the $80\text{Li}_2\text{S}$ – $20\text{P}_2\text{S}_5$ glass, Li_2S (99.9%; Idemitsu Kosan) and P_2S_5 (99%; Aldrich) were used as starting materials. These materials were mechanically milled at a rotating speed of 510 rpm for 10 h at room temperature using a planetary ball mill apparatus (Pulverisette 7; Fritsch) with a zirconia pot (volume of 45 mL) and 160 zirconia balls (5 mm in diameter). The obtained glassy powder was heated at 210°C for 2 h to yield the highly conducting $80\text{Li}_2\text{S}$ – $20\text{P}_2\text{S}_5$ glass-ceramic. Solid-state cells were constructed as follows: the LiCoO_2 and the glass-ceramic electrolyte powders with a weight ratio of 70:30 were mixed using an agate mortar to prepare composite positive electrodes. An indium foil with a thickness of 0.1 mm (99.999%; Furuuchi Chemical Corp.) was used as a negative electrode. A bilayer pellet consisting of the composite positive electrode (10 mg) and glass-ceramic solid electrolytes (80 mg) was obtained by pressing under 360 MPa ($\phi = 10 \text{ mm}$); then indium foil was attached to the bilayer pellet by pressing under 240 MPa. All processes were performed in a dry Ar-filled glove box.

Electrochemical impedance spectroscopy measurements of the cells $\text{In}/80\text{Li}_2\text{S}$ – $20\text{P}_2\text{S}_5$ glass-ceramic/ LiCoO_2 were performed using an impedance analyzer (SI 1260; Solartron) after charging them to 3.58 V at $0.13 \text{ mA}/\text{cm}^2$. The applied voltage was 50 mV and the frequency range was from 10 mHz to 1 MHz. The cells were charged and discharged using a charge–discharge measuring device (BTS-2004; Nagano). Charge–discharge performance of the cells was evaluated at room temperature in an Ar atmosphere. Morphologies of LiCoO_2 particles were observed using a field emission scanning electron microscope (FE-SEM/S4500; Hitachi).

3. Results and discussion

The surface morphology of the coated LiCoO_2 particles was investigated using FE-SEM observation. Fig. 1 shows FE-SEM images of the surface of the LiCoO_2 particles coated with 0.1 wt.% of TiO_2 and $\text{Li}_2\text{Ti}_2\text{O}_5$. The surface of non-coated LiCoO_2 is also shown for comparison. The surface of the LiCoO_2 particles with or without oxide coatings is relatively smooth. The weight ratio of the coating materials to the LiCoO_2 particles was 0.1/100. Estimated average thickness of coating materials was *ca.* 2 nm. Since the coating thickness is very small, the coating layer would not be confirmed in FE-SEM observation.

The all-solid-state cells $\text{In}/80\text{Li}_2\text{S}$ – $20\text{P}_2\text{S}_5$ glass-ceramic solid electrolyte/ LiCoO_2 were constructed and their electrochemical performance was investigated. Fig. 2 shows the impedance profiles of the all-solid-state cells with non-coated, TiO_2 -coated, and $\text{Li}_2\text{Ti}_2\text{O}_5$ -coated LiCoO_2 after charging to 3.6 V vs. Li–In electrode, which corresponds to 4.2 V vs. Li electrode, at the current density of $0.13 \text{ mA}/\text{cm}^2$. Two semicircles are observed and their peak top frequencies are about 1 kHz and 1 Hz in each impedance profile. The identification of the impedance components is as follows: the resistance observed at the high-frequency region ($>100 \text{ kHz}$) corresponds to the resistance of the solid electrolyte layer; the semicircles observed in the medium-frequency (about 1 kHz) and the low frequency region (about 1 Hz) are due to the resistances in the positive electrode layer (interfacial resistance between LiCoO_2 and solid electrolyte) and negative electrode layer, respectively [16]. The resistance of the solid electrolyte layer and that of the negative electrode layer of the three cells are about 150 and 50 Ω , respectively. Similar values of the resistances are observed in the three cells. The interfacial resistances in the positive electrode layer of the cells with non-coated, TiO_2 -coated, and $\text{Li}_2\text{Ti}_2\text{O}_5$ -coated LiCoO_2 are 270, 200, and 140 Ω , respectively. The interfacial resistances are decreased by the oxide coatings. The interfacial resistance of the cell with $\text{Li}_2\text{Ti}_2\text{O}_5$ -coated LiCoO_2 is lower than that with TiO_2 -coated LiCoO_2 . The lithium containing oxide is more effective in decreasing the interfacial resistance. This result corresponds to the previous results using the cells with the LiCoO_2 coated with Li_2O – SiO_2 glassy films [15–17]. The interfacial resistances of the cell with TiO_2 -coated LiCoO_2 and $\text{Li}_2\text{Ti}_2\text{O}_5$ -coated LiCoO_2 are respectively as small as those with SiO_2 -coated LiCoO_2 and Li_2SiO_3 -coated LiCoO_2 , indicating that the presence of transition metal oxide in coating materials is not so important to decrease the interfacial resistance. The resistance of positive electrode layer would be caused by the formation of high-resistance interface between LiCoO_2 and sulfide electrolyte. The oxide coatings would act as a buffer layer to prevent direct contact between LiCoO_2 and the sulfide solid electrolyte, resulting in the suppression of the formation of the highly resistive layer. Ohta et al. reported that the coatings of oxide films on LiCoO_2 brought about a significant decrease of the interfacial resistance [12–14]. They used $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiNbO_3 , and LiTaO_3 as coating materials in the all-solid-state cells $\text{In}-\text{Li}/\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (thio-LISICON)/ LiCoO_2 . The coating layers suppressed the formation of a highly resistive layer between the LiCoO_2 and solid electrolyte. They suggested

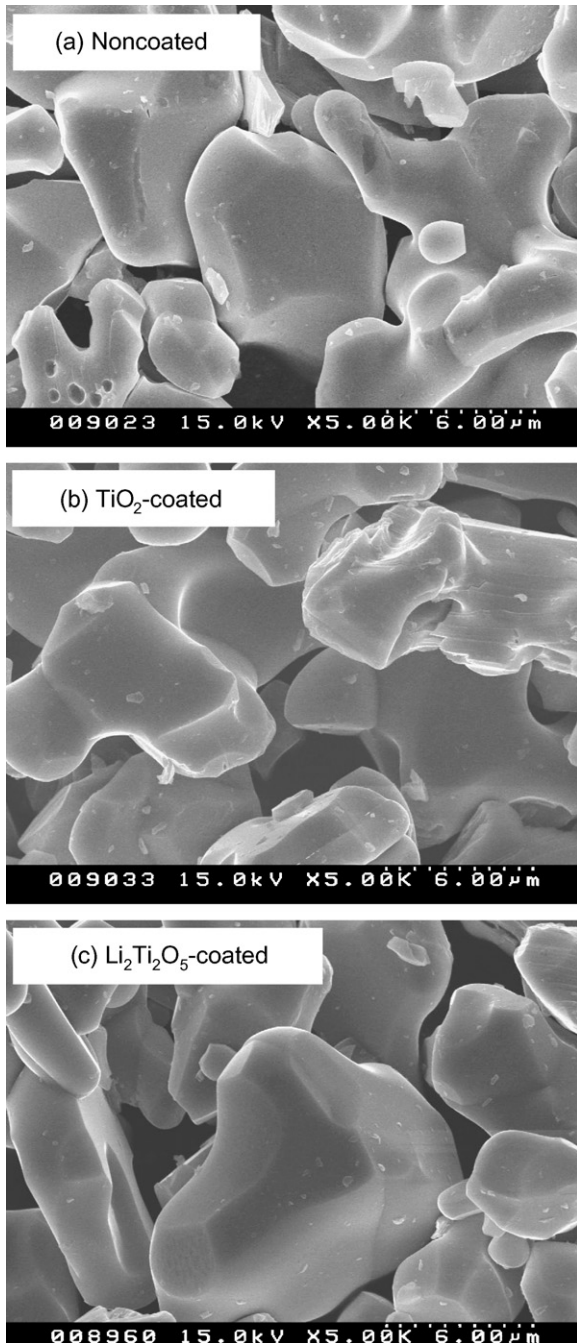


Fig. 1. FE-SEM images of (a) non-coated, (b) TiO_2 -coated, and (c) $\text{Li}_2\text{Ti}_2\text{O}_5$ -coated LiCoO_2 particles.

that LiNbO_3 and LiTaO_3 were more effective in improving the battery performance than $\text{Li}_4\text{Ti}_5\text{O}_{12}$ because LiNbO_3 and LiTaO_3 show higher lithium-ion conductivities. Our results are consistent with the conclusion by Ohta et al. [14].

Fig. 3 shows discharge curves of the all-solid-state cells In/LiCoO_2 with non-coated, and $\text{Li}_2\text{Ti}_2\text{O}_5$ -coated LiCoO_2 at a relatively high current density of $1.3 \text{ mA}/\text{cm}^2$ after charging to 4.2 V vs. Li electrode at the current density of $0.13 \text{ mA}/\text{cm}^2$. The average discharge voltages of the cells with non-coated and $\text{Li}_2\text{Ti}_2\text{O}_5$ -coated LiCoO_2 are 3.1 and 3.4 V vs. Li , respectively. The discharge capacities of those cells are 47 and $72 \text{ mAh}/\text{g}$, respectively. The discharge performance of the cell with $\text{Li}_2\text{Ti}_2\text{O}_5$ -coated LiCoO_2 is better than that with non-coated LiCoO_2 in a high current density operation. This improvement is attributable to the decrease

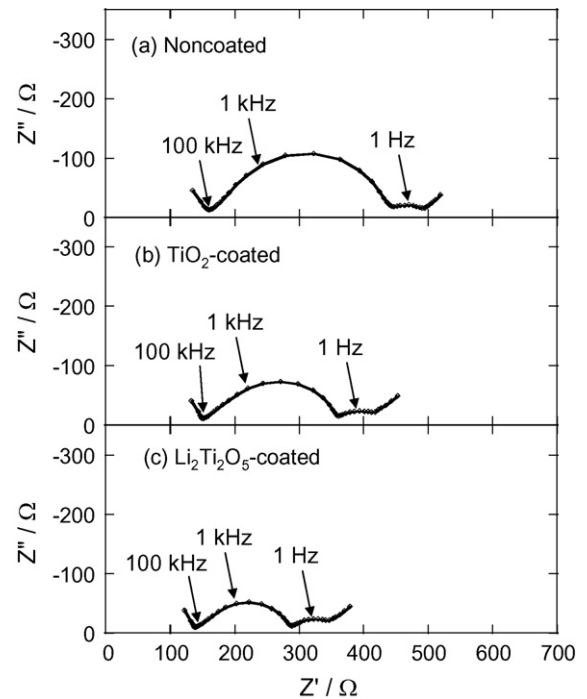


Fig. 2. Impedance profiles of the cells $\text{In}/80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass-ceramic/(a) non-coated, (b) TiO_2 -coated, and (c) $\text{Li}_2\text{Ti}_2\text{O}_5$ -coated LiCoO_2 .

of the resistance in the positive electrode layer by $\text{Li}_2\text{Ti}_2\text{O}_5$ coating.

The charge–discharge measurement of the all-solid-state cells were carried out at different cutoff voltage in order to investigate coating effects on the cell performance in different cutoff voltage operations. Cycle performances of the all-solid-state cells with non-coated, TiO_2 -coated, and $\text{Li}_2\text{Ti}_2\text{O}_5$ -coated LiCoO_2 are shown in Fig. 4. The current density was $0.13 \text{ mA}/\text{cm}^2$. The cutoff voltages are 2.6 – 4.2 V (until the 15th cycle) and 2.6 – 4.6 V (after the 16th cycle) vs. Li , respectively. The measurement was carried out after pre-cycles under high current densities over $1 \text{ mA}/\text{cm}^2$. The three cells are charged and discharged with the capacity of ca. $80 \text{ mAh}/\text{g}$ at a charging cutoff voltage of 4.2 V . In this cutoff voltage, the three cells do not show fading capacity. The capacities of the

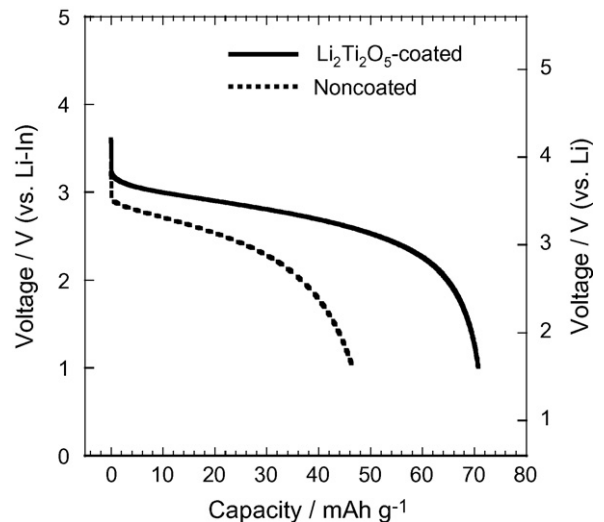


Fig. 3. Discharge curves of the cells $\text{In}/80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass-ceramic/non-coated and $\text{Li}_2\text{Ti}_2\text{O}_5$ -coated LiCoO_2 at the current density of $1.3 \text{ mA}/\text{cm}^2$.

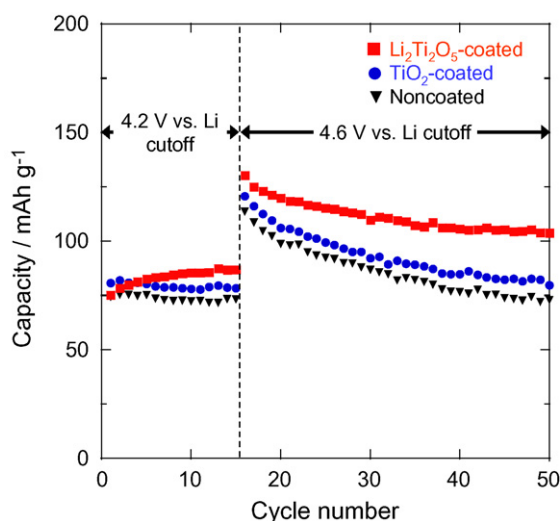


Fig. 4. Cycle performances of the cells In/80Li₂S-20P₂S₅ glass-ceramic/non-coated, TiO₂-coated, and Li₂Ti₂O₅-coated LiCoO₂ at the current density of 0.13 mA/cm². The cutoff voltages were 2.6–4.2 V (until 15th cycles) and 2.6–4.6 V (after 16th cycles) vs. Li, respectively.

cells increase by increasing cutoff voltage from 4.2 to 4.6 V. The 16th discharge capacities of the cells using non-coated, TiO₂-coated, and Li₂Ti₂O₅-coated LiCoO₂ are respectively 113, 121 and 129 mAh/g. At the high cutoff voltage, the decreases of the capacity are confirmed. The 50th discharge capacities of the cells using non-coated, TiO₂-coated, and Li₂Ti₂O₅-coated LiCoO₂ are respectively 73, 79 and 103 mAh/g. The cells with coated LiCoO₂ have better capacity retention than the cell with non-coated LiCoO₂; the cell with Li₂Ti₂O₅-coated LiCoO₂ exhibits better cycle performance than that with TiO₂-coated LiCoO₂. The 16th and 50th charge–discharge curves of the all-solid-state cells with non-coated and Li₂Ti₂O₅-coated LiCoO₂ are shown in Fig. 5. The charge–discharge capacities decrease during charge–discharge cycles in the cells with both non-coated and Li₂Ti₂O₅-coated LiCoO₂. The charging plateau voltages of the both cells increase during charge–discharge cycles. The discharging plateau voltage of the cell with non-coated LiCoO₂ slightly decreases with charge–discharge cycles at a high charging cutoff voltage of 4.6 V vs. Li, whereas the cell with Li₂Ti₂O₅-coated LiCoO₂ keeps almost the same discharging plateau voltage even after the 50th charge–discharge cycles. One of the causes of the fading capacity is the resistance increase, resulting in the decrease of the discharging plateau voltage. The discharging plateau voltage of the cell with non-coated LiCoO₂ decreases, indicating that the resistance of the cell increases. This resistance increase would be caused by the formation of high-resistance interface between LiCoO₂ and sulfide electrolyte by charging to a high voltage. The discharging plateau voltage of the cell with Li₂Ti₂O₅-coated LiCoO₂ hardly decreases, indicating that the resistance of the cell using Li₂Ti₂O₅-coated LiCoO₂ would not increase significantly. The Li₂Ti₂O₅ coating is effective in suppressing the resistance increase. In our previous report, the coatings of Li₂O–SiO₂ film on LiCoO₂ improved cyclability of the all-solid-state cells at the high cutoff voltage of 4.6 V vs. Li; coatings of lithium-ion conducting Li₂SiO₃ were more effective in improving cycle performance than those of an insulative SiO₂ [17]. The Li₂O–TiO₂ films with transition metal coated on LiCoO₂ by a sol–gel technique are also effective in improving cyclability of the all-solid-state cells at the high cutoff voltage as the Li₂O–SiO₂ coating films without transition metal. In addition, the Li₂Ti₂O₅ coating is more effective in improving cyclability than the TiO₂ coating. The existence of lithium in coating materials on the LiCoO₂ particles was more important than the kinds of coating oxide (SiO₂ or TiO₂) for electrochemical performance

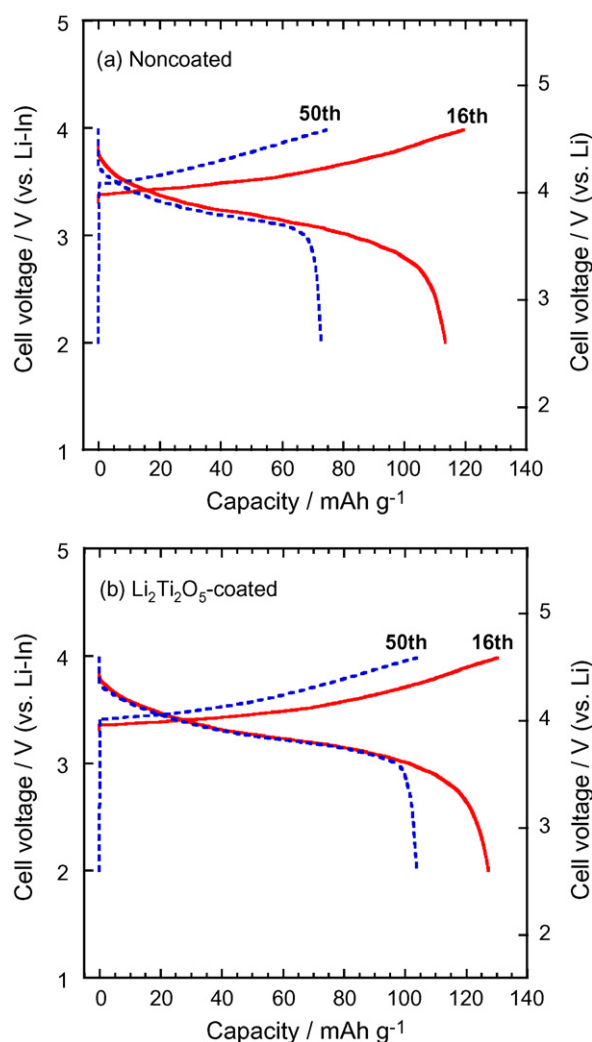


Fig. 5. The 16th and 50th charge–discharge curves of the cells In/80Li₂S-20P₂S₅ glass-ceramic/non-coated (a) and (b) Li₂Ti₂O₅-coated LiCoO₂. The current density and cutoff voltage were 0.13 mA/cm² and 4.6 V (vs. Li), respectively.

of all-solid-state lithium secondary batteries using Li₂S–P₂S₅ solid electrolytes.

4. Conclusions

LiCoO₂ particles coated with Li₂O–TiO₂ films were prepared by the sol–gel method and were applied to the all-solid-state lithium secondary batteries using Li₂S–P₂S₅ solid electrolytes. The interfacial resistance between LiCoO₂ and solid electrolyte was decreased with Li₂O–TiO₂ coatings. The resistance of the cell using the Li₂Ti₂O₅-coated LiCoO₂ was smaller than that of TiO₂-coated LiCoO₂. The discharge performance at a high current density of 1.3 mA/cm² was improved because of the decrease of the resistance by Li₂Ti₂O₅ coating. The cycle performance of the Li₂Ti₂O₅-coated LiCoO₂ cell under a high cutoff voltage of 4.6 V vs. Li was better than that of the TiO₂-coated cell and the non-coated LiCoO₂ cell. These results suggest that the lithium-ion conducting Li₂Ti₂O₅ coating on LiCoO₂ particles is effective in improving electrochemical performance of the all-solid-state lithium secondary batteries using sulfide solid electrolytes.

Acknowledgements

A Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan supported

this work. The New Energy and Industrial Technology Development Organization (NEDO) of Japan also supported this study.

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