Impact of Surface Coating on the Low Temperature Performance of a Sulfide-Based All-Solid-State Battery Cathode

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ABSTRACT
Cathode coating is a key technology in sulfide-based all-solid-state batteries (ASSBs). The coating serves as a protector, suppressing side reactions at the sulfide/cathode active material interface. Lithium niobate (LiNbO3) is a well-known coating material. In this study, sulfide-based ASSBs, which were uncoated and surface-coated with LiNbO3, are subjected to cell operation testing and electrochemical impedance spectroscopy (EIS) in a low-temperature environment (i.e., −60 °C), where a commercial liquid-type lithium-ion battery (LIB) is unable to operate because of partial freezing and significant viscosity increase. Unlike liquid-type LIBs, the coated and uncoated ASSBs successfully discharge at −60 °C, emphasizing their applicability in low-temperature environments. The coated ASSB exhibits better low-temperature performance than the uncoated one. In the absence of coating, the deconvoluted EIS resistance data show an increase in some resistance components at low temperature.

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1. Introduction
Considerable research has been conducted on lithium-ion batteries (LIBs) owing to their high demand as energy sources for consumer electronics, electric vehicles (EVs), and energy storage systems. In particular, all-solid-state batteries (ASSBs) that use solid electrolytes (SEs) have higher energy densities1,2 and are safer3 than general liquid-type LIBs. Among them, the ASSBs that use sulfide-based SEs have several advantages, including high ionic conductivity (>10 mS cm−1) and the plasticity of the sulfide itself; therefore, their rapid commercialization is highly desirable.4,5 In addition, expanding the operating temperature range, which is difficult for liquid-type LIBs, is expected to be easier for the ASSB.4,5 The operating range of the liquid-type LIBs is very narrow; at high temperatures (i.e., >60 °C), they suffer from major problems, such as battery-package swelling due to the gas generated by side reactions at the interface between the electrode active material and the organic solvent of the electrolyte,6 and the thermal decomposition of the electrolyte itself.10 At low temperatures (i.e., <30 °C), electrolytes begin to experience significant increase in viscosity or partial freezing.11,12 Unlike liquid-type LIBs, sulfide-based SEs thermally decompose at much higher temperatures (~200 °C)13 and do not freeze at low temperatures;4,5 thus, they exhibit a significantly wider operating range. Surface coating is a key technology for ASSB cathodes that use sulfide-based SEs,4 which serves as a protective layer that suppresses side reactions with a sulfide SE to reduce interfacial resistance. We have previously reported on its good performance in the case of a sulfide SE/Li3PO4 coated LiNi0.5Co0.2Mn0.3O2 (NCM523) in high-temperature environments (60 °C).5 Additionally, Kanno et al. have reported that ASSB using LiNbO3-coated LiCoO2 (LCO) exhibited better operational performance than a liquid-type LIB at a low temperature (~30 °C).5

In this study, we analyzed the effect of LiNbO3 surface coating on low-temperature battery operation through charge/discharge testing and electrochemical impedance spectroscopy (EIS) in detail.

2. Experimental
Cells were fabricated as described in our previous report.2 LiNi0.5Co0.2Mn0.3O2 (NCM523, Sumitomo Metal Mining, Japan) was used as the cathode active material. It was coated with LiNbO3 prepared with Li-Nb double ethoxide in anhydrous ethanol solution, using a rolling fluidized coating machine (MP-01, Powrex, Japan).4 The average thickness of the coating was approximately 2–10 nm (Fig. 1). Argyroite-structured Li1+xPS1-xCl (x ≈ 1, 2 × 10−3 S cm−1) (Mitsui Mining & Smelting, Japan) was used as the sulfide-based SE. The specific cathode active material, SE, and coating material were selected for the following reasons: NCM523 is classified as middle-Ni NCM, which is widely used because of its good balance between capacity and stability of the material itself. Argyroite-structured SE exhibits high conductivity1 and is cost effective.5 LiNbO3 is one of the most well-known materials used as a cathode coating; it is also easy to synthesize using the Li–Nb double alkoxide method.14 The NCM523 half-cell pellets consisted of three layers: (1) an ~60-µm-thick NCM523 cathode electrode layer (with or without (bare) the LiNbO3 coating) and an SE mixture 50:50 (v/v) as the working electrode; this was designed to achieve a cell capacity of 2 mAh based on the theoretical capacity of 160 mAh g−1 (NCM523) during operation at an upper voltage limit of 4.25 V vs. Li/Li+. (2) An SE separator layer of ~600 µm, and (3) an In–Li alloy counter electrode of ~600 µm. All processes were carried out in an Ar-filled glove box (dew point less than −80 °C, oxygen concentration <1 ppm).

EIS and cell operation testing were performed using a potentiosit/galvanostat with a frequency response analyzer unit (VSP-300, Biologic) in a thermostat chamber (SU-262, Espec). The half cells were charged to 4.25 V vs. Li/Li+ at a constant current (CC) of 200 µA cm−2 (0.1 C-rate) to maintain a constant...
potential (CP) of 4.25 V vs. Li/Li⁺ with a cutoff current of 20 
µA cm⁻² (0.01 C-rate). Then, the half cells were discharged to 3.0 V 
vs. Li/Li⁺ at a 0.1 C-rate CC to maintain a CP of 3.0 V vs. Li/Li⁺ 
with a 0.1 C-rate cutoff current. This charge/discharge process was 
performed over three cycles to activate the cell. Subsequently, EIS 
was conducted at 3.95 V vs. Li/Li⁺ in the temperature range of −60 
to 25 °C. The AC voltage amplitude was set to 10 mV, and a 10⁻²–
¹⁰⁵ Hz frequency range was used. Following the acquisition of the 
EIS spectra, cell operation testing was performed in the −60 to 
45 °C temperature range. The charging conditions were the same as 
those used to activate the cell at 25 °C (above). Discharging was 
carried out at a 0.1 and 0.01 C-rate in the temperature ranges of 
−40 to 45 °C and −60 to −40 °C, respectively. The wait time after 
reaching a specific temperature was set to 4 h in the temperature-
controlled process to ensure that the temperature inside the cell 
matched the target temperature.

3. Results and Discussion

Discharge curves acquired with and without the LiNbO₃ coating 
at several temperatures are shown in Fig. 2. It is noteworthy that the 
half cells successfully operated at −60 °C, where almost all 
commercial liquid-type LiB electrolytes partially froze.⁴,⁵,¹² This 
indicated that the sulfide-based ASSB was fundamentally more 
advantageous, even at extremely low temperatures. In contrast, 
we observed different temperature dependences of the discharge 
capacity at the 0.1 C-rate with and without the LiNbO₃ coating. The 
NCM523 active material exhibited an increasingly higher capacity 
in the presence of the coating than that in its absence with 
decreasing operating temperature. Considering that almost the same 
cell capacities were recorded with/without coating at 45 °C, the 
difference in the discharge capacity observed in the low-temperature 
region appeared to be the result of cell resistance, especially 
interfacial resistance at the sulfide-based SE/NCM523 active 
material boundary. To evaluate the differences in cell resistance 
from the discharge curves acquired with/without the LiNbO₃ 
coating, we analyzed the EIS spectra in the same temperature range 
(Fig. 3; EIS Nyquist and Bode plots). At least two semicircular 
shapes derived from the charge-transfer processes were observed for 
both the half cells. The charge-transfer resistance in the higher 
frequency region (HFR), Rₛ, was attributable to the NCM523 
surface components, while that in the lower frequency region (LFR), 
Rₓ, was mainly due to Li-ion intercalation/de-intercalation in 
NCM523, considering the relatively smaller resistance of the In–Li 
alloy counter electrode (e.g., ~1 Ω at 25 °C as previously reported)⁶ 
as an offset value common to cells with and without the coating. The 
intercept with the real component axis was determined by the ionic 
conduction resistance of the SE separator, R₁. Based on these 
attributes,⁷ the resistance components at each temperature are 
separated, as depicted by the equivalent circuit in Fig. 4a, with a 
fitted example (Fig. 4b). It is important to note that in this study, the 
well-known Warburg term denoting the diffusion of the Li-ion in the 
NCM lattice was excluded from the frequency range of fitting. The 
results of the capacitance values of each constant phase element 
(CPE) element from the fitting are summarized in Table 1. It was 
apparent from the digit deviation between C₂ and C₃, with or 
without the LiNbO₃ coating, that each was due to a different charge-
transfer process. In addition, the fact that the C₁ value, which was 
mainly attributed to Li-ion intercalation/de-intercalation for 
NCM523, was in agreement with the capacitance values of the 
lithium metal oxides previously reported,⁴,¹⁶,¹⁷ which supported its 
association with the element of Rₓ—CPE₃. The inverse of each 
resistance (1/Rₓ) was plotted against the reciprocal temperature 
(1000/T) to obtain the Arrhenius plots (Fig. 4c). Each resistance 
component clearly showed the Arrhenius-type temperature de-
pendence in the extreme low-temperature region (i.e., −60 °C); 
these plots also essentially revealed low-temperature operability. 
Although it was reasonable and natural that the resistance Rₓ derived 
from the SE separator was exactly the same, R₂ was higher while Rₓ 
was significantly lower over the entire temperature range for the 
LiNbO₃-coated sample. Interestingly, the slopes of the charge-
transfer resistance (R₂ and Rₓ) plots with and without coating were 
different, especially for Rₓ. The slope of each Arrhenius plot
provided the activation energy, $E_a$, for each process, which was calculated using the following equation:

$$1/R_x = A \cdot \exp(-E_a/RT),$$  \hfill (1)

where $R_x$ is each resistance component, $A$ is the frequency factor, $R$ is the gas constant, and $T$ is absolute temperature.

Figure 5 shows the activation energy of each resistance component calculated using Eq. 1. Consolidating the data from Figs. 4 and 5 shows that LiNbO$_3$ coating led to: (i) an increase in the charge-transfer resistance, $R_2$, derived from the NCM523 surface components, and a slight decrease in the associated activation energy; (ii) a significant decrease (by a factor of $\sim$100) in the charge-transfer resistance, $R_3$, derived from Li-ion intercalation/de-intercalation involving NCM523, accompanied by a significant decrease in activation energy. The notable decrease in the charge-transfer resistance $R_3$ and the corresponding activation energy correlated with the observed low-temperature operating performance (Fig. 2).
Finally, we discuss mechanistic considerations. The small increase in $R_2$ in response to the LiNbO$_3$ coating was most likely due to the low Li-ion conductivity of LiNbO$_3$ ($\sim$10$^{-8}$ S cm$^{-1}$).$^{16}$ The low ion-conductive surface layer of the coating appeared to increase the surface resistance, as compared to the bare surface. It is speculated that the low value of $R_2$, even in the absence of the coating (bare), is due to residual lithium compounds, such as LiOH and Li$_2$CO$_3$, which are particular to the NCM surface.$^{19}$ Although it was difficult to quantify the absolute amount, the surface carbonate concentration of bare NCM523 by X-ray photoelectron spectroscopy (XPS) analysis was $\sim$15 at%.$^{5}$ In contrast, the dramatic decrease in $R_1$ and associated activation energy in the coated sample was most likely caused by the suppression of the side reactions, such as elemental exchange$^{20}$ and the formation of a space charge layer (depletion layer)$^{21-23}$ Tateyama et al. proposed a coating effect for these side reactions at the interface with/without coating based on theoretical calculations, which is a well-known interfacial-design guideline for sulfide-based ASSBs. In other words, the presence of this side reaction layer increased the activation energy for Li-ion intercalation/de-intercalation to/from the active material, which was suppressed by the coating. In this study, we experimentally showed that the side reaction layer at the sulfide-based SE/cathode active material interface significantly impacted battery durability,$^{2,24,25}$ and low-temperature operations.

4. Conclusions

In this study, we investigated the impact of the well-known LiNbO$_3$ surface coating on low-temperature battery performance of all-solid-state cathode half cells using sulfide-based argyrodite-structured SE and LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$. Discharge curves acquired in the range of $-60$ to $45$ °C revealed that the coating reduced cell resistance, especially at low temperatures. Detailed EIS analyses revealed that the coating slightly increased the surface resistance of the active material but significantly reduced the resistance of the active material to Li-ion intercalation/de-intercalation. Furthermore, we found that the coating reduced the activation energy associated with the $R_2$ resistance component. We presumed that this effect was the result of the coating suppressing the elemental exchange and the formation of a space charge layer (depletion layer), experimentally demonstrating the significant impact of surface coating on the low-temperature operation of sulfide-based ASSBs.

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CRediT Authorship Contribution Statement

Yusuke Morino: Conceptualization (Lead), Investigation (Lead), Methodology (Lead), Validation (Lead), Visualization (Lead), Writing – original draft (Lead), Writing – review & editing (Lead)

Conflict of Interest

There are no conflicts of interest to declare.

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