



## A new structured composite membrane for fuel cell applications

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### ARTICLE INFO

#### Article history:

Received 12 October 2011

Received in revised form 8 February 2012

Accepted 16 March 2012

Available online 26 April 2012

#### Keywords:

Self-humidifying PEMFC

Passive DMFC

Micro fuel cell

HZSM-5

Nafion

### ABSTRACT

A new proton conducting membrane was prepared by confining sub-nanoliter volumes of perfluorosulfonic acid (PFSA) polymer within rigid pores clad with zeolite layers. Tests showed membrane-electrode assembly (MEA) made of confined Nafion PFSA-HZSM-5/Sil-1 structured composite membrane delivered an order of magnitude higher MPD (maximum power density) compared to a standard Nafion 117 MEA in a hydrogen PEMFC at high temperature operation under dry feed conditions. Similarly, 900% higher MPD was obtained from direct methanol fuel cell (DMFC) made of the new membrane. The zeolites are believed to play an active role in the water and methanol managements through adsorption and transport, and the confinement of the PFSA within zeolite environment changes its microstructure resulting in the improved thermal stability.

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### 1. Introduction

Most proton-exchange membrane fuel cells (PEMFCs) and direct methanol fuel cell (DMFC) use perfluorosulfonic acid (PFSA) membrane, particularly the commercial Nafion membrane. PFSA membrane in PEMFC is known for its high proton conductivity and long-term stability when operated under fully hydrated conditions. However, PFSA suffers sharp decrease in proton conductivity at low membrane hydration resulting in poor cell performance. This necessitates the use of external humidification equipment and thus complicating the system design and increasing the overall cost [1]. Also, the low glass transition temperature of polymeric PFSA membrane means that PEMFC must be operated below 80 °C [2]. This makes the fuel cell more sensitive to impurities in the fuel as well as makes the water and heat managements more difficult [3]. Compositing PFSA membrane with Pt/Zr(HPO<sub>4</sub>)<sub>2</sub> [4,5], Pt/M<sub>x</sub>O<sub>y</sub> [6–8], Pt/clay [9] and Pt/NaY [1] were used by various authors to create active sites for water generation within PFSA membrane. However, water is generated by consuming part of the hydrogen fuel and studies have shown that platinum promotes the formation of H<sub>2</sub>O<sub>2</sub> and HO• free radicals that can damage PFSA membrane [10–12].

DMFC is considered more competitive than PEMFC for powering portable electronic devices [13,14]. A passive DMFC that eliminates the need of ancillary devices such as pumps for fuel supply is particularly attractive for this application. However, the higher methanol feed concentration required by a passive DMFC [14] magnifies the problem of methanol crossover [15,16]. The review article by Jones and Roziere [17] shows that inorganic–organic composite membranes often have greater tolerance for liquid fuels and generally exhibit a lower fuel crossover. Indeed, zeolite–PFSA composite membranes containing zeolite beta [18,19], zeolite A [20], Fe-silicalite-1 [21] and ZSM-5 [22] are shown to lower methanol crossover and improve fuel cell performance. However, particles dispersed within PFSA tend to suffer from aggregation and phase separation resulting in poorer proton conductivity [18,23].

Our group had investigated zeolites as proton exchange membranes in miniature PEMFC [24,25] and DMFC [26]. Freestanding zeolite micromembranes were microfabricated and tested for gas, liquid and proton transports prior to their assembly into fuel cells [24,27–30]. It is possible to achieve excellent performance with power density approaching that of the PFSA fuel cell [24,26]. More recently, we prepared a new self-humidifying proton exchange membrane through confinement of subnanoliter volumes of PFSA within the zeolite-clad pores [31]. This architecture increased water retention in PFSA and the membrane displayed higher glass transition temperature. The PEMFC employing the new membrane had excellent tolerance for high temperature operation under dry conditions and delivered an order of magnitude higher power

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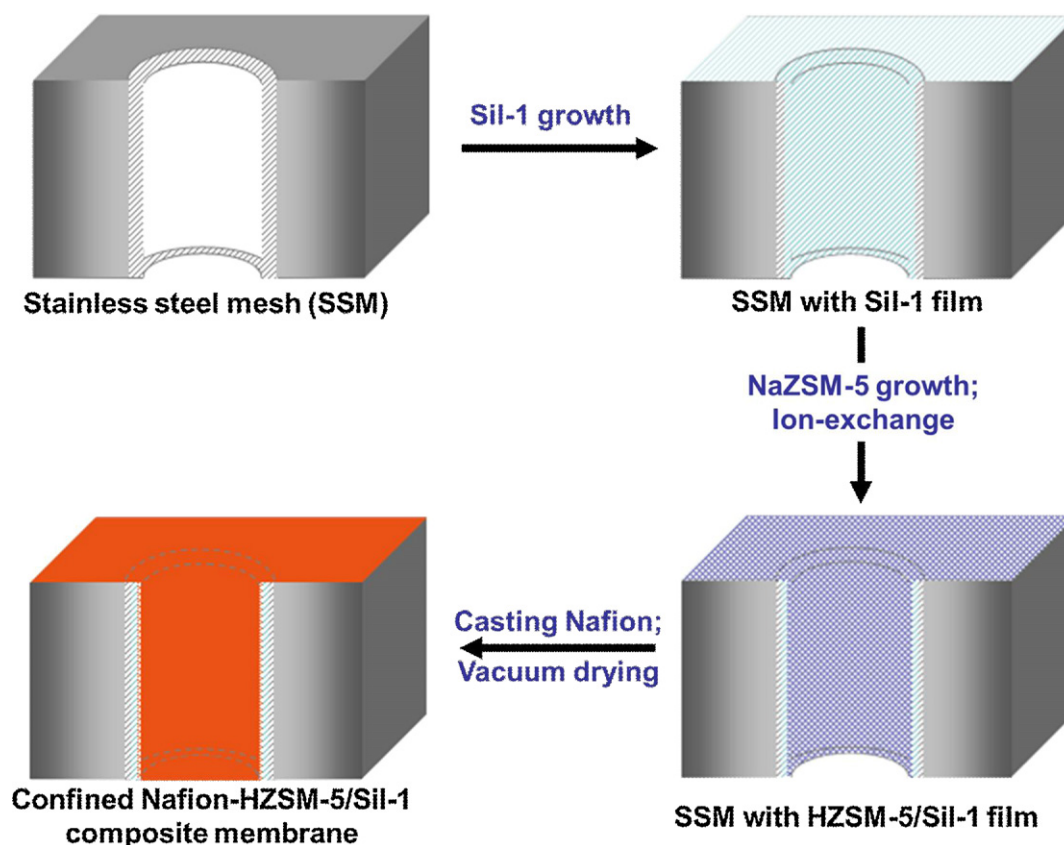


Fig. 1. Schematic diagram of the preparation procedure for confined Nafion-HZSM-5/Sil-1 composite membrane.

density than the standard Nafion PFSA PEMFC. The aim of this work is to further improve the properties of confined PFSA-zeolite structured composite membrane by using bi-layered zeolites. The membrane performance will be investigated in self-humidifying PEMFC and passive DMFC devices.

## 2. Experimental

### 2.1. Structured composite membrane: confined Nafion PFSA-HZSM-5/Sil-1

The process diagram shown in Fig. 1 describes the main steps in preparing the new structured composite membrane. A regular hexagonal array of pores was photochemically etched into a 50  $\mu\text{m}$  thick stainless steel foil to obtain a stainless steel mesh (SSM) [31]. An insulating layer of pure silica zeolite, silicalite-1 (Sil-1) was grown on SSM by a seeding and regrowth method. This zeolite layer also protects the SSM against corrosion. Seeding is important as it minimizes the effects of support chemistry [32–34] and enables the control of zeolite growth [35,36]. The stainless steel mesh was cleaned in acetone, water and ethanol, followed by surface grafting of 3-mercaptopropyl trimethoxysilane (Aldrich) before seeding with 100 nm TPA-silicalite-1 sol in water [37,38]. The synthesis condition dictates zeolite regrowth from the seed layer and affects the chemistry, microstructure and transport properties of the deposited zeolite [38–43]. The seeded stainless steel mesh was regrown in a synthesis solution of 16  $\text{SiO}_2$ :1 (TPA) $_2\text{O}$ :4000  $\text{H}_2\text{O}$  at 130  $^\circ\text{C}$  for 48 h. Tetraethyl orthosilicate and tetrapropylammonium hydroxide from Aldrich were used for silica precursor and structure directing agent.

A second layer of NaZSM-5 zeolite was deposited on the Sil-1 from a template-free synthesis gel with composition of 1  $\text{SiO}_2$ :0.0125  $\text{Al}_2\text{O}_3$ :0.268  $\text{Na}_2\text{O}$ :92  $\text{H}_2\text{O}$  after hydrothermal

regrowth at 180  $^\circ\text{C}$  for 16 h. The synthesis gel was prepared by dissolving 7 g of Ludox SM-30 colloidal silica (Aldrich) in a solution of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (0.27 g, Aldrich), NaOH (0.75 g, Scharlau) and distilled water (53.2 g) and aged for 24 h before synthesis. The NaZSM-5 was ion-exchanged with 0.05 M  $\text{H}_2\text{SO}_4$  (Fisher) thrice, each time lasting for 3 h. The pores of the zeolite-cladded SSM were filled with Nafion by repeated casting 1.6 wt.% Nafion precursor in water and 1,2-propanediol prepared from 10 wt.% Nafion resin aqueous suspension (Aldrich). The sample was vacuum dried at 80  $^\circ\text{C}$  and the procedure was repeated to give a final membrane thickness of 175  $\mu\text{m}$  that is comparable to commercial Nafion 117 membrane. The thickness of the confined Nafion-HZSM-5/Sil-1 structured composite membrane was measured with a microcaliper. Confined Nafion-Sil-1 structured composite membrane was also prepared for comparison by casting Nafion precursor into the pores of Sil-1-cladded SSM.

The membrane preparation was monitored and examined by microscopy. An Olympus BX41 microscope with fluorescence accessories was used to inspect the membrane for defects after each preparation step. Samples were taken for more detailed examination by scanning electron microscope (JEOL JSM-6300F & JSM-6390). The identities of the zeolites were confirmed by X-ray diffraction (Philips PW1830) and Fourier transformed infrared spectroscopy (Perkin-Elmer Spectrum GX), while the aluminum content of the HZSM-5 was determined by the energy dispersive X-ray spectroscopy (EDXS) accessory of the scanning electron microscope.

### 2.2. Membrane-electrode assembly (MEA)

MEA for self-humidifying PEMFC was prepared by hot-pressing the confined Nafion PFSA-HZSM-5/Sil-1 membrane between two pieces of porous stainless steel electrodes under 10 MPa pressure

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