



Short communication

A new method to prepare high performance perfluorinated sulfonic acid ionomer/porous expanded polytetrafluoroethylene composite membranes based on perfluorinated sulfonyl fluoride polymer solution



Libin Yang, Hong Li, Fei Ai, Xiaoyong Chen, Junkun Tang, Yan Zhu, Chaonan Wang, Wang Zhang Yuan*, Yongming Zhang*

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, No. 800, Dongchuan Road, Shanghai 200240, China

HIGHLIGHTS

- A simple but effective new method to fabricate PFSA/ePTFE membrane was developed.
- The hydrophobic PFSF solution was utilized to resolve the impregnation problem.
- The membrane properties are much better than those of traditional way made membrane.
- The new made membrane is totally comparable to Nafion 211 in PEMFC performance.

ARTICLE INFO

Article history:

Received 11 April 2013

Received in revised form

26 May 2013

Accepted 11 June 2013

Available online 18 June 2013

Keywords:

Perfluorinated sulfonyl fluoride solution

Fuel cell

Impregnated composite membrane

Perfluorinated sulfonic acid

Poly(tetrafluoroethylene)

ABSTRACT

Perfluorinated sulfonyl fluoride (PFSF) resin, the precursor of perfluorinated sulfonic acid (PFSA) ionomer is successfully dissolved in perfluorinated solvents, and its hydrophobic nature is utilized to resolve the difficulty of impregnating hydrophilic PFSA solution into hydrophobic porous expanded polytetrafluoroethylene (ePTFE). The composite membrane fabricated through such simple but effective method is well impregnated, leading to better ionic conductivity and lower gas permeability. The fuel cell constructed with PFSF solution based membranes shows superior performance as compared to that of its aqueous PFSA solution based counterpart, which is comparable to that of commercial Nafion® 211.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Since the first report by Penner and Martin in 1985 [1], PFSA/ePTFE composite membranes have drawn great attentions [2–8] due to their high tensile strength, excellent dimensional stability, and low cost. Thickness of the composite membranes can be reduced to as low as 5 μm with satisfactory conducting and mechanical properties [9–11], thus greatly lowering the production cost by reducing the amount of expensive polymer electrolyte [12–15]. Despite their promising perspective, it is still not particularly

suitable for commercial manufacturing operations owing to the difficulty of impregnating hydrophilic polymer electrolyte solutions into hydrophobic pores of ePTFE [16]. The voids or pinholes inside the composite membranes will reduce the ionic conductivity, meanwhile increase the gas permeability, subsequently deteriorating the fuel cell performance and operation stability. So far, tremendous efforts have been made to alleviate such thorny problem, but only met with limited success [17–23]. For instances, Oh hot-pressed hydrophobic PFSF resin on both sides of ePTFE, nevertheless the ePTFE membrane was not well impregnated due to the high viscosity of melting PFSF [17]. Shim sprayed PFSA solution on double surfaces of the ePTFE sheets, however, high gas permeability of the resulting membrane indicated the presence of undesirable pores or pinholes [18]. Lin adopted the surfactant of

* Corresponding authors. Tel.: +86 21 34202613; fax: +86 21 54742567.

E-mail addresses: wzhyuan@sjtu.edu.cn (W.Z. Yuan), ymzsjtu@yahoo.com.cn (Y. Zhang).

Triton X-100 to reduce PFSA aggregate sizes [19], and based on which, Ramya studied the solvent effect on the composite membranes [20]. Unfortunately, they did not inherently resolve the incompatibility problem; meanwhile, the troublesome procedure of impregnating ePTFE sheets with PFSA solutions for 24 h twice and additional removing process for the surfactant is inefficient for commercial fabrication. Although well impregnated membranes were also achieved through chemical modification of ePTFE to increase its hydrophilic [21,22] or utilizing vacuum pressure [23], such complicated processes inevitably increased the production cost.

Recently, we found that PFSF resins can be readily dissolved in such fluorocarbon solvents as hexafluoropropene trimer, perfluorotributylamine, tetrafluoroethylene oligomers and perfluoro [2-(2-fluorosulfonylethoxy) propyl vinyl ether at elevated temperatures [24,25]. The hydrophobic nature of PFSF solutions makes them excellent candidates for preparing PFSA/ePTFE composite membranes. Herein, we reported a facile new method for fabricating such composite membranes based on PFSF solutions. For comparison, a well used PFSA solution consisting of 4 g of PFSA and 100 ml of isopropanol/water (4:1 w/w) mixed solvent [20,26–28] was used as control. The results clearly suggest that the new technique can easily generate high performance composite membranes, whose fuel cell performance is comparable to well known Nafion® 211 membranes, thus exhibiting promising application prospect in future.

2. Experimental

2.1. Preparation of PFSA/ePTFE composite membranes

4 g of PFSF resin with an IEC value of 1.05 meq g^{-1} (Dongyue Shenzhou New Materials Company Ltd., China) was dissolved in 100 ml of perfluorotributylamine (Hubei Hengxin Chemical Co., Ltd). Herein, we chose perfluorotributylamine as solvent owing to its suitable boiling point ($\sim 178 \text{ }^\circ\text{C}$). For low boiling point perfluorinated solvents, a high-pressure autoclave must be involved; for those with even higher boiling points, they may not be easily evaporated.

The mixture was stirred and refluxed until a clear solution was achieved. After being washed with alcohol three times at room temperature and dried in an oven at $80 \text{ }^\circ\text{C}$, the porous ePTFE membrane (Shanghai Dagong Comp., $10 \mu\text{m}$ in thickness, 85% porosity, pore size $0.1\text{--}0.2 \mu\text{m}$) was immersed in the PFSF solution for 5 min. Then the impregnated membrane was dried at $120 \text{ }^\circ\text{C}$ for 5 min. After three cycles of repeated impregnation and drying processes, the PFSF/ePTFE membrane was annealed at $160 \text{ }^\circ\text{C}$ for 2 h. Then the membrane was transferred to 8 M NaOH solution and refluxed at $80 \text{ }^\circ\text{C}$ for 48 h to convert $-\text{SO}_2\text{F}$ into $-\text{SO}_3\text{Na}$ groups. After treatment, the membrane was repeatedly immersed (three times) in a fresh 5 M HNO_3 for 1 h to finally yield the new method made PFSA/ePTFE composite membrane (1#).

For comparison, 4 g of PFSA derived from the same batch of PFSF was dissolved in 100 ml of isopropanol/water (4:1 w/w) mixture. Subsequently, procedure similar to that of preparing the PFSF/ePTFE membrane was carried out to fabricate the traditional way made PFSA/ePTFE composite membrane (2#). In this work, the IEC value of PFSA was verified through titration according to the previously reported procedure [29].

2.2. Contact angle measurement

Contact angles were measured on an Optical Contact Angle Measuring Device (OCA20, DataPhysics Instruments GmbH, German) using a sessile drop method. ePTFE films after clean-up

process were extended on glass sheets to avoid significant changes of the membrane surface. A syringe was employed to take and generate a drop of 10 ml of sample solution close to the membrane surface.

2.3. Characterization of PFSA/PTFE composite membranes

The cross-section morphology of composite membranes was observed on a field emission scanning electron microscope (FESEM, JSM-7401F, JEOL Ltd., Japan). Samples were coated with gold before observation. Dimensional stability of the membranes was evaluated by measuring the change in three dimensions of dried (in vacuum at $80 \text{ }^\circ\text{C}$ for 24 h) and corresponding swollen (boiled in distilled water at $80 \text{ }^\circ\text{C}$ for 1 h) samples. Water uptake of the membranes was obtained from the difference between the weight of the dried and swollen membranes.

2.4. Areal proton resistance measurement

The swollen membranes were fixed in a home-made cell (as shown in Fig. 1) consisting of two mirror finished stainless steel electrodes with a holding setup for the membrane and electrodes, the clamping force originated from the stainless steel bolt was fixed at 2 N m^{-1} through a preset torque wrench in all test. Electrochemical measurement was carried out at 100% humidity and the membrane resistance was determined by AC impedance techniques using Ecochemie Autolab PGSTAT302 in the frequency range from 100 kHz to 100 Hz. The areal proton resistance of the membranes in the cross-section was obtained through dividing the membrane resistance by the active area.

2.5. Single cell evaluation and hydrogen crossover

Above composite membranes were hot-pressed with two pieces of standard electrodes (Shanghai Hephas Energy Co. Ltd) consisting of a gas diffusion layer and a catalyst layer (catalyst loading is 0.4 mg cm^{-2}) to obtain the electrode membrane assemblies (MEAs). The performance data were collected from single cells with an active area of 5 cm^2 . Hydrogen and air were used as fuel and oxidant, respectively. The cells were operated at $80 \text{ }^\circ\text{C}$ under a pressure of 29 psi. The hydrogen and air were humidified at $80 \text{ }^\circ\text{C}$. The gas flow rates at the anode and cathode were kept at 1 and 4 slpm, respectively.

Potential step experiments [30] were performed to evaluate fuel crossover using Ecochemie Autolab PGSTAT302 with a flow rate of

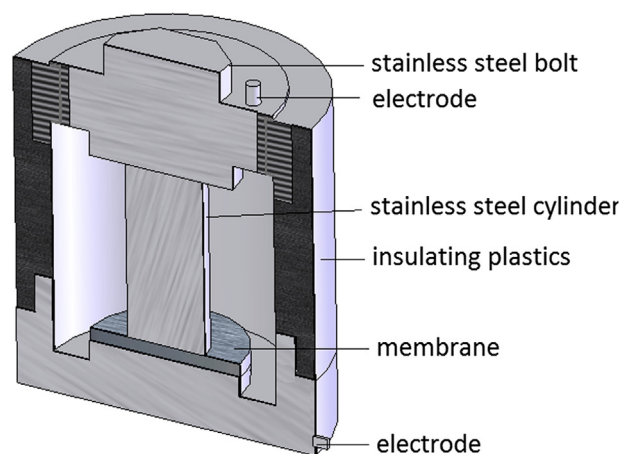


Fig. 1. Schematic illustration of the home-made cell for proton conductivity measurement.

Download English Version:

<https://daneshyari.com/en/article/7739427>

Download Persian Version:

<https://daneshyari.com/article/7739427>

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