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# **Synthesis and Proton transport property of Poly(aspartic acid) thin film on SiO<sub>2</sub> substrate**

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## ***Abstract***

Poly(aspartic acid) and its thin film were synthesized to study proton transport properties. The average degree of polymerization and molecular weight are 50 and 7000, respectively. The proton conductivities of the Poly(aspartic acid) and its thin film were  $4.3 \times 10^{-4}$  and  $5.1 \times 10^{-3}$  S cm<sup>-1</sup>, respectively under the relative humidity of 70 % and 298 K. The proton conductivity of the thin film is one order of magnitude higher than that of the pelletized Poly(aspartic acid). The activation energies for the proton conduction of the pelletized Poly(aspartic acid) and thin film are 0.65 and 0.53 eV, respectively. The open circuit voltage of the pelletized sample exhibited ~0.9 V under the relative humidity of 70 % and 298 K.

Keywords: proton conduction, thin films

## ***1. Introduction***

The design of highly proton-conductive solid electrolyte is essential to many applications in the research field of solid state ionics. One of the fundamental methods to make highly proton-conductive material is chemical modification. The properties of chemical stability and mechanical strength are often unfavorable by using chemical modification like sulfonation, however the proton conductivity exhibit excellent value. Due to such a trade-off relation between the proton conductivity, mechanical strength, and chemical stability, a new method to make highly proton-conductive material has been expected for a long time. The ionic conductivity enhancement in the 2-D system has been reported by many researchers [1 - 12]. These anomalies are supposed to be attributed to interfacial effects like structural effects and/or effects of a space charge region. The interfacial effects for the proton conduction in the 2-D system also attract considerable attention. But the enhancement of the proton conductivity has not been clearly reported in the thin films of the organic conductors.

Amino acid homopolymers and their derivatives, which have amide linkages as well as a peptide, have been known to exhibit interesting biochemical properties. Poly(aspartic acid) has free carboxylic acid groups at the side chains, and its proton at the free carboxylic acid groups is candidate for the mobile proton in the proton conduction. In this paper, we synthesized Poly(aspartic acid), and investigated the proton transport properties of the pelletized sample and its thin film.

## ***2. Experimental***

Poly(aspartic acid) was synthesized as shown in Scheme. D, L-Aspartic acid and *o*-phosphoric acid of reagent grade were commercially available and used without further purification. D, L-Aspartic acid of 1 g and 85 % *o*-phosphoric acid of 600  $\mu$ l were added to

100 ml round-bottom flask and mixed for 10 minutes under Ar atmosphere. The mixture was heated at 170 °C for 1 hour. The product was washed with methanol and water. The residue was washed with methanol and dried under reduced pressure. The dried sample of 0.7 g and a solution of sodium hydroxide of 0.3 g with a deionized water of 20 ml were added to a 200 ml beaker with stirring for 20 minutes. After the reaction, the pH of the solution was adjusted to ~6 by the addition of 35 % aqueous HCl into the solution. The white precipitate was obtained by adding methanol of 100 ml. The sample was washed with methanol, and was separated from the supernatant, in which the centrifuge technique was used in the washing and separation procedures. The obtained sample was dried under reduced pressure.

The quality of the sample was checked by the  $^1\text{H}$  NMR and Fourier-transform infrared (FT-IR) spectra measurements. The  $^1\text{H}$  NMR spectra in deuterium oxide, using Sodium 3-(trimethylsilyl)propionate-2,2,3,3-d<sub>4</sub> (TSP) as internal reference, were obtained on a ECA-600 (JEOL) operated at 14 T. For the FT-IR absorption measurements, the sample was diluted with KBr and the mixture was pressed into a pellet. The FT-IR spectra were measured with a PerkinElmer Spectrum GX in the frequency range of 400 – 4000  $\text{cm}^{-1}$ . The average degree of polymerization was determined by comparing the ratio of the peak area derived from the proton of  $-\text{CH}_2$  at the amino end groups to that of the intrachain  $-\text{CH}_2$  and  $-\text{CH}_2$  at the carboxyl end groups in the  $^1\text{H}$  NMR spectrum. The degree of protonation was determined by the titrimetric method.

The thin films were synthesized by using a Active ACT-200 Spincoater on amorphous  $\text{SiO}_2$  substrates. The thickness of the thin film was determined by using a KLA-Tencor P-10 contact stylus profiler. The obtained thin film is flat, and the thickness is 60 nm.

Impedance measurements of the pelletized sample and thin films were carried out in the relative humidity (RH) range of 40 – 70 % with a Solartron 1260 Impedance/Gain-Phase

analyzer and a 1296 Dielectric Interface system. The RH and temperature were controlled with an Espec Corp. SH-221 humidity- and temperature-controlled chamber. In the case of the impedance measurements of the pelletized sample, the sample was processed into pellets of 2.5 mm $\phi$  under pressure of  $\sim$ 1 GPa and porous gold paint (Tokuriki Chemical Research, SILBEST No. 8560) was used as electrodes. In the case of the impedance measurements of the thin films, the electrode configuration was selected to obtain measurements of the current flow in the plane parallel to the substrate surface. The size of the membrane on SiO<sub>2</sub> substrate is  $\sim$ 4.5 x 8.4 mm. The electrode by using Au paste is located at the edge of the membrane, and electrode configuration is parallel. The distance between electrodes is 4.0 mm. The Au electrode is also covered at the side of the membrane. The conductivity of the amorphous SiO<sub>2</sub> substrate is negligible because its resistance is quite higher than that of the thin film.

For the measurement of the open circuit voltage, the sample was processed into pellets of 13 mm $\phi$ . Pt-loaded carbon paper sheets (Pt: 1 mg cm<sup>-2</sup>) were used as electrodes. The pelletized sample was sandwiched between anode and cathode. Humidified hydrogen (100 ml / min) and oxygen (100 ml / min) were fed to anode and cathode, respectively. The cell temperature and relative humidity were controlled to be 298 K and 70 %, respectively.

### ***3. Results and Discussion***

#### **3.1 CHARACTERIZATION**

Figure 1 shows the NMR spectra of D, L-Aspartic acid and synthesized sample. The peak width in the synthesized sample becomes broad. This broad peak width suggests that the synthesized sample is polymerized. The similar spectrum of sodium polyaspartate was observed by Tabata *et al.* [13]. They determined that sodium polyaspartate was composed of 30 % of  $\alpha$ -amide and 70 % of  $\beta$ -amide units from the NMR spectrum as shown in Figure 2. Our sample is found to be composed of 24 % of  $\alpha$ -amide and 76 % of  $\beta$ -amide units. The

inset Figure 1 shows magnified figure for the chemical shift from 2.0 to 3.4 ppm in the NMR spectrum of synthesized polymer. These broad bands at 2.95 – 3.25 ppm are due to the proton of the  $-\text{CH}_2$  at the amino end groups. The average degree of polymerization was determined by comparing the ratio of the peak area derived from the proton of  $-\text{CH}_2$  at the amino end groups to that of the intrachain  $-\text{CH}_2$  and  $-\text{CH}_2$  at the carboxyl end groups. The average degree of polymerization is found to be ~50. The degree of protonation in the carboxylic acid groups was also determined by the titration method. The degree of protonation in the carboxylic acid groups is found to be 6 %. The average molecular weight is calculated by the degree of polymerization and the degree of protonation, and found to be ~7000. This synthesized polymer is determined to be called P-Asp in this paper.

Figure 3 shows FT-IR spectra of the D, L-Aspartic acid, Polysuccinimide, and P-Asp. In the spectrum of Polysuccinimide, the broad peak at  $1670 - 1770 \text{ cm}^{-1}$  can be assigned as the CO bond of the  $-\text{CO-N-CO-}$  (imide) groups. In the spectrum of P-Asp, two broad peaks are observed at  $1600$  and  $1650 \text{ cm}^{-1}$ . These peaks are due to the CO bond of  $\alpha$ -amide ( $-\text{CH-CO-NH-}$ ) and  $\beta$ -amide mode ( $-\text{CH}_2\text{-CO-NH-}$ ). These attributions are in accord with those of the NMR spectra. The spectrum of P-Asp exhibits the broad absorption band over  $3000 \text{ cm}^{-1}$ , which is due to the OH and NH bonds. This result is suggested that P-Asp can adsorb water molecules.

### 3.2 PROTON TRANSPORT PROPERTIES OF THE PELLETIZED P-ASP AND P-ASP THIN FILM

Figure 4 shows the RH dependence of the proton conductivity ( $\sigma$ ) for the pelletized P-Asp and P-Asp thin film. A resistance is directly given by the intersection of a depressed semicircle with the real axis in the complex plane impedance plots. In the proton conduction

of the pelletized P-Asp, the proton conductivity increases by over three orders of magnitude with increasing the RH from 40 to 70 %. Such a large dependence of the proton conductivity on the RH could arise from the proton conduction paths developed by the water uptake. The open circuit voltage of the pelletized sample exhibited  $\sim 0.9$  V, even if the tablet was found to be cracked after the measurement of open circuit voltage. This result indicates that the proton transport number is high and the carrier is proton in the sample, however we do not know yet whether  $\text{Na}^+$  ions affect AC conductivity or not. The proton conductivity of the pelletized P-Asp is  $4.3 \times 10^{-4} \text{ S cm}^{-1}$  under the RH of 70 % and 298 K. In the proton conduction of P-Asp thin film, the proton conductivity of the 60 nm thick thin film is found to be  $5.1 \times 10^{-3} \text{ S cm}^{-1}$  under the RH of 70 % and 298 K. This value is found to be over one order of magnitude higher than that of the pelletized P-Asp under the same condition, and is half of that of Nafion 117 membrane ( $1.3 \times 10^{-2} \text{ S cm}^{-1}$ ) [14].

Figure 5 shows the temperature dependence of the proton conductivity (Arrhenius plots) for the pelletized P-Asp and P-Asp thin film at the RH of 70 %. The proton conductivity of the thin film exhibits higher values than that of the pelletized P-Asp. The activation energy of the pelletized P-Asp and P-Asp thin film is 0.65 and 0.53 eV, respectively. The activation energy of P-Asp thin film is found to be 0.12 eV smaller than that of the pelletized P-Asp. One of the origins for increasing the proton conductivity of P-Asp thin film is due to the decrease of the activation energy for the proton conduction.

We observed the proton conductivity was enhanced by the synthesis of the thin film. In many kinds of the inorganic ionic conductors, some theoretical models including the space charge models for understanding the enhancement phenomena of the ionic conductivities have been discussed [15]. But the obvious thickness dependence of the proton conductivity for P-Asp thin films has not been observed yet. Therefore this enhancement phenomenon

could be originated from other effects like a molecular orientation by the synthesis of the thin film on the substrate rather than the interface effects like the space charge models in this system. The amide bond causes interchain hydrogen bonds between the polymers. The amide groups also exhibit the proton exchange property because of the amide/imidic acid tautomerism. The proton conduction paths could be expected to be formed by using these properties and water molecules including in the sample considering the relatively high activation energy. One of the possible reasons for this enhancement of the proton conductivity is due to the molecular orientation because it causes that the proton can easily move in the sample along these paths. This supposition can explain the reason why the activation energy for the proton conduction of the thin film decreases as compared to that of the pelletized sample. Further investigation is required to understand this phenomenon.

#### ***4. Conclusions***

Proton-conductive polyamide, Poly(aspartic acid), was synthesized to investigate the proton transport properties of the pelletized sample and its thin film. The average degree of polymerization and molecular weight are 50 and 7000, respectively. The degree of protonation in the carboxylic acid groups is 6 %. The open circuit voltage of the pelletized sample exhibited ~0.9 V under the relative humidity of 70 % and 298 K. The proton conductivity of the pelletized sample and its thin film is  $4.3 \times 10^{-4}$  and  $5.1 \times 10^{-3}$  S cm<sup>-1</sup>, respectively under the RH of 70 % and 298 K. The activation energy of the pelletized P-Asp and P-Asp thin film is 0.65 and 0.53 eV, respectively. The activation energy of P-Asp thin film is found to be 0.12 eV smaller than that of the pelletized P-Asp. We observed the proton conductivity was enhanced by the synthesis of the thin films.

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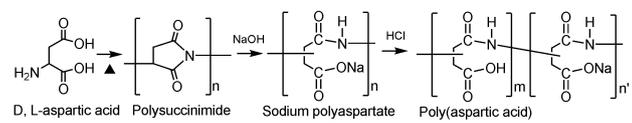
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***Scheme Caption***

Scheme : Chemical structure and reaction scheme of Poly(aspartic acid) from D, L-aspartic acid.



Scheme

### ***Figure Captions***

Fig. 1.:  $^1\text{H}$  NMR spectra of D, L-Aspartic acid and synthesized sample. Inset figure is magnified figure for the chemical shift from 2.0 to 3.4 ppm in the NMR spectrum of synthesized sample.

Fig. 2: Structure of sodium polyaspartate composed of 30 % of  $\alpha$ -amide and 70 % of  $\beta$ -amide units.

Fig. 3: IR spectra of the D, L-Aspartic acid, Polysuccinimide, and P-Asp.

Fig. 4: RH dependence of the proton conductivity with the pelletized P-Asp and its thin film.

Fig. 5: Temperature dependence of the proton conductivity with the pelletized P-Asp and its thin film.

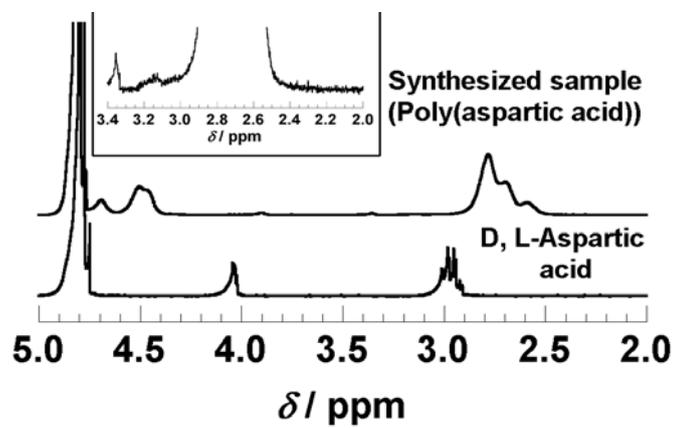


Fig. 1

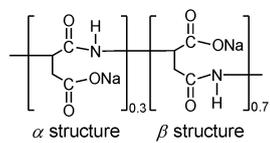


Fig. 2

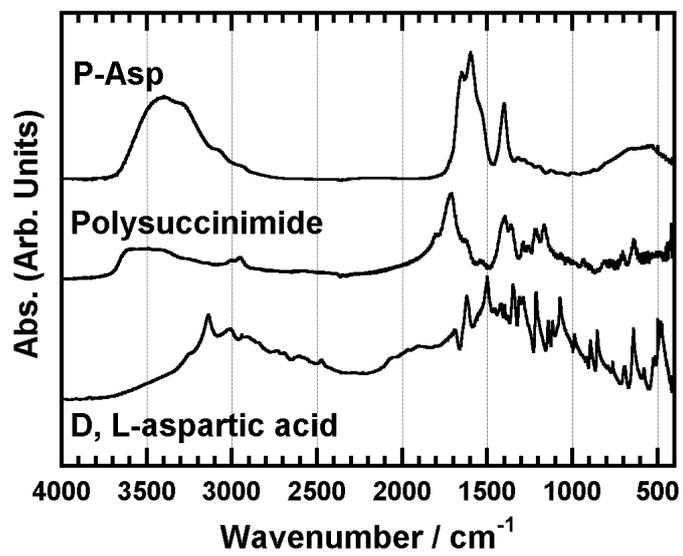


Fig. 3

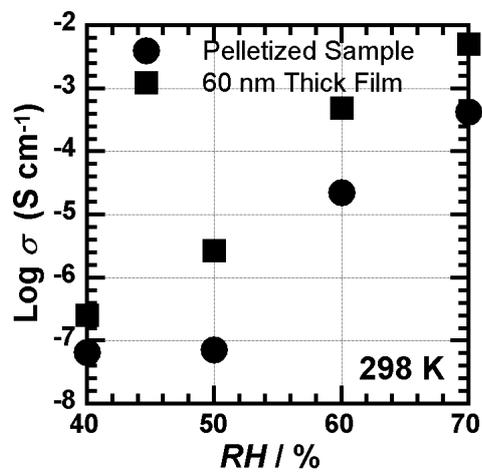


Fig. 4

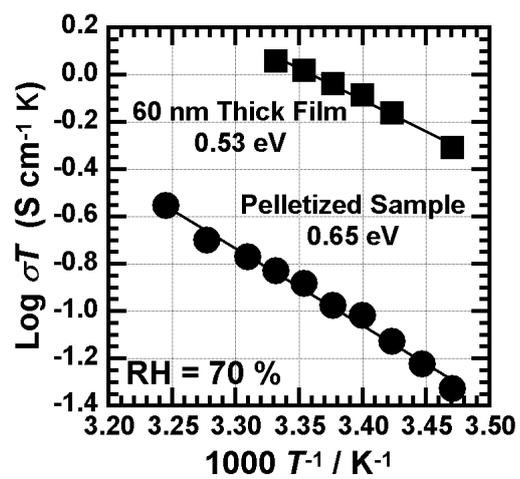


Fig. 5