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Pendant dual-sulfonated poly(arylene ether ketone) multi-block copolymer membranes for enhanced proton conductivity at reduced water swelling

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ABSTRACT

The proton exchange membranes are synthesized from poly(arylene ether ketone) (PAEK) multi-block copolymers with and without sulfonated groups. The hydrophilic PAEK block is dual - sulfonated at the pendant site to enhance the proton conductivity of the membrane, while the hydrophobic block length is enlarged to reduce its swelling (increase dimensional stability) associated with water accommodation. The chemical structures of the synthesized oligomers and copolymers are identified using ^{1}H and ^{19}F NMR, ATR-FTIR, and GPC. The ion cluster dimension of the membrane is analyzed by SAXS. The effect of copolymer composition on the membrane properties is investigated measuring the proton conductivity, water uptake, swelling ratio, and cell performance along with the thermal, mechanical, and oxidative stability. The prepared membranes exhibit lower swelling ratio but higher proton conductivity than Nafion115 membrane. Specifically, B.PAEK25-SDPA shows superior cell performance to Nafion115.

1. Introduction

As the polymer electrolyte membrane is a core component of the proton exchange membrane fuel cell (PEMFC), it must possess high proton conductivity, high thermal, mechanical, and dimensional stability along with cost competiveness [1]. One of the most commonly used commercial polymer electrolyte membranes for PEMFC is Nafion® by DuPont. Since its hydrophilic - hydrophobic phase separation is well developed in the presence of water, the percolated structure of ion clusters provides it with high proton conductivity. Nafion, however, has some weaknesses associated with low proton conductivity under low humidity conditions and uncompetitive cost due to its complex synthetic processes [2–5].

In order to replace the Nafion membrane, many researches have been actively pursued on the synthesis of hydrocarbon-based polymer electrolyte membranes [6–14]. As quite good membrane properties have been possibly obtained in proton conductivity, thermal and mechanical stability, and cell performance from their contributions, the major concern in its recent development is focused on its durability [15–19]. Along with the long term chemical stability associated with ·OH radical quenching process, the long term mechanical stability is the other potential issue, as it is related with the dimensional stability during the repeated wet/dry cyclic cell operations where the swelling/de-swelling of the membrane continuously takes place [20]. As the high proton conductivity is generally established by high degree of sulfonation, it is inevitable to imbibe large amount of water in membrane to realize high proton conductivity. This excessive water uptake, however, leads to unfavorably high swelling of the membrane, and thus the interfacial stability between catalyst layer and swollen membrane becomes being failed via long term wet/dry cyclic operations [21–23]. As the Nafion is composed of perfluorocarbon backbone molecules, the sulfonated repeating units are highly acidic and thus are easily phase separated from the non-sulfonated ones when compared with the hydrocarbon based membranes.

From those points of views, it is very important to enhance the proton conductivity of the hydrocarbon based polymer membrane at the reduced water swelling. A clue to achieve this is to utilize the block copolymer membranes where the distinct phase separation between hydrophilic domains and hydrophobic matrix occurs. From this distinguished phase separation, the hydrophilic blocks are independently percolated to provide it with high conductivity while the hydrophobic blocks provide it with high mechanical strength [24]. In this study, we synthesized the arylene ether ketone (AEK) based multi-block copolymers (BPAEK) with and without sulfonic acid groups. The sulfonated 3,3-diphenylpropylamine (SDPA) with two sulfonic acid groups was bonded to the pendant position of the hydrophilic block and the length of the hydrophobic block was enlarged to minimize the swelling of the membrane. By this maximization of hydrophilicity and hydrophobicity

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