Li⁺ Conduction in Li-Nb-O Films Deposited by a Sol-Gel Method

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Abstract

We fabricated amorphous Li-Nb-O films by a sol-gel method. The Li⁺ conductivities of Li-Nb-O films were analyzed by ac impedance **spectroscopy** after annealing at 300 to 450 °C. The highest Li⁺ conductivity and lowest activation energy were measured in Li-Nb-O films annealed at 400 °C. Films **annealed at 450 °C** were crystalized to form the non-Li⁺-conductive trigonal LiNbO₃ structure. Raman **spectroscopy** measurements revealed that Li-Nb-O films annealed at 400 °C had aligned NbO₆ octahedra in the structures,

although LiNbO_3 crystals were undetectable by X-ray diffraction. Additionally, it was found that Li-Nb-O films were preferentially crystalized near the Pt electrode surfaces rather than the quartz surfaces. Hence, Pt nanoparticles (NPs) were pre-deposited on quartz substrates by pulsed laser deposition (PLD) before spin-coating of Li-Nb-O films to investigate the effect of small LiNbO_3 crystals on the Li^+ conductivity. After annealing, the Li-Nb-O films fabricated on Pt-decorated quartz substrates exhibited higher Li^+ conductivity and lower activation energy in the in-plane direction compared to films on quartz substrates. Thus, it was considered that the amorphous/ LiNbO_3 crystal interfaces played an important role in fast Li^+ conduction. Although the mechanism of Li^+ conduction in the amorphous/crystal interfacial regions was not well understood, we suggest that reduced attraction between Li^+ and the terminal oxygen of NbO_6 octahedra in the amorphous/crystal interfacial regions contributed to fast Li^+ conduction.

Introduction

Many researchers have devoted significant effort into the development of high performance solid-state Li^+ conductors because all-solid-state-lithium batteries (SSLB) have been considered one of the leading candidates to achieve energy densities higher than those of lithium ion batteries with organic liquid electrolytes [1,2].

Inorganic solid Li^+ electrolytes for SSLB are mainly categorized into sulfide-based electrolytes [3] and oxide-based electrolytes [4-6] because lithium nitride and lithium halides have poor oxidative stability. LiBH_4 has good electrochemical stability and ionic conductivity, but it is a flammable material.

Sulfide-based electrolytes generally have higher Li^+ conductivities than oxide-based electrolytes, though the chemical instability of sulfide compounds in air is a significant challenge to overcome for use in practical applications. In comparison to organic liquid electrolytes, oxide-based electrolytes are stable in air and are non-flammable.

However, a critical problem for oxide-based SSLB is that usually there is a large resistance at the solid electrode/solid electrolyte interface and at grain boundaries because point contacts form at these interfaces. Electrode active materials such as LiCoO_2 have anisotropic Li^+ diffusivities depending on crystal orientation. Crystalline Li^+ electrolytes have anisotropic Li^+ conductivities as well. It is almost impossible to align the crystal axes for both materials in which Li^+ can move the fastest at all the interfaces in SSLB. To address this interfacial issue, an ideal interfacial structure could be a thin amorphous electrolyte filling the gap between the electrode active material and the crystalline electrolyte to decrease high interfacial and grain boundary resistances of oxide-based electrolytes. Since Li^+ conduction is isotropic in an amorphous film, the amorphous interlayer provides facile transport of Li^+ between the crystalline electrolyte and the electrode active material. However, amorphous Li^+ electrolytes such as LiPON [7] have lower ionic conductivity compared to crystalline Li^+ electrolytes such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) [5]. As such, amorphous interlayers need to be as thin as possible. A thin film deposition technique for preparing amorphous Li^+ electrolytes thus plays an important role.

Oxide-based amorphous electrolytes usually have Li^+ conductivities on the order of 10^{-8} to $10^{-6} \text{ S cm}^{-1}$ with activation energies from approximately 50 to 60 kJ mol^{-1} [7-12]. Among these, Glass *et al.* reported that $\text{Li}_2\text{O-Nb}_2\text{O}_5$ glass with an approximate molar

ratio of 1:1 had a high Li^+ conductivity on the order of $10^{-6} \text{ S cm}^{-1}$ [13]. They produced $\text{Li}_2\text{O-Nb}_2\text{O}_5$ glass by a roller quenching method. Since their report, no researchers have successfully produced Li-Nb-O glass with Li^+ conductivity on the same order of magnitude. For instance, Özer and Lampert fabricated amorphous Li-Nb-O films by a sol-gel method and reported $6-8 \times 10^{-7} \text{ S cm}^{-1}$ at room temperature [14].

The aim of this study was to synthesize thin films of amorphous Li-Nb-O with high Li^+ conductivity by the sol-gel method. We also investigated the reason that Li-Nb-O films annealed slightly below the crystallization temperature had high Li^+ conductivity.

Experimental

0.3 mol L^{-1} lithium ethoxide and 0.3 mol L^{-1} niobium ethoxide solutions were separately prepared by diluting 1.0 mol L^{-1} lithium ethoxide (95%, Sigma-Aldrich) and 4.0 mol L^{-1} niobium ethoxide (99.95%, Sigma-Aldrich) with dehydrated ethanol in an Ar atmosphere. These solutions were mixed in a 1:1 volume ratio. 100 μL of the mixed solution was dropped onto quartz substrates with interdigitated Pt electrodes (Fig. 1), and thin films were obtained by a spin-coating technique. The spin rate was maintained at 4000 rpm. Subsequently, samples were annealed in a tube furnace in an O_2 atmosphere for 1.0 hour. The annealing temperature (T_a) was set to be higher than 300 °C. The same procedure was repeated to increase the film thicknesses because cracks formed when a film was too thin. Cracking occurred because the film volume decreased after the solvent evaporated. Hence, the first deposited layer was annealed for 2.0 hours in total. The annealing duration will hereinafter be described as the duration for one uninterrupted

annealing process. The resultant thicknesses were approximately 100 nm, as measured by cross-sectional scanning electron microscope (SEM) observation.

The ionic conductivity of the samples was **primarily** measured in air with an impedance analyzer (4294A, Agilent Co.) using an amplitude of 20 mV in the frequency range from 40 Hz to 110 MHz. A few samples were measured in **an** Ar glove box to examine the effect of humidity.

Crystal microstructures of samples were examined by X-ray diffraction (XRD, CuK α , UltimaIV, Rigaku Co.). Molecular structures of the samples were analyzed by Raman **spectroscopy** (NRS-5100, Nihon Bunko Co.) with a green laser ($\lambda = 532$ nm). Raman spectra for LiNbO₃ powders (99%, Sigma-Aldrich) were also measured to compare with our samples.

Pt-nanoparticle (NP) films were deposited by pulsed laser deposition (PLD) with a YAG laser with the forth harmonic ($\lambda = 266$ nm, 480 mW). **The** PLD was performed for 10 seconds under a chamber pressure of 270 Pa in an Ar atmosphere. The Pt NPs were imaged by a dynamic-mode atomic force microscope (AFM, S-Image, Hitachi Co.).

Results & Discussion

Effect of annealing temperature

Figure 2 shows XRD patterns of samples annealed at (a) 300, (b) 350, (c) 400, and (d) 450 °C for 1.0 hour. It was found that samples were amorphous when the annealing temperature, T_a , was less than 450 °C. Diffraction peaks suddenly appeared when T_a was

450 °C. These peaks can be assigned to the trigonal LiNbO_3 crystal structure [International Center for Diffraction Data (ICDD) #00-020-0631]. Moreover, cracks were found in the sample (d) by SEM observation. These results indicate that the crystallization temperature of LiNbO_3 was higher than 400 °C [15]. It was confirmed that the oxidation and decomposition of organic compounds took place at temperatures higher than 150 °C by differential scanning calorimetry (DSC) (Fig. S1).

Figure 3 shows Nyquist plots (at 100 °C) for samples annealed at (a) 300, (b) 350, (c) 400, and (d) 450 °C for 1.0 hour. The semicircular arc in the higher frequency range ($> 10^4$ Hz) was associated with the Li^+ conduction in the Li-Nb-O film. The film resistance decreased with increasing T_a , but it suddenly increased at $T_a = 450$ °C (see the inset) because the LiNbO_3 crystal is not a Li^+ conductor. A slope with an approximately 45° angle appeared in a narrow frequency range on the order of 10^3 kHz in (a), (b), and (c). This slope is still under investigation, but it is suspected that a new phase formed after annealing at the interfaces between Pt electrodes and an amorphous Li-Nb-O film, such as thin Li-Pt alloy layer.

Figure 4 shows the Arrhenius plots for the Li^+ conductivities, σ , of samples that were evaluated by the arc diameters in Nyquist plots. σ was estimated by assuming rectangular Li^+ conduction paths (height : length : width = 100 nm : 3.0 μm : 2.0 mm) between 129 couples of Pt electrodes. However, the electric fields between Pt electrodes will be distorted in the vicinity of the Pt electrode edges (Fig. 1). This led to only 3% underestimation of σ based on the two-dimensional (2D) finite difference analysis. Hence, the effect of non-uniform electric fields was negligible.

All plots followed linear slopes in **Fig. 4**. The activation energy, E_a , for the Li^+ conduction decreased with increasing T_a to 400 °C. The LiNbO_3 -crystallized sample ($T_a = 450$ °C) had the lowest σ [(d) in **Fig. 4**].

Figure 5 (Top) and (Bottom) show σ (at 25 °C) and E_a of Li-Nb-O films as a function of T_a , respectively. The largest σ and the smallest E_a were measured at $T_a = 400$ °C. However, the σ and E_a values were significantly different depending on the sample at $T_a = 400$ °C (three or four samples were measured for each T_a). The $\text{Li}_2\text{O-Nb}_2\text{O}_5$ glass electrolyte produced by Glass *et al.* using a roller quenching method exhibited σ of $5 \times 10^{-6} \text{ S cm}^{-1}$ at 25 °C and E_a of 38.3 kJ mol^{-1} [13]. Some of our samples at $T_a = 400$ °C had σ and E_a values similar to the conductivity and activation energy by Glass *et al.* The σ of these samples were also measured in an Ar-filled glove box, but the results were still the same. At $T_a = 450$ °C, the σ significantly decreased due to the LiNbO_3 crystallization.

Figure 6 shows the Raman spectra of the samples ($T_a = 300, 350, 400, 450$ °C for 1.0 hour) and commercial LiNbO_3 powders. As described above, the σ was significantly different depending on the individual film. For clarity, the spectra for the samples with lower and higher σ at $T_a = 400$ °C were denoted as 400 °C^L and 400 °C^H , respectively, in **Fig. 6**. The Raman spectra clearly changed when T_a was higher than 350 °C. These spectra changed to be more similar to that of commercial LiNbO_3 powders with increasing T_a . The peaks at 630 cm^{-1} and 870 cm^{-1} indicate stretching modes associated with octahedral NbO_6 units [16, 17]. An increase in the integrated area of the peak at 630 cm^{-1} relative to the peak at 870 cm^{-1} meant the initiation of 3D ordering of octahedral NbO_6 units. At $T_a = 450$ °C, LiNbO_3 diffraction peaks appeared in XRD measurements (**Fig. 2**).

The Raman spectra of the samples annealed at 400 °C were different depending on the σ (400 °C^L and 400 °C^H in **Fig. 6**). The sample with higher σ (400 °C^H) exhibited a spectrum more similar to that of LiNbO₃. It is considered that the terminal oxygen of NbO₆ octahedra plays a critical role in fast Li⁺ conduction because neighboring NbO₆ octahedra share the corners that connect to each other with the terminal oxygen at neighboring positions (inset in **Fig. 6**) [18]. Li⁺ could hop to sites adjacent to the terminal oxygens to conduct unless Li⁺ is strongly attracted by the negative charges of the terminal oxygen. Electrically unbalanced space charge layers are developed in the interfacial regions between two different solid phases (e.g. amorphous and crystal). It is conceivable that the attraction of Li⁺ to the terminal oxygen can be relaxed by electric fields in these space charge layers.

The nuclear magnetic resonance (NMR) measurements by Heitjans *et al.* revealed that Li⁺ had higher mobility in the amorphous/crystal interfacial regions compared to the bulk in LiNbO₃ [19,20]. It is therefore possible that a large number of small LiNbO₃ crystals nucleated at 400 °C slightly below the crystallization temperature. The interfacial regions with high Li⁺ mobility should be developed in the peripheries of the LiNbO₃ crystals in the amorphous Li-Nb-O matrix, as in glass-ceramic electrolytes. Li⁺ conducted through these interfacial regions around the LiNbO₃ crystals. Hence, samples prepared just below the onset temperature of rapid LiNbO₃ crystallization were the most conductive. The reason that the measured σ values were significantly different depending on individual film at $T_a = 400$ °C in **Fig. 5** is probably because the nucleation condition was sensitive to unexpected contaminants or dust. It is suspected that a sample with a high σ at $T_a = 400$ °C contained small LiNbO₃ crystals with a large number density.

Effect of Pt NPs

XRD patterns of samples annealed at 425 °C for 2.0 hours on Pt and quartz substrates are shown in **Fig. 7**. Much stronger diffraction peaks of LiNbO₃ appeared on Pt than on quartz. It is thus suggested that Pt NPs acted as catalysts to trigger the nucleation of LiNbO₃ in a sample. The mechanism of LiNbO₃ crystallization on Pt surfaces has yet to be understood. The roles of the platinum oxide layer formation and interdiffusion between Pt and Li-Nb-O seem to be important. These need to be examined in the future. Nevertheless, it is obvious that Pt surfaces accelerated LiNbO₃ crystallization in **Fig. 7**. **As such**, Pt-NP films were deposited on quartz substrates with interdigitated Pt electrodes by PLD to introduce the preferential nucleation sites. The PLD duration was 10 seconds, which **was** too brief for Pt crystals to **electrically** short **the** interdigitated electrodes.

Figure 8 shows AFM images of Si wafers before and after depositing Pt NPs by PLD. Albeit with vibrational noises in AFM imaging for (a), small bumps indicating Pt NPs can be recognized after PLD in (b). It is observed that rather than forming contiguous Pt films, the short-duration PLD produced Pt “islands” with diameters less than 10 nm. The distributed Pt islands had separation distances less than 20 nm between the nearest neighbors.

Figure 9 shows σ (at 200 °C) and E_a of samples on quartz substrates with interdigitated Pt electrodes with and without Pt NPs as a function of annealing duration at $T_a = 425$ °C. Without Pt NPs, the σ decreased after 60 minutes **of** annealing, as shown in (a). The E_a increased simultaneously. In contrast, the σ with Pt NPs slightly increased until 60

minutes of annealing, as shown in (b). The E_a kept decreasing as the annealing proceeded. It is suspected that numerous small LiNbO_3 crystals nucleated on the Pt-NP surfaces, whence a large number of amorphous/crystal interfaces existed in the bottom region of the film as illustrated in the inset of **Fig. 9(Top)**. This situation provided highly- Li^+ -conductive regions in a Li-Nb-O film and was presumably similar to what occurred in a sample with relatively high σ annealed at 400 °C in **Fig. 5**. The cooling rates for the samples were possibly different so that the number density of LiNbO_3 crystals varied depending on the individual film resulting in a large deviation of σ at $T_a = 400$ °C. The reason that the σ started to decrease after 60 minutes in **Fig. 9** is because LiNbO_3 crystals grew to dominate the entire volume of the sample.

In conclusion, it is suggested that Li-Nb-O films can potentially become excellent amorphous Li^+ conductors if the amorphous/crystal interfaces can be controlled in the entire volume of the films. One effective approach is to introduce small catalytic particles in a film with a high number density to promote the nucleation of LiNbO_3 crystals.

Conclusions

We fabricated amorphous Li-Nb-O films by a sol-gel method and measured Li^+ conductivity and activation energy of the samples. A Li-Nb-O film annealed at 400 °C for 1.0 hour had the highest Li^+ conductivity and lowest activation energy. We considered that the structures of partially aligned octahedral NbO_6 units existing in the vicinity of the amorphous/crystal interfaces critically contribute to fast Li^+ conduction.

To verify this hypothesis, Pt NPs were deposited on a substrate before spin-coating of a Li-Nb-O film. A Li-Nb-O film with Pt NPs showed a slight increase in Li^+ conductivity due to the annealing at 425 °C. In contrast, the Li^+ conductivity of a sample without Pt NPs only decreased as the annealing proceeded.

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Figure 1. Schematic illustrations of plan and cross-sectional views for interdigitated Pt electrodes embedded in a quartz substrate. There are 65 electrodes for each pole (+, -). The effective lengths and widths of a single rectangular Pt electrode are 2.0 mm and 3.0 μm , respectively. The distance between two Pt electrodes is 3.0 μm .

Figure 2. XRD patterns of Li-Nb-O samples after annealing at (a) 300, (b) 350, (c) 400, and (d) 450 °C for 1.0 hour. The diffraction peak positions for the trigonal LiNbO_3 are presented on the bottom.

Figure 3. Nyquist plots (at 100 °C) for Li-Nb-O films annealed at (a) 300, (b) 350, (c) 400, and (d) 450 °C for 1.0 hour. The inset is for larger impedance values. Frequency: 10^n Hz.

Figure 4. Arrhenius plots for Li^+ conductivities, σ , of Li-Nb-O films annealed at (a) 300, (b) 350, (c) 400, and (d) 450 °C for 1.0 hour.

Figure 5. σ at 25 °C (Top) and E_a (Bottom) of samples as a function of annealing temperature. The annealing duration was 1.0 hour.

Figure 6. Raman spectra of Li-Nb-O samples with $T_a = 300, 350, 400,$ and $450\text{ }^{\circ}\text{C}$ and commercial crystalline LiNbO₃ powders. The annealing duration for **red** samples was 1.0 hour. The superscripts of L and H for $400\text{ }^{\circ}\text{C}$ **denote** samples with $E_a = 50\text{ kJ mol}^{-1}$ and 38 kJ mol^{-1} , respectively (see text). The inset illustrates corner-sharing NbO₆ octahedra with Li⁺ hopping on the terminal oxygen.

Figure 7. XRD patterns of samples after annealing at 425 °C for 2.0 hours on (a) Pt and (b) quartz substrates. The strongest peaks at the dashed lines in (a) indicate Pt diffraction peaks.

Figure 8. AFM images of Si wafer surfaces (a) without and (b) with Pt NPs deposited by PLD.

Figure 9. σ (200 °C) and E_a of samples as function of the annealing duration (a) without and (b) with Pt NPs on substrates. $T_a = 425$ °C. LiNbO₃ crystals nucleate on Pt-NP surfaces. Fast Li⁺ conduction occurs through the regions in the vicinity of the amorphous/crystal interfaces in a Li-Nb-O film in (b).