직접 메탄올 연료전지 응용을 위한 가교된 폴리(페닐렌 설파이드 설폰)(SPSSN) 막의 합성 및 특성 분석

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Synthesis and characterization of crosslinked sulfonated poly(phenylene sulfide sulfone) (SPSSN) membranes for Direct Methanol Fuel Cells applications

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1. Introduction

For proton exchange membrane (PEM) fuel cells, a solid polymer electrolyte is used to separate the fuel (H_2, Methanol) from the oxidant. Nearly all existing membrane materials for PEM fuel cells are based on absorbed water and its interaction with acid groups to generateproton conductivity. Membranes prepared from sulfonated poly(arylene sulfone)s are of considerable interest because these materials are well-known for their excellent thermal and mechanical properties as well as their resistance to oxidation and stability under acidic conditions [1].

Sulfonated poly(arylene ether sulfone)s are usually synthesized by standard polymerization process [2]. Following this process, aromatic diol or aromatic dithiol reacts with aromatic dichloride and sodium sulfonate aromatic dichloride to form sulfonate polymer under the presence of potassium carbonate.

In this study, a series of SPSSNs, a series of sulfonated poly(arylene ether sulfone)s (SPAESs), was synthesized by direct polycondensation. These membranes have proton conductivities similar to those of SPAESs. To further improve membrane properties for DMFC application, SPSSN membranes were crosslinked to reduce water uptake, methanol permeability and to increase mechanical properties.

2. Experimental

2.1. Preparation of SPSSNs and crosslinked membranes.

A series of copolymers was synthesized by direct polycondensation of monomers. The polycondensation reaction proceeded in N-methyl-2-pyrrolidone (NMP) as a solvent. After precipitation and removing inorganic salts and impurities, polymers in salt forms were dissolved in dimethylacetamide (DMAc) to fabricate SPSSN membranes. Membranes were formed by casting polymer solutions onto well leveled clean glass plates and then removing DMAc solvent. For fuel cell application, membranes in their sodium forms were converted to acid forms by conventional acidification method with 1M sulfuric acid solution at room temperature. Polymers in their acid forms were crosslinked by reaction of dicarboxylic acid with polymer chains under thermal treatment process. After crosslinking, membranes were re-acidified for characterization.

2.2. Characterization of SPSSNs and crosslinked membranes.

To conform the success of synthesis of SPSSN polymers, FT-IR, ^{1}H-NMR and ^{13}C-NMR were employed to analyze the chemical structures of SPSSN polymers. From the requirements for DMFC application, Water uptake, dimensional stability, mechanical strength and radical stability of SPSSN membranes have been measured. Methanol permeability and proton conductivity are critical properties for DMFC application and were measured between 30°C and 90°C. In addition, the effects of crosslinker on the properties of membranes were studied. Finally, to conform the advantage of SPSSN membranes over Nafion®117, DMFC single cell performance tests of SPSSN membranes were carried out.

3. Results and discussion

Similar to SPAES membranes, SPSSN membrane with degree of sulfonation of 40% has higher proton conductivity and lower methanol permeability than Nafion 117. It is showed in Figure 1 that SPSSN40 membrane also has higher proton conductivity than that of SPAES40 which has similar IEC value. That might be because of higher water uptake of SPSSN40. SPSSN membranes have stronger mechanical strength than Nafion 117. Due to the stability of sulfide linkages, SPSSNs have higher radical stability as compared with SPAESs. As a result, SPSSN membranes with degree sulfonation 40% had higher single cell performance than Nafion 117.

Crosslinking showed improvements of the water uptake, proton conductivity and methanol permeability properties for DMFC application. Crosslinking drastically reduced water uptake and dimensional change. This is important for fuel cell application because too much dimensional change causes delamination between catalyst layers and proton exchange membrane. That leads to reduce performance of single cell. As can be seen in Figure 2, single cell performance of crosslinked membrane is higher than those of non-crosslinked one and Nafion 117. More discussions on structural analysis, methanol permeability and proton conductivity will be showed in poster presentation.

4. Reference

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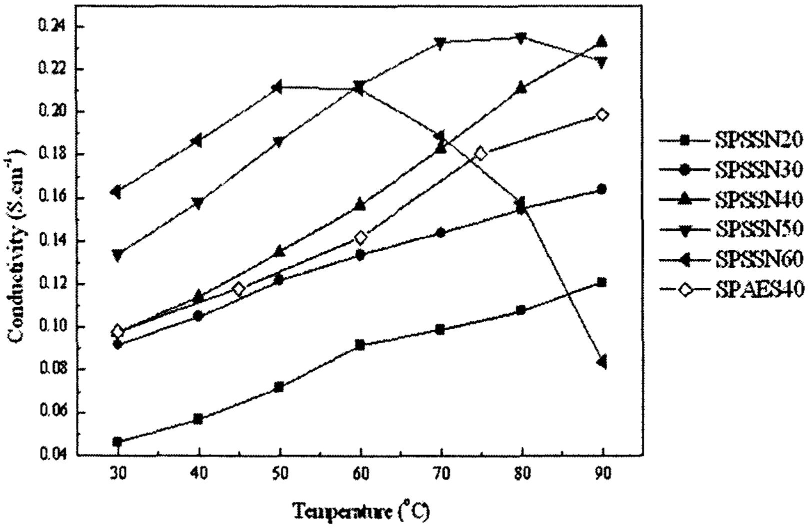

Figure 1. proton conductivity of SPSSN membranes as functions of tmeperature.

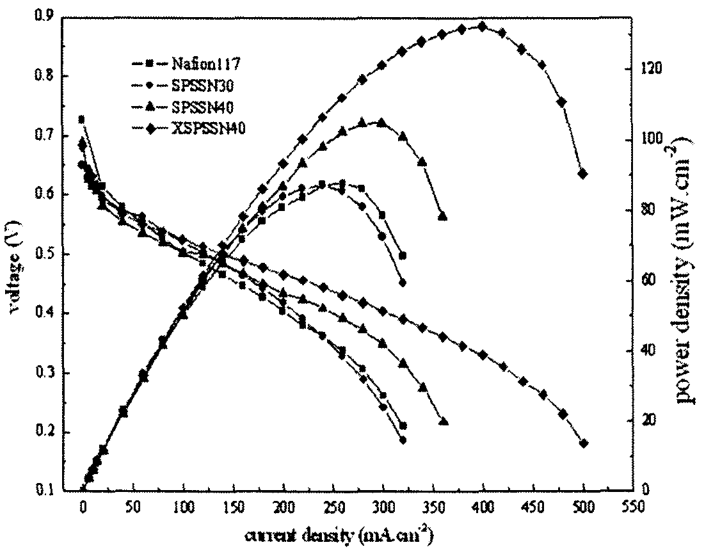

Figure 2. single cell perfomances of SPSSN and XPSSN membranes with 1M methanol solution at 90°C