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Substrate dependence of the proton transport and oriented structure in oligo[(1,2propanediamine)-*alt*-(oxalic acid)] thin films

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Three oligo[(1,2propanediamine)-*alt*-(oxalic acid)] thin films were prepared on SiO_2, R-plane sapphire, and MgO(100) substrates and their proton conductivities were investigated. Conductivity depended on the substrate and varied from 4×10^{-3} to 1×10^{-4} S cm^{-1} under the same conditions (80% relative humidity and 298 K). The thin films between the R-plane (1102) sapphire and MgO(100) substrates showed different molecular oriented structures. The thin film on the sapphire substrate, which shows higher proton conductivity, has a structure oriented parallel to the substrate. The molecular orientation in the thin film could be correlated with the proton transport property.

The design of highly proton-conductive solid electrolytes is necessary for many applications in the field of solid-state ionics. One fundamental method to create highly proton-conductive material is chemical modification by strong acid groups.[1] When using chemical modification such as sulfonation, the resultant chemical stability and mechanical strength are often unfavorable. However, the proton conductivity exhibits an excellent value. Because of this tradeoff between proton conductivity and mechanical strength and chemical stability, a new method to produce a highly proton-conductive material has been sought for a long time.

In a Nafion membrane, protons are known to be transported through nanochannels made of sulfonic acid groups and water clusters: a point that has been discussed intensively in the literature.[2] Nanochannels are created by phase separation with the amphiphilic character of Nafion. For a Nafion membrane, the high proton conductivity is known to result from phase separation. An earlier study by the author revealed that the proton conductivity of the Nafion thin film (400 nm) was much less than that of a commercial membrane.[3] In the thin film, sulfonic acid groups are highly oriented and mutually isolated from each other, producing poor conductive channel formation. Therefore, the proton conductive group orientation is important to improve proton conductivity.

A recent report has described anomalous proton conductivity by thin films based on oligomeric amides.[4] Thin films (ca. 200 nm) of oligomers on SiO_2 substrate exhibit about 10-times-higher proton conductivity than their pelletized sample (thickness ca. 0.5 mm). Although the reason for this enhancement in proton conduction remains unknown, application of this phenomenon shows promise as a new strategy to produce highly proton-conductive materials. Our group's previous report described that this origin for the proton conductivity enhancement by thin film can result from structural effects such as a molecular orientation by thin film on the substrate. This report explains the substrate dependence of the proton transport property in thin films, which had different molecular-oriented structure.

Proton conductive oligomeric amide (oligo[(1,2propanediamine)-*alt*-(oxalic acid)]) was synthesized as described elsewhere.[4] Details related to synthesis and characterization of the oligomeric amide are presented in an earlier report.[4(a)] The substrates were optically polished amorphous SiO_2, R-plane (1102) sapphire, and MgO(100) single crystals. The thin films were prepared by spin coating. The thin films on SiO_2, sapphire, and MgO substrates had respective thicknesses of 200, 180, and 150 nm.

Impedance measurements of the thin films were conducted at relative humidity (RH) of 60–80% using an impedance/gain-phase analyzer (SI1260; Solartron Analytical) and a dielectric interface system (1296; Solartron Analytical). The RH and temperature were controlled using a humidity-controlled and temperature-controlled chamber (SH-221; Espec Corp.). For impedance measurements of the thin films, the electrode was configured to obtain measurements of the current flow in the plane parallel to the substrate surface. Porous gold paint (Silbest No. 8560; Tokuriki Chemical Research Co., Ltd.) was used for electrodes.

The proton conductivity of each thin film on SiO_2, sapphire, or MgO substrate at each relative humidity (RH) is shown in Figure 1. Proton conductivity increased logarithmically with RH: a typical characteristic of proton conductive polymers. The conductivity value differed among the three thin films. Table 1 presents the proton conductivity of each thin film at 80% RH and 298 K. The conductivity values are 4×10^{-3} on SiO_2, 2×10^{-3} on sapphire, and 1×10^{-4} S cm^{-1} on MgO substrate. The proton conductivity on the MgO substrate exhibits a low value compared to others including the pelletized sample (3×10^{-4} S cm^{-1}). [4]

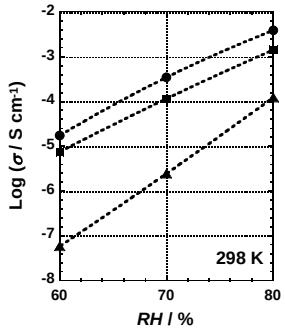

Figure 1. Relative humidity (RH) dependence of the proton conductivity. Thin films were prepared on SiO_2 (●), R-plane (1102) sapphire (Al_2O_3) (■), and MgO(100) (▲) substrates.

Table 1. Proton conductivity of thin films at RH = 80% and 298K.

	σ / S cm^{-1}
on SiO_2	4 x 10^{-3}
on sapphire	2 x 10^{-3}
on MgO(100)	1 x 10^{-4}

FT-IR is a powerful tool to investigate the amide group structure. To ascertain the structure, infrared p-polarized multiple-angle incidence resolution spectrometry (p-MAIRS) technique[5] has been applied. Infrared p-MAIRS is increasingly regarded as a powerful spectroscopic tool for revealing molecular orientation in the thin films. Information related to the spectra for in-plane (IP) and out-of-plane (OP) transition dipoles is distinguishable in an identical film. The p-MAIR measurements were taken using an FT-IR spectrometer (Nicolet 6700; Thermo Fisher Scientific Inc.) equipped with a mercury-cadmium-telluride (MCT) detector. Single-beam spectra were collected from 38° to 8° at 6° steps between the angle of incidence, as shown in Figure 2(a). Measurement details are given in Supporting Information. Figure 2(b) presents the incident angle dependence of the transmission IR spectra of the thin film on the MgO(100) substrate. Observed spectra depended on the incident angle. Absorbance of around 1680 cm^{-1} increased with the angle of incidence. This result suggests that these functional groups had a highly oriented structure. For a low incident angle, the peak was not observed around 1680 cm^{-1}. Therefore, no IP transition dipole moment exists around that wavenumber. However, the peak gradually appeared with the incident angle, meaning that OP transition dipole moments were excited by polarized light.

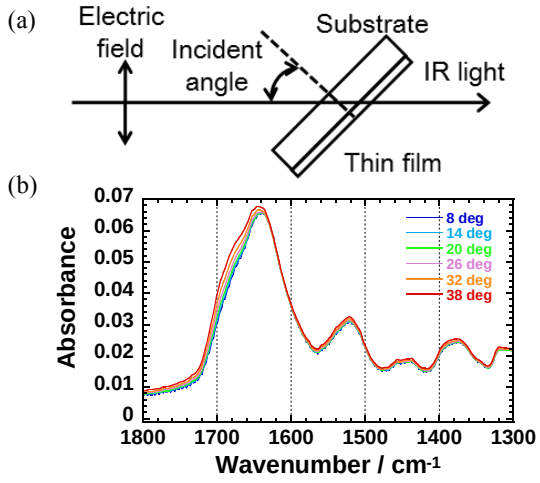

Figure 2. (a) Configuration of the polarized incident beam path and an incident angle. (b) Incident angle dependence of the transmission IR spectra of the thin film on the MgO(100) substrate.

The intensity of the 2×IP signal of p-MAIRS is twice that of the OP one when the transition moment vector is distributed isotropically (See Supporting Information). The OP and IP spectra of the thin film on MgO substrate are

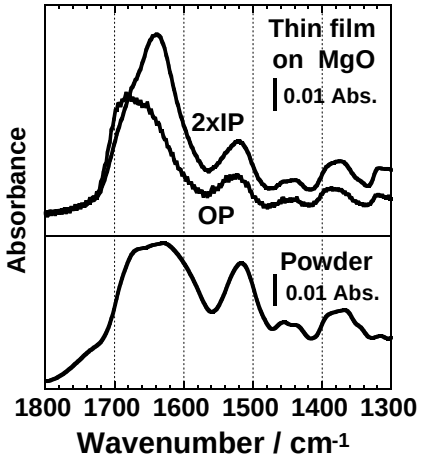

Figure 3. p-MAIR spectra of highly oriented oligomeric amide thin film on MgO(100) substrate. A powdered sample is shown as a reference.

shown in Figure 3. The peak top of the OP spectrum appeared at 1680 cm^{-1}. However, the peak top of the IP spectrum appeared at 1640 cm^{-1}. The absorption bands at 1680 and 1520 cm^{-1} in the OP spectrum were assigned respectively to the vibrational modes called Amide I and II. Wavenumbers simulated by software (Materials Studio ver. 6.0.0; Accelrys Software Inc.) suggest 1686 cm^{-1} for Amide I and 1510 cm^{-1} for Amide II (See Figure S1 in Supporting Information). The band position estimated by the quantum chemistry calculation is closely correspondent with the experimentally obtained result. The attribution of 1640 cm^{-1} is not fully analyzed yet because this absorption at 1640 cm^{-1} was not suggested by simulated results, using one isolating oligomeric amide chain for vibrational analysis. This absorption band might result from the coupling vibrational mode[6] between the many main chains through hydrogen bonds. The transition moment vector of the amide I band at 1680 cm^{-1} was highly oriented perpendicular to the surface. Other bands were nearly un-oriented. The spectrum of the powdered sample seems to be the mixed spectrum with the IP and OP spectra. This result suggests that the powdered sample has random orientation.

Attenuated total reflection (ATR) measurements were conducted to confirm the random orientation of the pelletized sample. Figure S3 shows the ATR spectra of the pelletized sample in each configuration (See Supporting Information). The inset shows the configuration between the pelletized sample direction and IR light direction. Both spectra exhibited the same spectral pattern. Therefore the oligomeric amide showed a random orientation in the pelletized sample. For the pelletized sample, no scaffold exists for inducing the oriented structure, which may result in a random orientation.

The proton conductivity of the thin film on the sapphire substrate is higher than that on the MgO substrate. The molecular orientation of the thin film on the sapphire substrate was investigated using p-MAIRS. Figure 4 shows the OP and IP spectra of the thin film on the sapphire substrate. The spectra differ greatly from the spectra of the thin film on the MgO substrate. The functional groups around 1690 cm^{-1} in the OP spectrum were un-oriented because the intensity of the 2×IP signal of p-MAIRS is twice of that of the OP one. Other parts were slightly oriented because the 2×IP components were apparently larger than the doubled OP components. These results suggest that the thin film on the sapphire

substrate has a structure oriented parallel to the substrate. This result presents an opposite trend compared to that of the MgO substrate. To attribute the oriented functional groups, the quantum chemistry calculation was conducted using dimer of the oligomers. Figure S2 shows the geometry-optimized dimer of the oligomers. (See Supporting Information) The amide groups were bonded between the oligomer chains by hydrogen bonds. The carboxylic acid groups at end groups also made hydrogen bonds to the amide groups. Based on the DFT calculation, the broad absorption around 1650 cm^{-1} in the IP spectrum corresponds to the amide I bands. The vibration mode corresponding to amide groups near the end groups tends to be a higher wavenumber than the others. This result suggests that the inside (not near the end groups) amide groups in the oligomer chain have stronger hydrogen bonds. The proton conductivity exhibited higher value in the case of thin film on the sapphire substrate compared to the MgO substrate probably because of these hydrogen bonding networks. The relation between the proton transport property and oriented structure has not been well-discussed yet. Recently Tamura and Kawakami found that the composite bulk membrane containing uniaxially aligned sulfonated polyimide nanofibers exhibited a high proton conductivity.[7] This result shows a possibility for improving the proton transport property using the molecular orientation. In this study, the hydrogen bonding networks between the main chains were able to contribute to the proton conduction. For the thin film of the SiO_2 substrate, the SiO_2 is not transparent substrate for IR region below 2000 cm^{-1}. Therefore, we were unable to characterize details about the oriented structure.

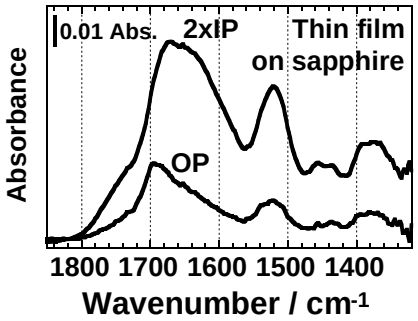

Figure 4. p-MAIR spectra of highly oriented oligomeric amide thin film on R-plane (1102) sapphire substrate.

To obtain effective and high-power energy sources of the fuel cell, understanding characteristics of the interface between the proton conductive materials and other materials is necessary. Many studies have investigated the interface between inorganic materials and proton conductive polymers.[8] Some reports have described that proton transport properties were improved by the fillers,[9] which presents advantages for the suppression of swelling and shrinking of the proton conductive membrane surrounded by water or other alcohol fuels. The improvement origin was inferred as related to their structural modification at the interface. Results contribute to the discussion of structural issues at the interface between the proton-conductive materials and inorganic materials.

In conclusion, the proton transport property of the thin films depends on the substrates. The proton conductivity of the thin films on SiO_2 and sapphire substrates was higher than that on the MgO substrate. The structure of the thin film on the MgO substrate was nearly un-oriented. However, the thin film on the sapphire substrate has an oriented structure that is parallel to the substrate. The molecular orientation in the thin film might be correlated with the proton transport property.

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