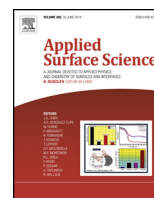




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Surface proton transport of fully protonated poly(aspartic acid) thin films on quartz substrates

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ABSTRACT

Thin film structure and the proton transport property of fully protonated poly(aspartic acid) (P-Asp100) have been investigated. An earlier study assessed partially protonated poly(aspartic acid), highly oriented thin film structure and enhancement of the internal proton transport. In this study of P-Asp100, IR *p*-polarized multiple-angle incidence resolution (P-MAIR) spectra were measured to investigate the thin film structure. The obtained thin films, with thicknesses of 120–670 nm, had no oriented structure. Relative humidity dependence of the resistance, proton conductivity, and normalized resistance were examined to ascertain the proton transport property of P-Asp100 thin films. The obtained data showed that the proton transport of P-Asp100 thin films might occur on the surface, not inside of the thin film. This phenomenon might be related with the proton transport of the biological system.

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1. Introduction

In biological systems, proton transfer in protein ionic channels has attracted many researchers since the 1960s [1]. Many have investigated the purple membrane including bacteriorhodopsin for its fundamental role in proton transport in biological systems [2–11]. Surface proton conduction at the lipid monolayer has also been studied intensively [12–18]. Reportedly, 20-times enhancement of proton diffusion on the surface was achieved compared to bulk water [12], but other researchers strongly disputed the contents of that report [13]. Nevertheless, enhancement of ionic transport at the interface still attracts many researchers of surface science and ionics.

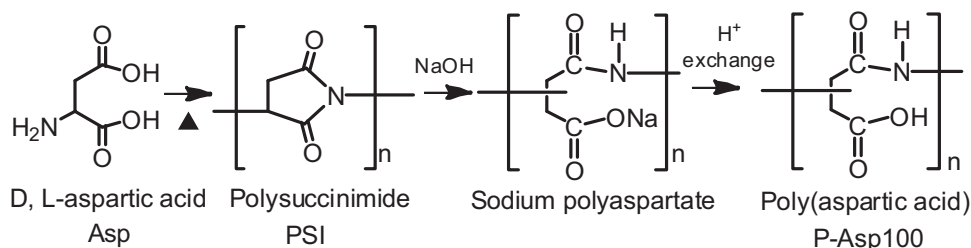
Regarding work in the solid state ionics research field, Liang reported approximately 50-times enhancement of Li⁺ ion conduction in 1973 [19]. The sample was simply mixed with inert Al₂O₃ ultrafine particles into LiI. However, ionic conductivity depends strongly on the contents of Al₂O₃ ultrafine particles. In most cases, when enhancement was observed, the second phase consisted of a nonconducting material such as SiO₂ or Al₂O₃, which is nearly insoluble in the host material. This finding gave us the opportunity to improve the ionic transport property by the inorganic–organic hybrid system. Recently many hybrid materials have been reported

for proton conductors with consideration of the pK_a difference between the proton donor and acceptor.

Many acid–base combinations of proton conductors have been reported for improving proton transport and stability or for anhydrous proton conduction [20–23]. The pK_a difference between the acidic and basic property of materials was applied for the proton transport system based on the concept of a proton donor and acceptor. Another familiar proton transfer with the pK_a difference is apparent in the biological system: bacteriorhodopsin. It pumps protons from the cell interior to the external medium when the light is irradiated. The retinal in bacteriorhodopsin receives light for the activation. Then it changes the pK_a-correspondent amino acid residues step-by-step around the retinal. The aspartic acid residue in bacteriorhodopsin polypeptides plays a crucial role in proton transport [2,7].

Recently, we have found markedly high proton conductivity in the thin films of partially protonated poly(aspartic acid) on quartz substrates [24]. This thin film exhibited highly molecular orientation spontaneously. The wavenumber of the IR spectrum suggests that this thin film has non-periodic secondary structures, e.g., β-turn [25] and α-sheet [26] structures. The proton conductivity of the thin film was one order of magnitude higher than the random oriented specimen. Results suggest that the origin for the proton conductivity enhancement is attributable to the oriented structural effects. However, a study of this enhancement of the proton transport using poly(aspartic acid) itself is insufficient to understand this phenomenon. In this study, fully protonated poly(aspartic acid) (P-Asp100) was synthesized to investigate the proton transport

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Scheme 1. Synthesis of fully protonated poly(aspartic acid) (P-Asp100).

properties of thin films. Although P-Asp100 has movable protons at the side chain, protons are not easily released and are hard to move to the next proton site in P-Asp100 because of the weak acid pK_a and fully protonated state. Therefore we speculated that the results obtained in the case of P-Asp100 would differ from those of the partially protonated poly(aspartic acid).

2. Experimental

Fully protonated P-Asp100 was synthesized according to Scheme 1. D,L-aspartic acid, o-phosphoric acid, methanol, sodium hydroxide, and HCl were purchased from Wako Pure Chemical Industries Ltd. D,L-Aspartic acid of 5 g and 85% o-phosphoric acid of 3 ml were added to a 100 ml round-bottom flask and were mixed for 10 min under Ar atmosphere. The mixture was heated at 170 °C for 16 h. The product was washed with methanol and water. The residue was washed with methanol and dried under reduced pressure. The dried sample of 3.6 g and a solution of sodium hydroxide of 1.5 g with 15 ml of deionized water were added to a 200 ml beaker with stirring for 20 min. A 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 washing and separation procedures. The obtained sample was dried under reduced pressure. For protonation, the sample was dissolved completely in distilled water. Then an ion exchange process was performed using Amberlyst. Using a rotary vacuum evaporator, the protonated sample was obtained and dried under vacuum. In fact, 100% of protonation was confirmed using the titration method. The obtained sample (P-Asp100) was characterized via ¹H NMR (Avance III; Bruker BioSpin Inc.) and FT-IR measurements using an ATR accessory (Nicolet 6700; Thermo Fisher Scientific Inc.). Gel permeation chromatography (ChromNAV-GPC; Jasco Corp.) showed the average molecular weight as ca. 6500, as determined.

The P-Asp100 thin films were prepared by spin coating using a spincoater (ACT-200; Active) on mirror-polished quartz substrates or Si wafer. The quartz substrate and Si wafer size were, respectively, 17 mmϕ × 1 mm and 20 × 30 × 0.5 mm. Before film deposition, each substrate was subjected to several cleaning processes. Then plasma treatment was performed using a vacuum plasma system (Cute-MP; Femto Science) to improve surface hydrophilicity. The thickness was determined using a contact stylus profiler (P-10; KLA Tencor Corp.). The roughness measurement showed that its smoothness was sufficient for IR measurement and impedance analysis.

For *p*-polarized multiple-angle incidence resolution (*p*-MAIR) spectroscopy [27–30], measurements were taken using a FT-IR spectrometer (Nicolet 6700; Thermo Fisher Scientific Inc.) equipped with a mercury–cadmium–telluride (MCT) detector. A mirror-polished Si wafer was used for *p*-MAIR measurements. Single-beam spectra were collected from 38° to 8° at 6° steps between the angle of incidence. The aperture was fully opened (size of 150) and a metal plate with small pores was placed in the

light path of the incident beam to prevent saturation. To obtain *p*-polarized light, a ZnSe polarizer was used. The cleaned Si wafer was used to obtain reference data.

For impedance measurements, the thin films were measured in relative humidity (RH) of 70–90% 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.). The temperature was set at 298 K. The thin films were prepared by spincoating on the quartz substrate. The thin film size was ca. 5 × 10 mm. The electrode configuration was selected to obtain measurements of the current flow in the plane parallel to the substrate surface. The electrode was located at the edge of the film, with a parallel electrode configuration. Porous gold paint (SILBEST No. 8560; Tokuriki Chemical Research) was used for electrodes and was covered at the side of the film. The inter-electrode distance was ca. 4.0 mm.

3. Results and discussion

3.1. Characterization of P-Asp100

Fig. 1 shows the ¹H NMR spectrum for P-Asp100. DMSO-*d*₆ was used for the solvent. The peaks at 4.5 and 2.6 ppm are attributed respectively to the CH and CH₂ groups. The peaks at 8.1 and 12.5 ppm respectively correspond to the protons of NH and COOH groups. Scheme 1 shows that integration of proton peaks in ¹H NMR spectrum produces good agreement with the number of protons.

Fig. 2 shows the ATR spectrum for P-Asp100. The amide I (CO of amide group) and amide II (NH of amide group) bands appeared respectively at 1650 and 1530 cm⁻¹. The wavenumbers of these bands are almost identical values to those of the partially protonated poly(aspartic acid) [24]. The new band at 1730 cm⁻¹ corresponds to the CO vibration mode of COOH at the side chain. Absorption around 1600 cm⁻¹ derived from the

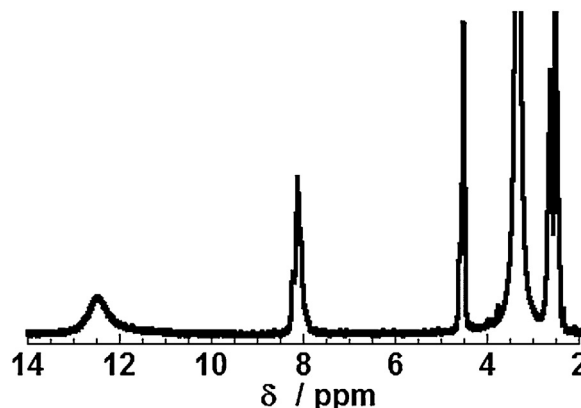


Fig. 1. ¹H NMR spectrum for P-Asp100.

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