PROPERTIES OF PARTIALLY-FLUORINATED POLYETHERSULFONE FOR HIGH TEMPERATURE PEM FUEL CELLS

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ABSTRACT

Proton exchange membranes were prepared by partial fluorination of polyethersulfone to have satisfactory thermo-mechanical stability for high temperature fuel cell application (>100°C). The base polymers were synthesized by polycondensation of hexafluoroisopropyliden diphenol, isopropyliden diphenol, and 4-fluorophenylsulfone, where the degree of fluorination was controlled by the amount of hexafluoroisopropyliden diphenol incorporated in the polymer. Diverse characterizations have been carried out on the synthesized membranes with two different degrees of fluorination (30% & 50% molar) and various sulfonation degrees in terms of thermal stability and proton conductivity, as a function of relative humidity and temperature. All the synthesized polymer membranes were found to be thermally stable up to 200°C, irrespective of the degree of fluorination and sulfonation, and their proton conductivities depend in a complicated way on the combination of fluorination and sulfonation in the F-PES polymer. High conductivity ($>10^{-2}$ S/cm) at relatively low relative humidity (~50%) was achieved for 50% fluorinated PES with an ion exchange capacity (IEC) of 1.43meq/g, a polymer which is also characterized by good thermal stability. Atomic force microscopy was performed to investigate the origin of the difference in the proton conductivity,

INTRODUCTION

Due to their inherently high energy efficiency and environment-friendly characteristics, fuel cells are rated to be among the most promising direct electrochemical energy conversion devices, and hence having generated a tremendous amount of research over the last decades. In particular, proton exchange membrane fuel cells (PEMFCs) have attracted a strong attention because of their potential application as vehicle power sources, portable electronic devices, etc (1,2). PEMFCs are commonly operated below 80 or 90°C for unpressurized systems, where CO poisoning of the Pt electrocatalyst is a problem. The necessity of higher temperature (>100°C) operation of PEMFCs arises from lower susceptibility to CO poisoning and enhanced reaction kinetics (3).

The typical membrane material that has been used in low temperature PEMFCs to date is Nafion®, a perfluorosulfonic acid polymer produced by DuPont de Nemours. Although Nafion® has many desirable properties including good mechanical strength, good chemical stability, and high ionic conductivity, use of this membrane at temperatures above the boiling point of water leads to dehydration, consequently a severe drop of proton conductivity, thus limiting the operating temperature range (4,5).

Many approaches have been attempted to develop novel proton-conducting alternative membranes in a variety of strategies. Among these polymers, modification of arylene main-chain polymers was motivated by their excellent chemical and mechanical stability (6-11). In this polymer family, we focus on polyethersulfone (PES), because, in addition to its extremely high resistance to hydrolysis, high thermal stability and oxidative resistance, PES also possesses very high group dipole moments and hence should result in much stronger dipole-dipole interactions with water than in the case of the other functional groups, thus the membrane should retain water at higher temperatures (12-14). The commercial PESs, which is highly sulfonated, show good conductivities up to around 120°C, but the mechanical properties deteriorate above 130°C, namely, the polymer film either dissolves completely or degrades in the presence of water.

For this reason, partial fluorination of polyethersulfone (F-PES) was explored for stabilizing the polymer in humid conditions at high temperatures. In addition, it is possible to change the hydrophobicity of polymer backbone by controlling the degree of fluorination, which means controlling the microstructure of hydrated membranes

In this paper, we address the preparation and detailed characterization of F-PES membranes, and give an insight into the factors controlling their electrical properties.

EXPERIMENTAL

Polymer Synthesis and Membrane Preparation

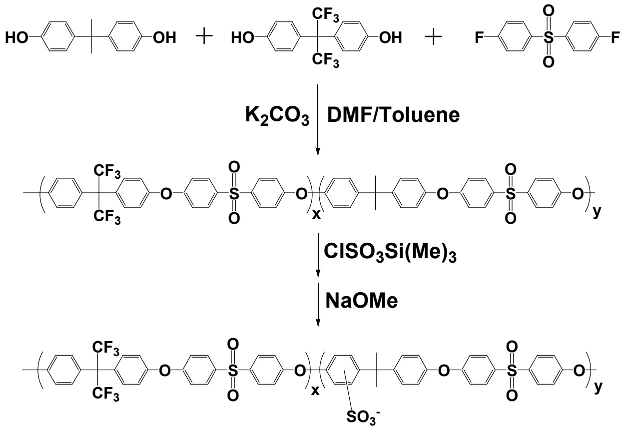

Fig.1. Synthesis route to F-PES and its sulfonation.

The synthetic scheme of sulfonated F-PES is shown in Fig. 1. Hexafluoroisopropyliden diphenol, isopropyliden diphenol, and 4-flourophenylsulfone were dissolved in 100 ml of dimethylformamide (DMF) and 10 ml of toluene. To investigate the effect of the degree of fluorination on the properties, two differently fluorinated PES were synthesized and the degree of fluorination was controlled by the amount of hexafluoroisopropyliden diphenol added and two differently fluorinated PESs (30 and 50%) for each degree of fluorination were prepared in order to investigate the effect of degree of fluorination and sulfonation on the microstructure and electrical properties. Then, the excess amount of K_2CO_3 was added as a catalyst. The reaction mixture was stirred at 150°C for 20h. After cooling to room temperature, the solution was precipitated into deionized water. Further purification was performed by precipitation from DMF solution to methanol. The polymer was dried in vacuum oven for 24h.

For sulfonation, the mother polymer was dissolved in chloroform and treated with trimethylsilyl chlorosulfonate to produce a silyl sulfonate poly(ether sulfone), where the amount of trimethylsilyl chlorosulfonate was determined by the desired sulfonation degree. Sodium methoxide was then used to cleave the silyl sulfonate moieties over 1h to yield the sulfonated polymer. The polymer solution was precipitated into deionized water and propanol. The polymer was dried in a vacuum oven for 48h at 55^{o}C after rinsing several times with deionized water. As a modification, isopropyliden diphenol (bisphenol-A) in the 50% fluorinated F-PES was substituted with diphenol. Polymerization procedure was same as described above.

The membranes of sulfonated poly(ether sulfone) were obtained by dissolving the polymer in *N*,*N*-dimethylformamide (DMF) and casting the polymer solution on a Telfon plate. Nafion®117 was purchased from Dupont and used as a evaluation standard. Prior to their use, sample membranes were pretreated in the conventional way ; they were boiled in a 3% H_2O_2 aqueous solution for 1h, boiled in 0.5M H_2SO_4 for 1h, and finally rinsed in deionized water (15).

Ion Exchange Capacity (IEC)

The ion exchange capacity (IEC, meq. SO_3H/g of dried polymer) of the sulfonated F-PESs and Nafion®117 is determined via titration using the following procedure ; 0.1g of membrane samples in the SO_3H form was immersed in 50ml of 2M NaCl solution for 24h, with stirring of the solution to convert the membrane from the H^+ to the Na^+ form completely. The NaCl/HCl solution was titrated against 0.01N NaOH to an end point at pH 7.0 using methyl red as a pH indicator.

Thermogravimetric Analysis (TGA)

Thermogravimetric analyses (TGA) for investigating the thermal stability of syntheized membranes were done on a SDT Q600, TA Instrument. The approximately 10-20mg samples were first immersed in deionized water for 24h, then heated from room temperature to 700°C at a rate of 10°C/min under a nitrogen atmosphere.

Conductivity Measurements

Proton conductivity of the membranes was measured by ac impedance spectroscopy using a 1286 Solartron Electrochemical Interface and a 1250 Solartron Frequency Response Analyser. Impedance spectra were recorded between 20kHz and 1Hz with an amplitude of 10mV.

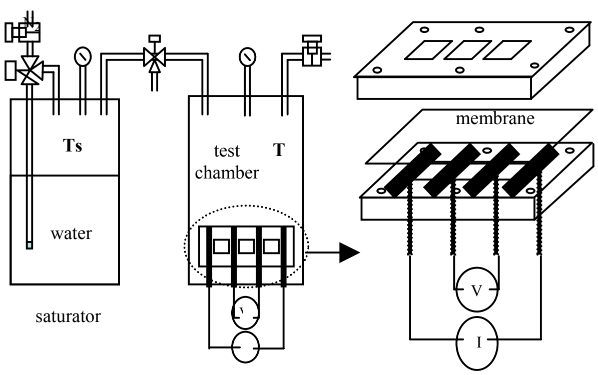

Fig.2. Schematic representation of humidity controller and conductivity cell.

A four probe conductivity cell (Figure 2) was constructed ; the membrane support incorporated square-shaped windows for exposure to water vapor with platinum wires as current-carrying electrodes and potential-sensing probes mounted on a Teflon sheet. Sample membranes are cut into 7cm×1cm strips and sandwiched between two Teflon sheets. This cell configuration allows for the membrane to be easily exposed to humid atmosphere and respond to alterations in relative humidity. The proton conductivity in the tangential direction was quantified according to the equation,

$$\sigma = \frac{1}{R}\frac{d}{A} \qquad [1]$$

where σ denotes the proton conductivity, d the distance between the potential-detecting reference electrodes, R the resistance of the membrane, and A the cross-sectional area of the membrane, respectively.

Experiments at various temperatures (80 to 140°C) and humidities (30 to 90%) were performed using the apparatus illustrated in Fig. 2. Nitrogen gas was saturated with water through the water-filled chamber (saturator). The transfer line was heated to prevent water from condensing before reaching the test chamber where the conductivity cell was installed. Relative humidity was determined by the ratio of the saturated-water vapor pressure at the saturator temperature (T_S) to that at the temperature of the test chamber (T) [$RH = 100 \times p(T_S)/p(T)$].

Atomic Force Microscopy

Samples (1.5cm in diameter) were prepared by spin-coating 5% polymer solution on a silicon wafer and dried at 60°C for 12h under vacuum. Those wafers were placed in a purpose-built environmental chamber to control humidity and temperature, which was attached to Molecular Imaging Picoscan AFM and imaged in the tapping mode with silicon cantilevers, in order to provide topographic and corresponding phase images at room temperature and relative humidities of 15 and 75%.

RESULTS AND DISCUSSION

Thermal Stability

Thermogravimetric analysis (TGA) was performed on sulfonated F-PESs and Nafion®117 to evaluate their thermal stability and the results are illustrated in Fig. 3a. The TGA curves indicate that the weight loss up to 200°C appears to be due to H_2O evaporation, whereas the weight loss at about 220°C is attributed to the desulfonation, which occurs at a markedly lower temperature than the degradation of the polyaromatic backbone (~400°C). All F-PES samples have similar TGA behavior, irrespective of the degree of fluorination and sulfonation. In addition, when bisphenol-A is substituted by diphenol, the peak temperature for desulfonation is increased by about 65°C (Fig.3b). This result indicates that use of a stiffer linkage, instead of bisphenol-A can improve the decomposition temperature without decreasing the IEC.

It should be noted that the thermal stability as quantified under the transient conditions of TGA experiments might be overrated to some degree. However, these TGA studies indicate that the sulfonated F-PESs should be thermally stable for the temperature range of PEMFC application (operation T=120-150°C).

Proton Conductivity

The typical impedance behavior (Bode plot) is shown in Fig. 4, where for Nafion®117, the magnitude of the

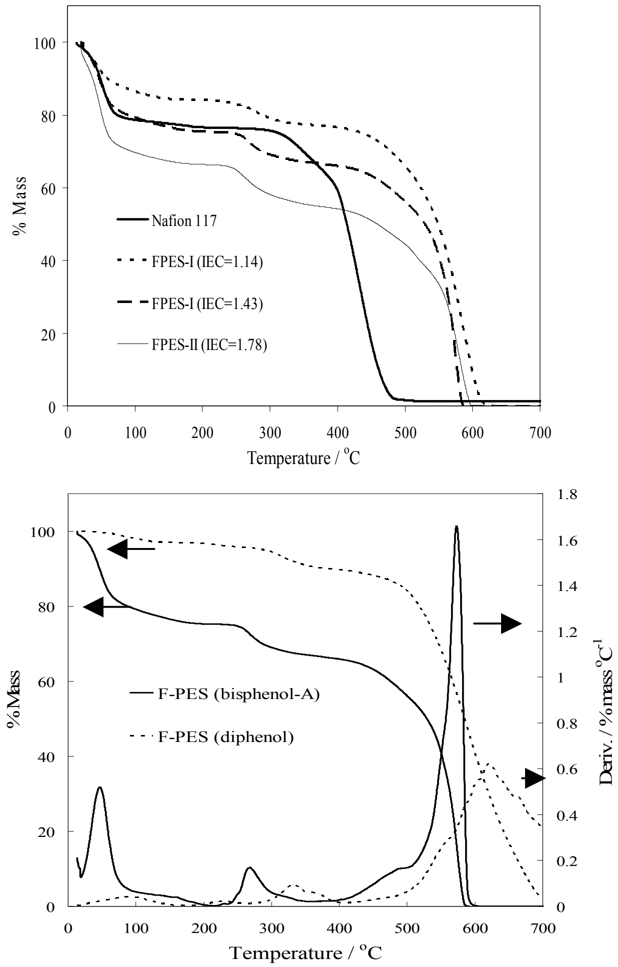

Fig.3. (a, top) Plot of weight loss vs. temperature of Nafion 117 and sulfonated F-PESs in nitrogen. (b, bottom) Plot of weight low and derivative of weight loss vs. temperature of F-PES(bisphenol A) and F-PES(diphenol) in nitrogen (F-PES(diphenol) :

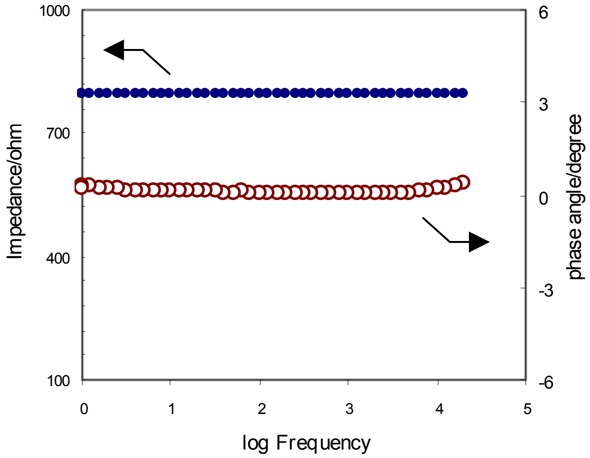

Fig.4. Typical impedance behavior (bode plot) of Nafion 117 in the four-probe conductivity measurements.

impedance is essentially invariant with frequency and the phase angle is close to zero over the full frequency range, as expected in the four-probe method.

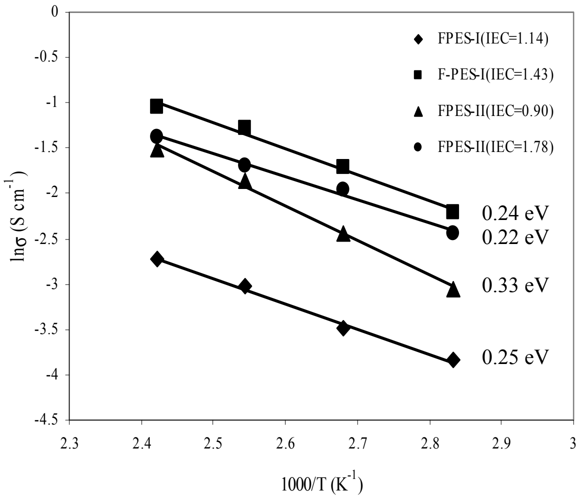

Fig.5. Proton conductivity for the sulfonated F-PESs as a function of temperature at 90% RH (FPES-I:50%fluorination degree, FPES-II:30% fluorination degree)

The conductivity as a function of the temperature for a fixed relative humidity (90%) is shown in Fig. 5 for F-PESs. Each point was obtained after equilibrating the sample at given conditions until the conductivity became stable. The protons are dissociated from the sulfonic acid groups, thus become highly mobile. Assuming that the overall mechanism for ion conduction is approximately an thermally activated process, the relationship between the ionic conductivity and temperature can be expressed by the Arrhenius law ;

$$\sigma = \sigma_o \exp(-\frac{E_a}{kT}) \qquad [2]$$

where σ_o is a pre-exponential parameter and *k* is the Boltzmann's constant (16). The results show that, under equilibrium conditions of hydration (i.e. after long equilibration at a given RH and in absence of a dc-current), F-PES membranes retain high proton conductivities up to at least 140°C and the values of the activation energies (E_a) obtained are between 0.22 and 0.33eV, depending on the degree of sulfonation and fluorination. These activation energies are substantially higher than the E_a of Nafion®117 (0.055eV) under the same conditions. The activation energy for Nafion®117 is in the same order of magnitude with the literature values (15, 17-19).

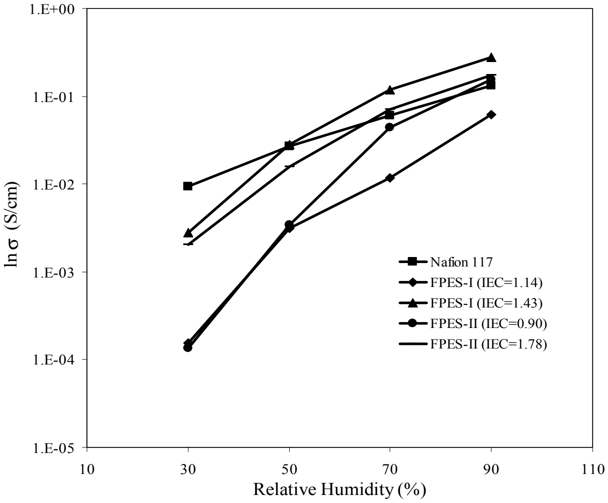

Fig.6. Conductivity at 120°C as a function of relative humidity for Nafion and sulfontated F-PESs (FPES-I:50% fluorination degree, FPES-II:30% fluorination degree)

Proton conductivity was also measured for F-PESs and Nafion®117 as a function of relative humidity at 120°C (Fig. 6). Following the general behavior of proton ducting membranes, the proton conductivity increases with RH for all membranes, due to the enhanced proton mobility resulting from the increasing water content. Also, the more highly-sulfonated F-PESs, the higher the proton conductivity, because higher sulfonation increases the number of protonated sites (SO_3H). At the highest humidity, SO_3H is driven towards full dissociation, and the difference in the protonic conduction between the examined membranes becomes progressively smaller. From the slope of the curves, it can be seen that the conductivity of Nafion® is less dependent on relative humidity than F-PESs. This may be because the acidity of Nafion® is stronger than that of F-PESs. Accordingly, Nafion® is still the best protonic conductor at low RH, but comparable with the other, less superacidic polymers for RH close to 100%.

Finally, the 50% fluorinated PES (IEC=1.43meq/g) shows slightly higher conductivity than the lower fluorinated one (30%, IEC=1.78meq/g), even though the former has lower IEC than does the latter. At first glance, this is contrary to what one might expect, but the strong increase in hydrophobicity across the polymer backbone seems to affect the conductivity more than the small change in the degree of sulfonation. This, along with the fact that the proton conductivity of F-PES is more dependent on temperature and relative humidity than that of Nafion®117, as noted earlier, can be the case when differences in microstructure occur.

In order to investigate the relevant microstructure, in-situ AFM images were obtained for membranes with different degree of sulfonation and fluorination. Fig. 7 shows the phase-contrast images for Nafion®117 and the 50% fluorinated PES at room temperature and two different humidities, 15 and 75%. There are clear differences between the various systems in their phase separation microstructure, and the samples with percolating hydrophilic phases correspond to those with the higher conductivities (Nafion®117, F-PES$_{IEC=1.43}$). It is qualitatively seen that, due to the phase separation at 15% RH, the most highly sulfonated membrane shows relative high conductivity even at low humidity.

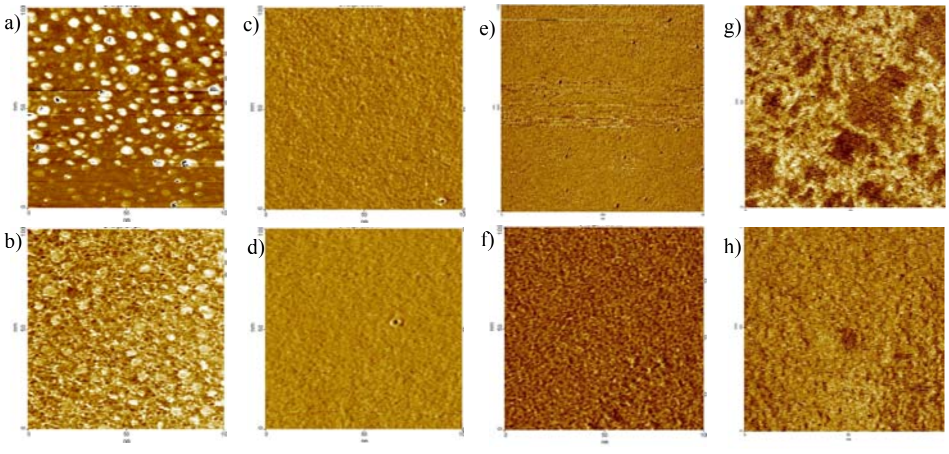

Fig.7. Phase separation images of Nafion117 and F-PESs at room temperature. a) Nafion117-10%RH, b) Nafion 117-75%RH, c) F-PES(50%DF, IEC=0.8meq/g)-15%RH, d) F-PES(50%DF, IEC=0.8meq/g)-75%RH, e) F-PES(50%DF, IEC=1.14meq/g)-15%RH, f) F-PES(50%DF, IEC=1.14meq/g)-75%RH, g) F-PES(50%DF, IEC=1.43meq/g)-15%RH, f) F-PES(50%DF, IEC=1.43meq/g)-75%RH.

CONCLUSIONS

Polyethersulfone was partially fluorinated in order to improve its thermal stability. Selected physical and electrochemical parameters have been measured for the synthesized membranes, which were sulfonated to various degrees.

It has been found that, irrespective of the degree of fluorination and sulfonation, all the synthesized polymer membranes are thermally stable up to 200°C, and the proton conductivity significantly varies with the degree of both fluorination and sulfonation. It can be concluded that the differences in conductivity of the examined membranes are buffered not only by high RH values, but also by increasing temperature. It is noteworthy that the highly sulfonated membranes with relatively high degree of sulfonation exhibited conductivities comparable to Nafion®117 under the same conditions of temperature and relative humidity, while maintaining the desired thermal stability. In addition, the degree of fluorination affected the proton conductivity more than the degree of sulfonation, and highly sulfonated F-PES (50% fluorination) has relatively high proton conductivity at low humidity, which appears to be due to its phase separation microstructure, as characterized by atomic force microscopy.

The partially fluorinated PESs (F-PESs) presented in this study show reasonable promise as candidate proton exchange membranes for high temperature PEM fuel cells, because it is possible to optimize the proton conductivity and thermal stability by controlling the degrees of sulfonation and fluorination.

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