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Anisotropic proton conductivity of poly(aspartic acid) thin films

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Abstract

Anisotropic proton conductivity was investigated in 60-nm-thick spin-coated thin films of partially protonated poly(aspartic acid)/sodium polyaspartate (P-Asp). The film showed large conductivity difference between in-plane and through-plane directions. The in-plane and through-plane conductivities to the substrate are 2.7×10^{-6} and 3.4×10^{-9} S cm^{-1}, respectively, at the same relative humidity (RH) of 50% and 298 K. The proton conductivity for the in-plane direction was three orders of magnitude greater than that for the through-plane direction. The anisotropic origin is derived from the reported highly oriented structure of the P-Asp thin film. The proton conductivity exhibits no difference for the two in-plane directions between radial and circumferential directions, which can be expected as anisotropic main chain orientation by a centrifugal force during spin-coating.

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Keywords: Centrifugal force; In-plane conductivity; Oriented thin film; Synthetic polypeptide; Through-plane conductivity

1. Introduction

Polymer electrolyte membrane fuel cells are ideal power sources promising high efficiency and high power-to-weight ratios. One issue hindering development of these fuel cells is the availability of a proton conductive material. Actually, a tradeoff relation exists between good proton conductivity, mechanical/chemical stability, and cost. One fundamental approach to the creation of highly proton-conductive materials is chemical modification. Usually, sulfonic acid groups are used as a proton conductive group because of their excellent proton conductivity [1–9].

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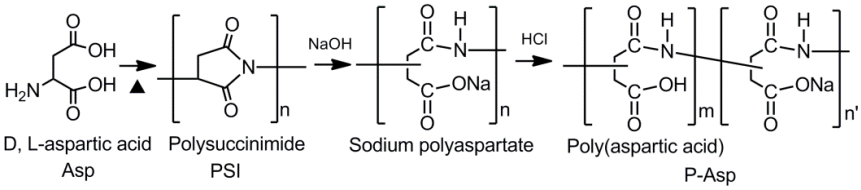
Nevertheless, the high acidity of sulfonic groups restricts the polymer backbone to fluoro or aromatic groups, which entails high production costs. Therefore, a new strategy to produce highly proton-conductive materials at low cost has been sought for a long time.

In a Nafion membrane, protons are well known to be transported through nanochannels made of sulfonic acid groups. In fact, many researchers have discussed this phenomenon intensively [1–4]. The nanochannels are created by phase segregation with the amphiphilic character of Nafion [1, 10]. Nafion's proton conductivity exhibits an excellent value for use in fuel cells at temperatures below 80°C. However, a limit exists on improvement of the proton transport properties and stability based on the concept of using microphase segregation by hydrophilic and hydrophobic parts. Nagao and coworkers proposed that not only microphase segregation but also molecular orientation is important for realizing high proton conductivity [11–21].

Our group investigated poly(aspartic acid) as a proton conductor with weak acid groups based on a different polymer design than that of Nafion [22–25]. Scheme 1 shows that it has free carboxylic acid groups at the side chains. The protons at these groups can be mobile for proton conduction. It is widely acknowledged that amino acid polymers take several hierarchical structures such as α-helix or β-sheets via hydrogen bonding between the amino acids. Our earlier study revealed that a thin film of a partially protonated poly(aspartic acid)/sodium polyaspartate (P-Asp) spin-coated onto quartz and magnesium oxide (MgO) (100) substrates exhibits in-plane orientation of the polymer backbones [22]. The thin films show higher in-plane proton conductivity parallel to the substrate by one order than a random oriented pelletized sample at the same relative humidity (RH). We proposed an ordered proton conductive channel formation which, as we speculated, enhances proton conductivity. It differs greatly from the case of a Nafion membrane, for which microphase segregation engenders high proton conductivity. This report describes high anisotropic proton conduction in the thin P-Asp film. Results demonstrated that the in-plane proton conductivity of the thin P-Asp film is about three orders of magnitude higher than that measured through the thickness direction (through-plane). Anisotropic conduction is well explained by our proposed oriented structure of P-Asp thin film.



Scheme 1. Synthesis of partially protonated poly(aspartic acid) / sodium polyaspartate (P-Asp).

2. Experimental

For these experiments, P-Asp was synthesized according to Scheme 1 [24]. D, L-aspartic acid, *o*-phosphoric acid, methanol, sodium hydroxide, and HCl were purchased from Wako Pure Chemical Industries Ltd. These reagents were used without further purification. The sample was characterized via ^{1}H NMR and FT-IR measurements. The average degree of polymerization was ca. 50. The degree of protonation was found to be 6% [24]. The P-Asp thin films were prepared by spin-coating using a spin-coater (ACT-200; Active Co. Ltd.) on mirror-polished quartz and indium tin oxide (ITO) substrates. The 17 mmϕ quartz substrate was purchased (Sendai Sekiei Glass Seisakusho Y.K.). The ITO substrate, which was prepared by sputtering on a glass substrate, was 15 × 15 mm^2. Before spin-coating, the substrates were irradiated by UV light for 1 hr to clean the surface. The thickness was found using a contact stylus profiler (P-10; KLA Tencor Corp.). The P-Asp thin films on quartz and ITO substrates were 60 nm thick.

Impedance measurements of the pelletized sample and thin films were conducted at relative humidity (RH) of 40–70% 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 pelletized sample, the sample was processed into pellets of 2.5 mmϕ under pressure of about 1 GPa and porous gold paint (SILBEST No. 8560; Tokuriki Chemical Research Co. Ltd.) was used for electrodes. For impedance measurements of the 60-nm thick thin film, one direction is parallel to the substrate (in-plane conductivity). Another is perpendicular to the substrate

(through-plane conductivity). The electrode configuration of the former was selected to obtain measurements of the current flow in the plane parallel to the quartz substrate surface. The thin film size on the quartz substrate was ca. 5 × 10 mm^2. The electrode using Au paste was located at the film edge with a parallel electrode configuration. The inter-electrode distance is 4.0 mm. The porous Au electrode is also covered at the side of the film. The quartz substrate conductivity is negligible because its resistance is much higher than that of the thin film. The electrode configuration of the latter one (through-plane direction) was selected to obtain measurements of the current flow through the thin film on the ITO substrate. The ITO was used as a bottom electrode. The Pt foil with 1 × 2 mm^2 was used as a top electrode. We were unable to obtain data in more than 60%RH because of short circuit problems in through-plane measurements.

3. Results and discussion

Typical complex impedance plots for P-Asp thin film measured through in-plane and through-plane directions are portrayed in Figures 1a and 1b. Resistance is given directly by the intersection of a semicircle with the real axis. The obtained proton conductivity values are, respectively, 2.7 × 10^{-6} S cm^{-1} for the in-plane direction and 3.4 × 10^{-9} S cm^{-1} for the through-plane direction at the 50%RH as shown in Figure 2. The proton conductivity for the in-plane direction was three orders of magnitude greater than that for the through-plane direction. We reported that the in-plane proton conductivity of the P-Asp thin film is one order of magnitude higher than that of the pelletized sample [22]. Figure 3 shows that the proposed enhancement of the proton conductivity in the thin film is attributable to the highly oriented structure of the P-Asp [22]. The polymer main chain aligns parallel to the layer plane. The high anisotropic ratio (790) for the proton conductivity can be supported by the proposed structure in which the proton conductive channel is aligned parallel to the layer plane. Through-plane conduction requires that a proton hops the main chains, which result in the low proton conductivity. Film structure details have been presented in an earlier report [22].

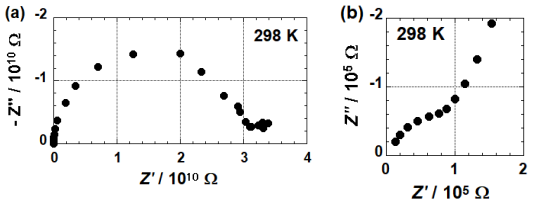


Figure 1. (a) Typical complex impedance plots of the P-Asp thin film on the quartz substrate at the RH of 50% and 298 K. Measurements were conducted parallel (in-plane) to the substrate. (b) Complex impedance plots of the P-Asp thin film on the ITO substrate at RH of 50% and 298 K. Measurements were conducted perpendicular (through-plane) to the substrate.

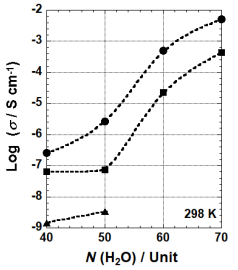


Figure 2. RH dependence of the proton conductivity: ●, in-plane proton conductivity [22].; ■, bulk conductivity of pelletized sample [22].; ▲, through-plane conductivity.

This anisotropic ratio of the proton conductivity was high compared to results described in earlier reports of the literature [26–28]. Ma and coworkers reported that anisotropic proton conductivity was observed in the Nafion 117 membrane [26]. The in-plane conductivity exhibits a higher value: moreover, the ratio of the anisotropy was 2.5–5. Holdcroft and coworkers also investigated the anisotropic proton conductivity in three given directions using a

fluorous block copolymer and a series of Nafion membranes [27]. The in-plane conductivity of Nafion membranes exhibits a higher value. The ratio of the anisotropy is 1.0–1.4. Results show that proton conductivity of the fluorous

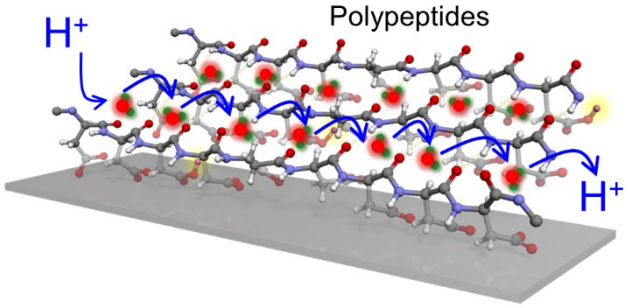


Figure 3. Proposed structure of the highly oriented P-Asp thin film [22]. Polymer backbones oriented parallel to the substrate surface. Pink atoms surrounded by yellow represent proton carriers of carboxylic acid groups: C, gray; N, blue; O, red; H, white.

block copolymer depends on the morphology and the in-plane conductivity in the case of perforated lamellar. Actually, lamellar morphologies exhibit larger values by factors of 2.4 and 5.5, respectively. The through-plane conductivity of the disordered fluorous copolymer exhibits a higher value. Park and Balsara reported heavy anisotropic proton conduction in the aligned block copolymer [28]. When the copolymer is pressed, the in-plane conductivity increases by 30% after alignment. The in-plane conductivity exhibits a higher value. The anisotropy ratio was 75. Matsui and coworkers reported high anisotropic proton conductivity using 2D proton conductive channels with Langmuir–Blodgett thin films [29–32]. The in-plane conductivity with carboxylic acid groups exhibits a higher value of 5×10^{-2} S cm^{-1}. The anisotropic ratio was greater than 10^{10} [31]. These results suggest that the oriented structure is a key property for improvement of proton conductivity. We demonstrated that an oriented proton conductive channel formation using poly(aspartic acid) thin films results in proton conductivity enhancement. This oriented structure might be derived from the secondary structure of polypeptides. Results suggest that the higher-order structure or hierarchical structure can contribute to improvement of the proton transport property. This concept is used naturally in the proton channel and pump in biological phenomena.

A spin-coated thin film is expected to undergo a centrifugal force. Some researchers have reported that the centrifugal force contributes to improvement of the functional and structural characteristics [33–37]. If the polymer is oriented in-plane in response to a centrifugal force, then the proton conductivity is expected to differ in direction A (radial) and direction B (circumferential). Two spin-coated films of equal thickness were formed on quartz substrates. Thin film 1 was formed so that the direction of impedance measurement is radial, as in direction A in Figure 4a. Thin film 2 was formed so that it is normal to the direction of measurement. The thin films were about 4×6 mm^2 in area; a pair of porous gold electrodes was attached, one to each end. Figure 4b presents the RH dependence of proton conductivity along the directions A and B. The proton conductivity in directions A and B presented the same value at each RH. For that reason, the proton conductivity of this polymer thin film presents no difference for the two in-plane directions between radial and circumferential directions. Therefore the polymer formed a uniform 2-D proton conductive channel through the layer plane.

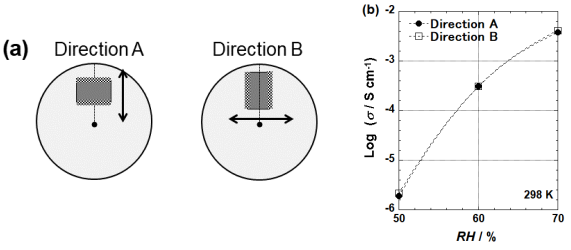


Figure 4. In-plane conductivity check between the two directions between radial and circumferential directions: (a) configuration of the impedance measurements; (b) RH dependence of the radial (Direction A, ●) and circumferential (Direction B, □) proton conductivity of the P-Asp thin films at 298 K.

4. Conclusion

To investigate the origin for improving the proton transport property in a P-Asp thin film, we specifically examined anisotropic conduction attributable to the oriented structure. Results demonstrate that the proton conductivity of the P-Asp thin film exhibits heavy anisotropy between the in-plane and through-plane directions. The proton conductivity for the in-plane direction was three orders of magnitude greater than that for the through-plane direction. The pelletized sample had no specific orientation. Therefore the proton conductivity of pelletized sample exhibited an intermediate value between in-plane and through-plane conductivity. A centrifugal force possibly acting on polymer chains by the spin-coat method brings about in-plane orientation and consequent in-plane anisotropy of the proton conductivity. However, proton conductivity in the radial and circumferential directions exhibited the same value at each RH. Results show that the proton conductivity of this polymer thin film had no in-plane orientation dependence.

Acknowledgments

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References

[1] W.Y. Hsu, T.D. Gierke, J. Membr. Sci. 13 (1983) 307–326.
[2] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29–39.
[3] K.A. Mauritz, R.B. Moore, Chem. Rev. 104 (2004) 4535–4585.
[4] A. Kusoglu, A.Z. Weber, Chem. Rev. 117 (2017) 987–1104.
[5] M. Rikukawa, K. Sanui, Prog. Polym. Sci. 25 (2000) 1463–1502.
[6] J.A. Kerres, J. Membr. Sci. 185 (2001) 3–27.
[7] K. Miyatake, B. Bae, M. Watanabe, Polym Chem. 2 (2011) 1919–1929.
[8] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Chem. Rev. 104 (2004) 4587–4611.
[9] Y. Yang, S. Holdcroft, Fuel Cells 5 (2005) 171–186.
[10] F.I. Allen, L.R. Comolli, A. Kusoglu, M.A. Modestino, A.M. Minor, A.Z. Weber, ACS Macro Lett. 4 (2015) 1–5.
[11] Y. Nagao, Langmuir 33 (2017) 12547–12558.
[12] Y. Nagao, Kobunshi Ronbunshu (In Japanese) advpub (2018) accepted.
[13] K. Krishnan, H. Iwatsuki, M. Hara, S. Nagano, Y. Nagao, J. Mater. Chem. A 2 (2014) 6895–6903.
[14] K. Krishnan, T. Yamada, H. Iwatsuki, M. Hara, S. Nagano, K. Otsubo, O. Sakata, A. Fujiwara, H. Kitagawa, Y. Nagao, Electrochemistry 82 (2014) 865–869.
[15] K. Takakura, Y. Ono, K. Suetsugu, M. Hara, S. Nagano, T. Abe, Y. Nagao, Polym. J. (2018) accepted.
[16] K. Krishnan, H. Iwatsuki, M. Hara, S. Nagano, Y. Nagao, J. Phys. Chem. C 119 (2015) 21767–21774.
[17] Y. Nagao, K. Krishnan, R. Goto, M. Hara, S. Nagano, Anal. Sci. 33 (2017) 35–39.
[18] Y. Ono, R. Goto, M. Hara, S. Nagano, T. Abe, Y. Nagao, Macromolecules 51 (2018) 3351–3359.
[19] Y. Nagao, Chem. Lett. 42 (2013) 468–470.
[20] Y. Nagao, N. Naito, F. Iguchi, N. Sata, H. Yugami, e-J. Surf. Sci. Nanotechnol. 7 (2009) 530–532.
[21] Y. Nagao, N. Naito, F. Iguchi, N. Sata, H. Yugami, Solid State Ionics 180 (2009) 589–591.
[22] Y. Nagao, J. Matsui, T. Abe, H. Hiramatsu, H. Yamamoto, T. Miyashita, N. Sata, H. Yugami, Langmuir 29 (2013) 6798–6804.
[23] Y. Nagao, Y. Imai, J. Matsui, T. Ogawa, T. Miyashita, J. Chem. Thermodyn. 43 (2011) 613–616.
[24] Y. Nagao, F. Iguchi, N. Sata, H. Yugami, Solid State Ionics 181 (2010) 206–209.
[25] Y. Nagao, M. Ando, H. Maekawa, C.H. Chang, F. Iguchi, N. Sata, ECS Trans. 16 (2009) 401–406.
[26] S. Ma, Z. Siroma, H. Tanaka, J. Electrochem. Soc. 153 (2006) A2274–A2281.
[27] T. Soboleva, Z. Xie, Z. Shi, E. Tsang, T. Navessin, S. Holdcroft, J. Electroanal. Chem. 622 (2008) 145–152.
[28] M.J. Park, N.P. Balsara, Macromolecules 43 (2010) 292–298.
[29] Y. Hashimoto, T. Sato, R. Goto, Y. Nagao, M. Mitsuishi, S. Nagano, J. Matsui, RSC Adv. 7 (2017) 6631–6635.
[30] T. Sato, M. Tsukamoto, S. Yamamoto, M. Mitsuishi, T. Miyashita, S. Nagano, J. Matsui, Langmuir 33 (2017) 12897–12902.
[31] T. Sato, Y. Hayasaka, M. Mitsuishi, T. Miyashita, S. Nagano, J. Matsui, Langmuir 31 (2015) 5174–5180.
[32] J. Matsui, H. Miyata, Y. Hanaoka, T. Miyashita, ACS Appl. Mater. Inter. 3 (2011) 1394–1397.
[33] H. Kimura-Suda, Y. Zhang, T. Sassa, T. Wada, H. Sasabe, Adv. Mater. 12 (2000) 1196–1199.
[34] H.F. Meng, B.L. Chen, K.C. Tzeng, S.F. Horng, Appl. Phys. Lett. 88 (2006) 023505(023501-023503).
[35] U. Bielecka, P. Lutsyk, K. Janus, J. Sworakowski, W. Bartkowiak, Org. Electron. 12 (2011) 1768–1776.
[36] Y. Hu, J. Wang, C. Li, Q. Wang, H. Wang, J. Zhu, Y. Yang, Langmuir 29 (2013) 15529–15534.
[37] T. Kobayashi, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A 314 (1998) 1–11.