

Anion-Conducting, Multiblock Copolymer Membranes: Structure-Property Relationships

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mPES-X_{6.7}Y_{7.7} and mPES-X_{6.7}Y_{11.1} samples did not lead to higher ionic conductivities in comparison to mPES-X_{6.7}Y_{3.4} can be explained by the fact that these two membranes had much longer relaxation times than the mPES-X_{6.7}Y_{3.4} membrane. This result indicates that the benefit of higher ion concentration was offset by the detrimental effect of the larger ion channel size, which led to a more inefficient water pathway.

Introduction

Anionic fuel cells are of interest because they have the potential to overcome cost and performance platinum usage issues with acid fuel cells. In this study, a series of anion-conductive multiblock copoly(arylene ether sulfone)s were synthesized. The block copolymer creates a nanochannel structure for ion conduction. The corresponding random copolymers were synthesized, enabling a comparison of properties. Measurements of NMR spin-relaxation times that probe the nanochannel structure of the polymers were employed, and then the morphology information extracted from the NMR relaxation times of water in the polymers were correlated with their ionic conductivity.

Results and discussion

A series of anion conductive multiblock copolymers (mPES) with different block lengths containing quaternary ammonium groups were synthesized by the polycondensation of separately prepared OH- and F-terminated oligomers. The F-terminated oligomer at which quaternary ammonium groups were attached become an ion-conductive hydrophilic block. The chemical structures of the synthesized polymers were analyzed by 1D and 2D NMR spectra and GPC.

The ion exchange capacities, the ion conductivities, and the relaxation times are summarized in Table 1. The relaxation times correspond to water in the polymer membranes rather than polymer protons, confirmed by the absence of peaks belonging to the polymers and the high water content of the membranes.

Table 1. Properties of mPES and rPES

| | IEC (meq/g) | Conductivity (mS/cm) | | T_1 (ms) | T_2 (ms) |
|--|----------------|-------------------------|----------|---------------|---------------|
| | | at 25 °C | at 60 °C | | |
| mPES-X _{11.3} Y _{3.4} | 1.06 | 2.4 | 5.0 | 309 | 28.0 |
| mPES-X _{9.2} Y _{3.4} | 1.45 | 4.9 | 12.7 | 304 | 33.3 |
| mPES-X _{6.7} Y _{3.4} | 1.38 | 15.7 | 37.7 | 224 | 20.2 |
| mPES-X _{6.7} Y _{2.5} | 1.02 | 3.2 | 7.2 | 229 | 22.2 |
| mPES-X _{6.7} Y _{7.7} | 2.28 | 13.9 | 27.9 | 376 | 48.0 |
| mPES-X _{6.7} Y _{11.1} | 2.82 | 14.2 | 29.0 | 483 | 95.6 |
| rPES-X _{0.5N} Y _{0.5N} | 2.17 | 11.5 | 25.0 | 324 | 57.2 |
| rPES-X _{0.67N} Y _{0.33N} | 1.38 | 5.7 | 13.6 | 212 | 50.2 |

Table 1 shows that mPES-X_{6.7}Y_{3.4} exhibited the shortest T_2 value and the highest hydroxide ion conductivity, which implies that narrow channels in mPES-X_{6.7}Y_{3.4} are the most efficient for water transport. The T_2 of mPES-X_{6.7}Y_{3.4} (20.2 ms) is significantly shorter than that of rPES-X_{0.67N}Y_{0.33N} (50.2 ms) in spite of their similar T_1 values (i.e., 224 ms for mPES-X_{6.7}Y_{3.4} and 212 ms for rPES-X_{0.67N}Y_{0.33N}). The observation in which higher IEC values in the