



Local structure and composition change at surface of lithium-ion conducting solid electrolyte



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ABSTRACT

In this study, three different surface-sensitive techniques, grazing incidence X-ray diffraction (GIXD), attenuated total reflectance Fourier transform infrared (ATR-FTIR), and X-ray photoelectron spectroscopy (XPS), were employed to analyze the local structure and composition around the surface region of a lithium ion conducting solid electrolyte sheet. It was revealed that the local structure and composition changed depending on depth from the top surface of the sheet. At the very surface, there was a layer with expanded lattice and high Li composition. And with increasing the depth from the surface, lattice shrank sharply, and then expanded again gradually. The change in the lattice seemed to be accompanied by Li and Al composition. It was supposed that the change in the Li composition and structure is induced by combination of chemical reaction, segregation, and defect distribution.

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1. Introduction

Recently, lithium ion conducting solid electrolytes attract many interests because of their potential application to all-solid-state batteries (ASSBs), which are supposed to be one of the candidates of next-generation energy storage devices with high safety and reliability [1–3]. Relatively poorer ionic conductivity has been a drawback of solid electrolytes in comparison to conventional electrolyte solutions with organic solvents. However, a door has been opened since novel solid electrolytes that are comparable or surpass liquid electrolytes in ionic conductivity were developed by pioneering works in the last few decades [2,4–8]. As a result of many efforts to increase lithium ion conductivity of bulk solid electrolytes, interfacial resistance especially between solid electrolytes and active materials appears as a next critical issue. The cause of interfacial resistance can be classified to two factors: extrinsic factors and intrinsic factors. One of the critical extrinsic factors is interfacial resistance arising from point–contact interface between solid electrolytes and active materials, which may be suppressed by employing solid electrolytes with plasticity [9,10] and/or low melting point [11]. On the other hand, intrinsic factors are unclear. Three plausible mechanisms have been reported as an origin of the intrinsic interfacial resistance: formation of interphases [9,12], depletion of mobile ions due to space charge layer (SCL) [1,13,14], and distortion of crystal lattice because of lattice mismatch [12]. According to the SCL model, the SCL is

about twice of Debye length in thickness and is calculated to be less than 1 nm for high ionic conductors. However, a few studies indicate that much thicker SCL. Iriyama's group investigated the potential profile at the interface between a cathode and a solid electrolyte of an ASSB by electron beam holography, and revealed that potential gradient in the solid electrolyte ranges about 1 μm in thickness from the interface [15]. We have so far studied the local structure at the interfacial region by fabricating nano-composites of active materials and solid electrolytes, and confirmed that the interfacial region with distorted lattice ranges for at least 20–50 nm in thickness [13,14]. To explain these discrepancies in the thickness of the SCL, we proposed the defect-pair model: interstitial lithium ions (denoted as Li_i^+ by Kröger–Vink notation) that are positive defects in a crystal lattice are bound to substituting ions (e.g. Al_{Ti}' for LATP) in high ionic conductors that are negative defects. Although more researches with variety of experimental analysis are required for further comprehension of the interfacial phenomena, difficulty in the analysis of solid/solid interface limits experimental tools.

It is known that the surface of solid electrolytes is also related to interfacial resistance. Kliever proposed cation depletion at surface of ionic crystals when free energy of defect formation is lower for cation than for anion [16]. In addition, we observed that ball-milling of a poor ionic conductor (Li_2SiO_3 , LSO) resulted in increase in ionic conductivity without change in activation energy [13,17]. This is interesting because size reduction of solid electrolyte particles generally increases grain boundary resistance, which is generally observed for high ionic conductor [14]. The enhanced ionic conductivity in the nano-LSO may be explained by three plausible mechanisms. One is related to packing of particles. The

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ball-milling causes not only reduce particle sizes, but also sharpens particle size distribution and particle shape becomes more spherical. The morphology change facilitates dense packing of particles and better contact among particles to improve the grain boundary resistance. The second mechanism is the formation of surface layer, i.e., change in phases, crystalline structure and/or distribution of ions (defects). The last is change in ion distribution, in other words, space charge layer (SCL) effect. With SCL model, conductivity enhancement in nano-LSO can be explained by type of charge carrier: Li vacancy (V_{Li}') for LSO and interstitial Li^+ (Li_i^+) for other high ionic conductors. The decreased Li^+ concentration at the surface means accumulation of carrier for LSO and depletion for the latter [17].

In this paper, local structure of surface of a solid electrolyte is focused on and investigated using various surface-sensitive analyses: grazing incidence X-ray diffraction (GIXD), attenuated total reflectance Fourier transform infrared (ATR-FTIR), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

Mirror polished solid electrolyte sheets (25.4 mm × 25.4 mm × 0.15 mm, LICGC, Ohara inc.) were used for analyzing their surface. This solid electrolyte is a glass-ceramic of NASICON-type one in the $Li_2O-Al_2O_3-TiO_2-GeO_2-SiO_2-P_2O_5$ system. According to the supplier, LICGC consists of $Li_{1+x}(Al_xGe_yTi_{2-x-y})(PO_4)_3$ as a main crystalline phase, and $Li_{1+x} + 3zAl_x(Ge,Ti)_{2-x}(Si_2PO_4)_3$ and $AlPO_4$ as subphases. Root-mean-square roughness of the sheets were 5.1 nm obtained by a scanning probe microscope (SPM-9600, Shimadzu Corp., see Supplementary Information S1). As shown in Fig. S1, the roughness of the sheet is mainly due to holes (10–20 nm in depth) on the surface of the LICGC, which is possibly formed by dropout of grains on the surface of LICGC on the polishing process. GIXD was conducted with asymmetric mode (or Seeman–Bohlin arrangement), which are explained in Supplementary Information, S2. GIXD profiles of LICGC were recorded on a SmartLab equipped with a rotating anti-cathode made of a Cu target (45 kV, 200 mA, Rigaku Corp.). Soller slits for the incident and the diffracted beams were both 5° and a parallel slit analyzer was 0.5°. A graphite monochromator was used to suppress fluorescent X-ray. X-ray was irradiated to the LICGC sheets with various incidence angles ranging from 0.2 to 1.5°. There is another mode for GIXD, in-plane mode, in which the detector is scanned around a normal vector of a sample (Supplementary Information, S2). In this work, the asymmetric mode was employed because influence of refraction at the surface for the in-plane mode is complex and it was difficult to discuss the change in the lattice parameters.

ATR-FTIR was carried out using an IR-Prestage21 (Shimadzu Corp.) with a single ATR attachment MIRacle A (Ge prism) for the wavenumber range from 700 to 4000 cm^{-1} . Penetration depth, D_p , of infrared beam in an object is given by the following equation:

$$D_p = \frac{\lambda}{2\pi n_c} \left[\sin^2 \phi - (n_s/n_c)^2 \right]^{-\frac{1}{2}} \quad (1)$$

where λ , n_c , n_s and ϕ are wavelength of infrared, a refractive index of a prism (Ge, $n_c = 4.0$ at $\lambda = 1000$ cm^{-1}), a refractive index of an object, and an incident angle, respectively. By assuming n_s of LICGC to be 1.4, which is similar to a value of typical oxide glass and ceramics, D_p is ca. 650 nm. To obtain bulk information, FTIR spectra of LATP powder obtained by milling LICGC with an agate mortar were also recorded by a conventional KBr method.

XPS was carried out using an AXIS-ULTRA DLD (Kratos Analytical Ltd.) with a monochromated $AlK\alpha$ (photon energy: 1.4867 keV, 15 kV, 10 mA). The detector of the photoelectrons was placed at 90° (perpendicular to the surface of LICGC). Spectra were recorded for C1s, Li1s, Al2p, Ti2p, Ge3p, Si2p, P2p, and O1s with a pass-energy of 40 eV. On measurements, a charge neutralizer was used to avoid charging of an

object. For the surface spectrum, contaminant carbon (285.0 eV) on the surface of LICGC was used for calibration of binding energy. To investigate depth profiles of elements, surface of LICGC was etched with coronene ion ($C_{24}H_{12}^+$) beam sputtering to minimize change in the concentration of mobile ions. According to Yamamoto, Ar ion beam, which is often used for depth profile analyses of metals and ceramics, causes change in the concentration especially for mobile ions, while C_{60} ion beam results in no change in ion distribution [18]. $C_{24}H_{12}^+$ beam used in this work exhibits similar etching ability to C_{60}^+ beam [19,20]. The acceleration voltage and the beam monitor current of the coronene ion beam were 7.9 kV and 2 nA, respectively. The ion beam injected with an incidence angle of 40° was scanned on the surface of the specimen for 2 mm × 2 mm in size. The etching rate was estimated from a result for a standard SiO_2 film on a Si substrate. Composition of elements was calculated by fitting each spectrum using pseudo-Voigt functions with a Shirley's background.

Bulk composition of LICGC was also analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) using an ULTIMA2 (HORIBA, Ltd.). For the analysis, LICGC was dissolved with hot sulfuric acid and hydrofluoric acid aqueous solution.

3. Results

3.1. GIXD

Fig. 1 shows asymmetric GIXD profiles of a LICGC recorded with various incidence angles, ranging from 0.2 to 1.5°. For the comparison, a profile by a conventional $2\theta/\omega$ scan is also exhibited. Although no impurity phase was confirmed for surface region (lower incidence angle in Fig. 1(a)), it is obvious that the peak position of diffraction peaks depended on incident angles (Fig. 1(b)). With increasing incidence angle, peaks shifted toward lower angles, meaning expansion of the crystalline lattice in the surface region. Unfortunately, it was impossible to precisely calculate lattice parameters of LICGC, because LICGC contains two similar crystalline phases of $Li_{1+x}Al_xGe_yTi_{2-x-y}P_3O_{12}$ and $Li_{1+x} + 3zAl_x(Ge,Ti)_{2-x}(Si_2PO_4)_3$. In this work, instead, d -values of (113) plane obtained by fitting each peak with a single Gaussian distribution function were compared (Fig. 2(a)). Interestingly, the d -value changed non-monotonically with increasing the attenuation length: the very surface region of LICGC is expanded, and d -value dropped sharply. Then, lattice expanded again after a minimum around an attenuation length of 40 nm. Next, the d -value exceeded bulk value again. Such expansion didn't relax even at 1500 nm in depth. Fig. 2(b) compares the expansion ratio of the d -value for 2 lattice planes (113) and (024), which agreed well with each other. This agreement suggests that the lattice expansion/shrinkage is isotropic.

3.2. FT-IR

To compensate GIXD, which is sensitive to crystalline phases, FT-IR was conducted to reveal the local structure in LICGC. Fig. 3 exhibits ATR and transmission FT-IR spectra of LICGC. For the transmission spectrum to obtain the bulk information, LICGC was milled with an agate mortar and a pestle, and then the obtained powder (1–10 μm in particle size) was mixed with KBr powder to form a pellet. As shown in Fig. 3(a), peaks attributed to hydroxyl group and chemisorbed H_2O on surface of LICGC were stronger in the ATR spectrum than for the powder [21–23], which confirms that the ATR method is sensitive to surface, while the transmission spectrum gives bulk information. Especially, a characteristic absorption peak attributed to a mono-layer chemically adsorbed hydroxyl group was confirmed. Therefore, information of very thin layer can be obtained by the ATR method. For the wavenumber below 1300 cm^{-1} , peaks related to LICGC structure were observed, all of which could be attributed to NASICON-type structure as summarized in Table 1 [24,25]. The ATR spectrum suggests that LiOH (or $LiOH \cdot H_2O$) and Li_2CO_3 may exist on the surface of LICGC. In Fig. 3(a), H_2O (1400–

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