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Title	Proton-Conductivity Enhancement in Polymer Thin Films
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Citation	Langmuir, 33(44): 12547-12558
Issue Date	2017-07-28
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/15729
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Description	

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Proton-Conductivity Enhancement in Polymer Thin Films

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ABSTRACT

Highly proton-conductive polymers have long attracted the attention of researchers for use in energy conversion, sensors, catalysts, and other applications. From the viewpoint of scientific history of creation of highly proton-conductive polymers, one fundamental approach is based on the strategy of phase-segregated structures with strong acid groups. This Feature Article presents a new approach to enhance the proton conductivity of the polymer thin films using an interface that can modify the degrees of freedom for a polymer structure through interaction between the substrate surface and polymers. The author introduces suppressed proton conductivity in Nafion thin films and then specifically examines the enhancement of proton conductivity by the molecular orientation in the polymers. As the last topic, the highly proton-conductive organized polyimide thin film is demonstrated using the lyotropic liquid-crystal property. Both molecular ordering and the in-plane oriented structure can enhance proton conductivity. Moreover, the

optical domain and degree of the molecular ordering derived from the molecular weight can contribute strongly to the proton transport property.

KEYWORDS: interface, oriented structure, substrate dependence, thickness dependence, organized structure, lyotropic liquid crystal property, molecular ordering, molecular weight dependence

Introduction

Proton transfer in ionic channels of biological proteins has attracted the efforts of many researchers since the 1960s.[1] Many have investigated the purple membrane including bacteriorhodopsin to elucidate its fundamental role in proton transport in biological systems.[2-5] Surface proton conduction at the lipid monolayer, including the phenomena of the proton diffusion enhancement at the interface, has also been studied intensively.[6, 7] Work in inorganic research fields indicates that diffusion at the interface or grain boundary plays an important role in the ionic conduction. Liang reported in 1973 approximately 50-times enhancement of Li^+ ion conduction using the non-conductive interface of the Al_2O_3.[8] The sample was simply mixed with inert Al_2O_3 ultrafine particles into LiI. In most cases, ionic conductivity enhancement was observed with non-conductive materials such as SiO_2 or Al_2O_3 as the second phase, which is nearly insoluble in the host material. To elucidate the enhancement phenomena of ionic conductivities at the interface, widely diverse 2D ion conducting materials have been reported from studies conducted over more than 30 years.[9-15] In 2000, Sata *et al.* demonstrated that ionic conductivity in solid electrolytes can be improved by introducing interfaces that redistribute ions in space-charge regions.[10] These findings gave us the opportunity to improve ionic transport

properties using an interface. In recent years, various thin materials have been reported on the high proton conduction using the interface concept: multilayer thin films by a layer-by-layer,[16-18] two-dimensionally confined Langmuir–Blodgett thin films,[19, 20] metal–organic framework thin films,[21] and graphene based thin films.[22, 23] Today, the proton transport property modulated by the interface attracts researchers of various research backgrounds.

Many proton conductive polymers have been reported and intensively studied.[24, 25] These designs are based on the phase segregation between the hydrophobic and hydrophilic parts with water uptake. Protons are considered to be transported through the hydrophilic parts. In the recent polymer research fields, taking advantage of the interface extends the molecular design such as the oriented structure and organized structure for the highly proton conductive materials. In this Feature Article, the author proposed the concept of molecular orientation to improve proton conductivity for various proton-conductive polymers using the interface of substrate surfaces.[26-33] The interface can modify the degrees of freedom for polymer structures through interaction for functional groups, wettability, and surface charge between the substrate surface and polymers. Some proton-conductive polymers exhibit an oriented structure by fabrication of thin films. Their oriented thin films show unique proton transport properties compared to those of non-oriented samples. Some polymer thin films exhibited not only higher proton conduction but also thickness-dependence or substrate-dependence for the proton transport property. Understanding the relation between the structure and proton transport property is fundamentally important, but this attempt has often been hampered in many highly proton-conductive polymers because of less structural information derived from amorphous or amorphous-like nature. Recent studies by the author and co-workers have demonstrated the organized polyimide structure using a lyotropic liquid crystal property in the thin films.[30-33] This organized thin film

shows a lamellar structure and exhibits in-plane high proton conductivity with more than 10^{-1} S cm^{-1}. The author introduces suppressed proton conductivity in the Nafion thin films, then specifically examines enhancement of proton conductivity by the molecular orientation and organized structure.

Suppressed Proton Conductivity in Nafion Thin Films

The Nafion membrane has been the most widely investigated polymer electrolyte for use in energy conversion as fuel cells for automotive, portable device and other applications since the 1960s because it exhibits high proton conductivity, good mechanical and chemical stability.[24, 34-36] Figure 1 shows the Nafion chemical structure, which comprises a perfluorocarbon backbone and side chains terminated with sulfonic acid groups. Protons at the sulfonic acid groups of the side chain can be transported through hydrated water channels in hydrophilic pathways, which are separated by phase segregation from the hydrophobic backbone.[24, 34-39]

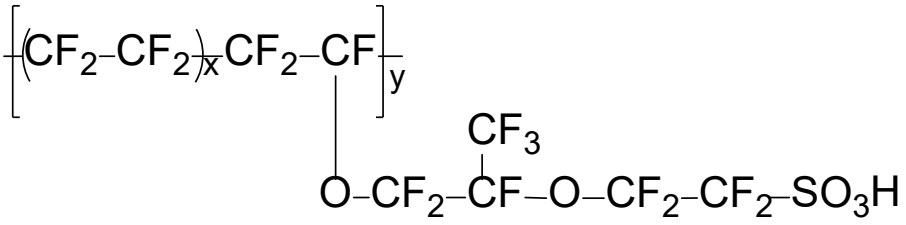


Figure 1 Nafion structure with equivalent weight of 1100: x=6-7 and y=1.

In 2008, Siroma *et al.* demonstrated the proton conductivity drop with decreasing thickness in a Nafion thin film.[40] Until now, the interfacial structure,[41-67] proton conductivity,[40, 50, 52, 53, 64, 65, 68-78] water uptake,[54, 60, 64, 76, 79-86] and diffusivity[81, 83, 85, 87-89] in the Nafion thin films have been reported. These structural and physical properties differ from those of the thick Nafion membrane and depend on the thickness and substrate. The Nafion thin films can be prepared

from a commercially available solution using spin casting, drop casting, Langmuir–Blodgett, Langmuir–Schaefer, spray deposition, or self-assembled adsorption on various substrates. One pioneer study for the interfacial structure of the Nafion thin film examined a multilayer lamellar structure between the SiO_2 substrate and Nafion thin film using neutron reflectometry (NR).[45] On the other hand, a single hydrated layer appeared at metal interfaces such as at Pt and Au surfaces.[44, 45] These results suggest that the interfacial structure of the Nafion thin film depends on the substrate surface. Kusoglu and Weber summarized recent studies of Nafion thin films conducted up through 2016.[36] The degree of micro-phase separation lessened with decreasing thin film thickness.[53] Less micro-phase separation can affect the proton conductivity drop.

In-plane proton conductivity of the Nafion thin film decreases concomitantly with decreasing film thickness as shown in Figures 2a and 2b.[40, 50, 52, 53, 65] Commercial Nafion membranes with thickness of more than several tens of micrometers exhibit good proton conductivity (10^{-1} S cm^{-1}). The proton conductivity and activation energy for the proton conduction of the Nafion thin films depend on substrate surfaces: quartz, MgO, and modified surfaces sputtered by Pt.[50, 52, 65, 77] Proton conductivity of the Nafion thin film on the quartz surface shows different thickness dependence from those on the MgO(100) and sputtered Pt surfaces.[50, 52, 65] As portrayed in Figure 2c, the activation energy of the Nafion thin film for the proton conduction on the quartz shows a higher value than that on the sputtered Pt surface, especially in the low RH condition.[65] These differences of the proton conductivity can be derived from different interfacial structures of the Nafion thin films and water uptake/diffusion properties.

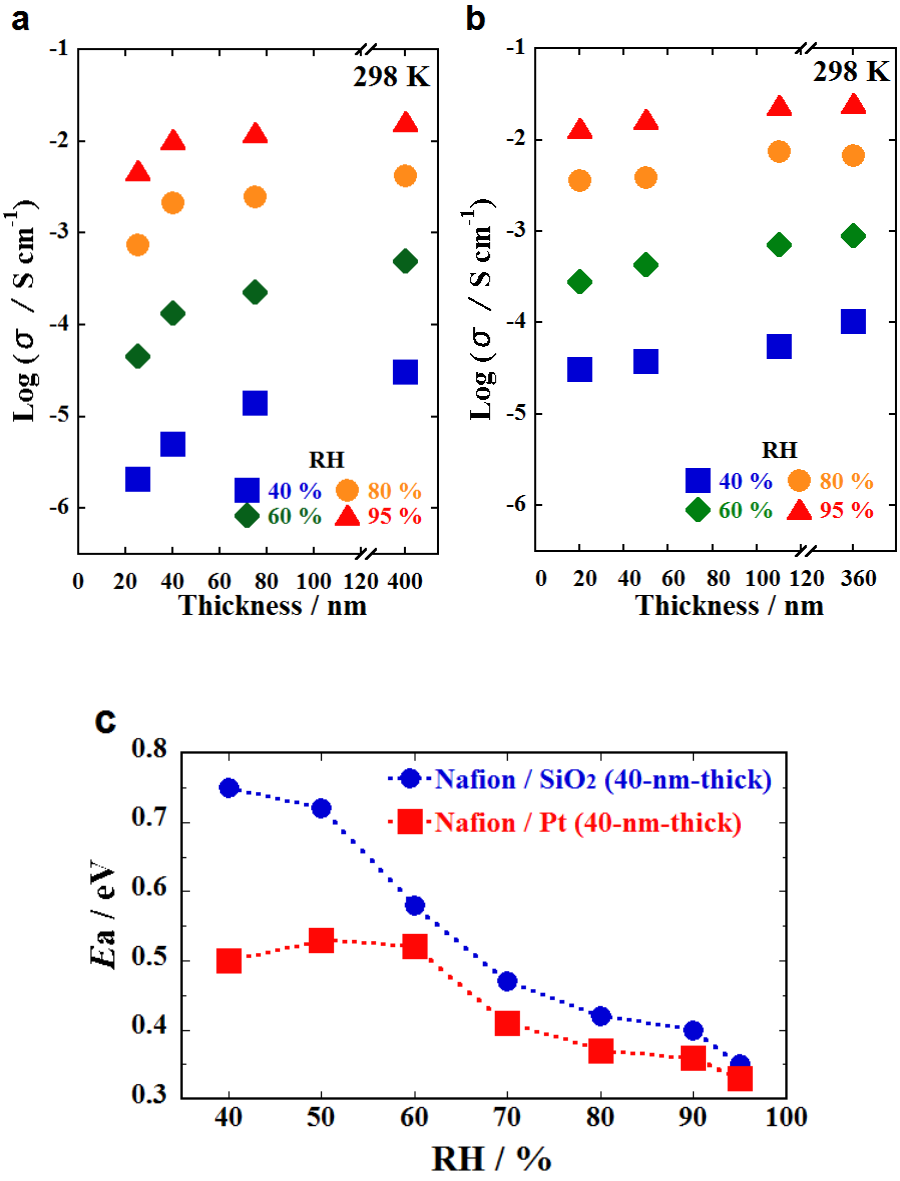


Figure 2. (a), (b) Thickness dependence of proton conductivity for Nafion thin films at various relative humidity (RH): (a) on SiO_2 and (b) on Pt-deposited surface. (c) Activation energy for the 40-nm-thick Nafion thin films on SiO_2 and Pt-deposited surface as a function of the RH. Adapted with permission from ref 65. Copyright 2016 American Chemical Society.

Oriented structures of Nafion thin films also receive attention. Anisotropic IR spectra between the in-plane (IP) and out-of-plane (OP) direction to the MgO (Figure 3a),[50] Si,[52] and Pt deposited[65] surfaces (Figure 3b) by p-polarized multiple angle incidence resolution spectrometry (pMAIRS)[90, 91] have been reported. The IR pMAIRS technique can provide opportunities to investigate pure IP and pure OP molecular vibrations to the substrate surface. The pMAIRS technique can reveal the degree of the molecular orientation quantitatively for each functional group according to the following equation (1) as

$$\varphi = \tan^{-1}\sqrt{\frac{2I_{IP}}{I_{OP}}}, \quad (1)$$

where I_{IP} and I_{OP} are the IP and OP peak absorbance and where φ denotes the orientation angle from the surface normal. For the Nafion thin film, the IP spectrum shows the well-known spectrum of the thick Nafion membrane.[92, 93] However, the OP spectrum differs greatly from the IP spectrum, as shown in Figure 3a. The characteristic absorption band at 1260 cm^{-1} is observed only in the OP spectrum. This band cannot be obtained in the IP spectrum. A few reports of the literature describe this peak located at 1260 cm^{-1} experimentally by polarization modulation infrared reflection absorption spectroscopy.[47, 88] They assigned different attributions of the band at 1260 cm^{-1} as $\nu(CF_2)$[88] and $\nu_{as}(CF_3) + \delta_s(COC)$[47] vibration mode, respectively. Zeng *et al*. assigned $\nu_{as}(CF_3)$ vibration mode at the 1269 cm^{-1} in the Raman spectra.[94] Malevich *et al*. and Korzeniewski *et al*. assigned attributions of the band at 1250–1350 cm^{-1} and 1249–1275 cm^{-1} as $-SO_3^-$ from a deconvoluted IR spectrum.[95, 96] Figure 3b shows that this absorbance of the band at 1260 cm^{-1} in the OP spectrum on the Pt deposited surface changes with decreasing thickness.[65] To discuss the absorbance change, the relative intensity ratio is calculated as

$$Intensity\ ratio\ = \frac{I_{OP}(1260\ cm^{-1})}{I_{2IP}(1215\ cm^{-1})}, \qquad (2)$$

where I_{OP} and I_{2IP} are derived from peak absorbance of IR p-MAIR spectra. Figure 3c shows that a threshold is observed around 50–70 nm in the case of the Pt-deposited surface. The ratio changes gradually with decreasing thickness on the MgO substrate surfaces, but no apparent threshold of the ratio is visible. This result suggests that the interfacial oriented structure depends on the substrate surface.

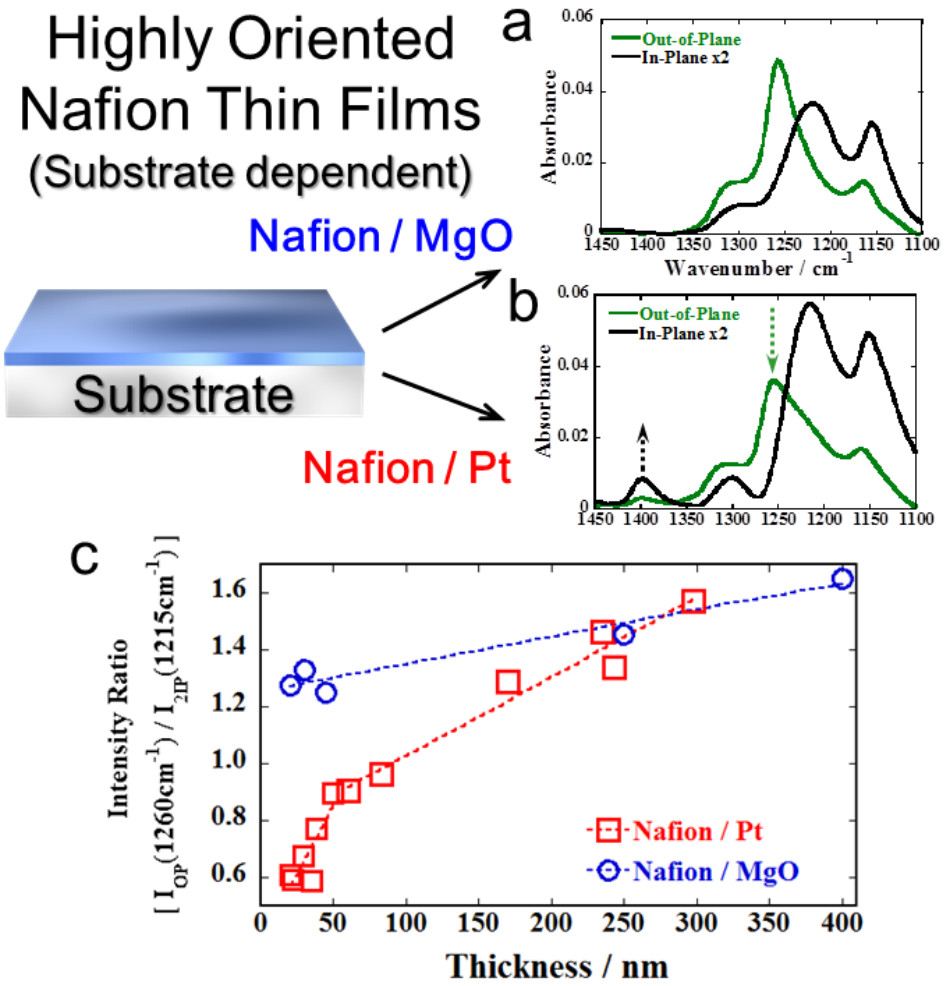


Figure 3 Oriented Nafion thin films. (a) pMAIR spectra on the MgO substrate. (b) pMAIR spectra on the Pt-sputtered surface. (c) Thickness dependence of relative intensity ratios

according to eq. (2). Adapted with permission from ref 65. Copyright 2016 American Chemical Society.

Other reports have described studies of the molecular orientation of the Nafion thin films. Kendrick *et al.* measured the polarization-modulated IR spectra of Pt-Nafion interfaces. The ordered structure of the SO_3^- groups on the Pt surface is well supported by their results and DFT calculations.[47] Yagi *et al.* discussed the orientation of SO_3^- groups in the ca. 5 nm region of the Nafion/Pt interface based on results of vibrational sum frequency generation spectroscopy.[59]

The adsorbed water also plays an important role in the proton transport property. The number of the adsorbed water and distribution of the water in the Nafion thin film can be investigated using an in-situ quartz crystal microbalance,[53, 54, 60, 76, 80, 82, 85] NR,[44-46, 54, 61, 81, 84, 86] and photoluminescence[82, 85] measurements. Compared to the thick Nafion membrane, the lower water uptake and lower effective diffusion coefficient of water in the Nafion thin film were discussed. Their properties were found to be dependent on the film thickness. Less water uptake of the Nafion thin films causes the proton conductivity drop. Water uptake of the 25-nm-thick Nafion thin film on SiO_2 shows less amount than that on Pt surface.[76] Ogata *et al.* reported that multi stepwise hydration was observed through the water uptake kinetics in ca. 50-nm-thick Nafion thin films on silver and quartz substrates by the surface plasmon resonance and NR measurements.[84] An NMR study for 10-nm-thick and 160-nm-thick Nafion thin films showed that the local mobility of the proton within the hydrogen-bonded domain is equivalent and that it is governed by the fast exchange limit in terms of NMR time scales.[89]

In summary, the Nafion thin film structure is unique and different from the thick Nafion membrane structure. The interfacial structure depends strongly on the thickness and substrate surface. To date, all results have shown that the proton conductivity of the Nafion thin film exhibits a lower value than that of the thick Nafion membrane. The proton conductivity of the Nafion thin film decreases concomitantly with decreasing thickness. Water uptake and diffusion of the Nafion thin film decrease compared to that of the thick Nafion membrane. The property of the Nafion thin film is related with the reaction sites for the polymer electrolyte fuel cells as an ionomer.[43, 97] Therefore, understanding the relation between the interfacial structure and proton transport property is necessary for both fundamental and application studies.

Enhancement of Proton Conductivity in Molecular Oriented Thin Films

Oriented Oligomeric Amide Thin Films

The proton conductivity of the Nafion thin films is lower than that of the thick Nafion membrane. Nagao and Naito *et al.* first reported the observation of anomalous proton conductivity in amide thin films of oligo[(1, 2-propanediamine)-*alt*-(oxalic acid)] in 2008.[98] From the results of ^{1}H NMR, FT-IR, and MALDI-TOF mass spectra, the synthesized amides are inferred as a mixture of the oligomers with different end groups and low-molecular-weights including the macrocyclic amides, as shown in Figure 4a. The oligomeric amide thin films were prepared by spin coating on the SiO_2 substrate with thickness of 60–400 nm. Figure 4b shows that the in-plane proton conductivity depended on thickness and showed 4.0×10^{-3} S cm^{-1} as a maximum value in the 200-nm-thick at the RH of 80%. For comparison between the thin film and bulk conductivity, the pelletized sample as bulk was processed into pellets of 2.5 mmϕ under pressure of approx. 1 GPa

because of failure of the self-standing membrane. The proton conductivity of the pelletized sample was 3.0×10^{-4} S cm^{-1}, which is one order of magnitude lower than that of the 200-nm-thick thin film. The activation energies of the 200-nm-thick film and pelletized sample were, respectively, 0.69 and 1.0 eV. Figure 4c shows that the substrate dependence of the proton conductivity was observed in the amide thin films.[26, 99] The amide thin films showed different proton conductivity on the SiO_2, R-plane sapphire, and MgO(100). The proton conductivity varied from 4×10^{-3} to 1×10^{-4} S cm^{-1} under the same condition of the 80% RH and 298 K. This difference of the proton conductivity is probably attributable to the difference of the interfacial structure. The pMAIRS results show that the spectra of the thin film on the R-plane (1102) sapphire (Figure 4d) differ greatly from those of the MgO substrate (Figure 4e). Both thin films show the anisotropic oriented structure from the IP and OP spectra. The absorption bands at 1680 and 1520 cm^{-1} in the OP spectrum on MgO substrate can be assigned respectively to the vibrational modes of Amide I and Amide II. The DFT calculation suggests that the wavenumber of the Amide I band depends on the oligomer–oligomer chain interaction through the hydrogen bonding networks. The difference of the proton conductivity can be derived from the differently oriented structure and hydrogen bonding networks in the thin films. Results obtained for the amide thin films demonstrate that the oriented structure in the thin films contributes to improvement of the proton conductivity. Therefore, preparing an oriented structure by thin films can be proposed as a new method to improve proton transport properties.

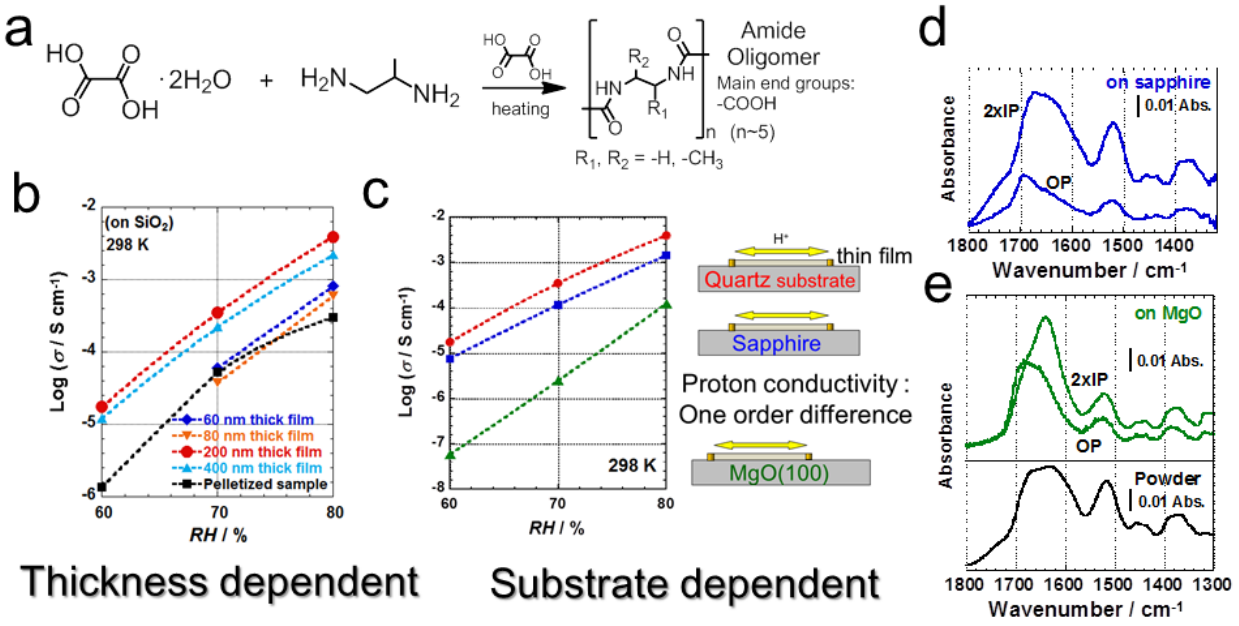


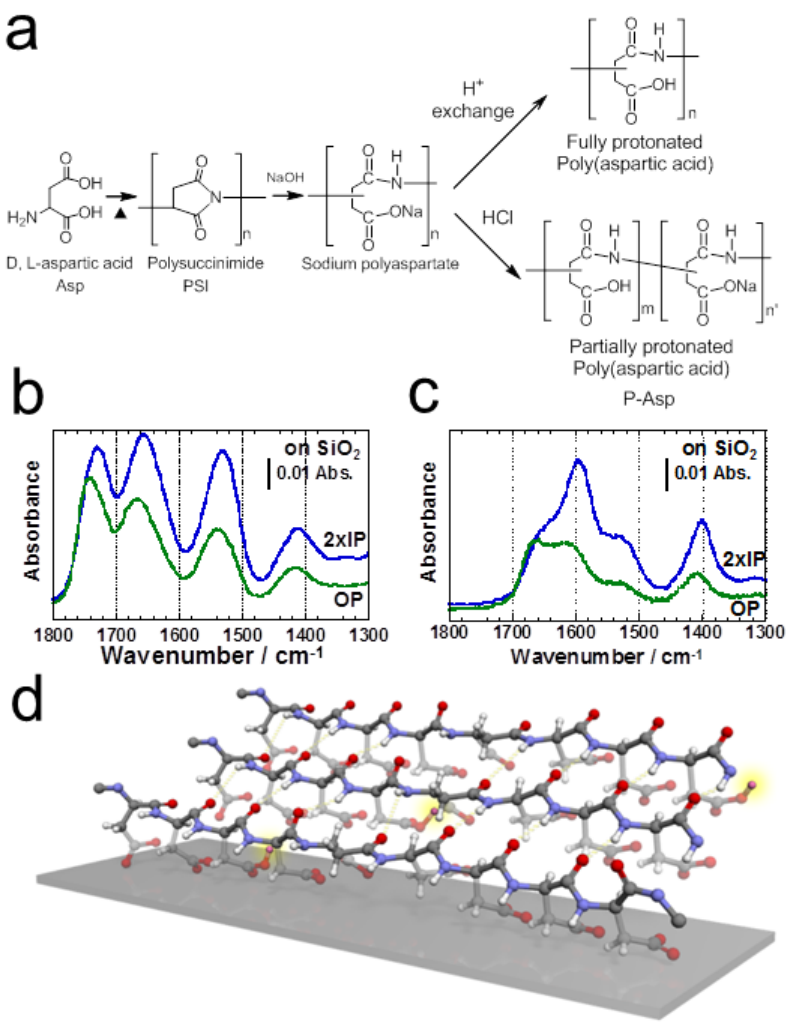
Figure 4 (a) Synthetic scheme of the oligomeric amide. (b) RH dependence of the proton conductivity of the amide bulk and thin films with thickness of 60 – 400 nm on SiO_2 substrates. (c) RH dependence of the proton conductivity of the amide thin films on different substrates. (d) pMAIR spectra of the amide thin films on sapphire substrate. (e) IR spectrum of the bulk powder and pMAIR spectra of the amide thin films on the MgO substrate. Figure 4b was adapted with permission from ref 98. Copyright 2009 Elsevier. Figures 4c-e were adapted with permission from ref 26. Copyright 2013 The Chemical Society of Japan.

Oriented Polypeptide Thin Films

An oriented polypeptide also improves the proton conductivity by thin films. Biological molecules and polymers with hydrogen bonding networks often exhibit hierarchical structures for the specific functionality. Proton transport into protein ionic channels has attracted many

researchers since the 1960s.[1] Polypeptides are widely acknowledged to take several hierarchical structures such as α-helix or β-sheets via hydrogen bonding between the amino acids. The poly(aspartic acid) has free carboxylic acid groups at the side chains. The protons at these groups are mobile as proton conduction in the synthetic scheme shown in Figure 5a.[27, 29, 100-102] The fully protonated poly(aspartic acid) thin film shows no oriented structure (Figure 5b),[29] although a partially protonated poly(aspartic acid) (P-Asp) thin film with 60 nm thick exhibits an anisotropic oriented structure between the IP and OP direction to the substrate by pMAIRS results, as depicted in Figure 5c.[27] The Amide I band is visible in both IP and OP spectra from pMAIR spectra at 1670 cm^{-1}. The peak position of the Amide I band is related to the polypeptide main-chain structure.[103, 104] It is plausible that the P-Asp thin film exists in neither regular secondary structures such as an α-helix or β-sheet nor in an irregular structure because these secondary structures respectively portray the Amide I bands at the range of 1640-1660, 1620-1640, and 1640-1660 cm^{-1}, respectively.[103, 104] Figure 5d portrays a proposed non-periodic α-sheet like model. High proton migration paths were realized through α-sheet layers with water uptake, which percolate in-plane, formed by the stacked layer structure in OP direction of the substrate. This model does not necessarily mean that the thin film is composed exclusively of α-sheet layers. For proton conductivity, the fully protonated poly(aspartic acid) thin film shows high surface conductivity. The proton conduction path is dominated on the surface rather than inside the thin film (Figure 5e).[29] By contrast, the oriented P-Asp thin film shows that protons can be transported easily inside the thin film and that they exhibit in-plane proton conductivity of 3×10^{-3} S cm^{-1} on the MgO substrate at 298K, as shown in Figures 5f and 5g.[27] It is remarkable that the proton conductivity shows such a high value by carboxylic acid groups as proton sources.[105] To compare proton conductivity between the oriented and random oriented P-Asp, the

randomly oriented sample is prepared using a pelletized sample.[27] The Amide I band appears correspondingly at ca. 1650 cm^{-1} in the IR ATR result, which is attributable to the existence of the irregular structure that produces the band at 1640-1660 cm^{-1}.[103, 104] The proton conductivity of the random oriented P-Asp shows 4×10^{-4} S cm^{-1} at 298 K and 70% RH, which is one order of magnitude lower than that of the oriented P-Asp thin film (Figure 5g). The activation energies for proton conductivity are 0.34 eV for the oriented P-Asp thin film and 0.65 eV for the random oriented P-Asp, as shown in Figure 5h. For comparison, examination using a quartz crystal microbalance is conducted for the water uptake between the oriented and random oriented P-Asp. Both the oriented and random oriented P-Asp show similar isotherm curves; both adsorb two water molecules per chain unit, at most (Figure 5i). Therefore, the results demonstrate that the oriented structure contributes to improvement of the proton transport property.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H+ exchange
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HCl
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Asp
Polysuccinimide
PSI
Sodium polyaspartate
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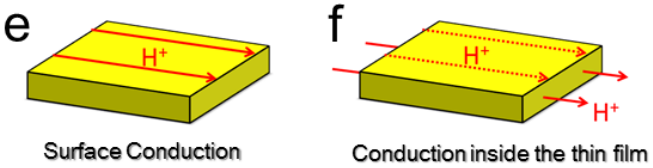
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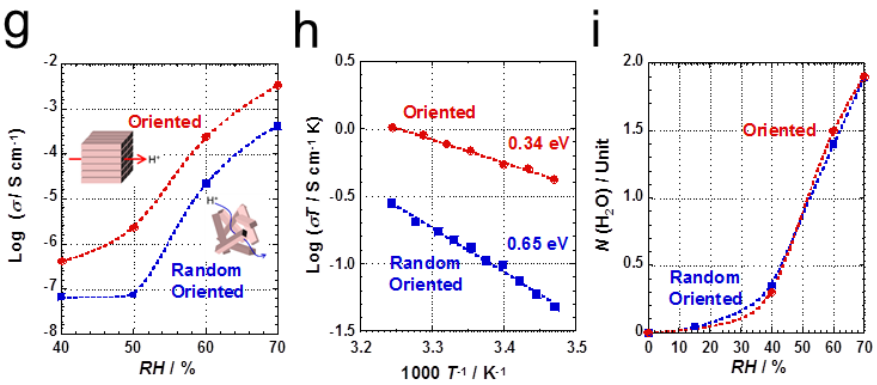
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Figure 5 (a) Synthetic scheme of fully and partially protonated poly(aspartic acid). (b) pMAIR spectra of the fully protonated poly(aspartic acid) thin film. (c) pMAIR spectra of the partially protonated poly(aspartic acid). (d) Proposed structure of P-Asp thin film with non-periodic α-sheet like. Pink atoms surrounded by yellow represent proton carriers of carboxylic acid groups: C gray, N blue, O red, H white. (e) Schematic view of surface proton conduction in the fully protonated poly(aspartic acid) thin film. (f) Schematic view of proton conduction inside P-Asp thin film. (g) RH dependence of proton conductivity by the oriented and random oriented structures. (h) Temperature dependence of proton conductivity by the oriented and random oriented structures. (i) Water isotherm curve between the oriented and random oriented structures. Figures 5b,e,f were adapted with permission from ref 29. Copyright 2014 Elsevier. Figures 5c,d,g-i were adapted with permission from ref 27. Copyright 2013 American Chemical Society.

Results obtained for both amide and polypeptide thin films demonstrate new aspects to enhance proton conductivity by the oriented structure induced by the interface. In the next chapter, a highly proton-conductive organized thin film designed to obtain higher proton conductivity will be demonstrated using not only an oriented structure but also molecular ordering, which can respond reversibly to humidity.

Enhancement of the Proton Conductivity in Highly Molecular Organized Thin Films of Sulfonated Polyimide

Relation between Lyotropic Organized Structure and Proton Conductivity

Sulfonated polyimides (SPIs) are promising candidates for use as polymer electrolytes for fuel cells because of their thermal and chemical stabilities. [106-113] Recently, highly proton-conductive oriented SPI thin films have been reported as shown in Figure 6a. [30-33] Many highly proton-conductive polymers are amorphous or amorphous-like. However, this SPI thin film presents an organized structure by water uptake based on the lyotropic liquid crystal property with more than 10^{-1} S cm^{-1}. This is the first report to demonstrate high proton-conduction by the oriented organized structure in the solid thin films, which responds reversibly by the humidified atmosphere. The organized structure and liquid crystal property of the SPI thin film on the quartz substrate were confirmed respectively by humidity-controlled in-situ grazing incidence small angle X-ray scattering (GISAXS) measurements and birefringence by polarized optical microscopy (POM) measurements. The SPI thin film shows lyotropic liquid crystalline lamellar behavior. The existence of high relative humidity induces expansion of the lamellar structure in the out-of-plane direction by water uptake, as shown in Figure 6b. Increasing intensity of the OP peak from the GISAXS profile (Figure 6c) by water uptake suggests improvement of the degree of molecular ordering. Along with the improvement of the degree of molecular ordering for the oriented lamellar structure, the in-plane proton conductivity also increases from 10^{-4} S cm^{-1} to 10^{-1} Scm^{-1} at 25 ºC. Not only because of the oriented lamellar structure but also because of the large scaled LC ordering and interchain *ch*-packing[114] of SPI thin films, the proton transport characteristic is much improved in the high-humidity condition.

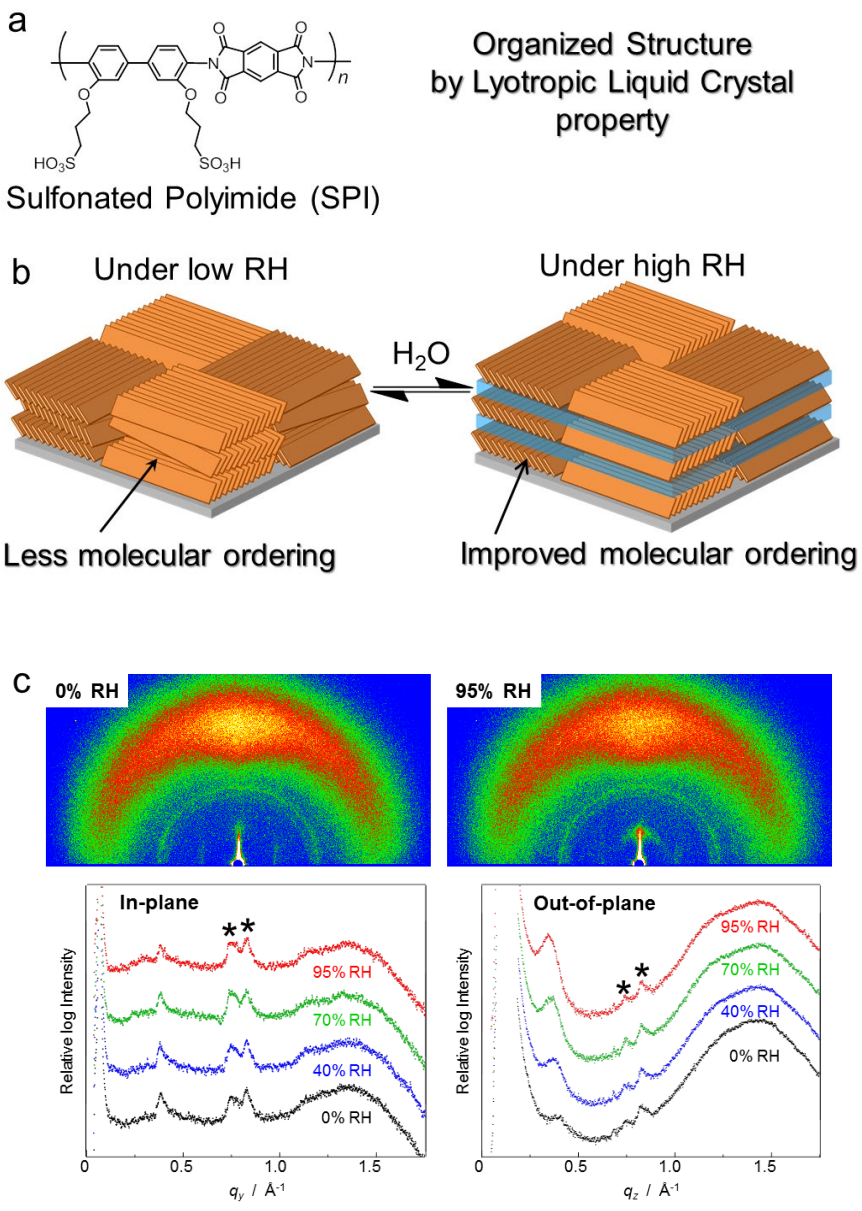

Figure 6 (a) Chemical structure of the sulfonated polyimide. (b) Schematic views of the organized lamellar structure. Molecular ordering improves with water uptake by the lyotropic liquid crystal property. (c) 2D GISAXS patterns at 0% RH and 95% RH, respectively, and humidity-dependent 1D GISAXS profiles in the IP and OP directions of the SPI thin film. Asterisks denote scattering from the Kapton windows. Adapted with permission from ref 32. Copyright 2015 American Chemical Society.

Effects of Molecular Weight to Proton Conductivity

Proton conductive polymers do not usually exhibit a strong effect of the molecular weight for proton conductivity when the molecular weight is greater than some thousands.[115, 116] However, the SPI thin films show strong correlation between the molecular weight and proton conductivity.[32] Analyses of the thin films by GISAXS reveal that the HM_w (M_w= 2.6 × 10^5) SPI film exhibits a higher degree of inherent liquid crystalline-like lamellar ordering than the LM_w (M_w= 1.3 × 10^4) SPI film does, as shown in Figures 7a and 7b. Such molecular ordering and the in-plane oriented structure can strongly influence the proton transport characteristics in thin films. The larger ordered domains in the HM_w SPI thin film with thickness of approximately 500 nm show marked proton conductivity enhancement to a value of 2.6 × 10^{-1} S cm^{-1} at 25ºC and 95% RH (Figure 7c), which is more than an order of magnitude higher value than that of the smaller ordered domains in the LM_w SPI thin film with less molecular ordering. The larger ordered domains in the HM_w SPI thin film (Figure 7d and 7e) influence the proton conducting characteristics attributable to the fewer liquid crystalline-like domain boundaries relative to the LM_w SPI thin films (Figure 7f and 7g). That influence derives from the smaller ordered domains in the LM_w SPI thin film, which more clearly exhibit large-scaled domain boundaries that can disrupt the fast ion transportation, as shown in Figure 7h and 7i. Revealing roles of the domain size and domain boundary for the high proton conduction in the SPI thin films is attractive issues to understand the proton conduction mechanism.

Degree of molecular ordering depends on molecular weight.

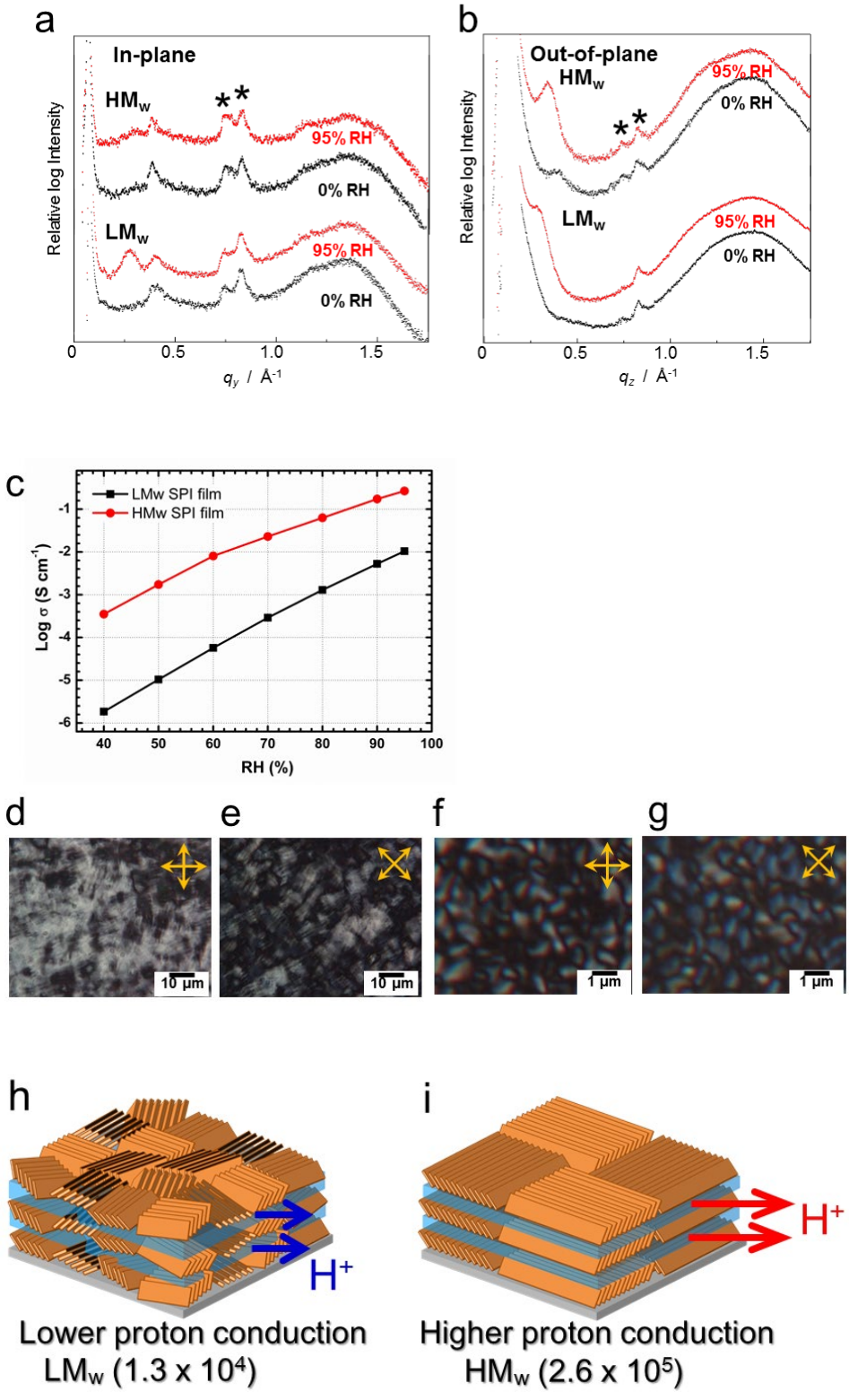

Figure 7 (a) RH dependence of 1D GISAXS profiles in the IP direction of both LM_w and HM_w SPI thin films. Asterisks denote scattering from the Kapton windows. (b) RH dependence of 1D GISAXS profiles in the OP direction of both LM_w and HM_w SPI thin films. (c) RH dependence of the proton conductivity for both LM_w and HM_w SPI thin films. (d), (e) POM images for larger domain size of HM_w SPI thin films at 0º and 45º, respectively. (f), (g) POM images for smaller domain size of LM_w SPI thin films at 0º and 45º, respectively. (h) Schematic view of the lower proton conductivity in LM_w SPI thin film with less molecular ordering in the out-of-plane direction and smaller domain. (i) Schematic view of the higher proton conductivity in HM_w SPI thin film with better molecular ordering in the out-of-plane direction and larger domain. Adapted with permission from ref 32. Copyright 2015 American Chemical Society.

Summary

From the viewpoint of the scientific history of the creation of highly proton-conductive polymers, one fundamental approach is based on the strategy of phase-segregated structures with strong acid groups. In this Feature Article, the author demonstrated another method to improve proton conductivity using the interface. The interface can modify the degrees of freedom for a polymer structure by interaction between the substrate surface and polymers. This approach enables us to discuss the relation between the interfacial structure and proton transport property. The Nafion thin film exhibits a thickness-dependent structure at the interface, with proton conductivity decreasing along with decreasing thickness. The oligomeric amide thin films show a substrate-dependent oriented structure. The polypeptide thin films show proton conductivity improvement by molecular orientation compared to the random oriented structure. As the last topic discussed

in this article, a highly proton-conductive organized polyimide thin film was demonstrated using the lyotropic liquid crystal property. Both molecular ordering and the in-plane oriented structure can enhance proton conductivity in SPI thin films. Moreover, the optical domain and degree of the molecular ordering derived from the molecular weight can contribute strongly to the proton transport property. Other studies have also specifically examined the molecular orientation or organized structure for obtaining the proton condustion.[19, 20, 117-120] Some issues still remain unsolved: roles of the surface wettability, functional groups, surface charge to understand the interfacial interactions. Moreover, a side of the free-surface of the thin films should be considered. An equilibrium structure expected from slow assembly vs kinetically frozen structure from spin coating is also one of the attractive issues. These discoveries are expected not only to encourage further discussion of the relation between the interfacial structure and proton transport properties but also to contribute to the development of Solid State Protonics.

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Notes

The author declares no competing financial interest.

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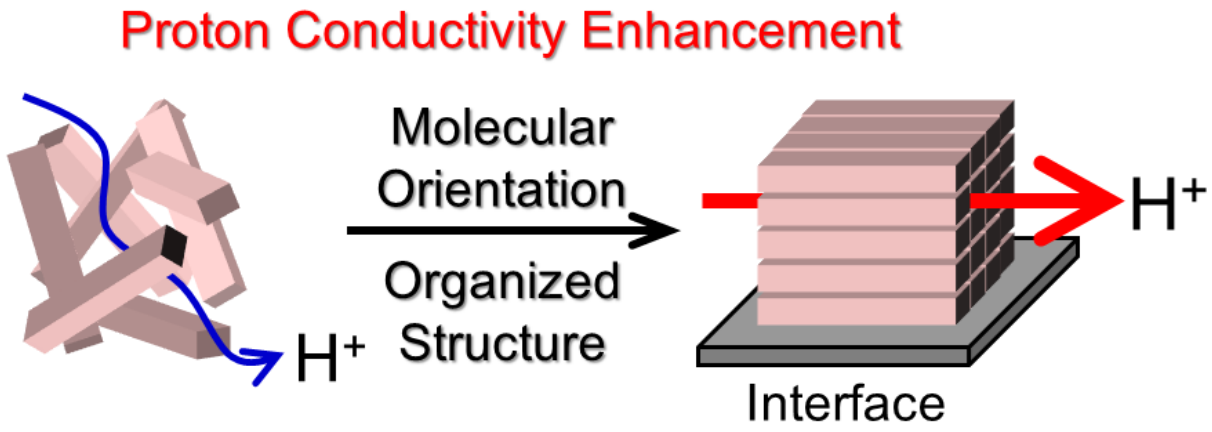
Acknowledgments

The author thanks Associate Professor Jun Matsui of Yamagata University, Associate Professor Shusaku Nagano, Dr. Mitsuo Hara, Ms. Hiroko Iwatsuki, and Mr. Ryosuke Goto of Nagoya University, and many collaborators. The author is thankful for the significant experimental efforts and results of Ms. Mie Sasaki, Mr. Nobuhiro Naito, Ms. Emi Urano, Dr. Karthik Krishnan, Dr. Zhuqing Wang, Mr. Takahiro Kubo, Ms. Yanglu Guo, Mr. Yutaro Ono, and many graduate students at Tohoku University, Kyoto University, and Japan Advanced Institute of Science and Technology. This work was supported in part by the Nanotechnology Platform Program (Molecule and Material Synthesis) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. This work was financially supported by Program for Improvement of Research Environment for Young Researchers from Special Coordination Funds for Promoting Science and Technology (SCF) commissioned by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan and the Japan Society for the Promotion of Science (JSPS) through the Funding Program (GR060) for Next Generation World-Leading Researchers (NEXT Program) initiated by the Council for Science and Technology Policy (CSTP). In addition, this work was partially supported research funds of Grant-in-Aid for Scientific Research for Young Scientists from JSPS of Japan (No. 18850005), JST-PRESTO, Tokyo Electric Power Company (TEPCO) Research Foundation, Research Foundation for the

Electrotechnology of Chubu (REFEC), Iketani Science and Technology Foundation, The Ogasawara Foundation for the Promotion of Science & Engineering, The Kyoto Technoscience Center, The Foundation Hattori-Hokokai, and The Murata Science Foundation.

TOC



Biography

Yuki Nagao was born in Tokyo, Japan in 1977. He received his B.Sc. in 2001 and M. Sc. in 2003 from University of Tsukuba and Ph.D. in 2006 from Kyushu University under supervision by Prof. Ryuichi Ikeda and Prof. Hiroshi Kitagawa. He was appointed an Assistant Professor of the Department of Mechanical Engineering, Graduate School of Engineering at Tohoku University

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