



Short communication

All-solid-state lithium secondary batteries with oxide-coated LiCoO_2 electrode and $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ electrolyte

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ABSTRACT

All-solid-state lithium secondary batteries using LiCoO_2 active materials coated with Li_2SiO_3 and SiO_2 oxide films and $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ solid electrolytes were fabricated and their electrochemical performance was investigated. The electrochemical performance of the all-solid-state cells at a high voltage region was highly improved by using oxide-coated LiCoO_2 . The oxide coatings are effective in suppressing the formation of an interfacial resistance between LiCoO_2 and the solid electrolyte at a high cutoff voltage of 4.6V (vs. Li). As a result, charge–discharge capacities and cycle performance at the cutoff voltage were improved. The cell with Li_2SiO_3 -coated LiCoO_2 showed a large initial discharge capacity of 130 mAh g^{-1} and a good capacity retention of 110 mAh g^{-1} after 50th cycles at the cutoff voltage of 4.6V (vs. Li).

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1. Introduction

Improvement of safety is an important issue to be resolved in lithium-ion batteries. It is expected that all-solid-state lithium batteries using inorganic solid electrolytes avoid the danger of fire and explosion. We reported that bulk-type all-solid-state batteries using LiCoO_2 and sulfide solid electrolytes exhibited long cycle performance [1]. However, further enhancements of electrochemical performance such as charge–discharge capacity are required for the all-solid-state batteries.

LiCoO_2 is typically used at the voltage up to 4.2V (vs. Li); the available capacity is about 140 mAh g^{-1} , which is only a half of the theoretical capacity about 280 mAh g^{-1} . In order to increase the available capacity of the LiCoO_2 , it needs to be charged above 4.2V. However, a significant capacity fading is observed at such a high voltage region. Oxide coatings such as Al_2O_3 , ZrO_2 , AlPO_4 , and Li_3PO_4 on LiCoO_2 have been reported as an effective approach to improve cycle performance at a high voltage above 4.2V in the batteries with organic liquid [2–6], polymer [7], and ionic liquid electrolytes [8].

In the all-solid-state batteries with sulfide solid electrolytes, which are very promising because of their high lithium-ion con-

ductivity and wide electrochemical window, the oxide coatings have been reported as a technique of the improvement of rate capability by Ohta et al. [9,10]. We also reported the improvement of rate capability of the all-solid-state batteries with $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass-ceramic electrolytes by using oxide-coated LiCoO_2 . We used Li_2SiO_3 -coated and SiO_2 -coated LiCoO_2 as electrode materials and found that the oxide coatings, in particular the lithium-ion conductive Li_2SiO_3 coating, are effective in decreasing the interfacial resistance between LiCoO_2 and the solid electrolyte [11]. On the other hand, few studies about the coating effect on the high voltage performance and cycle performance are reported in an all-solid-state battery system with an inorganic electrolyte. Very recently, Okamoto et al., have reported the high voltage performance of the all-solid-state batteries with LiCoO_2 electrode and the $0.01\text{Li}_3\text{PO}_4\cdot 0.63\text{Li}_2\text{S}\cdot 0.36\text{SiS}_2$ glass electrolyte [12]. They investigated the charge–discharge performance at various charging cutoff voltages between 4.1 and 4.7V (vs. Li); initial capacities of the cells increased with increasing the cutoff voltage. However, the charge–discharge curves of the cells which operated at a high cutoff voltage above 4.5V (vs. Li) were affected by large polarization, resulting in the capacity fading of the cells. It is expected that the oxide coatings are effective in decreasing the interfacial resistance at the high voltage region. The electrochemical impedance spectroscopy is a useful technique to investigate the internal resistance of the all-solid-state batteries [9,10,13,14]. We also have studied the internal resistance

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of all-solid-state batteries using the impedance measurements [11].

In the present study, we fabricated the all-solid-state cell In/80Li₂S-20P₂S₅ glass-ceramic/oxide-coated LiCoO₂ and studied the effect of oxide coatings on the charge–discharge performance at a high voltage of 4.0 V (vs. Li–In), which is equivalent to 4.6 V (vs. Li). The interfacial resistance between LiCoO₂ and the solid electrolyte was investigated using electrochemical impedance spectroscopy measurements. We used Li₂SiO₃ and SiO₂ glasses as coating materials for LiCoO₂ in order to investigate the importance of lithium-ion conductivity of coatings on electrochemical performance at a high voltage region.

2. Experimental

The amorphous Li₂SiO₃ coating layer on LiCoO₂ particles was formed by the sol–gel method [11]. Li₂SiO₃ sols were prepared from lithium ethoxide (LiOEt) and tetraethoxysilane [Si(OEt)₄] under N₂ gas atmosphere. SiO₂ sols were also prepared from EtOH, Si(OEt)₄ and hydrochloric acid. The sols were diluted by 1 wt% with dry ethanol, and the diluted sols were mixed with LiCoO₂ particles (Toda kogyo). After drying at room temperature, the mixture was heated at 350 °C for 30 min. The weight ratios of Li₂SiO₃ and SiO₂ coatings to LiCoO₂ particles were 0.06/100.

The 80Li₂S-20P₂S₅ (mol%) glass-ceramic for solid electrolytes was prepared by mechanical milling and subsequent heat treatment [15]. Li₂S (Idemitsu Kosan Co., 99.9%) and P₂S₅ (Aldrich, 99%) were used as starting materials for the preparation of the 80Li₂S-20P₂S₅ glass. The mechanical milling treatment was carried out for the batch (1.5 g) of the mixture of the starting materials placed into a zirconia pot (volume of 45 ml) with 160 zirconia balls (5 mm in diameter) under a rotating speed of 510 rpm for 10 h at room temperature using a planetary ball mill apparatus (Fritsch Pulverisette 7). The obtained glassy powder was heated at 210 °C for 4 h to yield highly conductive 80Li₂S-20P₂S₅ glass-ceramic.

All-solid-state cells were constructed as follows. Powders of LiCoO₂ and the glass-ceramic electrolyte with the weight ratio of 70:30 were mixed using an agate mortar to prepare composite positive electrodes. An indium foil (Furuuchi Chem., 99.999%) was used as a negative electrode. A bilayer pellet consisting of the composite positive electrode (10 mg) and the glass-ceramic electrolyte (80 mg) was obtained by pressing under 360 MPa ($\phi = 10$ mm), and then the indium foil was attached to the bilayer pellet by pressing under 240 MPa. All the processes were performed in a dry Ar-filled glove box.

The cells In/80Li₂S-20P₂S₅ glass-ceramic/LiCoO₂ were charged and discharged using a charge–discharge measuring device (BTS-2004, Nagano). Charge–discharge performances were evaluated at room temperature in an Ar atmosphere. Electrochemical impedance spectroscopy measurements of the cells were performed using an impedance analyzer (SI 1260, Solartron). The applied voltage was 50 mV and the frequency range was from 10 mHz to 1 MHz.

3. Results and discussion

The all-solid-state cells In/80Li₂S-20P₂S₅ glass-ceramics solid electrolyte/LiCoO₂ were constructed and their charge–discharge performances at a high cutoff voltage were investigated. Fig. 1 shows the charge–discharge curves of the all-solid-state cells with noncoated, SiO₂-coated, and Li₂SiO₃-coated LiCoO₂. The cutoff voltage is 2.0–4.0 V (vs. Li–In), which is equivalent to 2.6–4.6 V (vs. Li). The cutoff voltage of 4.6 V (vs. Li) was selected as a standard of high voltage in order to evaluate coating effects at high volt-

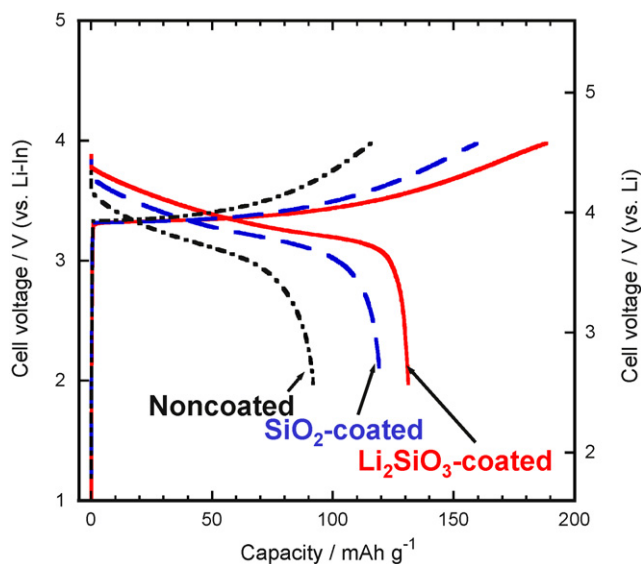


Fig. 1. Charge–discharge curves of the all-solid-state cells In/80Li₂S-20P₂S₅ glass-ceramic/LiCoO₂ with noncoated, SiO₂-coated, and Li₂SiO₃-coated LiCoO₂. The current density and cutoff voltage were 0.13 mA cm⁻² and 4.6 V (vs. Li), respectively.

age cutoff. The current density is 0.13 mA cm⁻². The initial charge capacities of the cells using noncoated, SiO₂-coated, and Li₂SiO₃-coated LiCoO₂ are respectively 120, 160, and 190 mAh g⁻¹. The initial discharge capacities of the cells are respectively 90, 120, and 130 mAh g⁻¹. The average discharge voltages of those are 3.7, 3.9, and 4.0 V, respectively. In our previous report [11], where charge cutoff voltage was 4.2 V (vs. Li), the initial discharge capacities of the cells using noncoated, SiO₂-coated, and Li₂SiO₃-coated LiCoO₂ were respectively 63, 70, and 95 mAh g⁻¹. The discharge capacities were increased by increasing cutoff voltage from 4.2 V to 4.6 V (vs. Li). Larger reversible capacities and higher discharge voltages are obtained in the cells with Li₂SiO₃-coated and SiO₂-coated LiCoO₂ than in the cell with noncoated LiCoO₂. The cell with Li₂SiO₃-coated LiCoO₂ showed superior charge–discharge capacity to the cell with SiO₂-coated LiCoO₂.

In order to investigate the coating effect in the high cutoff voltage of 4.6 V (vs. Li), the electrochemical impedance spectroscopy measurements of the all-solid-state cells were carried out. Fig. 2 shows the impedance profiles of the all-solid-state cells after the 1st charge process to 4.6 V (vs. Li) at a current density of 0.13 mA cm⁻². The large semicircle is regarded as the interfacial resistance between LiCoO₂ and Li₂S–P₂S₅ solid electrolytes and the resistance observed at the higher frequency region of the semicircle is attributed to the resistance of the solid electrolyte layer [11]. The resistance of the solid electrolyte layer shows almost no difference between the cells with coated LiCoO₂ and the cell with noncoated LiCoO₂; the resistance does not increase during a charge process. The interfacial resistances of noncoated, SiO₂-coated, and Li₂SiO₃-coated LiCoO₂ are respectively 1700, 900, and 750 Ω. The interfacial resistances after charging to 4.6 V (vs. Li) are larger than those after charging to 4.2 V (vs. Li) reported in our previous report [11]. The charge transfer resistance of the cell using LiCoO₂ is reported to increase at a high voltage region above 4.2 V (vs. Li) [6,13,14]. Similar behavior is observed in the all-solid-state cells with Li₂S–P₂S₅ solid electrolytes.

The interfacial resistances of the cells with Li₂SiO₃-coated and SiO₂-coated LiCoO₂ are smaller than that with noncoated LiCoO₂, indicating that the coatings are effective in suppressing an increase of the interfacial resistance. Li₂SiO₃ coating is more effective than SiO₂ coating in decreasing the interfacial resistance, indicating

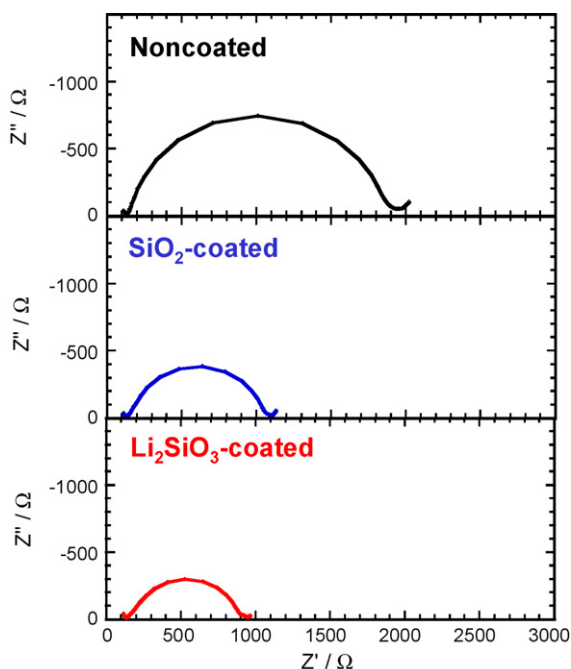


Fig. 2. Impedance profiles of the all-solid-state cells with noncoated, SiO₂-coated, and Li₂SiO₃-coated LiCoO₂ after the first charge process to 4.6 V (vs. Li).

that lithium-ion conductivity of coating materials is important for decreasing the interfacial resistance of the all-solid-state cells. It is noted that there is good relationship between charge–discharge capacities and cell resistances.

Fig. 3 shows the cycle performance of In/80Li₂S-20P₂S₅ glass-ceramic/LiCoO₂ cells. The reversible capacities of the cells with noncoated, SiO₂-coated, and Li₂SiO₃-coated LiCoO₂ at the 50th discharge process are respectively 60, 80, and 110 mAh g⁻¹. All the cells retain charge–discharge efficiency of 100% except for initial a few cycles. All the cells show relatively good capacity retention at a cutoff voltage of 4.6 V (vs. Li). The cells with coated LiCoO₂ have better capacity retention than the cell with noncoated LiCoO₂. In the case of using liquid and polymer electrolytes, it is reported that the capacity of the cells with noncoated LiCoO₂ decreased drastically during charge–discharge cycling at 0.1–1 C

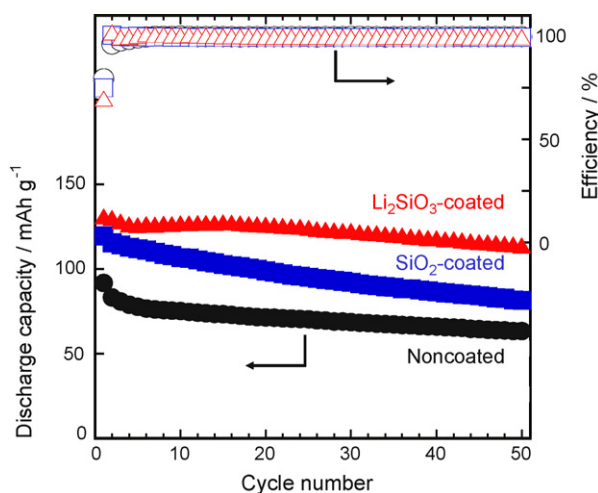


Fig. 3. Cycle performance for discharge capacity and columbic efficiency of the all-solid-state cells In/80Li₂S-20P₂S₅ glass-ceramic/LiCoO₂. The current density and cutoff voltage were 0.13 mA cm⁻² and 4.6 V (vs. Li), respectively.

under the cutoff voltage above 4.6 V (vs. Li) [4–8]. The all-solid-state cells operate stably even in the case using noncoated LiCoO₂ at 0.13 mA cm⁻² (0.1 C) under the high cutoff voltage of 4.6 V (vs. Li). This result indicates that the Li₂S–P₂S₅ solid electrolyte is more stable than the other electrolytes at the high voltage. In the cells with liquid and polymer electrolytes, the degradation of the cells at high voltages is explained as follows: (i) cobalt dissolution from LiCoO₂ to liquid electrolyte, (ii) structural change due to phase transition of LiCoO₂ between a hexagonal phase and a monoclinic phase, and (iii) impedance growth with cycling [3,6,7,14,16,17]. In the all-solid-state system, the Co dissolution would be suppressed at the interface between LiCoO₂ and the solid electrolyte, and thus the degradation of LiCoO₂ is restrained even in the case using noncoated LiCoO₂. However, the Co dissolution (diffusion) from LiCoO₂ to solid electrolyte could be strongly related to impedance growth. The capacity after 50th cycle of the all-solid-state cells using oxide-coated LiCoO₂ is larger than that with noncoated LiCoO₂. Chen and Dahn have reported that oxide coatings suppress side reactions between electrode and electrolyte [5,6]. We also assume that oxide coatings act as a buffer layer and suppress the reaction which forms highly resistive layer at the interface between LiCoO₂ and sulfide electrolyte. The electrochemical performances of the cell with Li₂SiO₃-coated LiCoO₂ at the high voltage are superior to those with SiO₂-coated LiCoO₂, indicating that lithium-ion conductivity of coating materials is important for improving the electrochemical performance of the all-solid-state batteries.

4. Conclusions

The improvement of the electrochemical performance of the all-solid-state cells In/80Li₂S-20P₂S₅ glass-ceramic/LiCoO₂ by coating Li₂SiO₃ and SiO₂ on LiCoO₂ was demonstrated. The cells with Li₂SiO₃-coated and SiO₂-coated LiCoO₂ showed larger initial charge–discharge capacities and higher discharge voltages than the cell with noncoated LiCoO₂ at a cutoff voltage of 4.6 V (vs. Li). The capacity after the 50th cycle of the cells with Li₂SiO₃-coated, SiO₂-coated, and noncoated LiCoO₂ were 110, 80, and 60 mAh g⁻¹, respectively. Cycle performance at high voltage was improved by the use of the cells with oxide-coated LiCoO₂ because the increase of interfacial resistance between LiCoO₂ electrode and Li₂S–P₂S₅ electrolyte at the high voltage was successfully suppressed. In particular, the lithium-ion conductive Li₂SiO₃ coating was more effective than SiO₂ coating in improvement of the electrochemical performance of the all-solid-state batteries.

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