# Lithium Ion Transfer at Electrolyte/Electrolyte Interface -Design of Highly Conductive Composite Electrolyte-

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Lithium ion transfer at interface between lithium ion conductive ceramic of  $La_{0.55}Li_{0.35}TiO_3$  (LLT) and polymer electrolyte of polyethylene oxide (PEO) complexed with LiCF<sub>3</sub>SO<sub>3</sub> (PEO-LiCF<sub>3</sub>SO<sub>3</sub>) was studied by an AC impedance spectroscopy for the system of Li / PEO-LiCF<sub>3</sub>SO<sub>3</sub> / LLT / PEO-LiCF<sub>3</sub>SO<sub>3</sub> / Li. The impedance ascribed to ion transfer through the interface was observed. The resistance due to the lithium ion transfer at the interface was larger than those through phases of LLT and PEO-LiCF<sub>3</sub>SO<sub>3</sub>, and the temperature dependence of the interfacial resistances was larger than those for lithium ion conduction in LLT and PEO-LiCF<sub>3</sub>SO<sub>3</sub>. The design of ion-conductive ceramic and polymer composite electrolytes is discussed based on the results.

Key words: polymer electrolyte, composite electrolyte, lithium ion transfer, interface

## 1. INTRODUCTION

polymer Solid electrolytes have been extensively studied since Wright et al. [1] reported that complex of alkali metal salts and poly(ethylene oxide) (PEO) exhibited good ionic conductivity. Solid polymer electrolytes have been received much attention for practical use of lithium ion batteries due to advantages such as high energy density, safety, and easv manufacturing as compared with the present commercialized lithium ion batteries using liquid electrolytes. However, low ionic conductivity and small lithium ion transference number of polymer electrolytes are serious problems to be solved for employing solid polymer electrolytes in commercial lithium ion batteries.

Many approaches have been done to enhance the ionic conductivities and transference number [2-10]. F. Croce et al. [11] reported that the polymer electrolytes containing nanometer-sized ceramic powders of  $TiO_2$  and  $Al_2O_3$  showed high and stable conductivity at moderate temperatures and also high lithium ion transference number. H. Y. Shu et al. [12] showed that the addition of ferroelectric materials as a ceramic filler into polyethylene oxide complexed with various lithium salt enhanced the ionic conductivity at lower temperatures and that interfacial resistance between lithium metal and polymer electrolyte decreased.

The above approaches should be based on the Lewis acid-base reactions between lithium salt and surface of ceramic filler, and the high ionic conduction path may be created near the ceramic surface [13].

K. Nairn et al. [14] used the highly ionically conductive ceramic to prepare polymer-ceramic composite electrolytes. Several studies using ion-conductive ceramics mixed with polymer electrolytes have been made. However, drastic enhancement of ionic conductivity has not been observed as compared with the polymer electrolytes. Polymer-highly ionically conductive ceramic composite electrolytes offer three ion conduction paths; 1) conduction solely through polymer electrolyte, 2) conduction in polymer electrolyte near the ceramic surface, and 3) conduction through ceramic electrolyte. When lithium ion moves through ceramic electrolyte in the composite electrolytes, lithium ion has to transfer across the interface between polymer and ceramic electrolytes. Therefore, the activation energy for lithium ion transfer at interface influences on the total ionic conductivity of composite electrolytes. Note that ceramic electrolytes should possess higher ionic conductivity than polymer electrolytes in this case. For the design of highly ionically conductive composite electrolytes using highly ionically conductive ceramic, lithium ion transfer at interface between polymer and ceramic electrolytes should be focused. However, little work has been done on this matter so far.

In this work, lithium ion transfer at interface between high lithium ion conductive ceramic of  $La_{0.55}Li_{0.35}TiO_3$  (LLT) and poly(ethylene) oxide (PEO) complexed with LiCF<sub>3</sub>SO<sub>3</sub> was studied by AC impedance spectroscopy.

## 2. EXPERIMENTAL

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LLT was prepared from reagent grade of La<sub>2</sub>O<sub>3</sub>,  $Li_2CO_3$ , and  $TiO_2$  (molar ratio of 11 : 40 : 7). A mixture of the powder was calcined at 800 °C and then at 1150 °C for given times. The calcined powder was pressed into pellet, which was sintered at 1250 °C. The pellet was polished and processed to give 1.0 mm thickness and 12 mm diameter. The detailed experimental procedure was followed by the previous literature reported by Inaguma et al. [15]. The resultant sample was characterized by X-ray diffraction (Rint 2200, Rigaku). PEO (Mw = 400,000) and LiCF<sub>3</sub>SO<sub>3</sub> were employed to prepare polymer electrolyte (PEO-LiCF<sub>3</sub>SO<sub>3</sub>) of 100 µm thickness and 13 mm diameter by using a normal casting method. Ratio of ethylene oxide unit to Li was kept at 20. Ionic conductivity of both ceramic and polymer electrolytes was measured by AC impedance spectroscopy (Solartron 1255) over the frequency region from 100 kHz to 10 mHz. To differentiate bulk and grain-boundary impedances of LLT, a wide frequency region from 10 MHz to 5 Hz using HP4192 was employed for measurement of bulk conductivity of LLT. Measurements of ionic conductivity for LLT were done by use of gold electrode, which was sputtered onto LLT, over the temperature range from 303 to 373 K. For polymer electrolytes, stainless steel disk or lithium metal was employed as electrodes.

Symmetrical cell of Li/ PEO-LiCF<sub>3</sub>SO<sub>3</sub>/Li was fabricated to investigate lithium ion transfer across the interface between PEO-LiCF<sub>3</sub>SO<sub>3</sub> and LLT. To make a good contact between PEO-LiCF<sub>3</sub>SO<sub>3</sub> and LLT, the symmetrical cell was pressed under heating at 353 K. Interfacial resistance was measured by AC impedance spectroscopy over the frequency region from 100 kHz to 10 mHz at various temperatures of 303 to 363 K.

#### 3. RESULTS AND DISCUSSION

XRD pattern of resultant LLT was in good agreement with the previous literature [15], and LLT possesses a cubic system in a primitive cell with a perovskite structure.

In Figs. 1(a) and 1(b) are shown cole-cole plots for cell of Au / LLT / Au at 303 K. Figure. 1(a) and Figure 1(b) show impedances which are ascribed to grain boundary and bulk resistances of LLT, respectively. The temperature dependence of ionic conductivity for bulk and grain boundary of LLT is shown in Fig. 2. Temperature dependence of ionic conductivity for PEO-LiCF<sub>3</sub>SO<sub>3</sub> is also plotted in the same figure for comparison. Lines were drawn by least squares fitting. The activation energies for bulk and grain boundary resistances of LLT were evaluated from the slopes in Fig. 2 to be 28.3 and 36.4 kJ mol<sup>-1</sup>, respectively. Inaguma et al. [16] reported the activation energy of bulk part of LLT to be 0.34 eV (32.9 kJ mol<sup>-1</sup>), and hence the present value seems valid.

Figure 3 shows a cole-cole plot for the symmetrical cell of Li / PEO-LiCF<sub>3</sub>SO<sub>3</sub> / LLT /







Fig.2. Temperature dependence of ionic conductivity for LLT bulk, LLT grain boundary, and PEO-LiCF<sub>3</sub>SO<sub>3</sub>.

PEO-LiCF<sub>3</sub>SO<sub>3</sub> / Li at 353 K. As is obvious from Fig. 3, two semi-circles are observed. Characteristic frequencies of both impedances are



Fig.3. Cole-cole plot for electrolyte / electrolyte interface of Li / PEO-LiCF3SO3 / La0.55Li0.35TiO3 / PEO-LiCF3SO3 / Li at 353 K. Numbers on the circles denote the values obtained by the legalisms of frequencies.

denoted in the figure as 10 kHz and 100 Hz. The symmetric al ce ll gives the following resistances as 1) interfacial resistance between Li / PEO-LiCF<sub>3</sub>SO<sub>3</sub>, 2) bulk resistance of PEO-LiCF<sub>3</sub>SO<sub>3</sub>, 3) interfacial resistance due to lithium ion transfer at interface between PEO-LiCF<sub>3</sub>SO<sub>3</sub> and LLT, 4) bulk resistance of LLT, and 5) grain boundary resistance of LLT. Among these factors, bulk resistances of LLT and PEO-LiCF<sub>3</sub>SO<sub>3</sub> are very small at this temperature of 353 K as shown in Fig. 2, and give no semi-circle in this frequency region of 100 kHz -10 mHz. Hence, impedances given in Fig. 3 are ascribed to resistances of 1), 3), and 5) accompanied with the corresponding capacitances.

To identify each impedance, cole-cole plots for Au / LLT / Au and Li / PEO-LiCF<sub>3</sub>SO<sub>3</sub> / Li were measured at the same temperature of 353 K. Au / LLT / Au gives only one semi-circle with a characteristic frequency of 10 kHz. As is mentioned above, the bulk resistance of LLT at 353 K is very small and gives no semi-circle in the frequency range of 100 kHz – 10 mHz. Hence, the impedance is ascribed to a grain boundary resistance. This frequency is the same as that observed for the impedance at higher frequency region in Fig. 3. In addition, the value of resistance is almost the same as that for the higher frequency region in Fig. 3.

Also only one semi-circle was given by using a cell of Li / PEO-LiCF<sub>3</sub>SO<sub>3</sub> / Li. Since AC impedance spectroscopy for the cell of stainless steel / PEO-LiCF<sub>3</sub>SO<sub>3</sub> / stainless steel gave no semi-circle at 353 K, the semi-circle should be due to the interfacial resistance of PEO-LiCF<sub>3</sub>SO<sub>3</sub> / Li. The characteristic frequency was around 5-6 kHz, which is also identical with the value observed for the impedance at higher frequency region in Fig. 3. In addition, the interfacial



Fig.4. Temperature dependence of interfacial impedance for Li / PEO-LiCF<sub>3</sub>SO<sub>3</sub> / La<sub>0.55</sub>Li<sub>0.35</sub>TiO<sub>3</sub> / PEO-LiCF<sub>2</sub>SO<sub>3</sub> / Li.

impedance between PEO-LiCF<sub>3</sub>SO<sub>3</sub> / Li at 353 K is very small.

It is now evident that the semi-circle at higher frequency region in Fig 3 can be assigned as a mixture of grain boundary resistance of LLT and an interfacial resistance between Li / PEO-LiCF<sub>3</sub>SO<sub>3</sub>. Thus the impedance at lower frequency region is identified as lithium ion transfer resistance at interface between LLT and PEO-LiCF<sub>3</sub>SO<sub>3</sub>.

Considering the above assignment, each resistance in Fig. 3 was fitted by the Randles type equivalent circuit, and the interfacial resistances between PEO-LiCF<sub>3</sub>SO<sub>3</sub> and LLT were plotted against the reciprocal temperatures as shown in Fig. 4. The line in the figure was drawn by the least squares fitting. The activation energy is evaluated from the slope to be 97.6 kJ mol<sup>-1</sup>. This value is much larger than the activation energies of lithium ion movement in polymer electrolyte of PEO-LiCF<sub>3</sub>SO<sub>3</sub>, and bulk or grain boundary of LLT (Fig. 2). Therefore, high activation barrier should exist at interface between LLT and PEO-LiCF<sub>3</sub>SO<sub>3</sub>.

Consequently, in designing of composite electrolytes containing PEO-LiCF<sub>3</sub>SO<sub>3</sub> and LLT, the interfacial impedance between them and its high activation energy should be taken into consideration.

#### 4. CONCLUSION

Lithium ion transfer at interface between polymer electrolyte of PEO-LiCF<sub>3</sub>SO<sub>3</sub> and La<sub>0.55</sub>Li<sub>0.35</sub>TiO<sub>3</sub> (LLT) was investigated by AC impedance spectrosc opy. Impedance ascribed to the interfacial resistance for lithium ion transfer between PEO-LiCF<sub>3</sub>SO<sub>3</sub> and LLT was observed. The activation energy for the interfacial resistance was higher than those for lithium ion conduction in PEO-LiCF<sub>3</sub>SO<sub>3</sub> and LLT. These results suggest that contact area between polymer electrolyte and ion conductive ceramic electrolyte should be as small as possible for attaining the high polymer-ion conductive ceramic electrolytes. In addition, glass electrolytes will be useful instead of using ceramic electrolytes due to no grain boundary resistances. We will report the lithium ion transfer at interface between polymer and glass composite electrolytes elsewhere.

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