Electrochemical analysis of the charge transfer reaction at the interface between sulfide-based solid electrolyte and positive electrode material with microelectrodes

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Introduction

All-solid-state batteries are considered as important candidate of post lithium ion batteries, because of its high safety and possibility for the use of Li metal negative electrode. Resent investigations about inorganic solid electrolyte realized sulfide-based solid electrolytes like $Li_2S-P_2S_5$ which shows high conductivity, wide potential window and non-flammability, so the performance of all-solid-state batteries improved dramatically during recent years [1]. For more progress of all-solid-state batteries, investigation of the charge transfer reaction at the interface between solid electrolyte and the electrode is important.

Previously we have studied about the charge transfer reaction at the interface between solid electrolyte and Li metal electrode and it was suggested that activation energy for the charge transfer reaction (E_a) between solid electrolyte and Li metal electrode is smaller than that between organic electrolyte and Li metal electrode due to the lack of the desolvation step[2]. However, the charge transfer reaction between solid electrolyte and the positive electrode material has not been obtained yet.

In this study, we investigated the microelectrode techniques to measure the E_a of charge transfer reaction at the interface between solid electrolyte and positive electrode materials. We attached the $LiNbO_3$-coated $LiCoO_2$ on Ni microelectrode and realized direct electrical bonding to $LiNbO_3$-coated $LiCoO_2$. This method can realize binder and conducting agent free electrochemical cells and makes it possible for us to measure the true E_a of charge transfer reaction.

Experimental

$Li_2S-P_2S_5$ solid electrolyte powders were prepared with Li_2S and P_2S_5 powder by mechanical milling technique[1]. In this study, $LiNbO_3$-coated $LiCoO_2$ was used as positive electrode materials because $LiNbO_3$ coating layer prevent the formation of a highly resistive layer, which is formed by Co diffusion from $LiCoO_2$ to sulfide electrolyte. The solid electrolyte powder was pelletized and sandwiched with $LiNbO_3$-coated $LiCoO_2$ as working electrode (WE) attached on φ50 μm Ni microelectrode by just pressing Ni electrode to $LiCoO_2$ particle and Li metal sheet was attached on the opposite side as counter and reference electrode (CE/RE). All procedure was executed in Ar-filled glove box.

Before performing electrochemical measurements, this cell was charged at SOC 50 %. In potential step method, the potential was stepped to 0, -10, +10, -20, +20 mV until the potential reached at ±300 mV (vs. OCV). Each potential was held for 5 s. Subsequently, micro-polarization method was performed. In this method, the potential was scanned from -20 to +20 mV (vs. OCV). All measurements were performed at various temperatures.

Results and discussions

To evaluate i_0, the steady-state current (i) measured at each overpotential (η) by potential step method was inserted into Allen-Hickling equation (1).

$$\ln\left[\frac{i}{1-\exp\left(\dfrac{F\eta}{RT}\right)}\right] = \ln i_0 - \frac{\alpha F}{RT}\eta \qquad (1)$$

where F is the Faraday constant, R is the gas constant, T is the absolute temperature and α is the transfer coefficient.

Fig. 1 shows Allen-Hickling plots by potential step method at various temperatures. All plots exhibited a linear relationship in the η range from -80 to +80 mV. From the intercept of each plot, i_0 was evaluated and then i_0 were plotted vs. the reciprocal of absolute temperature to calculate E_a using the following equation (2).

$$\ln i_0 = \ln A - \frac{E_a}{RT} \qquad (2)$$

where A is the frequency factor.

i_0 were also evaluated from micro-polarization method. In the small η range, i obeyed the following equation (3).

$$i = \left(\frac{F i_0}{RT}\right)\eta \qquad (3)$$

Fig. 2 shows Arrhenius plots of i_0 obtained from potential step method and micro-polarization method. We successfully measured the E_a of charge transfer reaction at the interface between solid electrolyte and positive electrode materials and the E_a calculated by potential step method is about 48 kJ mol^{-1}, which is almost the same as that by micro-polarization method.

Reference

1) A. Hayashi et al., J. Am . Ceram. Soc., **84**, 477 (2001).
2) M. Chiku et al., Electrochemistry, **80**, 740 (2012).
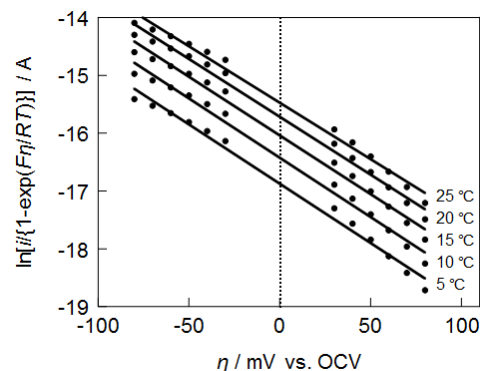
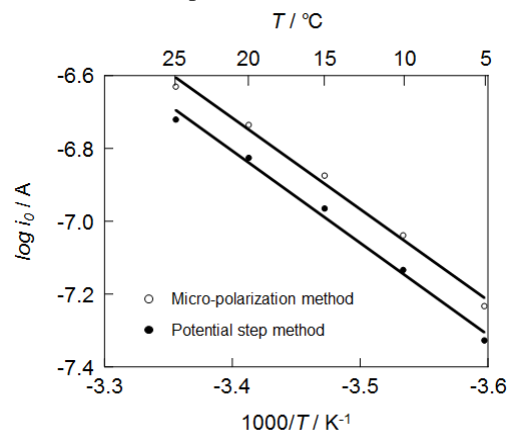Fig. 1 Allen-Hickling plots for the redox reaction of $LiCoO_2$ at various temperatures.

Fig. 2 Arrhenius plots of i_0 obtained from potential step method and micro-polarization method.