Li^+ and Na^+ transfer through interfaces between inorganic solid electrolytes and polymer or liquid electrolytes

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Abstract

Li^+-ion and Na^+-ion transfer at interfaces composed of inorganic solid electrolytes and polymer or organic liquid electrolytes were compared. $La_{0.55}Li_{0.35}TiO_3$ and $Na_3Zr_{1.88}Y_{0.12}Si_2PO_{12}$, which are conductive for Li^+ and Na^+, were selected for use as inorganic solid electrolytes. PC solution and PEO-based polymer electrolytes were added to Li salt or Na salt to give ionic conductivity. Using these electrolytes, solid electrolyte/liquid electrolyte or solid electrolyte/polymer electrolyte interfaces were constructed. The resistivities of Li^+ or Na^+ transfer through these interfaces were estimated based on the results of ac impedance measurements. In both solid/liquid and solid/polymer systems, the activation energies of Na^+-ion transfer at the interface were smaller than those of Li^+-ion. The Lewis acidity of both ions, Li^+ and Na^+, clearly explains this difference and supports the idea that the interaction between ion and solvents plays a major role in interfacial ion-transfer processes.
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1. Introduction

Lithium-ion batteries are widely used in portable electronic devices, such as cellular phones, notebook computers, and camcorders due to their high energy densities. Recently, lithium-ion batteries have attracted much attention for their use in hybrid electric vehicles (HEV) [1,2] and cordless electric tools.

These new fields of application require high power. To satisfy these high power requirements, lithium-ion batteries must have rapid charge and discharge properties. It is important that we understand the kinetics of the reactions in lithium-ion batteries to enhance the reaction rate. We have previously clarified the importance of lithium-ion transfer in these batteries [3,4]. This process can be divided into three steps: ion transfer inside the electrode materials, ion transfer in the electrolytes and ion transfer through the interface between the electrode materials and electrolytes. Among these, lithium-ion transfer at the interface can be the rate-limiting step in some cases where thin film-type electrodes or active materials of fine powders and a very thin electrolyte phase of fairly high ionic conductivity are used. The uncertainty regarding the effective surface area used in composite electrodes and the redox reactions of active materials in the solid phase caused by battery reactions has impaired the detailed analysis of interfacial ion transfer. To avoid these difficulties, interfaces between inorganic solid electrolyte and liquid or polymer electrolyte were constructed, where only lithium-ion transfer occurs.

We previously reported ion transfer through an inorganic solid electrolyte/polymer electrolyte interface, and found a large activation barrier for the reaction [3]. This large activation barrier was ascribed to the de-solvation of lithium ion at the interface between thin-film electrodes and the electrolyte solution [3,4].

In this work, interfacial lithium-ion transfer was compared to sodium-ion transfer inorganic solid electrolyte/liquid electrolyte or polymer electrolyte interfaces, which are conductive for Na^+. The Lewis acidity of Na^+-ion is weaker than that of Li^+-ion and the interaction between Na^+ and Lewis

base, solvent and polymer, is weaker than that with Li^+. This difference may influence interfacial ion transfer.

2. Experimental

Lanthanum lithium titanate (LLT) and Na^+-ion super conductor (NASICON) were selected as lithium-ion and sodium-ion conductors, respectively. $La_{0.55}Li_{0.35}TiO_3$ and $Na_3Zr_{1.88}Y_{0.12}Si_2PO_{12}$ were prepared by the traditional solid state reaction [6,7]. Polymer electrolytes ($LiCF_3SO_3$-PEO and $NaCF_3SO_3$-PEO) were prepared by an ordinary casting method [8]. Poly-(ethylene oxide) ($M_w = 400,000$ Aldrich) was used as a polymer matrix and $LiCF_3SO_3$ (Kishida Chemical) or $NaCF_3SO_3$ (Aldrich) as solute. The ratio of ethylene oxide unit (EO) to metal-cation (M^+) was maintained at $EO/M^+ = 20$.

2.1. Interfaces between inorganic solid electrolyte and liquid electrolyte

Interfaces between solid and liquid electrolytes were constructed using the cell depicted in Fig. 1. For lithium-ion transfer systems, LLT and propylene carbonate (PC) (Kishida Chemical) containing $1\,mol\,dm^{-3}$ $LiCF_3SO_3$ were used. For sodium-ion transfer systems, NASICON and PC containing $0.05\,mol\,dm^{-3}$ $NaCF_3SO_3$ were used. The geometric interfacial area was about $0.20\,cm^2$. Four-electrode ac impedance measurements were performed over the frequency range from 0.1 to 1 MHz at an applied potential of 30 mV. Electrodes for the ac current and reference electrode were Li metal for the LLT/PC system and Pt wire for the NASICON/PC.

2.2. Interfaces between inorganic solid electrolyte and polymer electrolyte

Interfaces between solid and polymer electrolytes were formed by piling up the polymer and solid electrolytes (end electrode/polymer electrolyte/solid electrolyte/polymer electrolyte/end electrode) as described in a previous report [3]. The geometric interfacial area was about $0.95\,cm^2$. The two end electrodes were Li metal for the lithium-ion system and SUS for the sodium-ion system. To obtain well-contacted
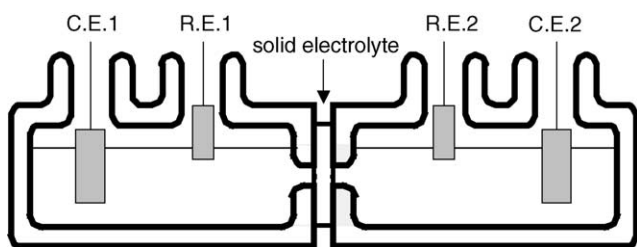
interfaces, the cell was kept at 353 K for 1 day, and then cooled to 333 K prior to measurements. Two-electrode measurements were conducted.

The cell-assembly and electrochemical measurements were conducted in an Ar-filled dry box, in which the dew point was kept under $-60\,°C$.

3. Results and discussions

Fig. 2(a) shows the ac impedance spectrum of Li/PC/LLT/PC/Li at 303 K. Two semi-circles were clearly observed with characteristic frequencies of about 1 kHz and 10 Hz. This spectrum must include three different impedance components: that due to ion transfer in the electrolyte solu-
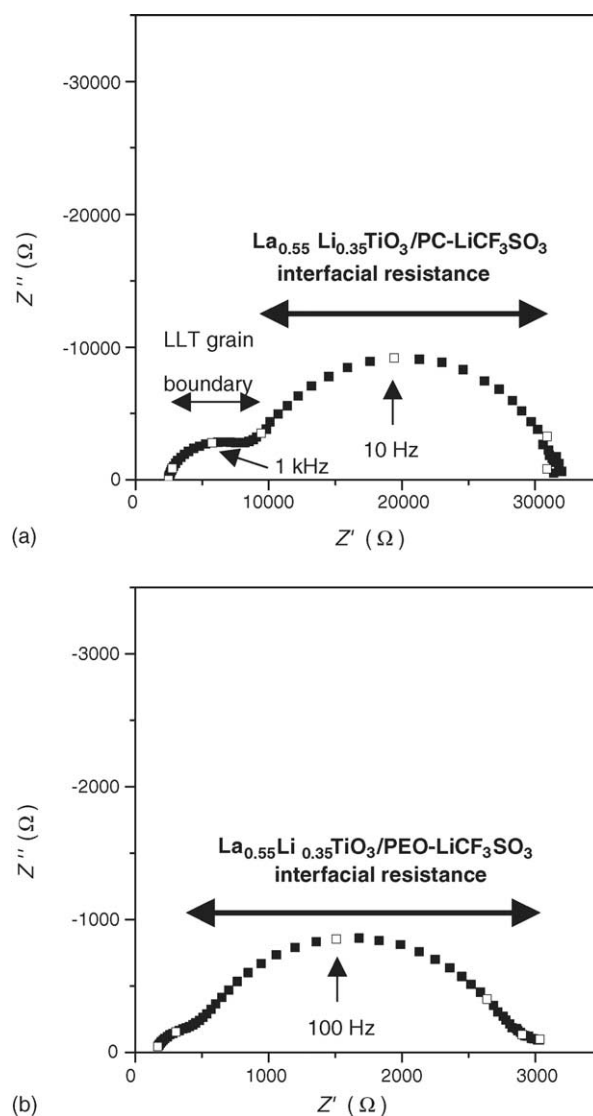

Fig. 2. Complex impedance plots of (a) Li/$1\,mol\,dm^{-3}$ $LiCF_3SO_3$-PC/LLT/$1\,mol\,dm^{-3}$ $LiCF_3SO_3$-PC/Li ($S = 0.20\,cm^2$, four-electrode, 303 K) and (b) Li/PEO-$LiCF_3SO_3$/LLT/PEO-$LiCF_3SO_3$/Li ($S = 0.95\,cm^2$, two-electrode, 303 K).

Fig. 1. Schematic diagrams of the four-electrode-electrochemical-cell for solid/liquid interface.
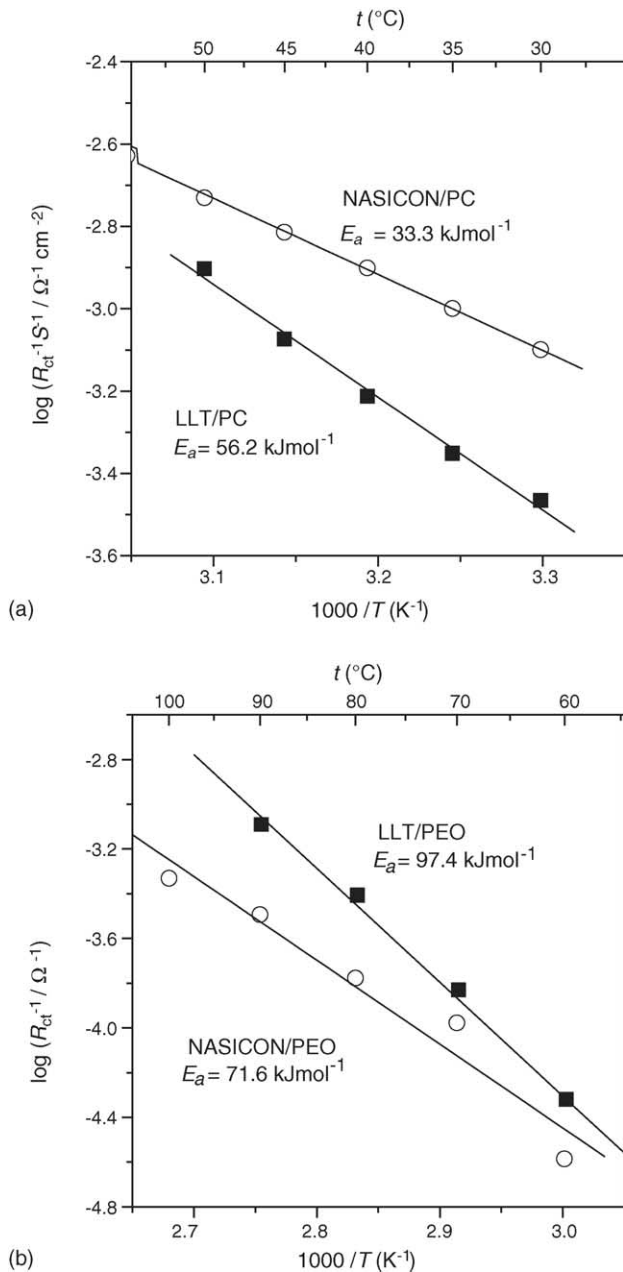
(a)

(b)

Fig. 3. Temperature-dependence of interfacial resistance for (a) solid/liquid and (b) solid/polymer electrolytes. Closed squares and opened circles represent the Li$^+$-ion and Na$^+$-ion systems, respectively.

tion, that due to ion transfer in the solid electrolyte, and that due to ion transfer at the interfaces between LLT and PC. Note that charge transfer resistance at the, Li/PC interface does not appear due to the use of four-electrode measurements. Among these impedance components, ion transfer resistance in the electrolyte solution generally appears at a frequency region higher than 1 MHz, and can be neglected here. The lithium-ion transfer in LLT was investigated separately using a Au/LLT/Au cell. Two semi-circles were observed, one with a characteristic frequency of about 1 kHz and another at a higher frequency region above 100 kHz and with a lower re-

sistivity than the former. The former was ascribed to the grain boundary resistance and the latter to the bulk resistance of LLT. This analysis permits us to reasonably assign the semi-circle in Fig. 2(a) with a characteristic frequency of 1 kHz to the grain boundary resistance of LLT, while the bulk resistance of LLT is not observed, and to assign the semi-circle in the lower frequency range to the charge transfer resistance at the solid electrolyte/liquid electrolyte interface.

Fig. 2(b) shows the impedance spectrum of Li/LiCF$_3$SO$_3$-PEO/LLT/LiCF$_3$SO$_3$-PEO/Li at 353 K. The semi-circle with a characteristic frequency of 100 Hz was ascribed to lithium-ion transfer at the LLT/polymer electrolyte interface according to our previous report [3].

The charge transfer resistance values for sodium-ion at the NASICON/PC and NASICON/LiCF$_3$SO$_3$-PEO interfaces were estimated in the same manner as descried above for lithium-ion transfer.

Fig. 3 (a) and (b) show the temperature-dependencies of the interfacial resistances for solid electrolyte/liquid electrolyte and solid electrolyte/polymer electrolyte, respectively. Arrhenius-type behaviors were observed in all of the systems examined. The activation energies of ion transfer were calculated for the four systems from the slopes of their linear relationships: 56.2 kJ mol^{-1} for LLT/PC, 33.3 kJ mol^{-1} for NASICON/PC, 97.4 kJ mol^{-1} for LLT/polymer, and 71.6 kJ mol^{-1} for NASICON/polymer system.

There are two important points regarding these activation energies. First, lithium-ion transfer requires higher activation energy than sodium-ion transfer in both PC and polymer systems. Second, polymer electrolyte gives higher activation energy than organic solution for both lithium-ion transfer and sodium-ion transfer. Since the activation energy is ascribed to a de-solvation process, as clarified previously [4], the former result is very reasonable; the solvation energy for lithium-ion is higher than that for sodium-ion. The stronger Lewis acid, Li$^+$, interacts more strongly with the oxygen of PC and PEO than Na$^+$. A detailed theoretical calculation to explain the difference in the activation energy values is now in progress. The latter results agree well with our previous work [4,5]. These results mean that polymer electrolyte gives a higher activation barrier for interfacial cation transfer than PC and that polymer electrolyte is inferior to liquid electrolyte for enhancing the rate performance of lithium-ion batteries.

4. Conclusions

Lithium-ion and sodium-ion transfer through interfaces between inorganic solid electrolyte/electrolyte solution and inorganic solid electrolyte/polymer electrolyte were studied by the ac impedance method. The charge transfer resistance at the interface due to ion transfer was observed. For both the solid/liquid and solid/polymer interfaces, the activation energy for sodium-ion transfer was smaller than that for lithium-ion. This difference can be explained based on the Lewis

acidity of the alkali ions, i.e., the strength of the interaction of cations with the Lewis base of the solution or polymer electrolyte. The results also indicate that it may be possible to give lithium-ion batteries high rate performance by lowering the interaction between the lithium-cation and Lewis base in electrolytes.

Acknowledgements

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