

고온형 PEMFC를 위한 술폰화 폴리이미드 전해질막

Effect of bulky bridging groups on the properties of sulfonated polyimides

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INTRODUCTION

Fuel cells are identified as the most feasible energy source with minimal amount of noxious emissions and it is in the limelight of academic and industrial interest for more than a decade now. Among the various kinds of fuel cells, due to the simplicity in operation, PEMFC are the forerunner in the field¹. The electrolyte is the most important component of any fuel cell system. Various Ionic membranes were extensively studied to serve as fuel cell electrolytes and Nafion[®] is the most well studied membrane of them¹. But there are few drawbacks associated with the perfluoro sulfonic acid membranes namely (1) the high cost make this product economically unviable for common applications (2) the rapid loss of ionic conductivity at high temperature and low humidity. These drawbacks triggered an extensive research to develop alternative PEM material for PEMFC^{2,3}. Polyimides possess many salient features to be used in PEMFC, still, the main drawback associated with polyimides are their hydrolytic stability, which is very sensitive to their chemical structure. The flexible systems are reported to exhibit more hydrolytic stability⁴ and moreover the T_g of these polymers will be low favoring easy migration of the protons. Also it has been reported that free volume in the non-sulfonated phase contribute to increased conductivity at elevated temperature^{5,6}.

In this study a series of six-membered polyimides were synthesized using non-sulfonated diamine monomers having different bridging groups (Figure 1). These

diamine monomers are selected on the basis of increasing bulkiness of the bridging atom and their effect on properties are studied in detail.

EXPERIMENTAL

Synthesis of random copolyimides

A series of six membered polyimides using NTDA as anhydrides, BDSA as sulfonated diamine and various non-sulfonated diamine comonomers with different bridging groups (cf. Figure 1) were synthesized by chemical imidization method.

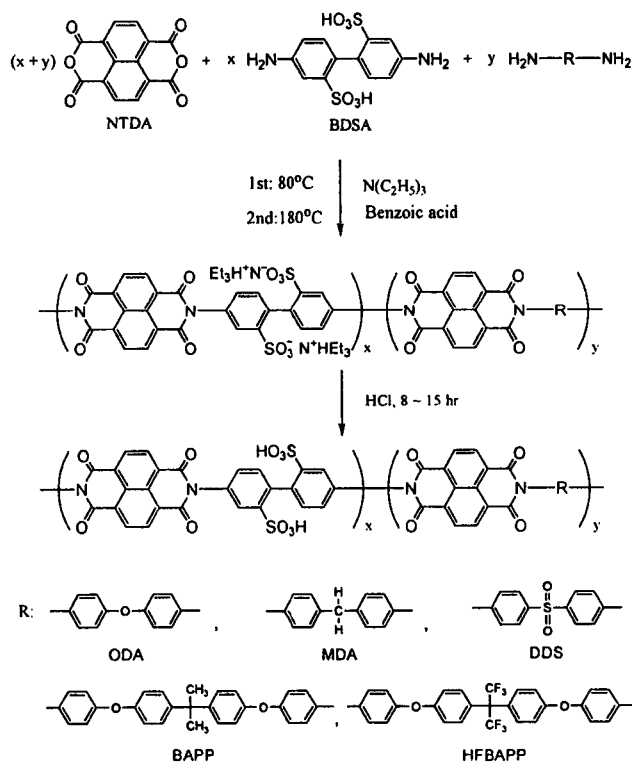


Figure 1. Synthetic scheme of sulfonated polyimides.

RESULT AND DISCUSSION

Spectral analyses

The chemical structures of synthesized polyimides were confirmed by FT-IR, which is shown in Figure 2.

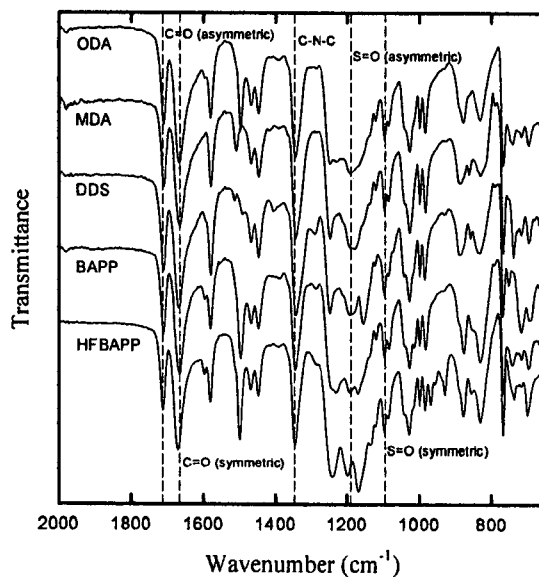


Figure 2. FT-IR spectra of sulfonated polyimides.

Solubility of sulfonated polyimides

All the polyimides are soluble in *m*-cresol. The solubility increased with increase in the bulkiness of bridging group. (Table 1)

Table 1. Solubility of sulfonated polyimides

| Polyimide | <i>m</i> -Cresol | NMP | DMAc | DMSO |
|------------------------|------------------|-----|------|------|
| NTDA-BDSA/ODA (1/1) | ○ | △ | × | △ |
| NTDA-BDSA/MDA (1/1) | ○ | × | × | △ |
| NTDA-BDSA/DDS (1/1) | ○ | ○ | ○ | ○ |
| NTDA-BDSA/BAPP (1/1) | ○ | △ | × | △ |
| NTDA-BDSA/HFBAPP (1/1) | ○ | ○ | ○ | ○ |

Thermal property

All the polyimide thin films exhibited three-step degradation pattern. The first weight loss was due to the loss of absorbed moisture. The second step of degradation corresponds to the degradation of aromatic sulfonyl groups. The third step indicates the decomposition of the polyimide backbones. All the polyimides showed thermal stability upto 500 °C. The thermal stability decreased with increase in both the bulkiness and the number of bridging groups

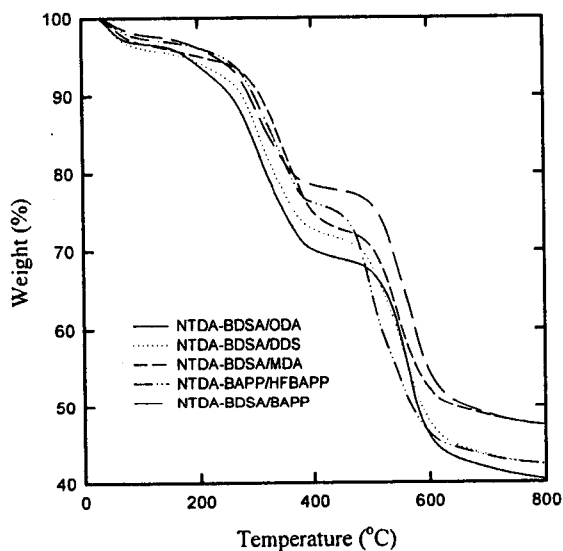


Figure 3. Thermal properties of sulfonated polyimides.

IEC and Water uptake of sulfonated polyimides

The water uptake and IEC values depend on the amount of sulfonyl groups present in the polymer. Both water uptake and IEC decreased with increase in both the bulkiness and the number of bridging groups. With increase in bulkiness molecular weight of the non-sulfonated diamine increases and hence the amount of sulfonic acid group in a particular weight fraction decreases. Hence both water uptake and IEC decreases.

Hydrolytic stability

The polyimides with bulky bridging groups showed increased hydrolytic stability. (Table 2) This must be due to flexibility of the polymer chain rendered by the bulky bridges. As reported, flexibility increases the molecular relaxation and hence increases the membrane stability⁴

Table 2. Water uptake, IEC and hydrolytic stability of sulfonated polyimides

| Polyimide | thickness (μm) | water uptake (%) | IEC (mequiv/g) | hydrolytic stability | | |
|-----------|--------------------------------|---------------------|-------------------|---------------------------------|-------------|------------------|
| | | | | temp. ($^{\circ}\text{C}$) | time (h) | stability |
| N-ODA | 19.42 | 26.3 | 2.01 | 80 | 90 | Somewhat brittle |
| N-MDA | 13.87 | 38.5 | 1.76 | 80 | 80 | brittle |
| N-DDS | 22.90 | 21.2 | 1.66 | 80 | 110 | good |
| N-BAPP | 22.10 | 20.6 | 1.48 | 80 | 110 | good |
| N-HFBAPP | 25.60 | 15.9 | 1.28 | 80 | 110 | good |

Conductivity

Nafion[®]115 showed high conductivity at low temperatures than polyimides due to high swelling and hydrophilic/hydrophobic phase separation. With increase in temperature the conductivity rapidly increased in the case of polyimides with bulky bridging groups. (Table 3) These bulky bridging groups lead to irregular packing thus increasing the free volume. Free volume in the non-sulfonated segment augment the water uptake in turn the conductivity of the polymer⁵.

Moreover water gets trapped in these voids and the evaporation of these trapped water is suppressed by rigid polyimide chains⁶. These trapped water account for the proton conduction at high temperature. This result is significant because the high conductivity is achieved despite low water uptake and IEC compared to ODA and MDA based polyimides. In polyimides having bulky bridging groups due to the increased free volume water molecules can easily diffuse and this accounts for

high conductivity. This can be inferred from the slope of polyimides and Nafion[®]115 systems.

Table 3. Proton conductivity of sulfonated polyimides

| Polymers | conductivity (S/cm) | | | | | | |
|----------|---------------------|--------|--------|--------|--------|--------|--------|
| | 30°C | 40°C | 50°C | 60°C | 70°C | 80°C | 90°C |
| N-DDS | 0.0050 | 0.0071 | 0.0085 | 0.0247 | 0.0605 | 0.1899 | 0.2218 |
| N-MDA | - | - | 0.0259 | 0.0538 | 0.0702 | 0.0790 | - |
| N-BAPP | 0.0037 | 0.0063 | 0.0758 | 0.1063 | 0.1509 | 0.1628 | 0.1966 |
| N-HFBAPP | 0.0020 | 0.0047 | 0.0318 | 0.0343 | 0.0580 | 0.1028 | 0.2828 |

CONCLUSIONS

The bulkiness and the number of the bridging groups in the non sulfonated diamine was systematically varied, for the first time to increase the free volume and these polyimides showed increased conductivity despite low water uptake and IEC and also showed very high conductivity than Nafion[®]115. The bulky bridging groups rendered high hydrolytic stability due to imparted flexibility. All the polyimides exhibited characteristic high thermal stability (> 470 °C).

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