"Crosslinked Sulfonated Polyimide Networks as Polymer Electrolyte Membrane in Fuel Cells"
"가교된 폴리이미드 구조의 연료전지용 전해질 막의 연구"

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1. Introduction

Crosslinking is a viable option to improve these properties without compromising on proton conductivity. By crosslinking the hydrolytic stability of the polymers can be greatly enhanced together with mechanical property and thermal stability. Interestingly the crosslinking can also reduce the methanol crossover to a greater extent. Also the mechanical integrity of the polymer with hot methanol can be increased.

2. Experimental

Materials and Synthesis of Sulfonated Polyimides

1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), 4,4'-diaminobiphenyl 2,2'-disulfonic acid (BDSA), 2-bis [4-(4-aminophenoxy)phenyl]hexafluropropane (HFBAPP) and m-cresol were purchased from Tokyo Kasei Co. Diaminoacrydine hemisulfate (DAA) and the crosslinkers – dibromo butane (DBB), dibromo hexane (DBH) and dibromo decane (DBD) were purchased from Aldrich Co. Triethylamine (Et₃N) was purchased from TEDIA. Benzoic acid was purchased from Duksan Co. NTDA, HFBAPP and BDSA were dried under vacuum before use. m-Cresol was distilled under reduced pressure. All other chemicals were used as received.

BDSA (8 mmol), m-cresol (60 mL), and triethylamine (6 mL) were successively added to a 250 mL 3-neck flask under nitrogen flow. When BDSA was completely dissolved, 8 mmol of HFBAPP and 4 mmol of DAA were added.

To this solution 20 mmol of NTDA and 28 mmol of benzoic acid were added. The mixture was stirred at room temperature for a few minutes until it became homogeneous and then they were chemically imidized. Detailed procedure is reported elsewhere. The synthesized sulfonated polyimides are precipitated in acetone and dried in vacuum.

Synthesis of Crosslinked Polymer Network

Synthesized sulfonated polyimide was taken in 100 mL three neck flask to which anhydrous m-cresol was added based on 30 weight % and was vigorously stirred at room temperature under N_2 purging until the sulfonated polyimide was completely dissolved (approximately 24 hours). Calculated amounts of dibromoalkanes were added, stirred at room temperature for 1 hour to effect homogeneous mixing and the solution was cast onto glass plates using spin coater. The spin coater allows preparing thin sulfonated polyimide films of uniform thickness, where the thickness can be effectively controlled by adjusting the RPM of the spin coater. The glass plate was pre-baked at 80 °C for 1 hour and then cured in a curing oven at 120 °C for 12 hours. The sulfonated polyimide films were soaked in deionised water over night to release the films from the glass plate. The as-cast films were soaked in methanol at 60 °C for 1 hour and in 1.0 M HCl at room temperature for 5 ~ 10 hours successively. The proton-exchanged films were thoroughly washed with deionized water and then dried in vacuum at 150 °C for 20 hours.

Result and discussion

FT-IR Analyses

The imide carbonyl absorption band around 1721 cm^{-1} and 1670 cm^{-1} and the C-N stretching vibration around 1346 cm^{-1} confirmed the formation of polyimides. Out of phase bending of imide ring was observed around 758 cm^{-1}. The SO_2 vibration of the sulfonic acid group was observed around 1178 cm^{-1} and band around 1022 cm^{-1}. Crosslinking leads to pyridinium cationomers, which show a new peak at 1543 cm^{-1} as reported in several references which may be specifically due to quaternisation of heterocyclic nitrogen which is absent in the uncrosslinked sulfonated polyimide. This confirms the successful synthesis of crosslinked sulfonated polyimides.

Thermal Stability

The thermal stability of the sulfonated polyimides was investigated by thermogravimetric analysis (TGA). The effect of crosslinking on the thermal stability of the sulfonated polyimides is not much pronounced. Since alkyl groups degrade at lower temperature than the polyimides, the actual effect of crosslinking is nullified. Despite this, a small increment in thermal stability is observed for crosslinked polyimides inthe third step degradation. When the polymer chains are crosslinked, the polymer cohesion and ordering increases and this may be the reason for the small increase in the thermal stability.

Ion exchange capacity

Many important properties of the sulfonated polyimide like the proton conductivity and the water uptake depend on IEC. IEC directly depends on the content of sulfonyl groups present in the polymer. The IEC decreased in the order PI-Uncrosslinked > PI-DBB > PI-DBH > PI-DBD. Here the same sulfonated polyimide was used to prepare crosslinked sulfonated polyimides using three different crosslinkers. Hence the amount of the sulfonic acid content is the same in all the sulfonated polyimides. The decrease in the IEC despite the same sulfonic acid content can be attributed to the molecular weight of the crosslinkers. The increase in the molecular weight of the crosslinkers reduces the amount of sulfonic acid in a unit weight of the crosslinked sulfonated polyimide. Hence the IEC of the sulfonated polyimides was reduced accordingly. Since water uptake depends on IEC linearly, it is expected that the water uptake will also reduce with increase in chain length of the crosslinker.

Water Uptake

The water uptake for the sulfonated polyimides was evaluated with micro balance at room temperature as reported earlier. The water uptake varied as follows PI-Uncrosslinked > PI-DBB > PI-DBH > PI-DBD. Water uptake value primarily depends on the sulfonic acid content. Since the sulfonic acid content is the same for all the polymers the variation in water uptake is attributed to the crosslinked structure.

Generally water uptake is lower for the crosslinked polymer than that of the uncrosslinked one. The crosslinking decrease the polymer swelling and this may be the reason for reduced water uptake of the crosslinked sulfonated polyimides. With increase in the alkyl chain length of the crosslinker, polymer flexibility will increase and hence it was expected that it would lead to higher swelling and thus higher water uptake. But in this study a reverse trend was observed as PI-DBB > PI-DBH > PI-DBD. It showed that the effect of sulfonic acid content i.e., IEC, seems to be dominant and hence with increase in the alkyl chain length, the water uptake decreased despite the increase in the flexibility of the crosslinking chains. In other words the increase in the molecular weight of the crosslinker reduces the amount of sulfonyl groups resulting in decease of the water uptake in the corresponding crosslinked sulfonated polyimide films. This is in accordance with the IEC trend.

Hydrolytic Stability

The poor hydrolytic stability may arise from two reasons. Due to the hydrophilic modifications in the polyimide backbone, the swell in water increases leading to poor mechanical properties of the film. The second reason is due to the chemical degradation of the polyimide backbone. The hydrolytic stability is analyzed by immersing the sample in water at 100 °C and the water is stirred at constant speed. The stirring exerts physical strain on the polymer films. The result may reflect the mechanical stability of the material. Nafion is more stable than the polyimides which originate from its highly hydrophobic, flexible polymer backbone. Also due to the unique much pronounced hydrophilic / hydrophobic phase separation the hydrophobic polymer backbone is not much affected by hydrolysis. The crosslinked sulfonated polyimidesexhibited higher hydrolytic stability than the uncrosslinked one. This may be because crosslinking can reduce the swelling to greater extent. It can be seen from the water uptake and IEC results that crosslinked sulfonated polyimide films exhibited lower IEC and water uptake than the uncrosslinked one.

Proton conductivity

The conductivity for all the sulfonated polyimides and the Nafion®115 were done at four different temperatures namely 30 °C, 50 °C, 70 °C and 90 °C. The proton conductivity of crosslinked sulfonated polyimide and Nafion increased with increase in temperature. The proton conductivity of all the sulfonated polyimides increased with increase in temperature which was due to the increased mobility of water and structural reorientation as well as increased chain mobility. When compared with benchmark Nafion membrane, the polyimides showed lower conductivity than Nafion at all temperatures. This is because of the flexible main chain of Nafion® which leads to high swelling of the membrane in hydrated state and lead to easy percolation of protons. On contrary, the polyimides having comparatively rigid backbone than that of Nafion®which resist the swelling in water and the water percolation, exhibited lower proton conductivity. Moreover due to the unique hydrophilic/hydrophobic phase segregated structure, Nafion® forms clusters with ion-rich channels accounting for high proton conduction at low temperature. But the loss in conductivity with increase in temperature is more pronounced in Nafion than the rigid polyimides. The proton conductivity of crosslinked sulfonated polyimides is almost similar to that of the uncrosslinked sulfonated polyimide indicating that the crosslinking did not affect the proton conductivity. This is an important result because with increase in crosslinking the hydrolytic stability can be increased, the methanol permeability can be reduced and these can be achieved without compromising on the proton conductivity.

Conclusions

Sulfonated polyimides are synthesized and they are crosslinked with various crosslinkers. The effect of the chain lengths of the dibromo alkanes are studied in detail. The quarternisation is confirmed by FT-IR measurements. Crosslinking did not show any pronounced effect on thermal stability, which may be due to the lower stability of the crosslinkers compared to polyimides. IEC decreased in the orderPI-Uncrosslinked > PI-DBB > PI-DBH > PI-DBD. IEC decreased with the increase in the molecular weight of the crosslinker due to the decreased sulfonic acid content in a unit weight of the polymer.

Water uptake decreased as follows PI-Uncrosslinked > PI-DBB > PI-DBH > PI-DBD. Water uptake was lower for the crosslinked sulfonated polyimides than that of the uncrosslinked one and it decreased with increase in alkyl chain length of the crosslinker. Hydrolytic stability of the crosslinked polyimides is higher than the uncrosslinked polyimides. Crosslinked polyimides have decreased swelling and hence good stability. Hydrolytic stability decreased with increase in the alkyl chain length of the crosslinker due to increase in flexibility and swelling. The conductivities for the crosslinked and uncrosslinked polyimides were almost similar indicating proton conductivity is not affected by crosslinking. Between the crosslinked sulfonated polyimides very small decrease in proton conductivity is observed with increase in alkyl chain lengths, which was due to the lower IEC of the corresponding crosslinked sulfonated polyimides.

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