



ELSEVIER

Contents lists available at ScienceDirect

## Journal of Membrane Science

journal homepage: [www.elsevier.com/locate/memsci](http://www.elsevier.com/locate/memsci)

# Polytetrafluoroethylene (PTFE)/silane cross-linked sulfonated poly(styrene–ethylene/butylene–styrene) (sSEBS) composite membrane for direct alcohol and formic acid fuel cells

Bo-Yan Wang, Chiyang Kevin Tseng, Chao-Ming Shih, Yu-Li Pai, Hsiu-Po Kuo, Shingjiang Jessie Lue\*

Department of Chemical and Materials Engineering, Chang Gung University, Kwei-shan, Taoyuan 333, Taiwan

## ARTICLE INFO

## Article history:

Received 11 November 2013

Received in revised form

30 March 2014

Accepted 31 March 2014

Available online 8 April 2014

## Keywords:

Direct alcohol fuel cell performance  
 Silane-crosslinked sulfonated poly(styrene–ethylene/butylene–styrene) (sSEBS)  
 Direct formic acid fuel cell  
 Ionic conductivity

## ABSTRACT

A novel polymeric electrolyte membrane for direct alcohol fuel cells (DAFCs) and direct formic acid fuel cells (DFAFCs) was developed using a pore-filling method. This composite consisted of a porous polytetrafluoroethylene (PTFE) microporous substrate filled with silane-crosslinked sulfonated poly(styrene–ethylene/butylene–styrene) (sSEBS). This composite membrane was characterized using field emission scanning electron microscopy, Fourier-transform infrared spectrometry, thermal gravimetric analysis, and differential scanning calorimetry. The thermal and mechanical stabilities of this composite membrane were good. The methanol and ethanol permeabilities of this composite membrane were lower than Nafion 117, and these two membranes had comparable ionic conductivities. The power densities in direct methanol fuel cells with this composite electrolyte were higher than with the Nafion electrolyte. A peak power density of  $91.4 \text{ mW cm}^{-2}$  was achieved at  $70^\circ\text{C}$  when the cell was fed with  $0.5 \text{ M}$  methanol. A direct ethanol fuel cell using this composite exhibited a peak power density of  $16.5 \text{ mW cm}^{-2}$  at  $60^\circ\text{C}$ . In a DFAFC, a peak power density of  $81.4 \text{ mW cm}^{-2}$  was achieved with this composite and  $3 \text{ M}$  fuel at  $60^\circ\text{C}$ . Long-term cell performance was sustained during a 180-h continuous operation using this pore-filled PTFE/sSEBS composite electrolyte. This PTFE/sSEBS composite membrane has potential for use in proton-exchange DAFC and DFAFC applications.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Alcohols are considered to be high energy density liquid fuels, and they may be used directly in fuel cells without the need of hydrogen reforming process [1,2]. One of the main challenges that currently limits the performance of direct alcohol fuel cells (DAFCs) is the high permeability of alcohols through electrolyte membranes. Perfluorosulfonated polymers, such as Nafion, are commonly used as fuel cell electrolyte materials because they have good proton conductivity, mechanical strength, chemical stability, and thermal stability under fuel cell operating conditions. Protons are transported through sulfonated polymer membranes primarily in the form of  $\text{H}_3\text{O}^+$  ions [3]. Consequently, the membranes must be swollen with water to function effectively in fuel cells. While water sorption enhances proton conductivity in sulfonated polymers, it also increases methanol fuel cross-over because water and methanol permeate through these membranes together [4,5]. This fuel cross-over causes voltage losses with increasing current

density in the polarization curves for a DAFC [6–8]. When an alcohol fuel passes through the membrane electrolyte from the anode to the cathode during fuel cell operation, the fuel loss lowers the fuel cell voltage and efficiency [9–11], and results in catalyst poisoning [12].

To suppress the fuel cross-over, composite electrolytes produced using pore-filling techniques have been proposed [13–17]. These electrolytes consist of electrolyte polymers embedded in porous films. The porous film imparts mechanical strength to the swollen electrolyte gel. The electrolyte possesses an appropriate chemical composition and sufficient conductivity for fuel cell applications. Nguyen et al. demonstrated that porous polyimide (PI) filled with sulfonated poly(styrene–ran-ethylene) electrolyte exhibited a methanol permeability one order of magnitude lower than that of the pure sulfonated poly(styrene–ran-ethylene) ( $0.13 \times 10^{-6}$  and  $2.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , respectively) [16]. Chen et al. reported that the methanol permeability is lower for the polytetrafluoroethylene (PTFE)/Nafion electrolyte than for Nafion 117 [17]. Other researchers prepared various porous film/electrolyte composites and confirmed that their methanol permeability was significantly lower than that of Nafion film [13–15]. Although the methanol permeability of pore-filled composite electrolytes was

\* Corresponding author. Tel: +886 3 2118800x5489; fax: +886 3 2118700.

E-mail address: [jessie@mail.cgu.edu.tw](mailto:jessie@mail.cgu.edu.tw) (S.J. Lue).

lower than that of Nafion or the corresponding nascent electrolyte, their proton conductivities were well maintained. Nguyen et al. reported that 80% of the ionic conductivity of pure sulfonated poly(styrene-ran-ethylene) was retained after it was used to fill the pores in a PI substrate ( $0.11$  and  $0.09 \text{ S cm}^{-1}$ , respectively) [16]. Kuzume et al. [14] demonstrated that a poly-2-acrylamide-2-methylpropane-sulfonic acid and poly-styrene sulfonic acid electrolyte (50:50 by weight) showed a conductivity value of  $0.08 \text{ S cm}^{-1}$ . Maintaining sufficient ionic conductivity is crucial for high performance DAFCs [18].

Additionally, pore-filled electrolytes within rigid substrates can suppress the swelling of the electrolyte [16,19,20]. Yamaguchi et al. reported that a PTFE/acrylic acid electrolyte (approximately 35% pore-filling ratio) showed an area change of 5% upon swelling in water, much less than that of Nafion (25%) [19]. Nguyen et al. reported that the dimensional change of a PI/sulfonated poly(styrene-ran-ethylene) electrolyte in water was reduced to one third of that for pure PI [16]. Yamaguchi et al. also reported that microporous high density polyethylene and PI electrolytes showed hardly any area change after immersion in water [20]. Small dimensional changes upon wetting/drying are essential for fuel cell electrolytes because this property ensures good contact between the electrolyte films and the gas diffusion electrodes, thus reducing interfacial resistance in a cell.

Limited reports on fuel cell performance using pore-filling electrolytes were found in the literature. Chen et al. [17] and Lin et al. [21] reported that direct methanol fuel cell (DMFC) power densities increased by 110% and 29%, respectively, when a PTFE/Nafion composite electrolyte was compared with Nafion 117 at a cell temperature of  $70^\circ\text{C}$ . Chen et al. attributed the increased cell performance to the lower methanol permeability of this PTFE/Nafion film [17]. Additionally, PI or PE porous supports filled with other polymer electrolytes demonstrated higher DMFC performance than the pristine Nafion series [14–16]. Although porous supports of PI [14,16,20], polyethylene [15,20] and polyvinylidene difluoride [13] have been employed as fortified framework materials for pore-filling membrane electrolytes, PTFE [17,19,20] is used widely for its chemical inertness and thermal and dimensional stability. A good porous substrate also enables the use of various proton-exchange electrolyte materials.

In addition to perfluorosulfonated ionomers such as Nafion analogs [17] acid-containing hydrocarbon-based polymer materials are potential electrolytes. Poly-styrene sulfonic acid [13,14], poly-2-acrylamide-2-methylpropane-sulfonic acid [14], sulfonated poly(phthalazinone ether ketone) (SPPEK) [15], sulfonated poly(styrene-ran-ethylene) [16], acrylic acid [19], poly(acrylamide-tert-butyl)sulfonic acid [20], sulfonated poly(ether ether ketone) (SPEEK) [22], and poly(benzimidazole) (PBI) [23] are some examples. Poly(styrene-ethylene/butylene-styrene) (SEBS) is an inexpensive triblock copolymer that consists of a thermoplastic phase (polystyrene) dispersed inside an elastomeric matrix (polyethylene/butylene). The polystyrene segments provide mechanical strength and the elastic polyethylene/butylene matrix demonstrates high polymeric free volume for permeate diffusion. The sulfonated SEBS (sSEBS) possesses good water uptake capacity and high ionic conductivity [24] and this material offers cost advantage as compared with Nafion [25–28]. It appears that sSEBS shows promise as an ionic polymeric electrolyte for DMFC applications but little cell performance data were found in the literature. From our previous experience the sSEBS film tended to deform under heat or pressure stress. Therefore reinforced composites need to be developed for sSEBS to be widely appropriate for practical applications. In addition to common alcohol fuels such as methanol and ethanol, the cell performance in acidic fuels (e.g., formic acid, which has a high thermodynamic cell potential of  $1.48 \text{ V}$  [29]) merits examination to further explore the composite electrolyte's potential.

In this study, we fabricate a PTFE/sSEBS composite membrane for proton-exchange direct-fueled fuel cell applications. This pore-filling electrolyte membrane is prepared by fortifying a PTFE porous film with crosslinked sSEBS. The surface and cross-sectional morphologies, thermal properties, ionic conductivities, fuel permeabilities of the composite membrane are evaluated. The performance of this composite membrane in a single cell was evaluated in direct methanol, ethanol, and formic acid fuel cells at various fuel concentrations and cell temperatures. The cell performance with this PTFE/sSEBS composite is correlated with the electrolyte characteristics, which include physical properties and conductive and transport features.

## 2. Experimental

### 2.1. Materials

The PTFE porous membrane (Advantec BN301, with a nominal porosity of 78% and a nominal pore size of  $0.5 \mu\text{m}$ ) was obtained from Toyo Roshi Kaisha Ltd., Tokyo, Japan. Silane-crosslinked sulfonated poly(styrene-ethylene/butylene-styrene) (sSEBS) and potassium hydroxide (KOH) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Nafion 117 membrane was purchased from DuPont Co. (Fayetteville, NC, USA). Methanol and ethanol (HPLC grade, 99.9%) were purchased from Acros Organics (Geel, Belgium). Hydrogen peroxide and sulfuric acid (99.9% purity) were obtained from Riedel-de Haen (Seelze, Germany). Gas diffusion electrodes (ELAT<sup>®</sup>) with  $6 \text{ mg cm}^{-2}$  Pt-Ru alloy (1:1 a/o) black as an anode and  $5 \text{ mg cm}^{-2}$  Pt black as a cathode were purchased from E-tek (BASF, Ludwigshafen, Germany). Deionized (DI) water with a resistivity of  $18 \text{ M}\Omega \text{ cm}$  was produced using a Millipore water purifier (Elix 5/Milli-Q Gradient system, Millipore Corp., Bedford, MA, USA).

### 2.2. Membrane preparation

A PTFE porous film was soaked in a 5 wt% sSEBS solution at  $25^\circ\text{C}$  for 15 min to fill the pores. The temperature was increased to  $120^\circ\text{C}$  for 2 h to evaporate the solvent from the sSEBS solution. The PTFE/sSEBS composite membrane was photopolymerized by UV light irradiation (500 W) for 2 h at  $25^\circ\text{C}$ . The resulting composite membrane was soaked in 1 M  $\text{H}_2\text{SO}_4$  at  $60^\circ\text{C}$  for 1 h to achieve thorough protonation of the sSEBS. The composite membrane was rinsed repeatedly with DI water to remove excess  $\text{H}_2\text{SO}_4$  prior to membrane characterization.

The Nafion 117 membrane was first boiled with 5% hydrogen peroxide for 1 h to remove organic matter, and was rinsed with DI water for 0.5 h. Then, the Nafion was boiled in 1 M sulfuric acid for 1 h to ensure complete conversion to the H-type exchange membrane and rinsed again with DI water.

### 2.3. Membrane characterization

The composite membrane was dried in a vacuum oven, quenched in liquid nitrogen, and sectioned with a surgical blade. The sample was sputter coated with platinum, and the surface and cross-sectional morphologies of the composite membrane were examined with a field emission scanning electron microscope (FESEM) (S-4800, Hitachi, Tokyo, Japan) [30]. The chemical structure was analyzed using a Fourier-transform infrared spectrometer (FTIR) (Perkin Elmer Spectrum One, Perkin Elmer Corp., Norwalk, CT, USA). The thermal stabilities of the membranes were analyzed using a thermo-gravimetric analyzer (TGA, TATGA Q-500, TA Instrument, New Castle, DE, USA) under a nitrogen atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$ . The temperature at which a 10 mg

Download English Version:

<https://daneshyari.com/en/article/633532>

Download Persian Version:

<https://daneshyari.com/article/633532>

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