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Short communication

Investigation of through-plane morphologies of multiblock copolymers based on poly(arylene ether sulfone)s

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ABSTRACT

Through-plane morphologies of multiblock copolymers based on poly(arylene ether sulfone)s were investigated by transmission electron microscopy (TEM) and through-plane conductivity measurements using a 4-probe method. The measured results showed that proton conductivity increased with a longer block length and that the optimal block length ranged from 5 to 7 K. TEM cross-sectional images also supported these results, indicating that a block length of 10 K is too well organized to conduct through-plane ion carriers.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) powered by hydrogen and oxygen have been researched extensively in recent years. A perfluorosulfonic acid (PSA) polymer, Nafion® developed by DuPont, has been used as a polyelectrolyte for both the membranes (PEMs) and the electrodes of the catalyst layers of fuel cells. However, PSAs also have some drawbacks, specifically, their low hydrated glass transition temperature that limits use above approximately 100 °C and their high fuel permeability that causes a short lifetime, in addition to their prohibitive material cost. Therefore, a number of alternative materials based on hydrocarbon membranes have been extensively developed over the last two decades, which may be much cheaper, more thermally stable, and have lower gas permeability than PSA membranes [1,2].

Although various kinds of alternative materials have been researched, few measurement techniques have been developed for obtaining an exact understanding of a material's potential for application to fuel cells in advance of fuel cell testing. During the last few years, several types of multiblock copolymers with a well-organized phase separation between the hydrophilic and hydrophobic sequences have been reported [3–7]. While it is interesting to discuss their morphological characteristics [8], it is very difficult to ascertain their through-plane proton conductivity, which may correspond to their real potential for fuel cell application. The reason is that almost all conductivity measurements can account for only in-plane performance, although a few researchers have started to tackle this issue [9].

It is imperative to develop a method of predicting PEM performance precisely without conducting fuel cell tests. Electrochemical atomic force microscopy (e-AFM) has recently been found to be a good tool for examining fuel cell performance [10,11], and the importance of understanding the morphological characteristics has been discussed using multiblock copolymers based on poly(arylene ether sulfone)s (PES) [12]. In this paper, we report the results of through-plane conductivity measurements made with a 4-probe method and present cross-sectional images obtained with transmission electron microscopy (TEM), in an effort to explain the correlation between fuel cell properties and morphological characteristics using PES multiblock copolymers.

2. Experimental

2.1. Materials

Disulfonated copolymers with both random and multiblock structures were provided by Dr. J.E. McGrath at the Virginia Polytechnic Institute and State University [3,13]. The membranes' materials discussed in this paper are the same as the ones in our previous report [12], and a practical example for forming membranes

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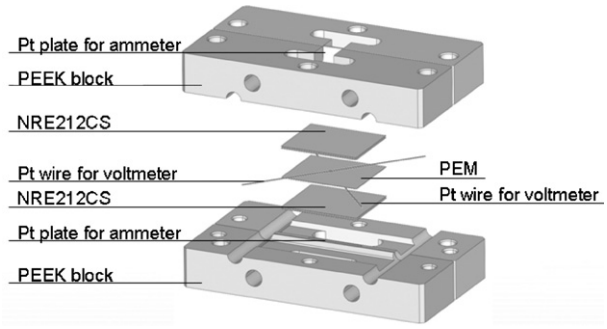

Fig. 1. A schematic view of through-plane conductivity measurement using a 4-probe method.

is shown as follows. A polymer solution was prepared in *N*-methyl-2-pyrrolidone (NMP, 5 wt.%) and filtered with a 7.0-μm porous cellulose membrane. The filtrate was cast onto a glass plate and dried in an oven at 80 °C for 24 h to form the membrane. The membrane was immersed in deionized water for a period of time to detach it from the substrate and then in 1 M HCl aq. for 48 h for acidification. Finally, it was rinsed several times and immersed in deionized water for 24 h. The ion exchange capacities (IEC) were 1.43 for the random structure, 1.45 for 3 K, 1.42 for 5 K, 1.45 for 7 K and 1.49 for 10 K, as determined by back-titration.

2.2. Through-plane properties

Cross-sectional images were obtained with two Hitachi TEMs (H-800 and H-9000UHR) in a voltage range from 200 to 300 kV. The TEM samples were prepared by ultramicrotomy (Ultracut S, Leica), followed by staining with barium ions.

Proton conductivity (PC) was measured with a 4-probe method at 80 °C under partially hydrated conditions in a window cell geometry using a Solartron 1260 Impedance/Gain-Phase Analyzer over the frequency range of 10 Hz–1 MHz. Membranes were equilibrated in a humidity–temperature oven at the specified relative humidity (RH) and temperature for at least 30 min before the measurement. To emphasize on, the experimental instrument for measuring through-plane PC is illustrated in Fig. 1, whereas in-plane PC was conventionally measured [14]. It was equipped with 2 dummy PEMs, 2 crossing Pt wires for the voltmeter, 2 Pt plates for the ammeter and a sample membrane. In this paper, NRE212CS was chosen as a dummy PEM because of its low modulus property and high conductivity to prevent the sample membrane from creeping.

3. Results and discussion

Fig. 2 shows a comparison of the in-plane PC and through-plane PC at 90% and 50% RH. It is observed that the in-plane PC increased with a longer block length at 90% RH, although the ion-exchange capacity (IEC) was almost the same for all the samples. At 50% RH, the in-plane PC apparently saturated when the block length was 5 K or longer. In contrast, the through-plane PC peaked at around 5–7 K and decreased at 10 K. This tendency was observed at both 50% and 90% RH. As reported previously [12], such tendencies were consistent with the performance results for single fuel cell test. That is to say, the longest block length, 10 K, showed the worst fuel cell performance, while it showed the worst through-plane PC of all multiblock copolymers. This suggests that measuring the through-plane PC can provide a useful and precise indication of the potential performance of a PEM when applied to a fuel cell.

To examine the morphological effect on performance visually, TEM cross-sectional images were investigated as shown in Fig. 3. In

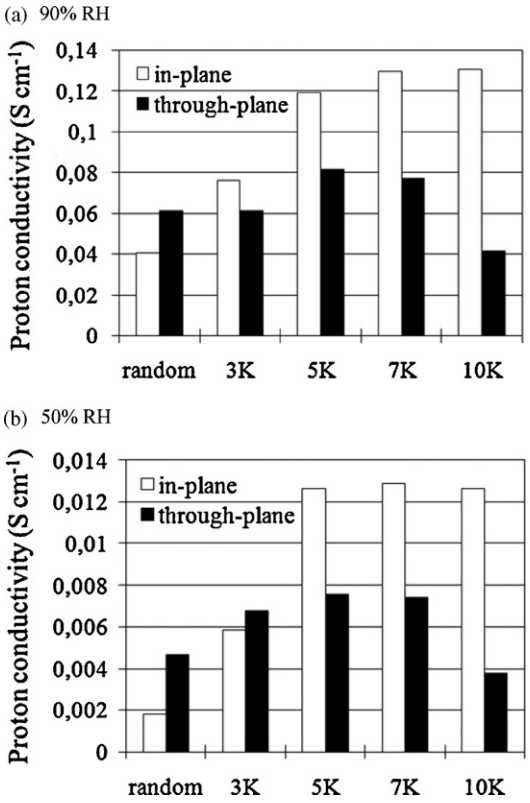

Fig. 2. Proton conductivities in both in-plane and through-plane directions at (a) 90% RH and (b) 50% RH.

the random structure, no phase separation was observed. Both the 5 and 7 K samples exhibited well-organized and continuous phase separations in the through-plane direction, whereas the 3 K sample did not show such specific separation. Some definite phase separations were seen in the 10 K sample and appeared to be obstacles for the proton/water paths through the membrane. As discussed in the references [3,4,8], multiblock copolymers are not swollen in an in-plane direction, whereas the through-plane swelling ratio is quite higher than the random copolymers. These results also suggest that the proton/water paths are horizontally laid down to the essential direction from the anode to the cathode in a single fuel cell.

From these TEM images and PC results as well as our previous findings, we conclude that multiblock copolymers have an optimal block length range that effectively promotes fuel cell performance, especially under a low RH. Presumably, an excessive block length results in a macromolecular alignment in the in-plane direction.

4. Conclusion

This paper has described in-plane and through-plane proton conductivity measurements and also transmission electron microscope images with the aim of obtaining a better understanding of the morphological impact of PES-based multiblock copolymers on actual fuel cell performance. The through-plane proton conductivity results suggest that there is an optimal block length range of 5–7 K that seems to achieve the best performance. The TEM results also support the observation that this block length range brings about the best phase separation for fuel cell performance. More efforts should be made such as non-solvent casting, different block length between hydrophilic and hydrophobic oligomers, and so

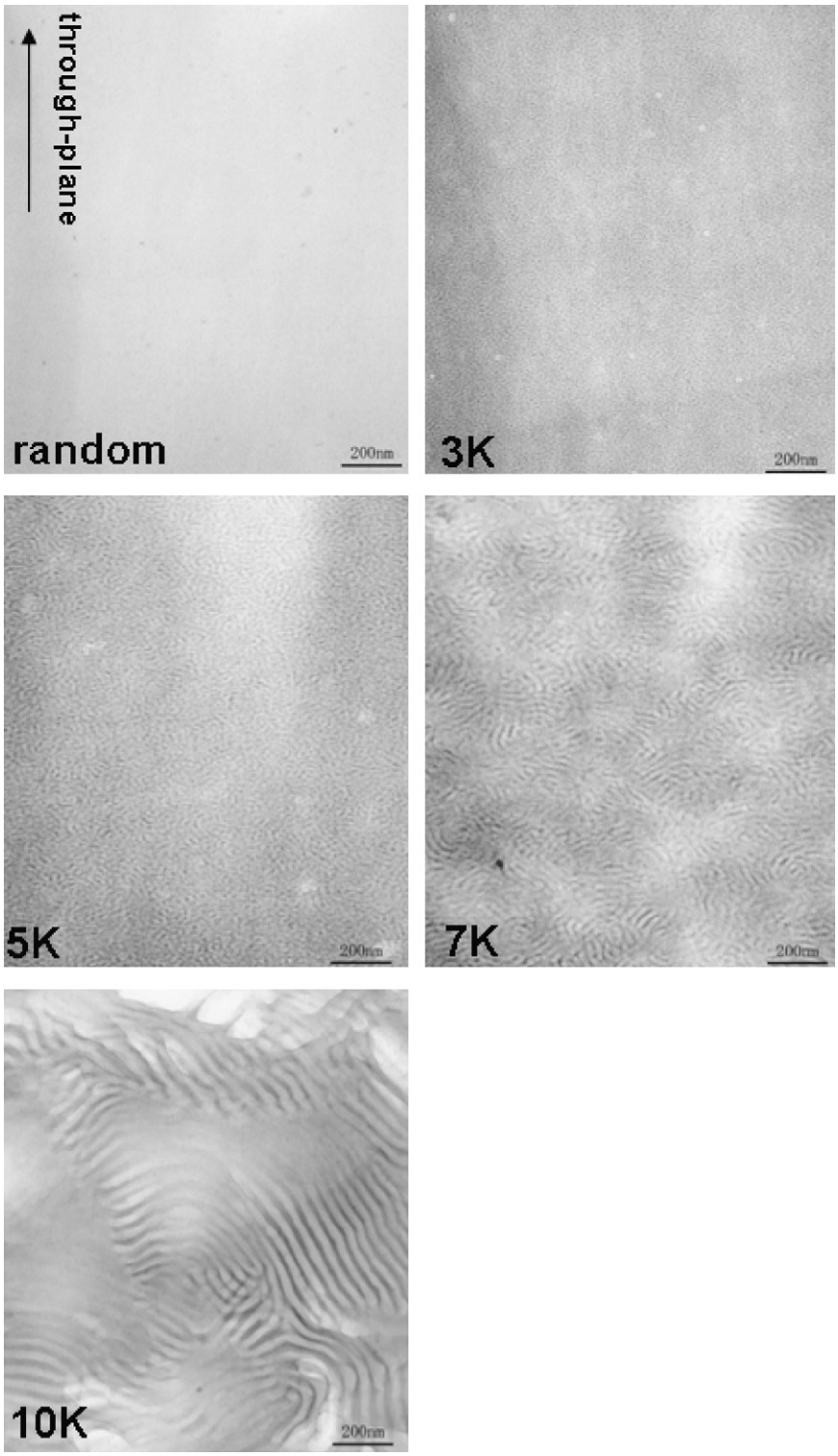

Fig. 3. TEM cross-sectional images of random and multiblock copolymers.

on, in order to enhance the fuel cell performance for multiblock copolymers.

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