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Sulfonated poly(styrene-*block*-(ethylene-*ran*-butylene)-*block*-styrene (SSEBS)-zirconium phosphate (ZrP) composite membranes for direct methanol fuel cells

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ABSTRACT

In this work, S40 (sulfonated poly(styrene-*block*-(ethylene-*ran*-butylene)-*block*-styrene) with 40% degree of sulfonation)-ZrP (zirconium phosphate) composite membranes, serving as proton conducting membranes for direct methanol fuel cells, were prepared via a precursor infiltration method. The obtained S40-ZrP membranes exhibited homogeneous distribution of ZrP nanoplatlets within continuous proton conducting sulfonated polystyrene domains of the microphase separated S40 matrix. Employing different solvent of the infiltrating ZrP precursor solution could tailor the loading, the geometry and the crystallinity of ZrP, which considerably affect the transport properties. S40-N3, the composite membrane containing only 3 wt% of ZrP using weak basic N-methyl-2-pyrrolidone as the solvent, exhibited a remarkable 16 fold increment in selectivity as compared to the parent S40 membrane due to enhanced proton conductivity and significantly suppressed methanol permeability. S40-N3 also exhibited improved mechanical properties to enable the integrity of the corresponding membrane electrode assembly during DMFC operation, leading to a power density of 66 mW cm^{-2} (1 M methanol at 60 °C) and a maximum current density of 450 mA cm^{-2} without cathode flooding. The DMFC performance was better than a DMFC single cell using Nafion 117 by 50% under the same setup. Enhancement in proton conductivity at low relative humidity was also observed for S40-N3 due to the strong water retention capability of ZrP, suggesting a good potential for both DMFC and PEMFC.

1. Introduction

Direct methanol fuel cells (DMFCs) offer great advantages for mobile power supply in the aspect of accessibility and safety of fuel. The high theoretical efficiency considering volumetric power density allows DMFCs a potential candidate to replace gasoline without expensive reforming processes [1]. As far, proton exchange membrane (PEM) based DMFCs are the most studied system; nevertheless, several major issues of PEMs prevent them from successful commercialization, including: (1) high methanol permeability resulting in open circuit voltage drop and lowered fuel efficiency; (2) dimensional instability and loss of mechanical strengths at hydrated state and elevated temperature; as well as (3) expensiveness and difficulty in ionomer synthesis and in membrane fabrication [2]. Therefore, it is strongly needed to develop PEMs concurrently achieving high proton conductivity, low methanol permeativity, mechanical robustness and good dimensional stability based on low cost ionomers.

The use of organic–inorganic composite membranes by incorporating inorganic fillers, such as TiO_2 [3–6], SiO_2 [7–12], ZrO_2 [13,14], and ZrP [15–18], in the ionomer matrix is one of most effective strategies to improve the performance of the existed PEMs. In general, comparing to the parent ionomer membrane, the composite membranes exhibited suppressed methanol crossover, improved dimensional stability and mechanical strengths as well as reduced oxidative degradation. The transport properties of the composite membranes are strongly affected by chemical structure, crystallinity, geometry, loading as well as distribution of the

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inorganic fillers [19,20], which offers a good opportunity to tailor the performance of a composite membrane by controlling the above properties of the inorganic fillers. Approaches to incorporate inorganic fillers into an ionomer matrix could be generally classified into two main categories: (1) blending of inorganic fillers in a polymer solution and following by the membrane casting [21–26]; and (2) infiltrating precursors of inorganic fillers into a preformed membrane with the following conversion [27–36]. The first method, denoted as blending method, often results in agglomeration of fillers due to the intrinsic incompatibility between the fillers and the ionomer, which aggravates the membrane performance. The second method, known as infiltration method (also called ″*in situ* method″ sometimes), would afford homogeneous distribution of smaller nanofillers in the resulting composite membranes. Comparing to the blending method, the infiltration method could provide the resulting composite membranes more effectively suppressed methanol crossover without sacrificing proton conductivity. For example, a 5 wt% zeolite dispersed in Nafion led to a 59% suppression in methanol permeability with merely 3% decrement in conductivity [32]. The incorporation of 6 wt% phosphonic acid-functionalized titania in SPEEK resulted in a 23% decrement in methanol permeability and even a 25% improvement in proton conductivity at 30 °C as compared with the parent SPEEK [37]. By incorporating 5 wt% phosphotungstic acid (CsPW) in Nafion, the resulting composite membrane exhibited a conductivity 1.8 times higher than the parent Nafion alone with a 4 fold suppression in methanol diffusion coefficient [38].

Among various inorganic fillers, zirconium phosphate (ZrP), an acidic filler containing phosphonic acids (HPO_4), has drawn a good attention for composite PEMs since the phosphonic acids could offer dissociative protons and entrap water to assist proton conduction [17,18,39–44]. In addition, the transport properties of ZrP nanoparticles could be feasibly tailored by varying the crystallinity and the geometry through tuning the synthesis parameters [45,46]. Several researches have employed the infiltration method to introduce ZrP nanoplatelets into a preformed ionomer membrane by immersing the parent membrane in a $ZrOCl_2$ aqueous solution to uptake the ZrP precursor $ZrOCl_2$ with the following treatment using a phosphoric acid aqueous solution to convent $ZrOCl_2$ to ZrP [47–60]. A wide variety of ionomer matrix, including Nafion [57–60], SPEEK (sulfonated poly(ether ether ketone)) [51], BPSH (disulfonated poly(arylene ether sulfone) random copolymer) [52] and SPAEK (Sulfonated poly (arylene ether ketone sulfone)) [53] have been employed, and the resulting composite membranes generally exhibited homogeneous distribution of semi-crystalline ZrP. The introduction of small amount ZrP would significantly suppress the methanol crossover, leading to improved DMFC performance. However, slight to moderate reduction in proton conductivity was generally observed for the composite membranes despite of the proton conducting nature of ZrP. Therefore, further improvement on the transport properties of the ZrP containing composite membrane should be achievable by delicately adjusting the crystallinity, the geometry and the distribution of ZrP as well as the morphology of the composite membrane.

Besides organic–inorganic composite membranes, the use of block copolymers is another attractive approach to improve the transport properties of a PEM through modulating the microstructure of the PEM. Block copolymers comprising of distinguishing hydrophobic segments and hydrophilic sulfonated segments could self-assemble into microphase separated nanostructures having distinctive proton conducting domains to efficiently utilize the sulfonic acids. Sulfonated poly(styrene-*b*-(ethylene-*r*-butadiene)-*b*-styrene) (SSEBS) triblock copolymer, consisting of two terminal sulfonated polystyrene (sPS) blocks and a central poly(ethylene-*r*-butadiene) (EB) block, has been the most studied system in the category [29,61–70]. SSEBS is attractive since well-defined molecular architecture with a wide variety of DS could be obtained by simple sulfonation of cheap SEBS synthetic rubbers. In addition, the microstructures of these PEMs could be tailored by varying the composition, the DS as well as the membrane fabrication conditions to tune the transport properties. Nevertheless, DMFC cell performance based on MEAs using SSEBS as PEM was rarely reported, probably owing to the dimensional instability and the mechanical weakness of the SSEBS membrane at the operation condition (60–80 °C) because of severe swelling and low glass transition temperature of hydrated sulfonated polystyrene (sPS) domains [69]. As far, only works employing composite membranes containing SSEBS, such as SSEBS-silica composite membrane and SSEBS infilled PTFE membrane, were able to provide DMFC performance [62,69].

Motivated by the good potential and the tunability of ZrP as well as the promising performance and the cost effectiveness of the SSEBS based membranes, ZrP nanofillers were introduced into a SSEBS matrix in this work to simultaneously take advantages of the microphase separated nanostructure of the SSEBS matrix and of the acidic ZrP nanofillers. The precursor infiltration method was employed to prepare the SSEBS-ZrP composite membranes to have ZrP nanoplatelets homogeneously distributed within the continuous proton conducting domains of the microphase separated SSEBS membrane. The schematic illustration of the membrane preparation procedure and the terminology used in this work are shown in Fig. 1. Different from most studies on ZrP containing composite membranes prepared from the infiltration method using water as the solvent for the $ZrOCl_2$ solution serving as ZrP precursor, the solvent of the $ZrOCl_2$ solution was intentionally varied to manipulate the morphology of the S40-ZrP composite membrane as well as the geometry and the crystallinity of the ZrP nanoplatelets. SAXS (small angle X-ray scattering) and TEM (transmission electron microscopy) were performed to identify the morphology of the membrane; while TEM, WAXS (wide angle X-ray scattering) and DMA (dynamic mechanical analysis) were carried out to retrieve the geometry, crystallinity and distribution of ZrP within the composite membrane. The loading of ZrP was suggested by thermal gravity analysis (TGA). The influence of the microstructure of the S40-ZrP membrane and the properties of ZrP on the transport properties, including water uptake, proton conductivity and methanol permeativity were systematically investigated. Temperature and relative humidity dependent proton conductivity was studied as well; and a proton conduction mechanism for the S40-ZrP membranes was proposed accordingly. Owing to the improvement in mechanical strength of the composite membrane to enable the corresponding membrane

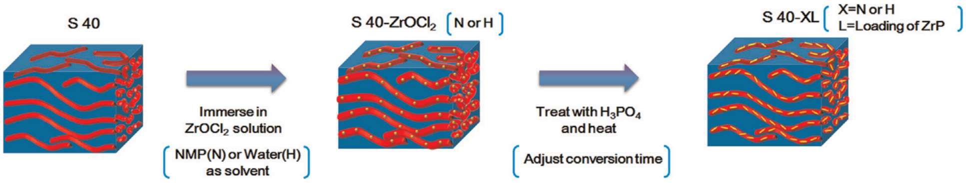

Fig. 1. Preparation of S40-ZrP composite membranes and associated nomenclature.