Journal of Membrane Science 333 (2009) 59–67

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Radiation-induced grafting of styrene onto ultra-high molecular weight polyethylene powder for polymer electrolyte fuel cell application

II. Sulfonation and characterization[☆]

Tauqir A. Sherazi[a,c], Shujaat Ahmad[b], M. Akram Kashmiri[a], Dae Sik Kim[c], Michael D. Guiver[c,*]

[a] *Department of Chemistry, GC University, Lahore 54000, Pakistan*
[b] *Pakistan Institute of Engineering and Applied Sciences, P.O. Nilore, Islamabad 45650, Pakistan*
[c] *Institute for Chemical Process and Environmental Technology, National Research Council of Canada, 1200 Montreal Road, Ottawa, ON, Canada K1A 0R6*

ARTICLE INFO

Article history:
Received 20 August 2008
Received in revised form 16 December 2008
Accepted 31 January 2009
Available online 10 February 2009

Keywords:
Proton exchange membrane
UHMWPE
Radiation grafting
Styrene
Methanol permeability
Proton conductivity
Fuel cells

ABSTRACT

Post-sulfonation of selective styrene-grafted ultra-high molecular weight polyethylene (UHMWPE-g-PS) films was carried out by chlorosulfonic acid and the properties of the membranes were investigated. The UHMWPE-g-PS films were previously prepared by initial γ-irradiation of polyethylene powder, grafting with styrene, followed by hot-pressing to process into films. The range of ion exchange capacities (*IECs*) obtained with different degrees of grafting (*DG*) of styrene was in the range of 0.97–2.77 mequiv./g. The water and methanol uptake of sulfonated films were studied on a weight and volume basis. FTIR spectroscopy and thermal gravimetric analysis (TGA) of control UHMWPE, UHMWPE-g-PS, and UHMWPE-g-PSSA were compared. The methanol permeability values at 30 °C for the series of UHMWPE-g-PSSA membranes were in the range 4.86×10^{-8} to 1.67×10^{-6} cm^2/s, with corresponding proton conductivities of 0.025–0.29 S/cm at 90 °C. The methanol permeability values of UHMWPE-g-PSSA were generally lower than that of Nafion 117 for comparable or even higher proton conductivity. Transmission electron microscopy (TEM) analysis was used to observe microstructure for evidence of nanophase separation of hydrophilic and hydrophobic domains. Owing to its low cost and the results of the current study, UHMWPE-g-PSSA is suggested as a viable proton exchange membrane for low temperature hydrogen and direct methanol fuel cell applications.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC)s are promising clean power sources for automotive and portable applications [1,2]. Proton conductive polyelectrolyte membranes (PEMs) are one of the key components in PEMFCs, which function to separate the reactant gases and conduct protons from the anode to the cathode [3]. Commercial PEMs are based mainly on perfluorinated sulfonic acid (PFSA) membrane materials, such as Nafion® (Du Pont, USA), Flemion® (Asahi Glass, Japan) and Aciplex® (Asahi Kasei, Japan). However, one of the key issues of PFSA-based PEMs is that dehydration occurs when used at temperatures above 80 °C, leading to lower proton conductivity [4]. In addition, the performance of PFSA-based direct-methanol fuel cells (DMFCs) is affected negatively due to the high permeability of methanol through the membrane, also known as methanol crossover [5]. Moreover, complex fluorine chemistry and raw material price of PFSA membranes contributes to their continuing high cost. The current price for Nafion membranes is of the order of US $100 per kilowatt of generated electric power [6]. These factors, in addition to environmental recycling uncertainties of perfluorinated membranes, have combined to limit their widespread commercial application in PEMFC and DMFC [7,8]. Currently, there is much ongoing research for developing non-perfluorinated polymers with better performance and lower cost as alternative PEM materials [7,9–11].

Besides the development of new polymer, the synthesis of PEM materials through grafting of functional monomer onto commodity polymer, followed by sulfonation is an attractive option [12]. Ionizing radiation such as γ-rays and electron beams are preferably used for radiation grafting reactions due to the facts that (1) there is relatively uniform formation of radicals with a thickness of the order of mm, (2) the process is free from contamination because it does not need initiator for radical formation, so that the purity of the processed products may be maintained [13].

Almost all commercially available fluorinated polymers, such as polytetrafluoroethylene (PTFE) [14,15], Teflon-FEP [16,17],

---

[☆] NRCC Publication No. 50941.

[*] Corresponding author. Tel.: +1 613 993 9753; fax: +1 613 991 2384.
E-mail address: michael.guiver@nrc-cnrc.gc.ca (M.D. Guiver).

0376-7388/$ – see front matter Crown Copyright © 2009 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2009.01.052

fluorinated ethylene propylene copolymer (FEP) [18,19], tetrafluoroethylene perfluoro(propyl vinyl ether) copolymer (PFA) [20,21], poly(vinylidene fluoride) (PVDF) [22,23], ethylene–tetrafluoroethylene copolymer (ETFE) [24,25], polychlorotrifluoroethylene (PCTFE) [26], etc., have been reported as being used for radiation-induced grafting with styrene using either simultaneous irradiation or pre-irradiation methods. Irradiation of polymer with ionization radiation produces several other chemical effects such as degradation, crosslinking, and co-polymerization, along with the desired grafting reaction in the presence of monomer [27]. Therefore, in the context of radiation grafting, the main disadvantage associated with fluorinated polymers in general is that they undergo main chain scission due to the relatively stronger C–F bond as compared with the C–C bond; thus a relatively low irradiation dose can effectively reduce the molecular weight of the PTFE [28–29]. Consequently, fluorinated polymers may not be the optimal substrates for radiation-induced grafting at low temperature. However, they could be crosslinked by irradiation above the melting temperature under an oxygen-free atmosphere [30]. In the present work, non-fluorinated polymer with grafting capability is being investigated as an alternative option for PEM development through the radiation grafting technique.

Ultra-high molecular weight polyethylene (UHMWPE) has long linear chains and high crystallinity, which provide chemical inertness and good mechanical strength [31]. Owing to its excellent bulk physical and chemical properties and low cost in comparison with perfluorinated polymer, UHMWPE appears to be a promising base material for the development of alternative hydrocarbon-based PEMs, after modification.

The grafting conditions and grafting reaction kinetics of styrene onto UHMWPE powder and the subsequent film formation process have already been discussed in our previous article [32]. The present work reports on the chlorosulfonic acid post-sulfonation reaction of various films of pre-irradiation styrene-grafted UHMWPE having different levels of grafting. The term post-sulfonation is used here to distinguish pre-fabricated films that were sulfonated, rather than films fabricated from sulfonated styrene-grafted polymer. Chlorosulfonic acid introduces sulfonic acid groups onto the styrene residue of grafted films, ultimately providing inexpensive PEM materials. This work is possibly one of the first detailed studies of PEM materials based on the post-sulfonation of films prepared by radiation-induced grafting of styrene onto UHMWPE. The study includes measurements of ion exchange capacity (*IEC*), degree of substitution (*DS*), water and methanol uptake. Membranes were also characterized by attenuated total reflection Fourier transform infrared spectroscopy (FTIR-ATR), thermal gravimetric analysis (TGA) and transmission electron microscopy (TEM). Measurements of proton conductivities and methanol permeabilities are also included.

2. Characterization and measurements

2.1. Materials

Styrene-grafted UHMWPE (UHMWPE-g-PS) films with a thickness of 80 ± 5 μm having different degree of grafting (*DG*) were prepared in our previous study. Styrene was first grafted onto UHMWPE and subsequently hot-pressed into film; the details of the grafting reaction and film formation were described [32]. The polymer sample size was 2 g for each of the grafting reactions. Chlorosulfonic acid ($ClSO_3H$) and 1,2-dichloroethane were obtained from Sigma–Aldrich Chemical Corp. Analytical grade dichloromethane was obtained from EMD Ltd. All chemicals were used as received.

2.2. Measurements

Following the styrene grafting reactions, the polymers were washed and dried under vacuum until constant weight was reached. The degree of grafting was obtained by using the following equation:

$$\text{degree of grafting}\,(\%) = \frac{W_g - W_0}{W_0} \times 100 \qquad (1)$$

where W_0 and W_g are the weights of polymer before and after the grafting reaction, respectively.

Sulfonation of the UHMWPE-g-PS films was carried out by immersing the films in a 0.2 M chlorosulfonic acid solution in dichloroethane for an initial period of 5 h at 50 °C, followed by overnight immersion at room temperature. After sulfonation, the membranes were removed from the sulfonating solution and immersed in fresh dichloromethane for 3 h, followed by washing with dichloromethane to remove any residual acid. After washing with dichloromethane, the films were thoroughly washed with deionized water.

2.3. Ion exchange capacity and degree of substitution

IEC of the sulfonated polymers was measured using a typical titration method. The dried membrane in the protonic form was immersed into 25.00 mL of 3 M NaCl solution for 24 h. A large excess of Na^+ ions in the solution ensured nearly complete ion exchange. Then, 10.00 mL of the 3 M NaCl solution containing the released H^+ ions was titrated against 0.05 M NaOH solution using phenolphthalein as indicator. The *IEC* was calculated using the following equation:

$$IEC_{\text{exp}} = \frac{0.05 \times V_{\text{NaOH}} \times n}{W_{\text{dry}}}\ (\text{mequiv./g}) \qquad (2)$$

where V_{NaOH} (mL) is the volume of the 0.05 M NaOH solution used for titration. n is the factor corresponding to the ratio of the amount of NaCl solution taken to immerse the polymer (25.00 mL) to the amount used for titration (10.00 mL), which is 2.5. W_{dry} (g) is the dry weight of the polymer electrolyte membrane in the protonic form.

Theoretical *IEC* (IEC_{theory}) can be calculated, making the assumption that 100% sulfonation of the grafted styrene occurs, i.e., one sulfonic acid group per styrene unit, by applying the following equation [33]:

$$IEC_{\text{theory}} = \frac{1000 \times DG/M_{\text{styrene}}}{100 + DG + (DG/M_{\text{styrene}}) \times M_{\text{sulfonate}}}\ (\text{mequiv./g}) \qquad (3)$$

where M_{styrene} is the molar weight of styrene unit and $M_{\text{sulfonate}}$ is the additional molar weight due to sulfonate.

The *DS* of sulfonic acid group indicates the percentage sulfonation level of the grafted styrene and can be calculated by simple relationship between experimental and theoretical *IEC* values as represented in the following equation:

$$DS = \frac{IEC_{\text{exp}}}{IEC_{\text{theory}}} \times 100 \qquad (4)$$

2.4. Water and methanol uptake

The water uptake and methanol uptake of the previously vacuum dried membranes in the sulfonic acid form were measured for 30 h in deionized water and methanol, respectively. The reported measurements are based on the average of two readings of each sample of dimension about 30 mm × 30 mm. Water uptake was measured at 30 and 80 °C while methanol uptake was measured at 30 °C. The temperature was controlled by means of a thermostatic