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고온 연료전지용 새로운 형태의 고분자 전해질막의 합성과 특성연구

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Synthesis and Properties of New Type of Proton Conducting Polymer Membrane for High Temperature Fuel Cells

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Abstract : Poly(benzimidazole-co-aniline) (PBIANI), a self-crosslinked, net-structured, proton conducting polymer has been synthesized for the membrane of high temperature proton exchange membrane fuel cells (HT-PEMFC) with improved proton conductivity and mechanical strength. The stress at break (26±3MPa)and proton conductivity (167 mS cm-1)of the phosphoric acid doped PBIANI (DPBIANI)membrane is much higher than those of other doped polybenzimidazole(PBI) type membranes.

Key words : Conducting polymers, Doping, Fuel cells, Polymeric materials

1. Introduction

Recent research in proton exchange membrane fuel cells (PEMFC) has focused on the development of a high temperature PEMFC (HT-PEMFC) that operates at 100-200°C. Polymers used to prepare HT-PEMFC membranes contain basic groups that can form complexes with stable acids. The phosphoric acid doped PBI membrane is the most preferred basic polymer membrane for HT-PEMFC.[1)] The operation of the fuel cell at higher temperatures ensue higher efficiencies, high power densities, reduced sensitivity to carbon monoxide poisoning of the electrode and better controllability. PBI type membranes are doped with an excess of phosphoric acid in order to increase their proton conductivity, which causes deterioration of the mechanical properties.[2)] The mechanical strength of PBI type membranes have been improved through the chemical cross-linking using *p*-xylene dihalides.[3-4)] The proton conductivity of PBI type membranes is also much lower than that of Nafion even after a high degree of doping.[1)] However, there is no literature showing a simultaneous improvement in the mechanical strength and proton conductivity of PBI type membranes.

In this study, a new self-crosslinked, net-structured, proton conducting PBI type of polymer membrane was synthesized for the HT-PEMFC. The aims of this research were to improve both the (i) mechanical strength and (ii) proton conductivity of PBI type membranes

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simultaneously by inserting an aniline monomer as an extra basic unit as well as a cross-linker between the benzimidazole units.

2. Experimental

2.1 Materials

3,3′-Diaminobenzidine (DAB) and 5-amino isophthalicacid (AIPA) were purchased from Tokyo Chemical Industry, Co. Ltd, Japan .Polyphosphoric acid (PPA), phosphoric acid, ammonium persulfate (APS) and toluene were obtained from Sigma Aldrich, Germany. Sulfuric acid and hydrochloric acid were acquired from Duksan Pure Chemicals Co. Ltd., Korea.

2.2 Synthesis of poly (benzi mid azole -co-aniline) (PBIANI)

The PBIANI was synthesized in two steps. In the first step, AIPA was polymerized to poly (5-aminoisophthalic acid) (PAIPA) by oxidative polymerization. In the second step, PBIANI was synthesized by condensation polymerization between PAIPA and DAB. The entire synthesis procedure is schematically presented in Fig. 1.

FT-IR: ν_{N-H}~3400cm^{-1}; $\nu_{(Q)}$~1620cm^{-1}; $\nu_{(B)}$~1460cm^{-1}; $\nu_{C=N}$~1170cm^{-1}; ν_{C-N}~1050cm^{-1}; γ_{C-H}(arom)~900-650cm^{-1}.[5] There is no residual carbonyl absorption between 1780 and 1650 cm^{-1},indicating a complete reaction between PAIPA and DAB and the formation of PBIANI.

2.3 Film Casting and doping

The PBIANI film was cast from H_2SO_4 at 250±5°C until completely dried. The film was then boiled with DI water for 2h. This film was designated UPBIANI. FT-IR: ν_{SO3H} ~1123 and 1395cm^{-1}.[5] The FT-IR result indicates that the some sulfonic acid groups are introduced in the structure of UPBIANI film during casting.

UPBIANI films were immersed in a 10M phosphoric acid solution and left for 4 weeks for complete acid doping.

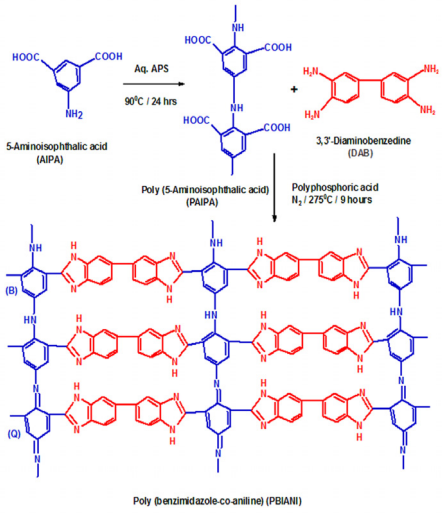

Fig 1. Schematics of the synthesis of PBIANI

2.4 Characterization

The FT-IR spectrum was recorded on a NICOLET 6700 FT-IR (Thermo scientific, USA).

The ultra high resolution microscopic study was accomplished using a field emission transmission electron microscope (FE-TEM), JEM-2200 FS from JEOL, Japan.

The thermogravimetric analysis (TGA) was carried out (TGA, Q50 from TA Instruments, USA) under a nitrogen atmosphere over 40°C to 900°C at a heating rate of 20°C min^{-1}.

The mechanical properties were measured using a universal test machine (LR5K plus model, Lloyd. Co.) according to the ASTM D412,at across head speed of 50 mmmin^{-1}.

The ion conductivity of the membranes was measured by the four-probe method using a BekkTech conductivity test cell in conjunction with a PGZ 301 Dynamic EIS Voltammeter. The temperature and humidification were controlled using a Globe Tech Computer Cell GT fuel cell test stand. [6]

3. Results and discussion

3.1 FE-TEM

The TEM image appears like a net consisting of highly ordered uniform rectangle units (Fig. 2). The TEM image confirms the formation of

self-cross-linked, net-structured PBIANI as shown schematically in Fig. 1.

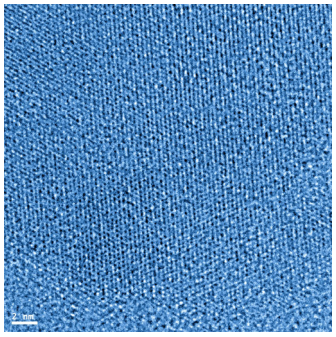

Fig 2. FE-TEM image of PBIANI

3.2 Thermogravimetric analysis (TGA)

The decomposition of the PBIANI powder and films is started from 230°C and continued up to the final experimental temperature, 900°C (Fig. 3). This means that the PBIANI can be used safely up to 200°C. The UPBIANI film shows more weight loss at around 230°C to 430°C compared to the PBIANI powder due to the decomposition of sulfonic acid groups. The phosphoric acid doped PBIANI film (DPBIANI) film shows further weight loss at the same temperature region compared to the UPBIANI film owing to the decomposition of both the sulfonic acid groups and doped phosphoric acid. The UPBIANI and DPBIANI films contain approximately 17.7 wt.% of sulfonic acid group with respect to the PBIANI powder and the DPBIANI film contains 45.0 wt.% of phosphoric acid with respect to the UPBIANI film (calculated from the residue at 900°C).

3.3 Mechanical properties

Table 1. lists the mechanical properties of the UPBIANI and DPBIANI films. Generally, for PBI type membranes, the stress at break deteriorates abruptly after doping with phosphoric acid and the value dwindles to as low as 3.4 MPa, which is not suitable for their application to HT-PEMFC.[2,7)]

The stress at break of UPBIANI and DPBIANI films are 32±3 MPa and 26±3 MPa, respectively.

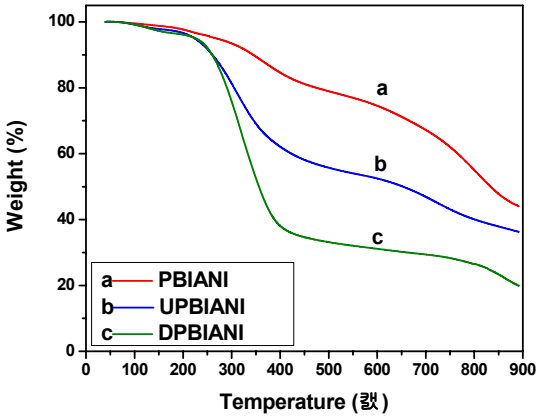

Fig 3. TGA plots of (a) PBIANI powder, (b) UPBIANI and (c) DPBIANI

The waning of stress at break for PBIANI is only ~20% after doping. However, the drop of mechanical strength of PBI after doping is as high as 92%.[7)] The self-crosslinked and net-structure of PBIANI assisted to overcome the problem of such weakening of the membrane after doping.

Table 1. Mechanical properties of the UPBIANI and DPBIANI films

Sample	Stress at break (MPa)	Elongation at break (%)
UPBIANI	32±3	13±4
DPBIANI	26±3	12±3

3.4 Proton conductivity

The proton conductivity of UPBIANI and DPBIANI increases with increasing temperature due to increase in activation energy (Fig 4). Hence, PBI type membranes can be used for HT-PEMFC. At 120°C and 100% RH, the proton conductivity of 45 wt% doped DPBIANI membrane is 167 mS cm^{-1}. Whereas, the proton conductivity of 75-500wt.% phosphoric acid doped PBI is 20-60mScm^{-1}.[2,8)] The higher conductivity is due to an increase in basicity through the introduction of an extra basic unit, aniline, to the molecular structure of the PBIANI.

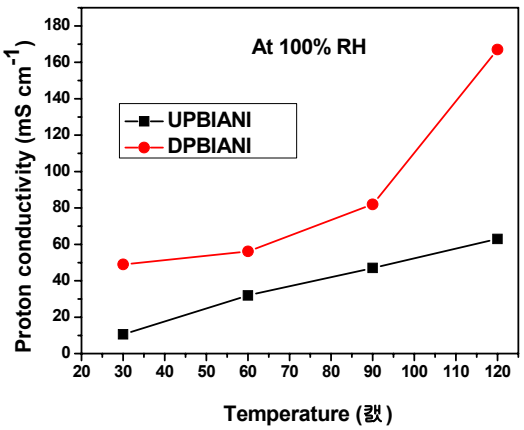

Fig 4. Proton conductivity of UPBIANI and DPBIANI films as a function of temperature

4. Conclusions

A new self-crosslinked, net-structured, proton conducting polymer, namely poly (benzimidazole -co-aniline) (PBIANI), was synthesized for a high temperature proton exchange membrane fuel cell (HT-PEMFC). The aniline monomer was inserted judicially as both an extra basic unit and cross-linker between the benzimidazole units, which improved the proton conductivity and mechanical strength of PBI type membranes, simultaneously.

The stress at break of the phosphoric acid doped PBIANI (DPBIANI) membrane (26±3 MPa) was much higher than that of the phosphoric acid doped PBI type membranes. The proton conductivity of the DPBIANI membrane (167 mS cm^{-1}) was much higher than that of PBI type membranes, as reported elsewhere.

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