주쇄구조가 다른 술폰화 폴리이미드 막의
열적 안정성과 가수분해 안정성의 특성 분석

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Thermal and Hydrolytic Stability of Sulfonated Polyimide Membranes with varying Chemical Structure

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Introduction

Fuel cells have been identified as a more feasible alternative energy source that is free from undesirable emissions. At present the polymer electrolyte fuel cell (PEFC) is the most promising of all the fuel cell systems whichare viewed as portable power systems for the use in vehicles. The most important component of a PEFC is polymer electrolyte membrane itself. Perfluoro sulfonic acid polymers (Nafion[®]) are currently used as proton exchange membrane (PEM) in commercial systems. These membranes are very expensive; moreover their conductivity decreases at low humidity and at higher temperatures. This lead to extensive research for alternate PEM materials and various sulfonated polymers are synthesized and reviewed for their possible application as PEM material.

Aromatic polyimides, due to its salient features like high thermal stability, thermo-oxidative stability, high mechanical strength and superior chemical resistance, are viewed as suitable PEM material to work in the more difficult fuel cell environment. Recently several aromatic polyimides are successfully synthesized with sulfonyl substitution and were tested in fuel cells.Generally the introduction of sulfonic groups in polyimides is achieved by using the sulfonated aromatic diamines. Control of sulfonation degree is of practical importance since high sulfonation lead to high swelling and even dissolution of the membrane in water whereas low sulfonation result in low conductivity. Hence often it is required to optimize the degree of sulfonation for the better performance of the polymer membrane. We

can tailor the degree of sulfonation according to our requirementby using another non-sulfonated diamine comonomer and just adjusting the mole ratio of them.

The rigidity and brittleness, which are the problems often encountered when polyimide based PEM materials are used in the fuel cell can be overcome by using monomers that import flexibility to the system. Moreover, the flexible systems are reported to have better stability towards water than the rigid polyimides. Hence all the monomers except BDSA were selected as if it contains a flexible bridge, to increase the flexibility of the system.

Hydrolytic stability of the sulfonated polyimide membrane is a limiting factor, which affects the lifetime of these membranes in fuel cell applications. Hence several studies focusing on the various aspects to increase the water stability were carried out. The hydrolytic stability and proton conductivity exhibited dependence on chemical structure of the polymer backbone and polymer morphology. The effect of various morphological aspects including phase separation, graft and random copolymerization, flexibility of the main chain, the ring structure of the polyimide etc on the proton conductivity and hydrolytic stability were studied. The flexible systems exhibit better hydrolytic stability than the rigid polymer backbone. Like-wise the hydrophilic-hydrophobic phase separation facilitates the formation of ionic clusters and result in better ionic conductivity.

To study the hydrolytic degradation of polyimides, two series of polyimides with different chemical backbone structure were synthesized from dianhydrides and diamine comonomers with flexible linkages along with 4,4'-diaminobiphenyl 2,2'-disulfonic acid (BDSA) whichwas used to provide the required sulfonic acid groups. To study hydrolytic stability, less stable phthalic derivatives were used in the polyimide synthesis and they were compared with the naphthalenic derivatives. The polyimides were characterized by FT-IR and thermal stability. The proton conductivity, water uptakeand ion exchange capacity of the polyimides with different chemical backbone structure were investigated.

Experimental

In a three-necked round bottom flask fitted with a magnetic stirrer, thermometer and nitrogen inlet, BDSA, triethylamine and m-Cresol were added and kept at 30 °C till BDSA completely dissolved in m-cresol. To this solution ODA or MDA with different mole ratio was added under nitrogen atmosphere. To this solution, equimolecular of 6FDA or ODPA to total diamines was added in N_2atmosphere and stirred for 24 hrs at 0°C and the viscous copoly(amic acid) solutions were obtained. All other polyimides were prepared by adopting the

same procedure, by varying the mole ratio of the monomers and the solid content was fixed at 15% by adjusting the amount of solvent.

The poly(amic acid) solutions were spin coated onto substrates like silicon wafers. The thickness of the films can be adjusted by varying the spin speed. Then the poly(amic acid)films were kept in the curing oven. The following curing cycle was followed-the films were cured at 80°C for one hour. Then the temperature was increased to 200°C at a rate of 2°C per minute and the films were cured for another 24 hrs at 200°C. Then they were cooled to 50°C at a cooling rate of 1°C/min. The copolyimide films were obtained and they were removed from the substrate, soaked in boiling methanol and then soaked in 1.0 M HCl for 10 hrsto regenerate the sulfonic acid. The films were thoroughly washed with deionised water and then dried.The copolymides were named as the first two letters represent the anhydride and the next letter gives the comonomer. The following numeral gives the percent of BDSA content. 6FDA 20 gives the polymide from 6FDA, ODA, and the BDSA content is 20 %.

The polyimide thin films after exchange of protons, dried in vacuum oven at 100^oC for 24 h. For these polyimide thin films water uptake values were measured at four different temperatures 25^oC, 40^oC, 60^oC and 80^oC at 100 % relative humidity and also as a function of time by using a thin film diffusion analyzer (Cahn Instruments Co., model D-200) with a resolution of 0.1 g. The detailed procedures were given in our previous studies.

The ion exchange capacity (IEC) was measured by titration method. The sulfonated polyimide films were soaked in 1 M HCl for 10 hrs to regenerate the protons from the salt form, if any. They were thoroughly washed with deionised water for several times and were soaked in 0.1 M NaCl for 15hrs. The protons released due to the exchange reaction with Na^+ ions were titrated against 0.1 M NaOH, using phenolphthalein indicator.

Results & Discussion

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