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Effect of crosslinking on the durability and electrochemical performance of sulfonated aromatic polymer membranes at elevated temperatures

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ABSTRACT

End-group crosslinked sulfonated poly(arylene sulfide nitrile) (XESPSN) membranes are prepared to investigate the effect of crosslinking on the properties of sulfonated aromatic polymer membranes at elevated temperatures (>100 °C). The morphological transformation during annealing and crosslinking is confirmed by atomic force microscopy. The XESPSN membranes show outstanding thermal and mechanical properties compared to pristine and non-crosslinked ESPSN and Nafion[®] up to 200 °C. In addition, the XESPSN membranes exhibit higher proton conductivities (0.011–0.023 S cm⁻¹) than the as-prepared pristine ESPSN (0.004 S cm⁻¹), particularly at elevated temperature (120 °C) and low relative humidity (35%) conditions due to its well-ordered hydrophilic morphology after crosslinking. Therefore, the XESPSN membranes demonstrate significantly improved maximum power densities (415–485 mW cm⁻²) compared to the ESPSN (281 mW cm⁻²) and Nafion[®] (314 mW cm⁻²) membranes in single cell performance tests conducted at 120 °C and 35% relative humidity. Furthermore, the XESPSN membrane exhibits a much longer duration than the ESPSN membrane during fuel cell operation under a constant current load as a result of its improved mechanical and thermal stabilities.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been investigated as alternative energy sources due to their high

energy conversion efficiencies and environmental friendliness [1]. In addition, PEMFC operation above 100 °C (elevated temperature) has further advantages such as a low level of carbon monoxide poisoning, easy water management, and a comparatively simple operating system [2]. However, there

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are a few drawbacks of elevated temperature PEMFCs including a relatively low proton conductivity and the poor thermal and mechanical stabilities of polymer materials operated at elevated temperatures [2–5].

In PEMFCs, protons are transported through an electrolyte membrane by a vehicle and the Grotthuss mechanism using water molecules and/or sulfonic acid groups in sulfonated polymers [2]. The low proton conductivity at elevated temperatures is attributed to the evaporation of water molecules above 100 °C. Therefore, water retention in polymer membranes is one of the critical factors which affect the fuel cell performance, particularly at medium to high temperatures [6]. Various types of polymer membranes such as sulfonated aromatic polymer membranes, inorganic–organic composite membranes, and acid–base polymer membranes have been developed to overcome these drawbacks [7–17]. These modified membranes have higher proton conductivities and PEMFC performances at elevated temperatures than pristine membranes because inorganic materials, ionic liquids, and polyacids act as proton conductors under anhydrous or low relative humidity (RH) conditions. However, some drawbacks such as toxicity and leakage of composite materials still need to be overcome for practical applications.

In general, highly sulfonated polymers are strong candidates as electrolytes operating at elevated temperatures because they have high water uptakes due to the strong hydrogen bonding between water molecules and sulfonic acid groups. Although most of the water evaporates at elevated temperatures, highly sulfonated polymers have great potential for excellent proton conduction due to their high ion exchange capacity, which can transport protons via the Grotthuss mechanism [1]. However, the high degree of sulfonation in polymer membranes causes poor mechanical stability resulting in membrane dissolution in water. Moreover, harsh operating conditions such as elevated temperatures and backpressure can cause failure of the membrane electrode assembly (MEA). Therefore, the mechanical and thermal stabilities of sulfonated hydrocarbon membranes are very important properties of fuel cells operating at elevated temperatures. Many researchers have focused on enhancing membrane stability by employing a rigid backbone structure in polymer and fabricating inorganic composites, re-inforced membranes, and crosslinked membranes [10,18–25]. One of the promising solutions for the stability issue in hydrocarbon membranes is to crosslink the membranes. Different crosslinking agents and sulfonic acid groups have been studied for sulfonated polymers [26,27]. However, this method uses sulfonic acid groups to crosslink the membranes, which obviously results in decreases of the ion exchange capacity and proton conductivity. One novel strategy of crosslinking is to use the end-groups in the polymer as sites for thermal crosslinking to improve the membrane stability without any performance loss.

Crosslinking induces a well-defined morphology because polymer chains are rearranged [28]. Sulfonated polymers with a hydrophilic and hydrophobic phase separated morphology generally have a high proton conductivity as well as good PEMFC single cell performance under low RH conditions [1]. Therefore, the formation of an effective membrane morphology is important for proton transport under anhydrous or low RH conditions. In addition, the retention of water in membranes is affected by the hydrophilic ionic domain size

at elevated temperatures and low RH conditions [29]. Therefore, it is crucial to form a well-defined morphology for enhanced elevated temperature fuel cell performance.

In our previous study, we reported that the electrochemical performance of crosslinked sulfonated poly(arylene sulfide nitrile) (ESPSN outperformed Nafion® at a low temperature (80 °C, 50% RH)) [28]. However, the physical properties and electrochemical performances at elevated temperatures (>100 °C) can be significantly different due to the evaporation of water molecules. In the present study, by using end-group crosslinked sulfonated polymers with a high degree of sulfonation, we investigated the effects of crosslinking as well as the morphological transition of ESPSN membranes on their mechanical properties and electrochemical performances particularly at elevated operating temperatures (120 °C, 35% RH). The mechanical properties were obtained by room temperature stress–strain tests and dynamic mechanical analysis (DMA) to verify the mechanical and thermal stabilities at various temperatures. The influence of crosslinking on fuel cell performance and durability at elevated temperatures was also studied.

2. Experimental

2.1. Membrane preparation

End-group crosslinkable sulfonated poly(arylene sulfide nitrile) (ESPSN) random copolymers were synthesized by nucleophilic aromatic substitution reaction. The degree of sulfonation of ESPSN was controlled to 50 and 60 mol% by changing the feed ratio of sulfonated monomer. Pristine (ESPSN_{xx}, where xx is the molar ratio of the hydrophilic repeating unit) and crosslinked (XESPSN_{xx}, where xx is the molar ratio of the hydrophilic repeating unit) membranes were fabricated using the method reported in our previous study [28]. End-group crosslinking was conducted by thermal treatment at 250 °C for 100 min under argon atmosphere. All membranes were acidified while Nafion® 212 was used as received.

2.2. Thermal and mechanical properties

The tensile stress and strain of the membranes were measured using a universal test machine (UTM, AGS-J 500N, Shimadzu, Kyoto, Japan) at room temperature following the ASTM D882 method. In addition, dynamic mechanical analysis (DMA) was performed using a TA DMA Q800 (TA Instrument, DE, USA) to estimate the thermal and mechanical stabilities of the membranes in the tensile mode at 1 Hz from 60 to 450 °C with a ramp rate of 5 °C min⁻¹. The membranes were dried at 120 °C under vacuum to remove residual water and then were punched into 0.9 cm wide, 4 cm long samples.

2.3. Morphology

Atomic force microscopy (AFM) analysis was performed using a Digital Instruments Multimode 8 (Veeco, Plainview, NY, USA) instrument with a diNanoScope V controller (Veeco) to obtain morphology images of the membrane samples. A silicon probe (Nanosensors, Switzerland) with a force constant of

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