

Kinetics of Interfacial Lithium-ion Transfer between a Graphite Negative Electrode and a $\text{Li}_2\text{S-P}_2\text{S}_5$ Glassy Solid Electrolyte



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ABSTRACT

All-solid-state lithium-ion batteries that use sulfide solid electrolytes have attracted much attention due to their high safety and wide electrochemical window. In this study, highly oriented pyrolytic graphite (HOPG) and $75\text{Li}_2\text{S-25P}_2\text{S}_5$ (mol%) glass were used as a model graphite negative electrode and a sulfide solid electrolyte, respectively. Interfacial lithium-ion transfer between $75\text{Li}_2\text{S-25P}_2\text{S}_5$ glass and the HOPG electrode was studied by AC impedance spectroscopy measurements. The activation energy of the interfacial lithium-ion transfer was estimated to be around 37 kJ mol^{-1} , which was much smaller than that at the interface between organic liquid electrolytes and HOPG electrode, indicating that the lithium-ion transfer at the interface between $75\text{Li}_2\text{S-25P}_2\text{S}_5$ glass and HOPG electrode proceeded quite rapidly. Furthermore, surface deposition of TiO_2 and surface oxidation on HOPG electrodes were performed using the atomic layer deposition (ALD) method. Interfacial lithium-ion transfer between $75\text{Li}_2\text{S-25P}_2\text{S}_5$ glass and ALD-modified-HOPG electrodes was also investigated. The activation energies of the interfacial lithium-ion transfer were slightly higher than that of HOPG, but the resistance of the charge-transfer process was lower, indicating that the affinity of the HOPG electrode for the glass electrolyte was improved by surface modification.

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Keywords : All-solid-state Lithium Secondary Batteries, Interfacial Lithium-ion Transfer, Graphite Negative Electrode, Sulfide-based Solid Electrolyte

1. Introduction

There has been a growing demand for next-generation lithium-ion batteries (LIBs) with higher energy densities and improved safety performance to support, among other applications, the rapid development in electric vehicles (EVs). Traditional lithium-ion batteries use an organic liquid electrolyte composed of lithium salt and organic solvents to transfer the ions between the cathode and anode electrodes during energy storage and consumption.¹ However, the ionic conductivities of currently used organic liquid electrolytes are quite low at low temperature.² Besides, in some extreme cases, the risks associated with a volatile and flammable organic liquid electrolyte have also been one of the main limitations on the application of lithium-ion batteries in EVs.^{3,4} Over the past two decades, replacement of the traditional organic liquid electrolyte by a non-flammable inorganic solid electrolyte with high conductivity in all-solid-state lithium-ion batteries has been considered as a potential approach to address these issues.⁵⁻⁷ Due to their high lithium-ion conductivity, wide electrochemical and temperature windows, as well as excellent mechanical behaviors for constructing a solid-solid interface between an electrolyte and electrode, sulfide solid electrolytes have been the focus of considerable attention.^{8,9} However, most sulfide solid electrolytes are extremely sensitive to

moisture in the air.¹⁰ The hydrolysis reactions of a sulfide solid electrolyte can greatly modify its structure and increase risks by forming the toxic gas H_2S .¹¹

$75\text{Li}_2\text{S-25P}_2\text{S}_5$ (mol%) glass is a type of sulfide solid electrolyte that shows a high ionic conductivity of around 10^{-4} – 10^{-2} s cm^{-1} at room temperature.^{12,13} This value is almost the same as that in currently used organic liquid electrolytes. Furthermore, it shows excellent chemical stability toward moisture in the air compared to other sulfide solid electrolytes.¹⁴⁻¹⁶ Therefore, $75\text{Li}_2\text{S-25P}_2\text{S}_5$ glass has attracted much attention for development of next-generation all-solid-state lithium-ion batteries.

Graphite has been widely used as a negative electrode in traditional lithium-ion batteries due to its high theoretical capacity of 372 mAh g^{-1} ,¹⁷ low negative redox potential of around 0.1 V (vs. Li^+/Li)¹⁸ and excellent cycling performance.¹⁹ However, the application of graphite as a negative electrode in all-solid-state lithium-ion batteries has been limited by the poor rate performance and high interfacial resistance caused by the poor solid-solid contact between the sulfide solid electrolyte and graphite electrode,^{20,21} and the details have not been reported.

Atomic layer deposition (ALD) is usually used to create smooth thin films with a precise thickness and high conformality.²² For LIBs with organic liquid electrolyte, the ALD-modification on the surface of graphite have been reported to effectively increase the active sites of graphite as well as improve the cycling and high-rate performances of the LIBs.^{23,24} However, the effect of the ALD-modification on graphite in LIBs with sulfide solid electrolyte has not been systematically investigated.

In this study, we chose $75\text{Li}_2\text{S-25P}_2\text{S}_5$ glass as the sulfide solid electrolyte and highly oriented pyrolytic graphite (HOPG) as a model electrode to investigate the interfacial lithium-ion transfer

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between a sulfide solid electrolyte and a graphite electrode. Furthermore, surface modification of HOPG electrodes was conducted by ALD method and the effect of the surface modification of HOPG electrodes on the interfacial lithium-ion transfer between the sulfide solid electrolyte with the ALD-modified-HOPG electrodes is discussed.

2. Experimental

A basal plane of HOPG (ZYH grade, Momentive Performance Materials Quartz, Inc.) was used as a model electrode. The surface of the HOPG electrode was carefully cleaved with Scotch[®] tape before the electrochemical measurements. A HOPG electrode without any further modification was denoted as pristine HOPG electrode. Surface modification of the HOPG electrodes was carried out with an ALD device (SUGA SAL 1500-CAT) and the as-prepared HOPG electrodes were considered ALD-modified-HOPG electrodes. TiO₂ was deposited on the HOPG electrode by alternately introducing tetrakis(ethylmethylamido)titanium (TEMAT, Nacalai Tesque Inc.) and deionized water into the ALD device. Nitrogen was used as the carrier gas and the flow rate of nitrogen gas was set at 10 sccm during the ALD process. The temperature of the ALD substrate was set at 200 °C. The detailed steps were as follows: (1) a 10 ms supply of water with a 5 s purge, and (2) a 1000 ms supply of TEMAT with a 15 s purge of the oversupplied water and any coproduct. This 2-step sequence was used as one cycle of the ALD process of TiO₂. The cycle number was set to be 1 or 5 and the as-prepared HOPG electrodes were denoted as ALD-TiO₂-1-HOPG and ALD-TiO₂-5-HOPG, respectively. For comparison, a sequence without TEMAT and with only deionized water was conducted for 5 cycles and the as-formed HOPG electrode was denoted as ALD-Oxidized-HOPG.

For electrochemical measurements, unless otherwise stated, a three-electrode cell with HOPG as the working electrode and lithium foil as both the counter and reference electrodes was used, as shown in Fig. 1. In this study, we focused on the interfacial Li⁺ transfer between sulfide solid electrolyte and graphite, therefore, a three-electrode cell with a combination of both organic liquid electrolyte and sulfide solid electrolytes were used to eliminate the interference from the positive electrode. The organic liquid electrolyte was 1 mol dm⁻³ (M) LiClO₄ dissolved in propylene carbonate (PC) (Tomiya Pure Chemical Industries). As for the sulfide solid electrolyte, the starting materials of Li₂S (Furuuchi Chem., 99.9%) and P₂S₅ (Aldrich, 99%) were mixed in a molar ratio of 75 : 25 by ball-milling and the as-prepared material was denoted as the 75Li₂S-25P₂S₅ glass powder.²⁵ 140 mg of the 75Li₂S-25P₂S₅ glass powder

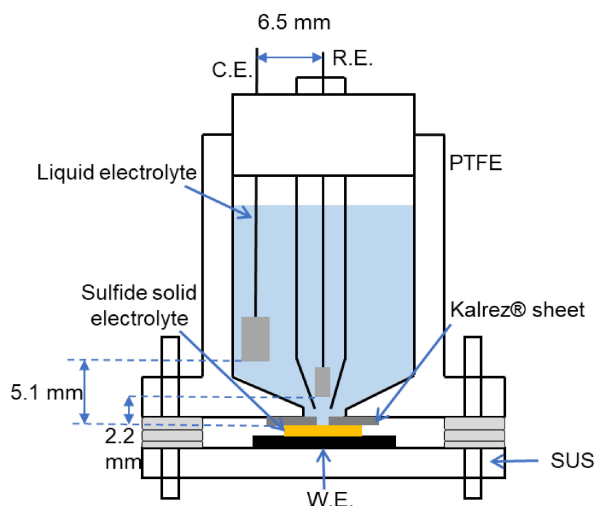


Figure 1. Schematic diagram of a three-electrode cell.

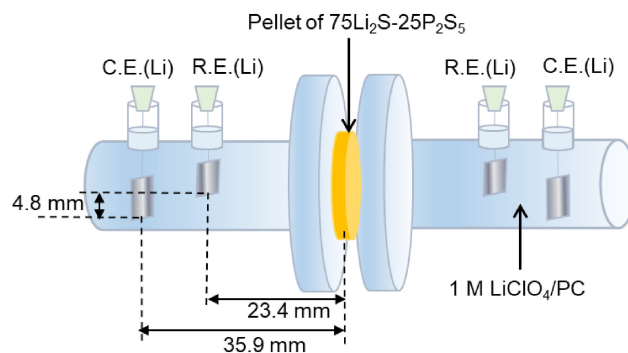


Figure 2. Schematic diagram of a four-electrode cell with a pellet of 75Li₂S-25P₂S₅ glass. Cross-sectional area of the tube: 0.2 cm².

was compressed by uniaxial cold-press molding with a pressure of 360 MPa at room temperature for 30 minutes to obtain a pellet of sulfide solid electrolyte with a diameter of 1 cm. The as-prepared pellet was fixed between the polytetrafluoroethylene (PTFE) of the cell and the HOPG electrode.

Cyclic voltammetry (CV) was carried out for 5 cycles within a potential range of 0–2.5 V with a sweep rate of 0.1 mV s⁻¹ by HSV-100 (Hokuto-Denko). AC impedance spectroscopy measurements were performed over a frequency range of 100 kHz–100 mHz and the applied AC voltage was set at 5 mV using a Solartron 1480 MultiStat (Solartron Analytical) together with an SI 1255 frequency response analyzer (EG&G Princeton Applied Research). ZPlot software (Solartron Analytical) was used to analyze the Nyquist plots.

The interface between the organic liquid electrolyte of 1 M LiClO₄/PC and the pellet of 75Li₂S-25P₂S₅ glass was constructed by using a four-electrode cell (cell constant: 21 cm⁻¹), as shown in Fig. 2. The contact area between the organic liquid electrolyte and the pellet on each side was fixed to be about 0.07 cm². Lithium foil was used for both the counter and reference electrodes. AC impedance spectroscopy measurement was conducted with a VSP-300 (Bio-logic) within a frequency range from 100 kHz to 10 mHz and the applied AC voltage was 300 mV. All the electrochemical measurements were carried out in an argon gas atmosphere.

3. Results and Discussion

3.1 Lithium-ion charge-transfer between 75Li₂S-25P₂S₅ glass and a pristine HOPG electrode

Cyclic voltammograms of the pristine HOPG electrode are shown in Fig. 3. Oxidation and reduction current peaks within a potential range of 0–0.6 V were assigned to the intercalation and deintercalation of lithium ion to the HOPG electrode. During scanning for five cycles, the obtained cyclic voltammograms were similar with regard to peak current and the center of the current peaks did not show any shift to other potentials, indicating the intercalation and deintercalation of lithium ion occurred at the interface between the electrolyte and the HOPG electrode. In this study, although both organic liquid electrolyte (1 M LiClO₄/PC) and 75Li₂S-25P₂S₅ glass were used as a composite electrolyte in the three-electrode cell, only a single side of the pellet of 75Li₂S-25P₂S₅ glass was in contact with the HOPG electrode. Besides, PC has been widely reported to participate in a destructive reaction toward graphite;^{26,27} thus, the reversible intercalation and deintercalation of lithium ion cannot occur on the interface between PC and graphite. Therefore, in this study, the reduction and oxidation current peaks observed in cyclic voltammograms were attributed to the smooth intercalation and deintercalation of lithium ion at the interface between 75Li₂S-25P₂S₅ glass and the HOPG electrode.

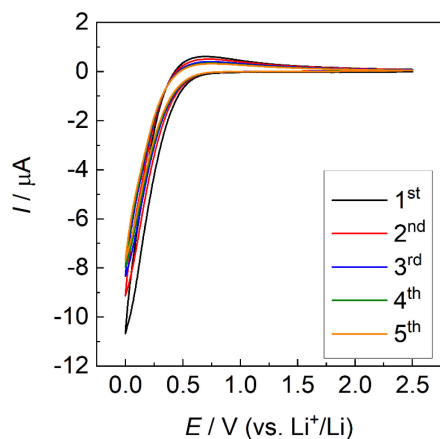


Figure 3. Cyclic voltammograms for the three-electrode cell of HOPG. The scan rate was 0.1 mV s^{-1} .

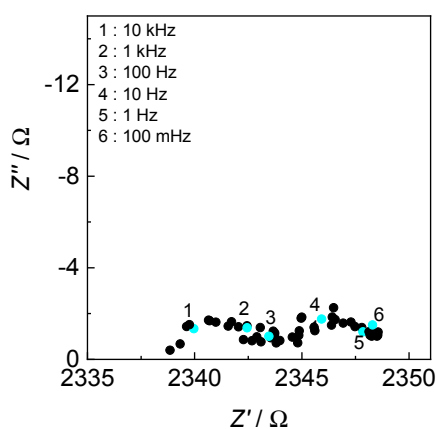


Figure 4. Nyquist plot of the four-electrode cell at room temperature.

As shown in Fig. 4, the diffusion of lithium ion in the bulk of the pellet of $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass, and the interfacial transport of lithium ion between the organic liquid electrolyte and the pellet of $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass are discussed based on the obtained Nyquist plot with a four-electrode cell by AC impedance spectroscopy measurements. Two semi-circles were observed and the semi-circle at the high frequency region was attributed to the grain boundary resistance of the bulk of the pellet of $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass. The semi-circle observed in the middle to lower frequency region (1 Hz–100 mHz) was assigned to the interfacial transport of lithium ion between the organic liquid electrolyte and the pellet of $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass, and its resistance was estimated to be around $0.9 \Omega \text{ cm}^2$.²⁸

To further discuss the kinetics of the interfacial lithium-ion transfer between $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass and the HOPG electrode, AC impedance spectroscopy measurements with a three-electrode cell were carried out following the cyclic voltammetry tests to achieve a relatively stable interface between the solid electrolyte and HOPG electrode. The obtained Nyquist plots might reflect the following components of resistance: (1) the diffusion of lithium ion in the organic liquid electrolyte; (2) the interfacial transport of lithium ion between the organic liquid electrolyte and the pellet of $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass; (3) the diffusion of lithium ion in the bulk of the pellet of $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass; (4) the interfacial transfer of lithium ion between the pellet of $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass and the HOPG electrode; (5) the diffusion of lithium ion in the bulk of the HOPG electrode; and (6) electron transport in the bulk of the HOPG electrode and at the interface between the HOPG electrode and the current collector.

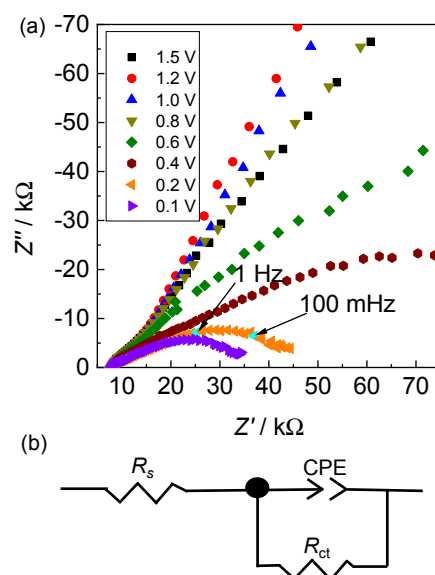


Figure 5. (a) Potential-dependence of Nyquist plots for the three-electrode cell of HOPG. (b) Equivalent circuit used for fitting Nyquist plots.

In the frequency region we used in the AC impedance measurements, the diffusion of lithium ion in the organic liquid electrolyte (1), the diffusion of lithium ion in the bulk of the pellet of $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass (3), and the electron transport in the bulk of the HOPG electrode and at the interface between the HOPG electrode and the current collector (6) usually do not give any semi-circle in Nyquist plots.²⁹ The diffusion of lithium ion in the bulk of the HOPG electrode (5) usually shows a straight line from the Z' axis with an angle of 45° as reported in the literature.³⁰

The potential dependence of Nyquist plots obtained within the potential range of 0.2–1.5 V is shown in Fig. 5a. In the middle to lower frequency region, Nyquist plots within the potential range of 0.8–1.5 V showed blocking electrode-type behavior and no semi-circle was observed, indicating the intercalation and deintercalation of lithium ion to the HOPG electrode did not occur at these potentials, which was consistent with the results in the cyclic voltammograms. When the potential was lower than 0.6 V, a semi-circle began to appear in the middle to lower frequency region and its diameter decreased with a decrease in the potential, suggesting that the interfacial intercalation and deintercalation of lithium ion on the HOPG electrode occurred at these potentials. The resistance for the semi-circle obtained in the middle to lower frequency region was estimated to be around $35.3 \text{ k}\Omega \text{ cm}^2$ (at 0.2 V) from the equivalent circuit shown in Fig. 5b, which was much larger than that of the interfacial transport of lithium ion between the organic liquid electrolyte and the pellet of $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass (2) estimated with a four-electrode cell to be around $0.9 \Omega \text{ cm}^2$. Therefore, the semi-circle observed in the three-electrode cell in the middle to lower frequency region was assigned to the interfacial charge-transfer of lithium ion between the pellet of $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass and the HOPG electrode (4).

3.2 Interfacial lithium-ion charge-transfer between $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass and ALD-modified-HOPG electrodes

To investigate the electrochemical behavior of interfacial lithium-ion charge-transfer between $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass and ALD-modified-HOPG electrodes, ALD- TiO_2 -HOPG and ALD-Oxidized-HOPG electrodes were prepared and used as working electrodes in the following electrochemical measurements.

Cyclic voltammograms obtained with the ALD-modified-HOPG electrodes are shown in Fig. 6. The reduction and oxidation current

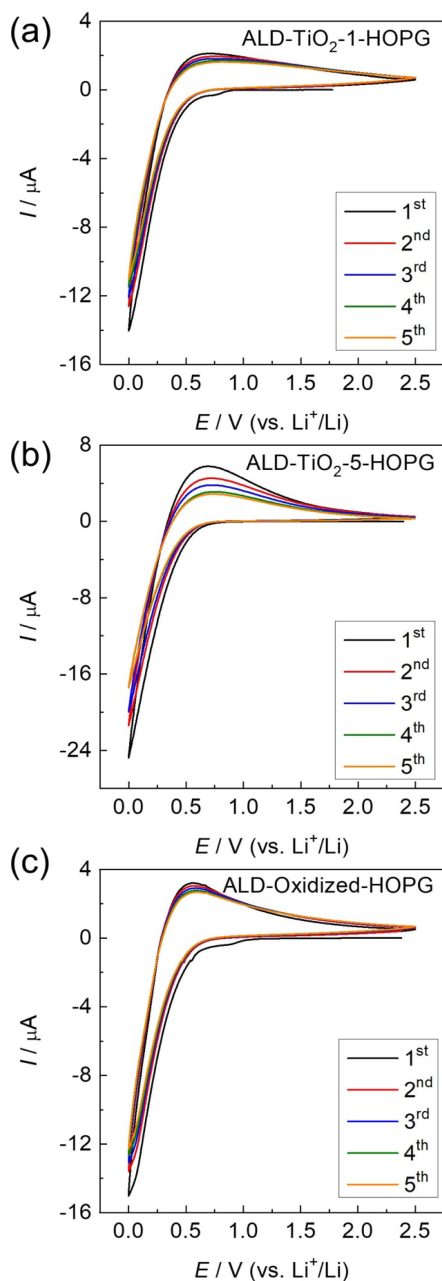


Figure 6. Cyclic voltammograms of three-electrode cells of (a) ALD-TiO₂-1-HOPG, (b) ALD-TiO₂-5-HOPG, and (c) ALD-Oxidized-HOPG.

peaks observed in the potential range between 0–0.6 V were assigned to lithium-ion intercalation and deintercalation to the ALD-modified-HOPG electrodes. The peak current of the reduction and oxidation current peaks of the ALD-modified-HOPG electrodes was much higher than that of the pristine HOPG electrode, indicating that the intercalation and deintercalation process could proceed smoothly at the interface between 75Li₂S-25P₂S₅ glass and the ALD-modified-HOPG electrodes and the reactivity of the basal plane of the HOPG electrodes might be enhanced through surface modification by the ALD method. These results were also consistent with the result that we reported at the interface between organic liquid electrolyte and ALD-modified-HOPG electrodes. Several factors, such as the diffusion of lithium ion in the electrolyte, and the number of active sites on the HOPG electrode, might influence the value of the peak currents. First, the organic liquid electrolyte and 75Li₂S-25P₂S₅ glass we used in each cell were the same, and

therefore, the activity of lithium-ion diffusion in the electrolyte should be almost the same. Second, the basal-plane of the HOPG electrode was cleaved with tape very carefully before use and the results obtained from the cyclic voltammograms were very repeatable, hence the difference in the number of edge-plane sites on each HOPG electrode before surface modification by ALD could be ignored. Here, we attribute the increase in the value of the current peaks in the cyclic voltammograms to the increase in the number of active sites on HOPG electrodes by ALD modification as well as the improvement in solid-solid contact between 75Li₂S-25P₂S₅ glass with the ALD-modified-HOPG electrodes compared to the pristine HOPG electrode.

According to the cyclic voltammograms for the pristine HOPG electrode as shown in Fig. 3, the oxidation current nearly disappeared after scanning for 5 cycles, suggesting the poor stability of the interface between pristine HOPG electrode and 75Li₂S-25P₂S₅ glass electrolyte. As for the cyclic voltammograms for the ALD-modified-HOPG electrodes as shown in Fig. 6, the current peaks kept relatively stable except for ALD-TiO₂-5-HOPG electrode. Because the deposition of TiO₂ layer was conducted with the temperature of substrate being set at a relatively low temperature of 200 °C, at which the deposited TiO₂ layer should be in an amorphous structure,³¹ which may be unstable during cycling. Besides, it is also well-known that the precursor of TEMAT for the deposition of TiO₂ often causes residual carbon, which might further cause dielectric degradation and side reactions³² so that the ALD-TiO₂-5-HOPG electrode would suffer obvious current fading during the scanning for 5 cycles. For ALD-TiO₂-1-HOPG electrode, the deposited TiO₂ layer was very thin compared to that of ALD-TiO₂-5-HOPG and the cycle number for ALD processing was only one, thus the negative influence of the TiO₂ layer on cycling stability might be hard to be observed.

AC impedance spectroscopy measurements were conducted to further discuss the kinetics of the interfacial lithium-ion charge-transfer between 75Li₂S-25P₂S₅ glass and ALD-modified-HOPG electrodes. The potential dependences of the Nyquist plots with the ALD-modified-HOPG electrodes are shown in Fig. 7. In the potential range of 1.5–0.8 V, a straight line with an angle of about 45° from the Z' axis was observed in the middle to lower frequency region, indicating that the intercalation and deintercalation of lithium ion did not occur at these potentials, which is consistent with the results with the pristine HOPG electrode. Similar to the results with the pristine HOPG electrode, a semi-circle in the frequency range of 1 Hz–100 mHz began to appear and was attributed to the interfacial lithium-ion charge-transfer between the pellet of 75Li₂S-25P₂S₅ glass and the ALD-modified-HOPG electrode when the potential was lower than 0.6 V. The diameter of the semi-circle decreased with a decrease in the potential. The value of R_{ct} at a potential of 0.2 V was estimated by fitting with an equivalent circuit and was chosen for comparison of the pristine and ALD-modified-HOPG electrodes. As a result, the value of R_{ct} decreased with either the surface deposition of TiO₂ or the surface oxidation of HOPG electrodes compared to the results with the pristine HOPG electrode, suggesting that a more conductive interface might be formed, and an increase in the number of active sites on the ALD-modified-HOPG electrodes compared to the pristine HOPG electrode might be brought about by the surface modification of HOPG electrodes by the ALD method, which is consistent with the discussion of the results in the cyclic voltammograms. The values of R_{ct} are summarized in Table S1 (Supporting Information).

At a certain potential, the value of R_{ct} varies according to the surface reactivity of the HOPG electrode. However, for the poor solid-solid contact of the interface between the pellet of 75Li₂S-25P₂S₅ glass and the HOPG electrode, the surface reactivity of the HOPG electrode might be greatly affected. Hence, it is not enough

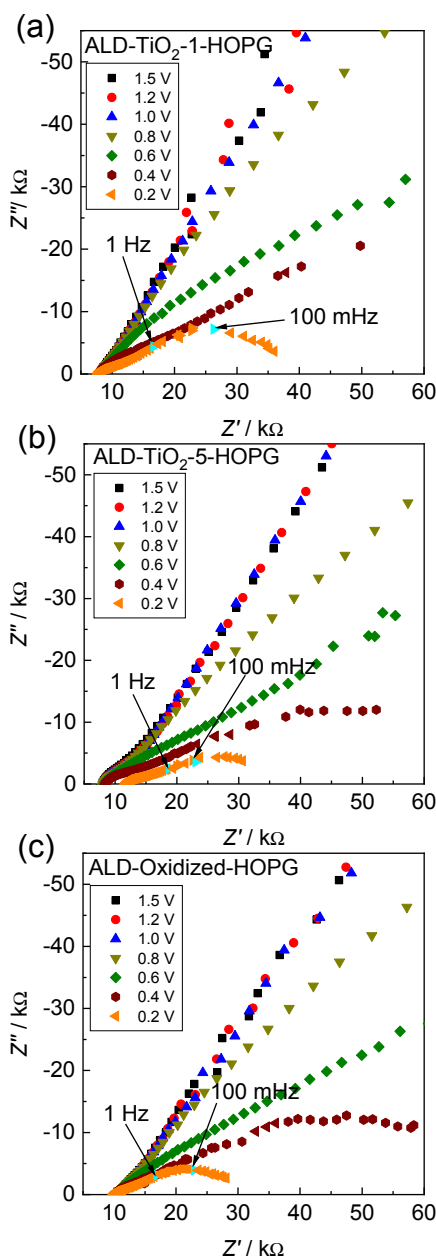


Figure 7. Potential-dependence of Nyquist plots: (a) ALD-TiO₂-1-HOPG, (b) ALD-TiO₂-5-HOPG, and (c) ALD-Oxidized-HOPG.

to evaluate the interfacial transfer of lithium ion by considering only the value of R_{ct} . To further evaluate the interfacial lithium-ion charge-transfer process without considering the surface reactivity, the activation energy (E_a) was calculated based on the temperature-dependence in the temperature range of 10–30 °C with an R_{ct} obtained from the fitting result of Nyquist plots at 0.2 V. The value of E_a was estimated from the slope of Arrhenius plots according to the Arrhenius equation, $1/R_{ct} = A \exp(-E_a/RT)$, where A , E_a , R , and T refer to the frequency factor, activation energy, gas constant, and absolute temperature, respectively.

As shown in Fig. 8, the activation energy of the interfacial charge-transfer of lithium ion between the pellet of 75Li₂S-25P₂S₅ glass and the pristine HOPG electrode was estimated to be around 37 kJ mol⁻¹. Compared to the value of E_a of around 50–60 kJ mol⁻¹ reported by our group for the interface between an organic liquid electrolyte and HOPG electrode,³³ the value of E_a for the lithium-ion transfer process at the interface between 75Li₂S-25P₂S₅ glass and the pristine HOPG electrode was much smaller, suggesting that

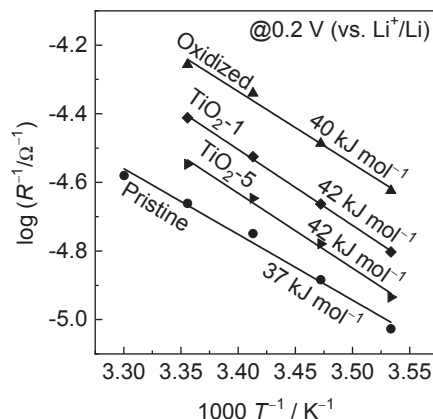


Figure 8. Temperature dependences of interfacial conductivities ($1/R_{ct}$) between 75Li₂S-25P₂S₅ glass and HOPG electrodes at 0.2 V.

interfacial lithium-ion transfer might proceed much faster at the interface between a HOPG electrode with 75Li₂S-25P₂S₅ glass than with organic liquid electrolyte. Hence, the rate-performance of LIBs with graphite as a negative electrode might be enhanced using 75Li₂S-25P₂S₅ glass instead of a traditional organic liquid electrolyte.

In addition, the value of E_a at the interface of 75Li₂S-25P₂S₅ glass and ALD-TiO₂-1-HOPG, ALD-TiO₂-5-HOPG, and ALD-Oxidized-HOPG was calculated to be 42, 42, and 40 kJ mol⁻¹, respectively. The value of E_a for the ALD-modified-HOPG electrodes was slightly higher than that of the pristine HOPG (37 kJ mol⁻¹).

4. Conclusion

Lithium-ion transfer at the interface between 75Li₂S-25P₂S₅ glass and graphite was studied by cyclic voltammetry as well as AC impedance spectroscopy measurements. The interfacial lithium-ion transfer between 75Li₂S-25P₂S₅ glass and a graphite electrode was found to be very rapid. By surface modification of graphite, we found that although the surface deposition of TiO₂ or surface oxidation of HOPG electrode might slow the interfacial lithium-ion transfer compared with pristine graphite, considering the activation energies, the interfacial lithium-ion charge transfer resistance could be clearly decreased by surface modification. The surface modification of graphite by ALD showed different properties between the interface with organic liquid electrolyte or 75Li₂S-25P₂S₅ glass, indicating different interfacial lithium-ion transfer kinetics between graphite and liquid electrolyte or 75Li₂S-25P₂S₅ glass.

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CRedit Authorship Contribution Statement

Danni Yu: Data curation (Lead), Writing – original draft (Lead)
 Meiqi Huang: Conceptualization (Lead)
 Yuto Miyahara: Methodology (Lead)
 Kohei Miyazaki: Writing – review & editing (Lead)
 Akitoshi Hayashi: Resources (Lead)
 Masahiro Tatsumisago: Resources (Lead)
 Takeshi Abe: Supervision (Lead), Writing – review & editing (Lead)
 Tomokazu Fukutsuka: Conceptualization (Lead), Supervision (Lead)

Data Availability Statement

The data that support the findings of this study are openly available under the terms of the designated Creative Commons License in J-STAGE Data listed in D1 of References.

Conflict of Interest

The authors declare no conflict of interest in the manuscript.

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