Proton Conductive Polyether Membranes Containing Sulfofluorenyl Groups

Yohei Chikashige, Kenji Miyatake and Masahiro Watanabe

(Interdisciplinary Graduate School of Medicine and Engineering, Clean Energy Research Center, University of Yamanashi)
4 Takeda, Kofu, 400-8510, Japan

INTRODUCTION

Proton conductive polymer membranes have been attracting more and more attention as an electrolyte material for polymer electrolyte fuel cells (PEFCs) and direct methanol fuel cells (DMFCs). Alternative membranes rather than perfluorinated ionomers have been in great demand. One of the available approaches is to functionalize hydrocarbon polymers with acid groups.

We have recently found that the introduction of bulky hydrophobic component fluorenylbiphenyl groups into sulfonated polyimides improves water holding capability at high temperature, resulting in the very high proton conductivity of 1.67 Scm^{-1} at 120 °C. [1)] In this study, we describe the synthesis and properties of novel poly (arylene ether) bearing sulfofluorenyl moieties. [2)]

EXPERIMENTAL

The parent polyethers were synthesized by common procedure[3)]. They were reacted with chlorosulfonic acid in dichloromethane to give the title polymers 1 and 2. The sulfonated polyethers were dissolved in N,N-dimethyl-acetamide and the solution was cast onto a glass plate at 60 °C for 15 h. The obtained membranes were acidified by soaking in 1.0N nitric acid.

The sulfonated polyethers 1 and 2 were characterized by ^{1}H-NMR and IR spectroscopy. TG/DTA analyses were carried out to investigate thermal properties. The hydrolytic stability was evaluated by treating the membrane sample at 140 °C and 100% RH for 24 h. The oxidative stability was evaluated by soaking the membrane sample into Fenton's reagent at 80 °C. Tensile tests were carried out to investigate mechanical strength. Proton conductivity of polyethers were measured using a four-point-probe electrochemical impedance spectroscopy technique.

RESULTS AND DISCUSSION

Two kinds of sulfonated polymers 1 and 2 were synthesized (Fig.1). The degree of sulfonation (x) could be controlled by simply changing the amount of chloro-sulfonic acid used in the reaction. ^{1}H-NMR spectra indicated that the sulfonic acid groups were substituted only on fluorenyl groups.

The stability of the polyethers was investigated under both dry and wet conditions. The result of TG/DTA analysis showed two step weight losses: the first one from 50 to 180 °C due to the desorption of water molecules and the second one above 250 °C due to the degradation (loss of sulfonic acid groups). The high thermal stability is comparable to that of other sulfonated hydrocarbon polymers or perfluorinated ionomers. The membrane did not display any changes in appearance (color, flexibility, and toughness) after the hydrolytic stability test. Since there were not any changes observed in ^{1}H-NMR and IR spectra, it is assumed that the sulfonic acid groups are intact during the treatment. The membrane retained its flexibility over 40 minutes in the Fenton reagent at 80 °C.

Under heated and humidified conditions, polymer 1 exhibited better mechanical properties (lower elongation and higher maximum stress at break) than those of Nafion112 (Fig.2), despite the higher IEC (1.14meq/g) of the polymer 1 than that of Nafion112 (0.91meq/g). It is noticeable that the polymer 1 showed even better mechanical properties at 120 °C than at 85 °C.

Proton conductivity of the polymer 1 (IEC = 1.14meq/g) membrane was measured at 100% RH and compared with that of Nafion112 in Fig.3. At temperatures below 100 °C, both membranes showed almost the same conductivity of 0.1-0.2 Scm^{-1}. While Nafion112 lost its conductivity at 140 °C down to 60% of the value at 100 °C, the conductivity kept increasing even above 100 °C for polymer 1.

Other electrolyte properties (water uptake, humidity dependence of the proton conductivity, gas permeation, etc) will also be reported.

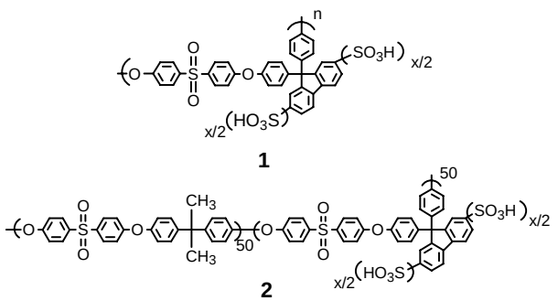

Fig.1 Chemical structure of sulfonated polyethers.

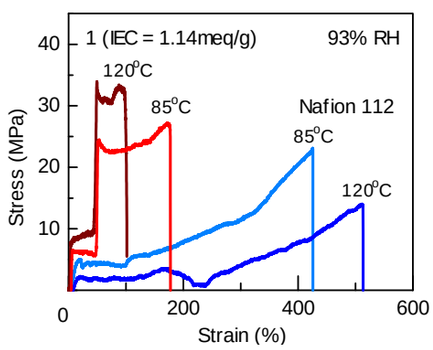

Fig.2 Stress-strain curves of sulfonated polyether and Nafion112.

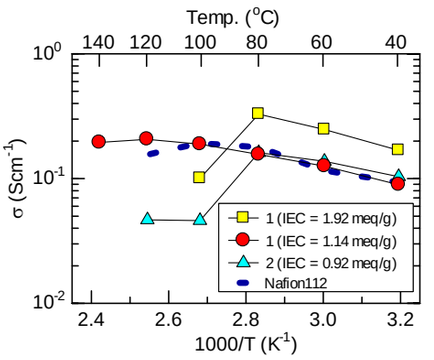

Fig.3 Temperature dependence of the proton conductivity at 100% RH.

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3. P. M. Hergenrother et al., *Polymer*, 29, 358-369 (1988)