Direct Observation of Ion Concentration Distribution in All-Solid-State Rechargeable Battery Using *operando* X-ray Radiography and Silver-Ion Conductor

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**ABSTRACT**

To improve the performance of all-solid-state rechargeable batteries, it is important to understand the distribution behavior of carrier ions in electrolytes and electrodes. However, few methods are available for observing carrier ions directly inside an all-solid-state rechargeable battery because lithium, a common carrier ion, is a light element, making observing it directly difficult. In this study, the dynamic behavior of the reaction distribution of an all-solid-state rechargeable battery with a silver-ion solid electrolyte was investigated by using a high-energy X-ray radiography method. The use of silver ions improves the X-ray absorption contrast of carrier ion concentration because silver is a heavy element. In the solid electrolyte, no change in the concentration of carrier ions is detected. By contrast, in the composite electrode, a preferential reaction at the electrode/electrolyte interface is confirmed in the initial stages of charge and discharge. Although a change in the concentration of the solid electrolyte would be an advantage, reaction distribution in the composite electrode is one of the important issues from the viewpoint of practical application of high-energy-density, all-solid-state rechargeable batteries.

**Keywords**: All-Solid-State Battery, Solid Electrolyte, Reaction Distribution, *operando* X-ray Radiography

1. Introduction

All-solid-state rechargeable batteries are expected to be used widely owing to their safety, long lifecycles, and high energy densities. Historically, the ionic conductivity of the solid electrolytes used in all-solid-state batteries has been lower than that of the liquid electrolyte. Recently, in 2011, Kamaya, et al. reported a Li$_{10}$GeP$_2$S$_{12}$ (LGPS) solid electrolyte, which has a three-dimensional structure that exhibits a high ion conductivity of 12 mS cm$^{-1}$ at room temperature. In addition, in 2016, Kato, et al. reported that the lithium-ion conductor, Li$_{0.5}$Si$_{0.5}$P$_{1.5}$S$_{1.5}$C$_{3.0}$, has the highest lithium-ion conductivity, exceeding that of liquid electrolytes at room temperature.

However, it remains a challenge to exceed the performance of a liquid-type lithium-ion battery, primarily because of inadequate optimization of the processes of fabrication of the composite electrode structures and cell stacks used in all-solid-state batteries. To improve the performance of all-solid-state batteries at the cell level, it is important to not only enhance the ionic conductivity of the solid electrolyte but to also understand the reaction mechanisms peculiar to the solid electrolyte and composite electrode of an all-solid-state battery.

Regarding the characteristic mechanism of the battery cell, inhomogeneous concentration distribution of the carrier ion in the composite electrode and electrolyte in a conventional lithium-ion battery that employs a liquid electrolyte has been reported. The electrode of a lithium-ion battery is composed of active material, conductive carbon, and binder. The liquid electrolyte is poured into the porous space in the composite structure, which facilitates ion transport from the bulk electrolyte to the active material. In a direction perpendicular to the composite electrode, electrons are supplied from the current-collector side, and ions are supplied from the opposite separator side. Generally, because ionic conductivity is not relatively higher than electronic conductivity, the effective ionic conduction resistance is different along the depth direction of an electrode. Therefore, under charge-discharge in the high-rate condition, resistance distribution in the perpendicular direction becomes remarkable, and a reaction distribution occurs, which leads to a decrease in electrode utilization.

Moreover, another distribution phenomenon occurs in a conventional liquid electrolyte because the reported lithium-ion transport number is considerably lower than 1.0. In the presence of an electric field, mass transport in a liquid electrolyte is facilitated by migration and diffusion. In a cell during charging, an electric field that creates an ohmic potential gradient in the electrolytic solution causes electrophoresis, in which the resulting cations move toward the anode and anions move toward the cathode. While lithium ions are consumed in the reactions at the electrode, the anions do not react and remain near the electrode. Consequently, the concentration of cations increases near the cathode to maintain local electrical neutrality, inducing a salt concentration gradient in the electrolyte.

Krachkovskiy, et al. analyzed the distribution of salt concentration in an Li | 1 mol dm$^{-3}$ LiPF$_6$ (ethylene carbonate + dimethyl carbonate 1:1 v/v) | C cell via $^{7}$Li- and $^{13}$C-nuclear magnetic resonance (NMR). A concentration distribution of 0.78–1.27 mol dm$^{-3}$ along a perpendicular direction to plane of electrolyte between electrodes was observed in the 1 mol dm$^{-3}$ LiPF$_6$ liquid electrolyte. Because the conductivity of the organic electrolyte depends greatly on the salt concentration, the distribution of salt concentration influences the effective ionic resistance as well, resulting in a reaction distribution along a direction perpendicular to the composite electrode.
In the case of all-solid-state rechargeable batteries, the situation should differ drastically. The lithium-ion transport number of a lithium-ion solid conductor, such as Li$_2$S-P$_2$S$_5$ or Al-doped Li$_2$La$_2$Zr$_2$O$_12$, is 0.9999 or higher.\textsuperscript{15,16} Thus, the carrier ion concentration distribution does not exist in principle because only the lithium ion can move in a solid electrolyte. However, to the authors’ knowledge, there is no report on the direct measurement of carrier-ion concentration distribution in solid electrolytes during the charge-discharge of all-solid-state batteries in the literature.

Direct observation is difficult owing to the lightness of the lithium ion, which is generally difficult to detect. Although heterogeneous reaction of LiCoO$_2$ thin films at the nanoscale has been observed by \textit{operando} scanning transmission electron microscopy and electron energy-loss spectroscopy,\textsuperscript{17} the macroscopic reaction distribution phenomena in all-solid-state batteries has not been understood thus far. Observation of the solid electrolyte and composite electrode over hundreds of micrometers is necessary to understand the characteristic behavior of all-solid-state rechargeable batteries.

To detect the macroscopic diffusion phenomena occurring in an all-solid-state battery, synchrotron X-ray radiography was applied to an all-solid-state battery system with a silver-ion solid electrolyte, which is reportedly a superionic conductor.\textsuperscript{18} Because silver is a considerably heavier element than lithium, its diffusion behaviors in the electrolyte and electrode can be visualized based on changes in the transmittance of X-rays. The present study examines whether the concentration distribution of the carrier ion can be observed in the solid electrolyte and composite electrode of an all-solid-state rechargeable battery.

2. Experimental

2.1 Battery assembly

A silver-ion conductor, Ag$_6$I$_4$WO$_4$, was prepared as a solid electrolyte for all-solid-state silver batteries. Ag$_2$WO$_4$ and AgI powders were mixed using a molar at an atomic ratio of 1:4. Then, the mixture was pressed into pellets and sintered in an argon atmosphere at 280°C for 20 h. X-ray diffraction (XRD) analysis was performed using a diffractometer to confirm the crystal phase. The Ag composite electrode was prepared by mixing Ag powder (with a secondary particle size of approximately 50 µm) and the electrolyte in a weight ratio of 1:1. By using the electrolyte and electrode powder, symmetric Ag || Ag$_6$I$_4$WO$_4$ || Ag cells with a diameter of 10 mm were fabricated. Ag$_6$I$_4$WO$_4$ powder was pressed at 10 MPa in a ceramic tube. Then, the mixture of Ag powder and the electrolyte was poured on both sides of the pressed Ag$_6$I$_4$WO$_4$ pellet and pressed at 10 MPa. The loading density of Ag active material was 0.064 g cm$^{-2}$. Finally, the cells were assembled by fastening the assembly with screws tightened to a torque of 5 N m. AC impedance measurements by using the symmetric cell were performed at 5, 10, 15, 20 and 25°C at an amplitude of 10 mV and a frequency of 1 MHz to 0.1 Hz to calculate the ionic conductivity of the solid electrolyte.

Furthermore, the silver-ion transport number of the solid electrolyte was calculated using the Tubandt method.\textsuperscript{19} Figure S1 in the Supporting Information (SI) shows a schematic diagram of the cell used for calculating the transport number. In the cell considered for calculations with the Tubandt method, an Ag electrode as a source of silver-ions, three electrolyte pellets, and a Pt electrode as an ion-blocking electrode were stacked. A total charge of 0.18 C was applied galvanostatically to the stacked cell to initiate and sustain the Ag stripping and plating reactions on the Ag electrode and the Pt electrode, respectively. The weight change of each of the pellets after this reaction was measured, and the Coulomb efficiency at the Ag/Ag$_6$I$_4$WO$_4$ interface was obtained from the relationship between decrease in weight of Ag electrode and total charge. In the present study, we could confirm that the Coulomb efficiency was almost 100%, which indicated the absence of electrical conduction in the electrolyte. Furthermore, the ion transport number of the electrolyte can be calculated from the relationship between increase in Ag weight on the Pt electrode and the total charge.

2.2 Observation in electrolyte using X-ray transmission imaging method

To observe the ion concentration distribution in the electrolyte by means of X-ray radiography, a sliced Ag || Ag$_6$I$_4$WO$_4$ || Ag symmetric cell was fabricated. A pressed Ag$_6$I$_4$WO$_4$ electrolyte and Ag electrode pellets were sintered at 280°C for 20 h in an Ar atmosphere and, then, cut into approximately 250-µm-thick slices. The electrode part of the sliced symmetric cell was connected to a Ni wire by using Ag paste. Synchrotron X-ray radiography measurements were performed on BL33XU in SPring-8 (Japan, Hyogo). Transmission images of the charge-coupled device detector during current flow were acquired by using X-rays at 33 keV. The detection area was 1.3 × 1.3 mm, and the detection speed was approximately 1 s per image. Figure S2(a) in SI shows a schematic illustration of the experimental setup. Differential images were prepared to investigate the magnitude of change in X-ray transmission intensity from the initial state before charge/discharge. Figure S3 in SI shows the method of preparation of the difference images from the transmission images. The reference samples were prepared by mixing Ag$_2$I$_4$WO$_4$ powder, boron nitride, and silver powder. The quantity of silver powder in these samples varied (Ag$_6$I$_4$WO$_4$; x = 0, 0.06, 0.17, and 0.31). Each sample was pressed into a pellet with a diameter of 10 mm.

2.3 Observation of bulk-type all-solid-state rechargeable battery using X-ray transmission imaging method

To observe the ion concentration distribution in the bulk-type all-solid-state rechargeable battery, an Ag || Ag$_6$I$_4$WO$_4$ || TiTe$_2$ cell was fabricated. TiTe$_2$ purchased from Mitsuwa Chemicals Co., Ltd. was used as the cathode active material. A mixture of the active material, electrolyte, and acetylene black in a weight ratio of 10:10:1 was used as the cathode powder. The cylindrical cell was fastened with screws torqued to 10 cmN. The loading density of Ag and TiTe$_2$ active materials were 0.25 and 0.24 g cm$^-2$, respectively. For X-ray radiography, an Ag || Ag$_6$I$_4$WO$_4$ || TiTe$_2$ cylindrical cell with a diameter of 1 mm was used. An X-ray energy of 65 keV was employed. The detection speed of the detector was approximately 10 s per image. Figure S2(b) in SI shows a schematic illustration of the experimental setup.

3. Results and Discussion

3.1 Characterization of prepared solid electrolyte

Figure 1 shows the XRD pattern of the prepared Ag$_6$I$_4$WO$_4$ used in this study. The diffraction peaks were indexed in a monoclinic system, and the calculated lattice constants were $a = 16.74 \pm 0.04$ Å, $b = 15.52 \pm 0.04$ Å, $c = 11.81 \pm 0.03$ Å, $\alpha = \gamma = 90°$, and $\beta = 103.9°$. Although Ag$_6$I$_4$WO$_4$ has been reported to exhibit high conductivity,\textsuperscript{20,21} to the best of our knowledge, structure refinement analysis results for Ag$_6$I$_4$WO$_4$ have not been reported in the literature thus far. When compared with the results obtained for a similar composition Ag$_{25}$La$_{18}$WO$_{126}$,\textsuperscript{22} the present results agree well in terms of the XRD pattern and lattice constant.

Figure 2(a) shows a Nyquist plot prepared based on AC impedance measurements of the Ag || Ag$_6$I$_4$WO$_4$ || Ag symmetric cell at various temperatures. Because the semicircular component was not confirmed in the Nyquist plot and the plot produced a straight line with an inclination of about 45°, ionic conductivity was calculated using the intersection point with the horizontal axis. Thus, the calculated conductivity was 47.0 mS cm$^{-1}$ at 298 K. Figure 2(b) shows the Arrhenius plot of the ionic conductivity, and the
activation energy calculated from the slope of this straight line is 21.4 kJ mol$^{-1}$. These values are comparable to the conductivity and activation energy of Ag$_6$I$_4$WO$_4$ reported by Takahashi, et al.\textsuperscript{20} The conductivity value obtained in this study is slightly higher than the values obtained for lithium-ion conductors, such as the LGPS system\textsuperscript{3,4} and Li$_2$S–P$_2$S$_5$ glass ceramics.\textsuperscript{23} Moreover, the silver-ion transport number of the solid electrolyte evaluated using the Tubandt method was 0.99 ± 0.01, indicating pure silver-ion conduction in Ag$_6$I$_4$WO$_4$.

3.2 Ion concentration analysis in solid electrolyte

First, we investigated the detection limit of changes in the concentration of silver-ions in the electrolyte. Figure 3(a) shows X-ray radiography images of Ag$_{6+x}$I$_4$WO$_4$ reference samples ($x = 0, 0.06, 0.17, 0.31$). The contrast in these figures was set to be equal. As the concentration of silver increases, the intensity of the transmission images decreases. Figure 3(b) shows the average X-ray transmission intensity calculated from Fig. 3(a) as a function of silver concentration. Therefore, in this X-ray radiography measurement, silver-ion concentration changes of 1% in the electrolyte were detected.

Next, we examined changes in electrolyte concentration during the current flow by using the sliced symmetric Ag | Ag$_6$I$_4$WO$_4$ | Ag cell. Figures 4(a) and (b) show the X-ray radiography images before (0 s) and after charging for 60 s with a current density of 33.4 mA cm$^{-2}$, respectively. The left and right sides of the images correspond to the Ag electrodes; the current flowed in the direction.
The left and right sides show silver electrodes. (c) Di and con reported by Y.G. Guo, et al. The crystal structure of TiTe$_2$ was observed during charging for 60 s at a current density of 33.4 mA cm$^{-2}$.

The concentration of the electrolyte changed linearly from 0.78 to 1.28 mol dm$^{-3}$ under a current density of 0.9 mA cm$^{-2}$. The signal became noisy when using the silver-ion solid electrolyte. The apparent concentration change in the electrolyte was not observed. This change corresponds to an approximately 20% increase in the concentration. By contrast, in the silver-ion solid electrolyte used in this study, we employed TiTe$_2$ as the cathode active material.

Figure 4 shows the X-ray radiography images of sliced symmetric Ag | Ag$_2$I$_4$WO$_4$ | Ag cell before charging (0 s) (a) and during charging for 60 s at a current density of 33.4 mA cm$^{-2}$ (b). The left and right sides show silver electrodes. (c) Differential plot of X-ray transmittance during current flow at a position along the direction perpendicular to the electrode as the horizontal axis.

Figure 5 shows the results of the X-ray radiography during the charging cycle of an Ag | TiTe$_2$ | Ag$_2$I$_4$WO$_4$ | Ag cell at a current density of 10.4 mA cm$^{-2}$ (corresponding to the 1 C rate). Figure 5(a) shows the charge curve during the measurements, and Figs. 5(b)–(g) show the differential X-ray transmission images obtained at each point. The left and right sides show the Ag, TiTe$_2$, and Ag electrodes, respectively. In terms of the charging reactions, Ag, TiTe$_2$ becomes bright, which is related to the extraction of silver ions. By contrast, the black shadows originate from the silver electrode on the electrolyte side due to the plating and growth of silver from the anode.

Figure 6 shows the differential changes in X-ray transmittance at each time during charging. The increase in X-ray transmission on the cathode side is due to the extraction of silver ions from the cathode. By contrast, the slight increase that occurred in this study was observed at the end of charging for 1000 s. This was presumed to be caused by mechanical distortion of the electrolyte due to slight changes in the positions of both electrodes and the growth of silver metal in the electrolyte.

Finally, we focused on the reaction distribution of the cathode part using a TiTe$_2$ | Ag$_2$I$_4$WO$_4$ | Ag cell. Figure 7(a) shows the discharge curve of the cell at a current density of 2.1 mA cm$^{-2}$ during X-ray radiography measurements, and Figs. 7(b)–(g) show the differential X-ray transmission images at each point in Fig. 7(a). As the discharge reaction progressed, a decrease in X-ray transmittance due to insertion of silver into the cathode could be confirmed. Figure 8 shows the differential changes in X-ray transmittance during discharge.

At the start of discharge, the transmission intensity on the cathode side decreased near the interface with the electrolyte. This phenomenon indicates that a preferential reaction at the cathode/electrolyte interface occurred during discharge. This reaction distribution relaxed gradually in the subsequent discharge and disappeared at approximately 2000 s. The change in X-ray intensity on the electrolyte side near the cathode/electrolyte interface exhibited spiked behavior because of changes in the electrode position due to volume expansion of the active material.

As described above, during charging and discharging, a remarkable ion concentration distribution does not occur in the electrolyte of the all-solid-state rechargeable battery. This feature helps realize a thicker composite electrode than that of the conventional lithium-ion battery because conductivity distribution in the perpendicular direction due to changes in concentration does in which silver stripping occurred at the left electrode, and the plating occurred on the right side. In Fig. 4(b), the dark area on the right side denotes plating of the silver after the flow of current.

The differential plot of X-ray transmittance during current flow is shown in Fig. 4(c), with the positions in the direction perpendicular to the electrode shown as the horizontal axis. During current flow, the apparent concentration change in the electrolyte was not observed, even though the signal became noisy. When using the solid electrolyte, the ion concentration distribution was observed under a current density of 0.9 mA cm$^{-2}$ in the electrolyte (i.e., the salt concentration changed linearly from 0.78 to 1.28 mol dm$^{-3}$). This change corresponds to an approximately 20% shift in the salt concentration. By contrast, in the silver-ion solid electrolyte used in this study, such a concentration distribution with a uniform slope was not observed. The concentration detection resolution of this measurement was 1%; therefore, no change in ion concentration in the electrolyte during current flow was demonstrated. The transition to noisy X-ray transmittance started post the position change of the electrolyte due to the growth of the silver metal.

3.3 Ion concentration change in bulk-type all-solid-state battery

Ion concentration change was studied in both the composite electrode and electrolyte for the bulk-type all-solid-state battery configuration. Titov et al. reported the electrochemical reaction between Ag and TiTe$_2$ at 400 K. Based on the potential-composition profile of Ag$_x$TeTe$_2$ and XRD measurements, the following reaction formula can be expressed:

\begin{align}
\text{TiTe}_2 + \frac{1}{2} \text{Ag}^+ &\rightleftharpoons \text{Ag}_x\text{TiTe}_2 \\
\text{Ag}_x\text{TiTe}_2 &\rightleftharpoons \frac{1}{4} \text{Ag}^+ + \frac{3}{4} \text{Ag}_x\text{TiTe}_2 \\
\text{Ag}_x\text{TiTe}_2 &\rightleftharpoons \frac{1}{2} \text{Ag}^+ + \frac{3}{2} \text{Ag}_x\text{TiTe}_2
\end{align}

When these reactions have progressed completely, the theoretically gravimetric capacity of TiTe$_2$ is 88 mA h g$^{-1}$. Guo et al. reported that charge/discharge reaction at room temperature was possible with the TiTe$_2$ cathode and silver-ion solid electrolyte. Therefore, in this study, we employed TiTe$_2$ as the cathode active material.

Figure 5 shows the X-ray radiography during the charging cycle of an Ag | TiTe$_2$ | Ag$_2$I$_4$WO$_4$ | Ag cell at a current density of 10.4 mA cm$^{-2}$ (corresponding to the 1 C rate). Figure 5(a) shows the charge curve during the measurements, and Figs. 5(b)–(g) show the differential X-ray transmission images obtained at each point. The left and right sides show the Ag, TiTe$_2$, and Ag electrodes, respectively. In terms of the charging reactions, Ag, TiTe$_2$ becomes bright, which is related to the extraction of silver ions. By contrast, the black shadows originate from the silver electrode on the electrolyte side due to the plating and growth of silver from the anode.

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not occur in the solid electrolyte. However, a preferential reaction at the electrode/electrolyte interface is observed, which is similar to the phenomenon observed in a lithium-ion battery. The preferential reaction is caused by the lower ionic conduction of the composite electrode as opposed to electronic conduction. Even in all-solid-state batteries, the ionic conduction in the composite electrode limits the electrode thickness and, therefore, the performance of all-solid-state rechargeable batteries. The ion concentration behavior can be related to current density, electrode thickness, porosity, and other factors. Further research should be conducted by varying these conditions to understand the mechanism of all-solid-state secondary batteries.
4. Conclusion

The ion concentration distribution phenomena in the electrolyte and the composite electrode of an all-solid-state silver-ion battery as a model system were examined using X-ray radiography. Ion concentration distribution in the solid electrolyte with an ionic transport number of 1 does not occur during current flow. This feature can increase the thickness of the composite electrode relative to that of lithium-ion batteries, which employ an organic liquid electrolyte. However, in the process of charging and discharging, a preferential reaction in the composite electrode at the electrode/electrolyte interface occurs as it does in lithium-ion batteries. Ion conduction in the composite electrode is an important factor limiting the electrode thickness of the all-solid-state rechargeable battery.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-00011.

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