

Preparation and characterization of chemically stable polymer electrolyte membranes by radiation-induced graft copolymerization of four monomers into ETFE films

Jinhua Chen^{*}, Masaharu Asano, Tetsuya Yamaki, Masaru Yoshida

Department of Material Development, Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

Received 31 March 2005; received in revised form 14 June 2005; accepted 16 June 2005
Available online 28 July 2005

Abstract

To develop a highly chemically stable polymer electrolyte membrane for application in a direct methanol fuel cell (DMFC), four styrene derivative monomers, *m,p*-methylstyrene (MeSt), *p-tert*-butylstyrene (*t*BuSt), divinylbenzene (DVB) and bis(*p,p*-vinyl phenyl) ethane (BVPE) were graft copolymerized into poly(ethylene-co-tetrafluoroethylene) (ETFE) films followed by sulfonation and hydrolysis. The latter two monomers were used as crosslinkers. The graft copolymerization was carried out by the γ -ray preirradiation method. The influence of the preirradiation dose and the grafting kinetics were investigated in detail. Sulfonation of the grafted ETFE films was performed in a chlorosulfonic acid solution, by which the sulfonation ratio reached about 90%. By means of the FT-IR and TG-DTA measurements, it was evident that the monomers were grafted into the ETFE films and that the sulfonic acid groups were attached to the aromatic rings of the graft chain. Assessing their potential to serve as polymer electrolyte membrane in a DMFC was performed by measurement of the ion exchange capacity, proton conductivity, water uptake, chemical stability and the methanol permeability. The newly obtained membrane possesses significantly higher chemical stability than the traditional styrene/DVB-grafted membrane and six times lower methanol permeability compared to the Nafion[®] 112 membrane. Therefore, this study reveals the possibility of the developed inexpensive four monomers-grafted membranes, which could provide an attractive alternative as a substitute for the expensive Nafion[®] membranes for DMFC applications.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Polymer electrolyte membrane; Radiation grafting; Proton conduction; Methanol permeability; Chemical stability; Direct methanol fuel cell

1. Introduction

The direct methanol fuel cell (DMFC) has strongly emerged as a viable alternative source of power due to its high power density relative to other power sources [1]. In the DMFC, the polymer membranes used as electrolyte for proton transport are the perfluorosulfonic membranes, such as Nafion[®] membranes. However, without large cost reductions, these inherently expensive membranes are difficult to use in large-scale commercial applications [2]. Therefore, it is necessary to develop an alternative membrane which is less

expensive and has high performance. To date, the new membranes being developing as alternatives to the Nafion[®] membranes include hydrocarbon polymers [3], organic/inorganic hybrid membranes [4,5], acid–base polymer complexes [5] and radiation-grafted membranes [6,7].

The radiation-grafted membranes have been reviewed by Nasef and Jegzey [7]. The advantages of radiation-grafted membranes include the lack of need for chemical initiators or catalysts, the easy preparation from the already prefabricated base film, and the easy control of the degree of grafting and ion exchange capacity of the membranes. The grafting can be initiated by high-energy irradiation such as γ -ray, electron-beam and swift heavy ions. The base film in the polymer electrolyte membrane functions as hydrophobic host that

^{*} Corresponding author. Tel.: +81 27 346 9413; fax: +81 27 346 9687.
E-mail address: chen@taka.jaeri.go.jp (J. Chen).

constrains the membrane swelling in water and provides the mechanical strength and dimensional stability. In addition, the price of commercial radiation-grafted membranes is said to be in the range of 50–100 US\$ m⁻² [8], which is far lower than that of the Nafion[®] membranes (about 800 US\$ m⁻²). Typically binary monomers of styrene/divinylbenzene (DVB) have been used to graft because the monomer units can be easily sulfonated to introduce sulfonic acid groups into the membranes. The bifunctional monomer of DVB is used as crosslinker to improve the chemical stability of the radiation-grafted membranes. Other crosslinkers such as bis(vinyl phenyl) ether (BVPE) [9,10], triallyl cyanurate (TAC) [11] and *N,N*-methylene-bis-acrylamide [12] with different addition amounts were also attempted.

The current–voltage behaviors of fuel cells containing such radiation-grafted membranes compare favorably with those of cells containing Nafion[®] membranes under the same operating conditions, and the longest durability of the styrene/DVB-grafted membranes was reported to be over 10,000 h in a working fuel cell fed with hydrogen and oxygen [13,14]. Even then, the lifetimes of these membranes are not long enough for the commercial applications [15]. The lower durability is due to the lower chemical stability of the sulfonated graft chains in the oxidant environment of the fuel cells [16]. The method of radiation grafting also allows for further changes by choosing other monomers or crosslinkers in order to find membranes with improved properties [17–21]. Chemically more stable but also more expensive membranes have been prepared at RAI Co. and Chlorine Engineers Co. by either simultaneous or preirradiation grafting of α,β,β -trifluorostyrene onto base polymer films [19,20]. Chloromethyl styrene and α -methylstyrene have been also studied as alternative monomers in order to increase the chemical stability [21]. Therefore, the strategies in our development of the radiation-grafted membranes are to find alternatives to replace the styrene monomer. The main challenge in this field is how to improve the membrane durability without the large sacrifice of the other properties such as proton conductivity and mechanical strength.

In our previous study [18], we found that the *m,p*-methylstyrene (MeSt)-grafted membrane showed a high proton conductivity and that the *p-tert*-butylstyrene (*t*BuSt)-grafted membrane showed a very high chemical stability. We also found that the addition of a DVB crosslinker greatly improved the chemical stability of the membrane. For instance, the durability time of the MeSt/DVB-grafted polymer electrolyte membrane in 3% H₂O₂ solution at 60 °C was 78 h, while that of the only MeSt-grafted one was 36 h. However, the addition amount of over 5% DVB resulted in brittleness and low mechanical strength of the membranes. In this study, The BVPE having flexible structure and two isolated vinyl groups used as an additional crosslinker together with the above-mentioned MeSt, *t*BuSt and DVB were grafted into the poly(ethylene-co-tetrafluoroethylene) (ETFE) films. We fixed the weight ratios of the four monomers, MeSt, *t*BuSt, DVB and BVPE, at 40.0/40.0/2.5/17.5. In other

words, the total weight amount of the DVB and BVPE crosslinkers in the monomer mixture was 20 wt.%.

The ETFE was used as the base film for the grafting. ETFE polymer occupies a special position among fluoropolymers as it contains alternating structural units of polyethylene (PE) and poly(tetrafluoroethylene) (PTFE) that confers it a unique combination of properties imparted from both fluoro resin and hydrocarbon resin. For instance, ETFE is less dense, tougher, stiffer and higher mechanical strength than the fully fluorinated polymer i.e. PTFE, poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(tetrafluoroethylene-co-perfluorovinyl ether) (PFA). It also offers an excellent thermal stability and superior resistance to common solvent. In addition, its higher resistance to radiation makes possible to be preirradiated under the γ -rays for the subsequent grafting [22,23], and its higher resistance to fatigue makes possible to be tolerated in a DMFC stack for a long time.

The grafting was performed using the preirradiation method. That is, the ETFE films were activated in a preirradiation step and then grafted with monomers in a subsequent step. Sulfonation of the grafted films was carried out in a chlorosulfonic acid solution to introduce the sulfonic acid groups into the membranes. Characterization of the new polymer electrolyte membranes was carried out by means of the Fourier transform infrared (FT-IR) and thermogravimetric analysis (TG–DTA), together with the measurement of the ion exchange capacity, water uptake, proton conductivity, chemical stability, and methanol permeability.

2. Experimental

2.1. Preparation of the polymer electrolyte membranes

The monomers of *m,p*-methylstyrene (MeSt, 99%, inhibited with 50 ppm 4-*tert*-butylcatechol) and *p-tert*-butylstyrene (*t*BuSt, 93%, inhibited with 100 ppm *p-tert*-butylcatechol) were purchased from Aldrich. Divinylbenzene (DVB, 55% mixture of isomers, 45% of ethylvinylbenzene) and bis(*p,p*-vinyl phenyl)ethane (BVPE) were purchased from Wako Pure Chemical Ind., Ltd., Japan. The DVB and BVPE were used as crosslinkers. The monomers (containing crosslinkers) were used without further treatment. The ETFE film, with a thickness of 50 μ m was kindly provided by Asahi Glass Co., Japan and was washed with acetone to remove any impurity on its surface before use. The crystallinity of the ETFE films, determined by DSC was about 35%. The chemical structures of the ETFE film and monomers are shown in Scheme 1.

The process for the preparation of the new polymer electrolyte membranes is shown in Fig. 1. As the first step, the glass tube with added ETFE films in the size of 2 cm \times 3 cm was degassed for 12 h, and argon gas was then filled in the tube for the γ -ray preirradiation at room temperature. Two total preirradiation doses of 15 and 30 kGy (1 Gy = 1 J g⁻¹ energy absorbed) were performed for the samples. The dose rate

Download English Version:

<https://daneshyari.com/en/article/639721>

Download Persian Version:

<https://daneshyari.com/article/639721>

[Daneshyari.com](https://daneshyari.com)