



# Toughened polymer electrolyte membranes composed of sulfonated poly(arylene ether ketone) block copolymer and organosiloxane network for fuel cell

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## ABSTRACT

The semi-interpenetrating polymer network (semi-IPN) based electrolyte membrane was synthesized from the poly(arylene ether ketone)-b-ketone sulfonated poly(arylene ether ketone) multi-block copolymer (PAEK-b-KSPAEEK) and the organosiloxane organic-inorganic hybrid polymer network (OSPN) pre-synthesized. The chemical structure of the synthesized PAEK-b-KSPAEEK and semi-IPN was identified using  $^1\text{H}$  and  $^{19}\text{F}$  nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy, and the dimension of the phase separated ionic clusters was examined by small angle X-ray scattering spectroscopy. Introduction of OSPN to PAEK-b-KSPAEEK improved not only the thermal and mechanical stability (toughness) but also the oxidative stability. The performance of the membrane electrode assembly fabricated with the semi-IPN electrolyte membranes was superior to that of the pure block copolymer membrane because of the enhanced proton conductivity and toughness. While the semi-IPN24 membrane showed the comparable proton conductivity and cell performance to Nafion 115 membrane, its methanol permeability was significantly lower than that of Nafion 115 membrane.

## 1. Introduction

The polymer electrolyte membrane is one of the most important components in proton exchange membrane fuel cell system. In order to realize the satisfactory cell performance, the membrane must possess high proton conductivity as well as good thermomechanical stability. Nafion® is a well-known commercial electrolyte membrane illustrating such properties. However, as Nafion® is quite expensive [1–4], a variety of studies on its replacement with the hydrocarbon based polymer membranes have been actively pursued [5–15]. Even though some of the arylene based polymer membranes have been successfully synthesized to show excellence in proton conductivity, tensile strength, thermal and chemical stability, the cell performance was not always satisfactory, especially in long term basis. It is because the cell performance is affected by not only membrane properties but also the interfacial stability between the membrane and catalyst layer. Under the same type and content of the catalyst and ionomer binder, the enhancement of toughness of the membrane is quite essential to improve the interfacial stability between the membrane and catalyst layer, because it mitigates the interfacial stress given by the repeated wet/dry cyclic cell operation. In this manuscript, we tried to show the synthesis

and properties of such toughness enhanced membranes based on poly(arylene ether ketone)-b-ketone sulfonated poly(arylene ether ketone) multi-block copolymer (PAEK-b-KSPAEEK), one of the recently developed membranes from our laboratory [16]. In the previous study [16], when the PAEK-b-KSPAEEK membranes were compared with the poly(arylene ether ketone)-r-ketone sulfonated poly(arylene ether ketone) random copolymer (PAEK-r-KSPAEEK), the mechanical and oxidative stability of the PAEK-b-KSPAEEK was better than PAEK-r-KSPAEEK with reduced methanol permeability. Also, PAEK-b-KSPAEEK exhibited much higher conductivity than PAEK-r-KSPAEEK ascribed to more distinct hydrophobic-hydrophilic phase separation. However, KSPAEEK block in the PAEK-b-KSPAEEK membrane was too rigid to sustain long term dry-wet cyclic operation [17]. In this study, we prepared the semi-IPN type electrolyte membranes from PAEK-b-KSPAEEK and organosiloxane polymer network (OSPN) to enhance the toughness of the PAEK-b-KSPAEEK membrane [18–25]. The PAEK-b-KSPAEEK was pre-synthesized using hydrophobic and hydrophilic oligomers of the same molecular weight and the OSPN was also pre-prepared from 1-hydroxyethane-1,1-diphosphonic acid and (3-glycidioxypropyl) trimethoxysilane. Because of the presence of the numerous phosphoric acid groups in OSPN, the semi-IPN membrane was expected to possess high proton conductivity.

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