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Anomalous behavior of proton transport and dimensional stability of sulfonated poly(arylene ether sulfone) nonwoven/silicate composite proton exchange membrane with dual phase co-continuous morphology



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ABSTRACT

Herein, anomalous behavior of proton conductivity and dimensional stability of sulfonated poly(arylene ether sulfone) (SPAES) nanofiber nonwoven fabric/silicate composite membrane (denoted as 'SN/S membrane') featuring dual phase co-continuous morphology, which could be potentially applied to proton exchange membrane fuel cells (PEMFCs), is systematically investigated. The SN/S membrane is fabricated via *in situ* sol-gel synthesis of tetraethoxysilane (TEOS)/3-glycidyloxypropyltrimethoxysilane (GPTMS) mixture directly inside the electrospun SPAES nonwoven. In comparison to a typical SPAES (matrix)/silicate (domain) composite membrane, the SN/S membrane having structural uniqueness provides significant improvement in relative humidity (RH) variation-driven dimensional change, although its proton conductivity is decreased due to the presence of ionically inert continuous silicate phase. A noteworthy finding of this study is that the phase morphology of composite proton exchange membranes plays a crucial role in determining the membrane properties such as proton conductivity and dimensional stability.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have drawn increasing attention as an eco-friendly and efficient energy conversion system for a wide range of applications such as smart mobile devices, electric vehicles, and residential energy supplies [1,2]. Here, a proton exchange membrane is considered a core component that significantly influences electrochemical performance of PEMFCs [3,4]. Among various proton exchange membranes, water-swollen polymer electrolytes containing sulfonic acid groups such as perfluorosulfonic acid polymers (e.g., Nafion) and sulfonated hydrocarbon copolymers have been extensively investigated due to their advantageous attributes for practical use in PEMFCs.

In general, proton transport of these water-swollen polymer electrolyte membranes is known to highly depend on their degree

of hydration [3–5]. When the hydrated membranes are exposed to harsh operating conditions such as high temperature and low humidity, they tend to be easily dehumidified, consequently impairing their hydration-dependent proton conductivity. Moreover, this deterioration of proton conductivity at dehumidified conditions is often accompanied by dimensional change (i.e., area (or volume)-based dimensional expansion/shrinkage). Consequently, this gives rise to weakening of membrane/electrode interface in a confined membrane-electrode assembly (MEA) unit and also mechanical failure of the membranes during fuel cell operation [6]. For this reason, fabrication of new proton exchange membranes that can provide satisfactory level of proton conductivity and also dimensional stability is urgently needed.

One promising approach to resolve the drawbacks of water-swollen polymer electrolyte membranes is the incorporation of hygroscopic inorganic fillers such as SiO₂, TiO₂, and ZrO₂ into polymer electrolyte membranes [7–9]. Unfortunately, in these membranes, the inorganic particles generally exist as a dispersed phase (not a highly interconnected continuous phase), thereby insignificantly improving the dimensional stability of the composite membranes.

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Meanwhile, reinforced composite membranes consisting of mechanically reinforcing porous substrates and proton-conductive electrolytes have drawn considerable interest owing to their superiority in membrane thickness, mechanical strength, and dimensional change. The incorporation of porous substrates such as poly(tetrafluoroethylene) (PTFE) [10], polypropylene [11], and polyimide [12], however, causes unwanted loss of proton conductivity, because the porous substrates are generally ionically inert. Recently, polymer electrolyte nanofiber-based porous substrates, which can offer proton conductivity, have been proposed as a new approach to overcome the shortcomings of conventional reinforced composite membranes [13–15].

In the present study, as an ongoing effort to develop advanced composite proton exchange membranes with excellent electrochemical performance and also dimensional stability, the influence of phase morphology of composite proton exchange membranes on their proton conductivity and relative humidity (RH) variation-driven dimensional change is systematically investigated. Herein, two distinctively different composite membranes are prepared as model systems and compared in terms of their morphological difference: sulfonated poly(arylene ether sulfone) (SPAES) nanofiber nonwoven fabric/silicate composite membrane with dual phase co-continuous morphology (denoted as 'SN/S membrane') versus SPAES/silicate composite membrane ('S/S membrane') composed of SPAES matrix (as a continuous phase) and silicate domains (as a dispersed phase). In these composite membranes, the SPAES is chosen as a representative example of water-swollen polymer electrolyte membranes.

The SN/S membrane is fabricated via *in situ* sol-gel synthesis of tetraethoxysilane (TEOS)/3-glycidyloxypropyltrimethoxysilane (GPTMS) mixture directly inside an electrospun SPAES nonwoven, wherein the TEOS is introduced to form mechanically stiff silicate

network and the GPTMS bearing epoxy ring and flexible hydrocarbon chain [16,17] is added to mitigate the brittleness of the TEOS only-based silicate and also enhance interfacial adhesion between the TEOS/GPTMS silicate and SPAES nonwoven substrate. Meanwhile, the S/S membrane, a kind of typical composite membrane, is fabricated through a simple blending technique, where the S/S membrane has the same chemical composition as that of the SN/S membrane.

Here, it should be noted that, in comparison to the S/S membrane having conventional domain (silicate)/matrix (SPAES) phases, a distinctive structural feature of the SN/S membrane is the dual phase co-continuous morphology (i.e., multi-fibrous SPAES nonwoven phase combined with three-dimensionally interconnected silicate phase). Based on the structural characterization of the composite membranes, their temperature-dependent proton conductivity and RH variation-driven dimensional change are investigated and also discussed with an in-depth consideration of the morphological difference.

2. Experimental section

2.1. Fabrication of SPAES/silicate composite membranes: SN/S membrane and S/S membrane

Prior to the fabrication of the SPAES/silicate composite membranes, SPAES (degree of sulfonation = 49.3%, inherent viscosity = 2.02 dl g⁻¹) was synthesized via nucleophilic aromatic substitution polymerization of 4,4'-dichlorodiphenylsulfone, 3,3'-disulfonated 4,4'-dichlorodiphenylsulfone and 4,4'-biphenol. The detailed synthesis and characterization of SPAES were described in previous publications [4,5,18,19]. As a first step for the fabrication

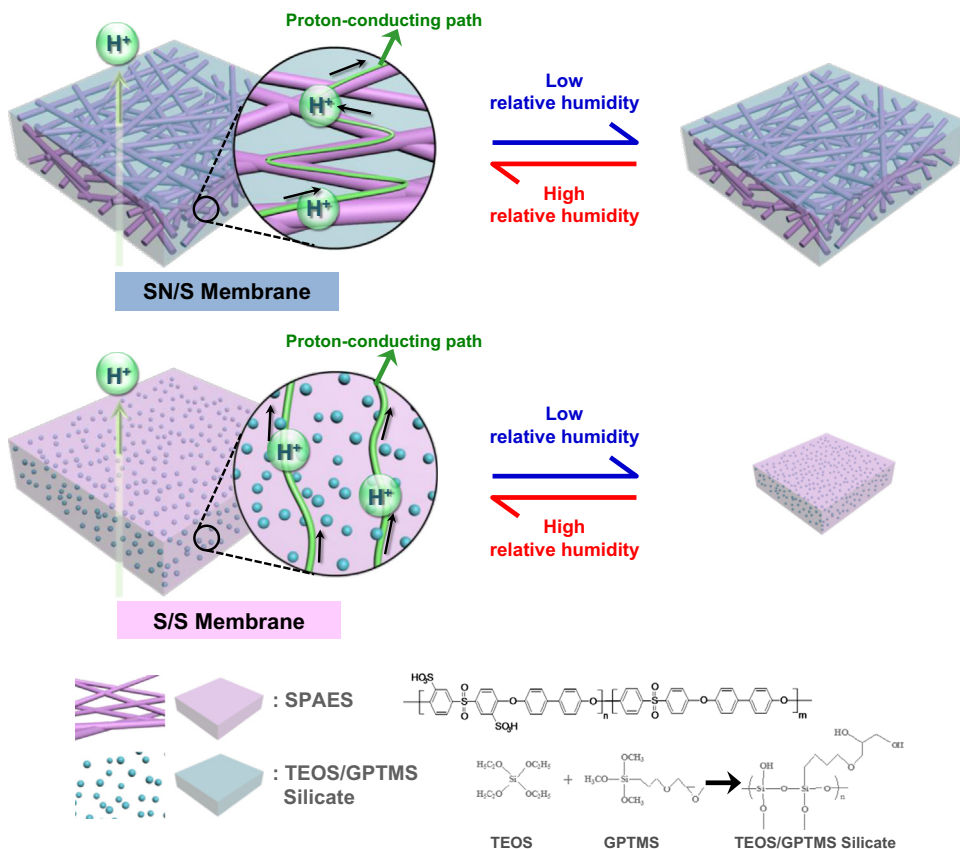


Fig. 1. A schematic illustration depicting phase morphologies of SN/S and S/S membranes and their relative humidity (RH) variation-driven dimensional change, wherein conceptual pathways for proton transport is also provided (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).

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