

A facile method for the preparation of poly(vinylidene fluoride) membranes filled with cross-linked sulfonated polystyrene



Naeun Kang ^a, Junhwa Shin ^b, Taek Sung Hwang ^c, Youn-Sik Lee ^{a,*}

^a Division of Chemical Engineering, Chonbuk National University, 567 Baekje-Daero, Deokjin-gu, Jeonju, Jeonbuk 561-756, South Korea

^b Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, Jeongeup-si, Jeollabuk-do, South Korea

^c Department of Chemical Engineering, College of Engineering, Chungnam National University, Daejeon 305-764, South Korea

ARTICLE INFO

Article history:

Received 7 October 2015

Received in revised form 1 December 2015

Accepted 10 December 2015

Available online 12 December 2015

Keywords:

Organic-soluble ion-pair monomer

Pore-filling polymerization

Pore-filled poly(vinylidene fluoride)

membrane

Sulfonated polystyrene

ABSTRACT

Pores of poly(vinylidene fluoride) (PVDF) membranes were filled with tetrabutylammonium 4-vinylbenzene sulfonate (TVS), a cross-linking agent, and a radical initiator in dimethyl sulfoxide, followed by radical polymerization and subsequent replacement of tetrabutylammonium ions by protons. This pore-filling method using an organic-soluble sulfonate monomer was very efficient and convenient, as it avoids the highly acidic sulfonation step. The dimensional changes in the length of the PVDF membranes filled with cross-linked sulfonated polystyrene were similar to Nafion 212, but their water uptakes were higher and they exhibited greatly improved mechanical moduli and elongations. Proton conductivities of the modified membranes were also higher than Nafion 212 under identical conditions.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Perfluorosulfonic acid membranes, such as Nafion, have been widely used in polymer electrolyte membrane fuel cells (PEMFCs) because of their good mechanical properties, high thermal and chemical stability, high proton conductivity, and long-term durability [1–3]. However, those polymer membranes have some limitations such as high cost and low conductivity at high temperatures due to decreased humidity [4,5]. In order to overcome these limitations, alternative membranes such as poly(ether sulfone), poly(ether ketone), poly(phenylene), poly-imide, poly(ether ether ketone) and polybenzimidazole have been developed [6–11]. Aromatic hydrocarbon polymers have appreciable thermal and chemical stability, and exhibit high proton conductivity when highly sulfonated. However, in general, such highly sulfonated polymer membranes exhibit severely decreased dimensional stability and mechanical strength due to excessive water uptake [12,13]. In order to overcome issues associated with excessive water uptake, cross-linked membranes, inorganic/polymer nanocomposite membranes, grafted membranes, and pore-filled membranes have been actively investigated [12–18].

Poly(vinylidene fluoride) (PVDF) membranes have been extensively used for scientific research and industrial processes because of their good mechanical properties and high thermal and chemical stability [19–21]. Yamaguchi et al. successfully imparted a proton-conducting

property as well as hydrophilicity to porous PVDF membranes via pore-filling polymerization [18,22]. PVDF membranes filled with sulfonated polystyrene have also been prepared by filling the pores with styrene, irradiating with an electron beam, and sulfonating with chlorosulfonic acid [23]. Dobrovolsky and coworkers reported that PVDF membranes could be filled with a solution of styrene and divinylbenzene in toluene, followed by radical polymerization and subsequent sulfonation with sulfuric acid to prepare PVDF membranes filled with sulfonated polystyrene [24]. In these studies, sulfonic acid groups were incorporated into the PVDF membranes filled with polystyrene using sulfuric acid or chlorosulfonic acid. One problem associated with these pore-filling methods is degradation of the polymer chains [25].

The highly acidic sulfonation step would be avoided if styrene was replaced by sodium 4-vinylbenzene sulfonate. In other words, polymerization of PVDF membranes filled with sodium 4-vinylbenzene sulfonate would obviate the need of a sulfonation step. The ionic monomer, however, is not compatible with the hydrophobic PVDF membrane and does not efficiently fill the membrane pores. One possible way to overcome this pore-filling problem is to replace the sodium counterion with tetrabutylammonium ion, because the resulting ion-pair monomer, tetrabutylammonium 4-vinylbenzene sulfonate (TVS), will be organic-soluble.

In this study, sodium 4-vinylbenzene sulfonate was treated with tetrabutylammonium hydroxide to synthesize organic-soluble TVS. PVDF membranes were filled with TVS, *N,N'*-methylenebisacrylamide (cross-linking agent), and 2,2'-azobisisobutyronitrile (AIBN, initiator)

* Corresponding author.

E-mail address: yosklear@jbnu.ac.kr (Y.-S. Lee).

in dimethyl sulfoxide (DMSO), followed by radical polymerization and subsequent washing with dilute HCl solution to replace the tetrabutylammonium ions with protons and to remove any unreacted cross-linking agent together with the monomer (Scheme 1). To the best of our knowledge, this is the first study of its kind where PVDF membranes filled with cross-linked sulfonated polystyrene (CSPS) were directly prepared using an organic-soluble sulfonate monomer without the highly acidic sulfonation step. In this study, the preparation of PVDF membranes filled with CSPS is described, together with their properties such as ion-exchange capacity (IEC), dimensional stability, thermal stability, mechanical properties, oxidative stability, and proton conductivity.

2. Experimental

2.1. Materials

PVDF membranes (thickness: 90 μm , porosity: 80%) were provided by Amgreentech, South Korea. Sodium 4-vinylbenzene sulfonate, DMSO, and *N,N'*-methylenebisacrylamide were purchased from Sigma-Aldrich Chemical Co. Tetrabutylammonium bromide was purchased from Sejinco Co. Hydrochloric acid (35–37%), 1.0 N hydrochloric acid solution, magnesium sulfate, sodium chloride, sodium hydroxide, methylene chloride, and acetone were purchased from Samchun Pure Chemical Co., Ltd. AIBN, aqueous phenolphthalein (1%), and hydrogen peroxide (35%) solutions were purchased from Dae-Jung Chemicals & Metals Co., Ltd. All the aforementioned chemical reagents and solvents were used as received.

2.2. Synthesis of TVS

Sodium 4-vinylbenzene sulfonate (1.0 g, 4.85 mmol) and tetrabutylammonium bromide (1.55 g, 4.85 mmol) were dissolved in water (6 mL) and acetone (5 mL), respectively, and the two solutions were mixed in a two-neck flask. The solution was left undisturbed at room temperature for 6 h under an argon atmosphere. Then, excess acetone was added to the reaction mixture to precipitate sodium bromide, and unreacted acetone was evaporated using a rotary evaporator. The residue was extracted with methylene chloride, and the mixture of organic solutions was dried over magnesium sulfate and concentrated using a rotary evaporator to yield a yellow gel-like product (2.0 g, 95%). ^1H nuclear magnetic resonance (NMR) (400 MHz, CDCl_3 , ppm): 7.8–7.83 (d, 2H), 7.24–7.33 (d, 2H), 6.62–6.69 (dd, 1H), 5.68–5.73 (d, 1H), 5.19–5.27 (d, 1H), 3.19–3.24 (t, 8H), 1.53–1.61 (m, 8H), 1.32–1.41 (m, 8H), 0.92–0.95 (t, 12H). Elemental analysis: calculated for $\text{C}_{24}\text{H}_{43}\text{NO}_3\text{S}$: C 67.72%; H 10.18%; N 3.29% and S 7.53%. Found: C 67.10%; H 10.87%; N 3.46% and S 6.99%.

2.3. Preparation of PVDF–CSPS

PVDF membranes were immersed in a solution of TVS, *N,N'*-methylenebisacrylamide (cross-linking agent), and AIBN (radical initiator, 0.5 wt.% with respect to the total amount of TVS and cross-linking agent) in DMSO for 3 h. The following three weight ratios of TVS to *N,N'*-methylenebisacrylamide were used: 90:10, 85:15, and 80:20. The membranes were sealed between two glass plates, polymerized at 70 $^\circ\text{C}$ for 12 h in an oven, and then washed with methylene chloride to remove any unreacted compounds. The resulting membranes were immersed in a 1.0 N HCl solution and kept for 24 h to replace tetrabutylammonium ions with protons, washed with water, and dried in a vacuum oven. The resulting membranes filled with CSPS were designated PVDF–CSPS-10, PVDF–CSPS-15, and PVDF–CSPS-20, respectively, where the numbers indicate the loading of cross-linking agent with respect to the TVS used.

2.4. Instruments

Fourier-transform infrared (FTIR) spectra were recorded on a JASCO 4100E FTIR spectrometer under ambient conditions over the wave number range of 4000–600 cm^{-1} . ^1H NMR spectra were recorded on a JEOL FT-NMR (400 MHz) spectrometer in CDCl_3 . Sample membranes were dried in a vacuum oven at 80 $^\circ\text{C}$ for 24 h before measurement, and the contact angles were measured directly after dropping water on the membrane surface (Surface Electro Optics Phoenix 150). Thermal stability of the sample membranes was measured on a SDT Q600 Thermogravimetric Analyzer at a heating rate of 10 $^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Mechanical properties of the membranes (60 \times 5 mm) were measured on a universal testing machine (UTM, LR5K Plus, Lloyd Instruments). All values were calculated thrice and their averages were measured. Membrane surface images were recorded on a field emission scanning electron microscope (FESEM, Hitachi SU-70).

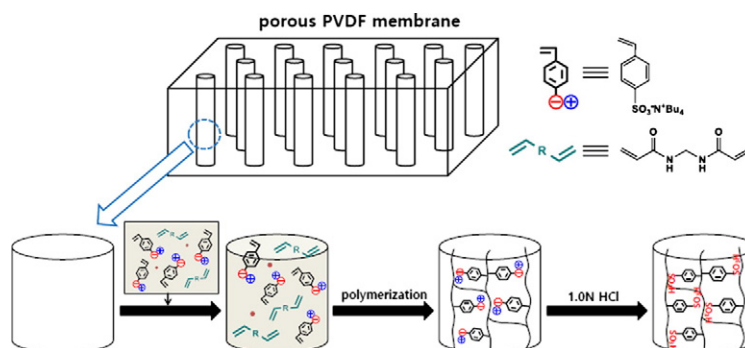
2.5. Measurements

2.5.1. Ion exchange capacity

The PVDF–CSPS membranes were immersed in a 2.0 N HCl solution and kept for 24 h. After washing several times with water, the samples were placed in an aqueous 3.0 M NaCl solution for 24 h, and then removed. The resulting solution was titrated with 0.01 N NaOH, and the IEC values were calculated from the following equation:

$$\text{IEC (mmol/g)} = [\text{C}_{\text{NaOH}} \times V_{\text{NaOH}}] / W_{\text{dry}}$$

where C_{NaOH} is the concentration of NaOH solution, V_{NaOH} is the volume of NaOH solution, and W_{dry} is the weight of sample membranes.



Scheme 1. Experimental procedure for the preparation of PVDF membranes filled with cross-linked sulfonated polystyrene using organic-soluble TVS.

Download English Version:

<https://daneshyari.com/en/article/5209623>

Download Persian Version:

<https://daneshyari.com/article/5209623>

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