설폰화 폴리아릴렌 공중합체의 제조 및 특성

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Preparation and Charaterization of Sulfonated Poly(arylene ether sulfone) Copolymers with Carboxylic Acid Groups

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1. Introduction

Fuel cells are electrochemical devices that convert chemical energy from fuels such as hydrogen or methanol directly into electrical energy. They are enviornmentally friendly energy sources because, ideally, water and heat are the only byproducts from hydrogen/air systems. PEMFC or DMFC based fuel cell systems are a very promising power source for portable, transportation, and stationary power. Theses systems produce electric power from two electrochemical reaction: the oxidation of hydrogen at the anode and the reduction of oxygen at the cathode. The electric circuit is completed by the transport of protons through the polymeric membrane. Nafion represent the current state of the art PEMs. These membranes have good mechanical, thermal, and chemical stability along with good conductivity at temperatures less than or equal to 80℃ and high humidity. However, Serveral questions, such as high methanol permeability and reduction in conductivity at high temperature and low humidity, have limited their applicability. As a result, the development of competitive and less expensive PEMFC or DMFC that will overcome these problems is important. Poly(arylene ether sulfone)s are important, well-known engineering thermoplastics that display excellent thermal and mechanical properites, as well as resistance to oxidation and acid catalyzed hydrolysis.[1-4]

The objective of this study is to synthesize the sulfonated poly(arylene ether sulfone) copolymers with carboxyl group. To achieve this goal, sulfonated poly(arylene ether sulfone) membranes containing a carboxyl group in its side chain have been synthesized by the nucleophilic displacement reaction of 4,4'-dichlorodiphenyl sulfone, sulfonated 4-4'-dichlorodiphenyl sulfone, and phenolphthalin. The proton conductivity and methanol permeability were evaluated for future DMFC application.

2. Experimental

A. Synthesis of the 3,3'-disulfonated 4,4'-dichlorodiphenyl sulfone (SDCDPS): SDCDPS was synthesized by sulfonating dichloro diphenyl sulfone(DCDPS) using fuming acid and sulfuric acid at 110℃ for 6 hours. The resulting acidic compound was neutralized first by sodium chloride and subsequently at room temperature with sodium hydroxide. The sulfonated monomer grade was generated by recrystallization from a mixture of methanol and deionized water.

B. synthesis of sulfonated poly(arylene ether sulfone): A typical synthetic procedure to prepared sulfonated copolymers (S-DCDPS/DCDPS = 40/60) was described. phenolphthalin (3mmol), DCDPS (1.8mmol), and SDCDPS (1.2mmol) were added into 50ml 3-neck flask equipped with mechanical stirrer, nitrogen inlet and a Dean Stark trap. The solvent (usually, DMAc/toluene = 2/1 v/v) was introduced to afford a 20% solid concentration. After solvent was mixed in the system, anhydrous potassium carbonate was added as an azeotropic agent.

The reaction mixture was heated under reflux at 150℃ for 4 hours until there was no water observed in the Dean-Stark trap. Finally, the temperature was gradually increased to 190℃ for 18 hours during dehydration and removal of toluene from the reaction mixture.

The solution was diluted with DMAc, filtered to remove inorganic salts, and isolated by coagulation in ethanol. The precipitated copolymers were washed several times with ethanol and dried in a vacuum oven at 120℃ for 24 hours.

C. Membrane preparation: The sulfonated polymer was dissolved in DMAc and poured onto a glass to prepare sulfonated membrane. The membranes were carefully dried at gradually increasing temperature (up to 60℃) and then vacuum dried at temeprature up to 120℃for 48 hours. The membrane was converted into the acid form with 2N H_2SO_4 for 24 hours. Finally the membrane was washed with deionized water and dried at 80 ℃

for 1 day.

3. Results and discussion

FT-IR and ^{1}H NMR were used to identify and characterize the sulfonated copolymers. The IEC value and water content of the membranes were listed in Table 1.

The prepared proton exchange membranes at each condition possessed the IEC in the range of 0.61 - 1.45 meq./g-dry membranes. The total IEC value and water content increased with the sulfonated monomer content due to increasing charged ionic content($-SO_3^-$) in membranes.

Figure 1. shows the proton conductivities of the membranes as a function of the relative humidity(RH). The proton conductivity increases with RH and depends on both the containing of SDCDPS mol % and relative humidity(RH). Proton conductivities and methanol permeabilities of the membranes ranged from 10^{-3} - 10^{-2} S/cm, and 10^{-7} - 10^{-8} cm^2/s, respectively. These characteristic of the sulfonated poly(arylene ether sulfone) copolymers with carboxylic acid group are desirable for future application related to direct methanol fuel cell.

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Table I. IEC Values and Water Content of Membrane

Sample	mol % SDCDPS	IEC (meq./g)	Water content (%)
PDS 0	0	0.61	14.6
PDS 10	10	0.76	29.9
PDS 20	20	0.99	37.6
PDS 30	30	1.27	48.4
PDS 40	40	1.45	55.3

PDS0-PDS40: Containing of SDCDPS mol %

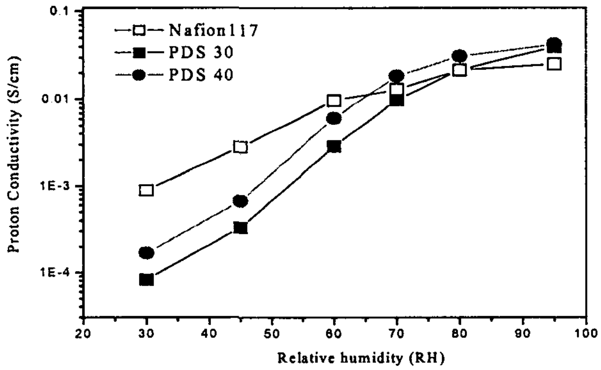

Fig.1 Proton conductivities of poly(arylene ether sulfone) and Nafion 117 with relative humidity(RH%) at 30℃