

Nafion/Acid Functionalized Mesoporous Silica Nanocomposite Membrane for High Temperature PEMFCs

Zhongwei Chen*, Ryan S. Hsu

Department of Chemical Engineering, Waterloo Institute of Nanotechnology, Waterloo Institute for Sustainable Energy, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada,

This study reports the synthesis and the characterization of proton conducting composite membranes prepared by dispersing in Nafion matrix with highly acid functionalized mesoporous silica (KIT-6). Nafion/KIT-6 composite membranes were studied for operation in hydrogen/oxygen polymer electrolyte membrane fuel cells (PEMFC) at 120 °C with different relative humidities (72%RH and 100%RH). The Nafion/KIT-6 composite membrane demonstrated little improved fuel cell performance to that of the Nafion membrane at 100% relative humidity (RH), however, it was much higher at low RH (72%). These results suggest that this new type of Nafion composite membrane may be successfully used as an improved proton exchange membrane in high temperature PEMFC.

Introduction

Polymer electrolyte membrane fuel cell (PEMFC) has been developed for both stationary and mobile power generation because it was recognized as high operational efficient and environmentally clean power source.¹ Operation of PEMFCs at temperatures above 100 °C would significantly boost PEMFC performance, enhancing important parameters, such as electrode reaction kinetics and CO tolerance, and allowing an easier thermal and water management of the system. However, high temperature operation of PEMFCs is not practical due to the low proton conductivity of the state-of-the-art perfluorosulfonic acid (PFSA) polymer electrolyte membranes under these conditions.¹⁻⁴ Nafion, one of the oldest but still one of the best available electrolytes, limits the operation temperature of PEMFCs to 80 °C under strict humidification requirements. The reduced water content at higher temperatures results in a strong decrease of the performance. Additionally, at higher temperatures the mechanical stability is reduced resulting in crack formation and crossover of the fuel.¹⁻⁴

In order to achieve higher temperature stability, either new polymer membranes have to be developed or established materials like Nafion have to be modified. A common concept to improve and fine-tune materials properties is the preparation of organic/inorganic hybrid materials with nanosized interfaces as composite material. Large efforts have also been made to modify Nafion with hydrophilic particles like by a variety of organic and inorganic materials such as silicon oxide, zirconia, titania, alumina, zirconium phosphates, Pd, polypyrrole, polyfurfuryl alcohol and polyoxyalkylenes.¹⁻⁸ These attempts lead to enhanced temperature stabilities of the membranes up to 120 °C and allow sufficient proton conductivity at a relative humidity (RH) of only 26%.

Additionally, the incorporation of inorganic particles provides higher mechanical stability which is especially relevant if methanol is used as liquid fuel.

Mesoporous silica materials particles are proton conducting, hygroscopic, and mesoporous materials, and have been used as inorganic fillers in composite membranes.⁷⁻¹² Mesoporous silica materials possess desirable traits including large internal surface areas, mechanically stable frameworks, chemical inertness, and negligible electronic conductivity. Furthermore, acid functionalized silica materials have shown proton conductivities on the order of Nafion. Pore structure (i.e., pore size and dimensionality) has been proven to influence proton transport greatly. Mesoporous MCM-48 with large pore size and three dimensional interconnected pore structures have demonstrated better proton conductivity than small pore zeolite Beta and one dimensional pore structure MCM-41.¹³ While the pore size of most mesoporous materials used in the composite membranes for fuel cells in the literature are less than 4 nm.¹³

In order to further improve proton conductivity, here acid functionalized KIT-6 with large pore (8 nm) and three dimensional interconnected pore structures was synthesized and used successfully as inorganic filler in composite membranes.¹⁴ The effects of KIT-6 in Nafion composite membranes on the methanol permeability and proton conductivity were examined. The performance of these composite membranes in high temperature has been evaluated and the results are discussed.

Experimental

Synthesis of powdery mesoporous silica¹⁴

The large mesoporous silica with cubic Ia3d symmetry (designated as KIT-6) is prepared in aqueous solution using a 1: 1 (wt%) mixture of Pluronic P123 (EO20PO70EO20, MW = 5800, Aldrich) and butanol, around 0.5 M HCl concentrations at 25–35 °C. Tetraethoxysilane (TEOS) is acceptable as a silica source. In a typical synthesis batch with TEOS, 6 g of P123 was dissolved in 217 g of distilled water and 11.8 g of conc. HCl (35%). To this, 6 g of butanol (Aldrich, 99.4%) was added under stirring at 35 °C. After 1 h stirring, 12.9 g of TEOS (ACROS, 98%) was added at 35 °C (TEOS : P123 : HCl : H₂O : BuOH = 1 : 0.017 : 1.83 : 195 : 1.31 in mole ratio). The mixture was left under stirring for 24 h at 35 °C, and subsequently heated for 24 h at 100 °C under static conditions in a closed polypropylene bottle (The latter is referred to as hydrothermal treatment). The solid product obtained after hydrothermal treatment was filtered and dried at 100 °C without washing. The template was removed by extraction in an ethanol–HCl mixture, followed by calcination at 550 °C. The calcined KIT-6 was then soaked in 100 ml NaOH aqueous solution at pH 10.0 for 1 h, followed by filtration and drying.

Modification of mesoporous silica

The KIT-6 was evacuated at 120 °C for 8 h, cooled to room temperature, and a solution of reactant (1,2,2-trifluoro-2-hydroxyl-1-trifluoromethyl-ethane sulfonic acid beta-sultone, 1.0 g) was then added to 50 ml dry toluene. The mixture was refluxed for 24 h. The solid was filtered and washed thoroughly with toluene and finally dried at 100 °C overnight.

Fabrication of composite membrane

To prepare a composite membrane, a desired amount of prepared sulfonated mesoporous silica (KIT-6-SO₃H) was added to a 5 wt% Nafion® solution (EW1100, DuPont Co., USA), then the volume of the resulting suspension could be doubled, if desired, using N,N-dimethylformamide (DMF) as an additional high boiling aprotic solvent and stirred mechanically and degassed by ultrasonication. The desired membrane thickness was obtained by variation of the amount of membrane casting solution used. The top of the vessel was covered with a watch glass, and the vessel was put on a level surface in a convection oven. In the absence of DMF the casting mixture was held at 60°C until dry, and then the oven temperature was raised to 120°C for 1 day to remove any remaining trace solvent. If DMF was used as a cosolvent, the caster was held at 80°C until half of the mixture volume evaporated. Then the temperature of the oven was raised to 100°C until the solution was dry, and finally the oven temperature was raised to 140°C for 1 day to remove any remaining trace DMF solvent. The casting vessel was then removed from the oven and allowed to cool. Once cool, double deionized (DDI) H₂O was poured in the vessel to loosen the membrane from the glass. After the membrane was removed from the casting vessel, the edges were trimmed. After these treatments, the membranes were further treated before characterizations by first boiling in 3wt% H₂O₂ for one hour followed by rinsing with boiling DDI H₂O. Then they were boiled in a 0.5M sulfuric acid solution for one hour, followed by rinsing with boiling DDI H₂O. Finally, the membranes were boiled for 1 hour in DDI H₂O, and then allowed to cool, after which the membranes were ready for testing.

Physical Characterization

X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance Diffractometer (Bruker AXS) using aCu K α radiation. The dried membranes were mounted on an aluminum sample holder. The scanning angle ranged from 5° to 50° with a scanning rate of 3° min⁻¹. All the spectra were taken at ambient conditions. The morphologies of the surfaces and the cross-sections of the membranes were investigated with a Philips XL30-FEG scanning electron microscope. For the cross-sectional SEM samples, the membranes were freeze-fractured in liquid N₂.

Single cell performance

The carbon backing layers used in the membrane/electrode assembly (MEA) were purchased from SGL Carbon Group (Model GDL 30BC). The GDL were used on both the anode and cathode. Anodes used in this study were prepared in a conventional manner by airbrush spraying a sonicated catalyst ink mixture of 20 wt % Pt/XC-72 (E-TEK), 5 wt % Nafion solution (Ion Power, Inc.), water, and isopropyl alcohol onto the GDL. The resulting loadings on the GDL are 0.2 mg Pt/cm² and 35 wt % Nafion loading with respect to total dry weight of the ink. An membrane electrode assembly (MEA) with an active electrode area of 5 cm² was obtained by pressing the cathode and anode onto each side of a pre-treated composite membrane at 140 atm and 135°C for 3 minutes. The MEA was then assembled into a single cell fixture. Cell potential vs current density measurements were performed under the desired conditions of temperature and pressure in the PEMFC. Identical procedures were followed for all of the membranes. All PEMFC experiments were carried out at cell temperatures 120 °C with the total pressure (reactant gas plus water vapor pressure) at 3 atm, respectively. Initially, data were collected at 100% relative humidity, and the temperature of the humidifier bottles was decreased to record performance data at lower relative humidities. In all cases, a flow rate of 40 mL/min was employed. A 1 h period was used between changes in systems temperatures

and collection of current-voltage data to permit temperature and potential stabilization before data acquisition.

Results and discussion

The high quality of the cubic Ia3d silica product is judged by the powder X-ray diffraction (XRD) pattern (Figure 1), transmission electron microscopy (TEM) images (Figure 2) and pore size distribution (Figure 3). The material consists uniquely of large ordered domains of pure bicontinuous mesostructure. The 3-D structure is shown to be commensurate with cubic Ia3d symmetry, as illustrated by the images viewed along various directions. TEM image of KIT-6 indicates large domains of 3-D networks, thus revealing the interconnectivity in the pore structure of the parent cubic silica. The material typically synthesized at 100 °C has average pore size of 8 nm.

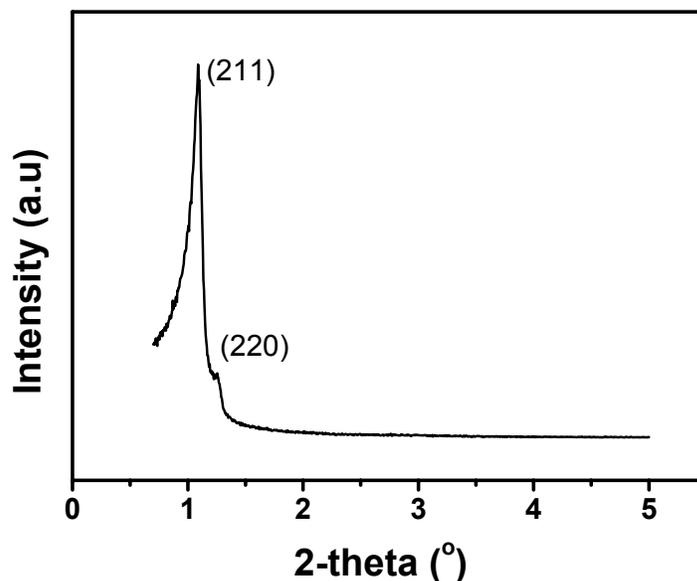


Figure 1. Powder XRD patterns for calcined mesoporous silica (KIT-6) samples.

The microstructures of Nafion and Nafion/KIT-6 composite membrane were observed using a scanning electron microscope (SEM). Figure 4 presents the SEM images of the casted Nafion and Nafion/KIT-6 composite membrane. The SEM microphotograph (a) in Figure 4A demonstrates that neat Nafion® membrane has a homogenous structure. Fig. 4B shows membranes with 2.5 wt% KIT-6-SO₃H particles in the ionomer matrix. These images clearly show that the particulate sizes are 1 μm or less, and the distribution of the silica particles is relatively uniform.

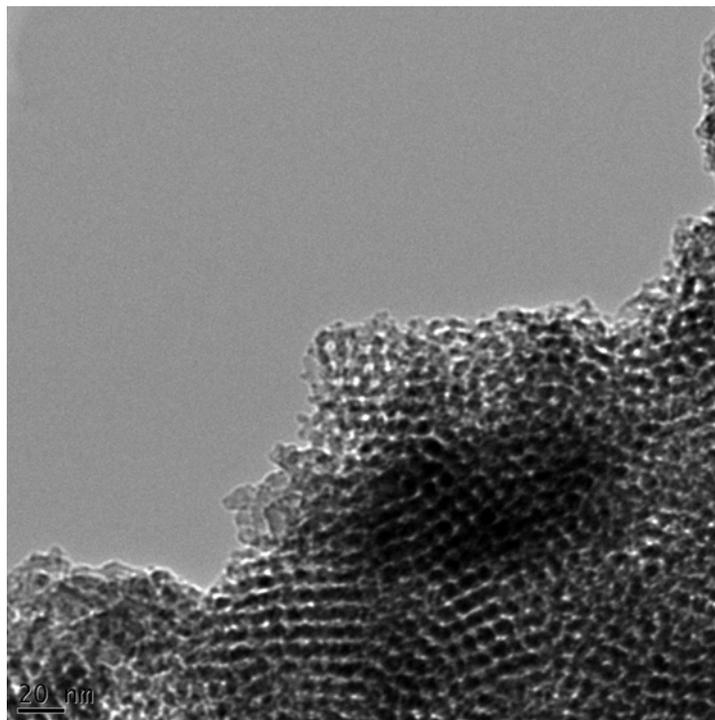


Figure 2. TEM images of the KIT-6.

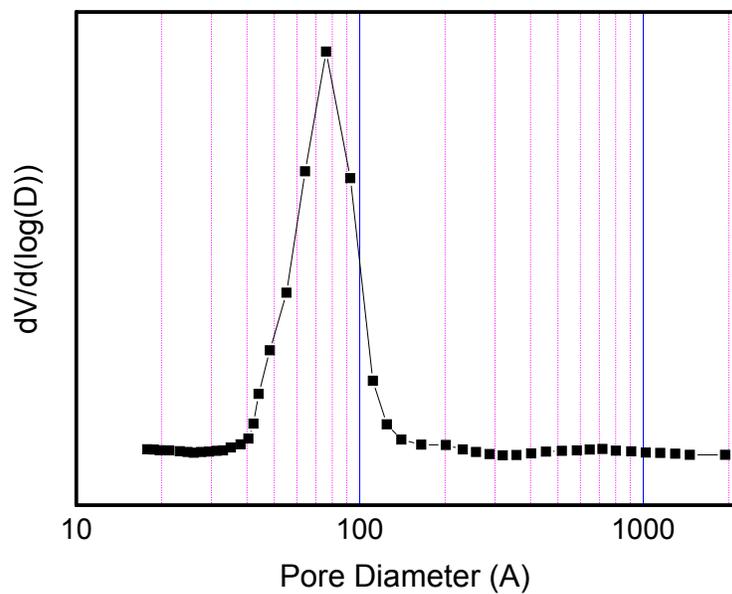


Figure 3. Pore size distributions of KIT-6 synthesized at 100 °C. . The sized was analyzed with the adsorption branch using the BJH algorithm.

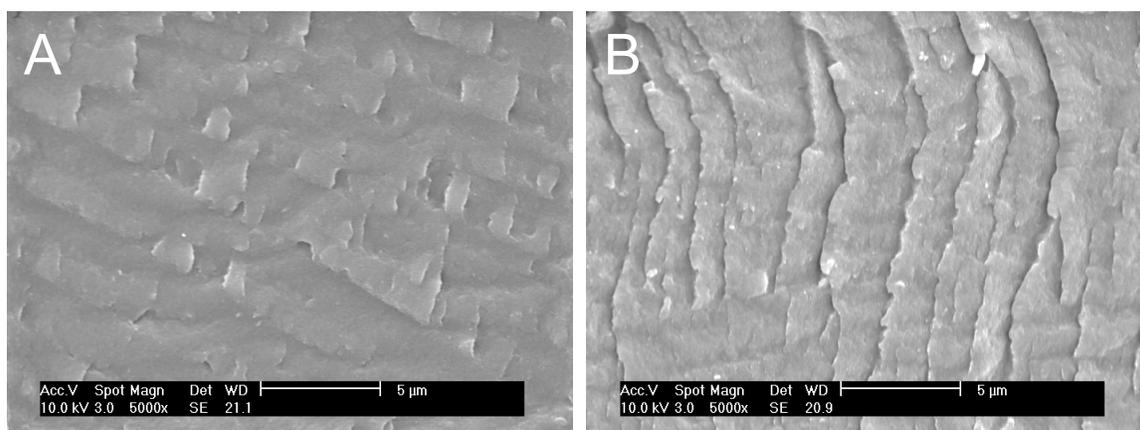


Figure 4. SEM images of the membranes: (c) cross-section of Nafion; (d) cross-section of Nafion/KIT-6 composite membrane.

The fuel cell performance of a single cell with Nafion membrane and Nafion/KIT-6 composite membranes under fully and partially humidified conditions at 120 °C is shown in Figure 5. There is only slight improvement in performance of fuel cell at 100%RH for Nafion/KIT-6 composite membrane as compared to pure Nafion membrane, while Nafion/KIT-6 composite membrane has about 310 mA/cm² higher current at 0.6V compared to Nafion® membranes at 80% RH. This improved performance of the cell with Nafion/KIT-6 composite membrane is attributed to higher proton conductivity in the nanocomposite at low relative humidity. Nafion/KIT-6 composite membrane showed higher proton conductivity compared to Nafion membrane at the same temperature and lower humidity conditions due to the improved water uptake, provision of strong acid sites and higher bulk to surface water ratio, which is critical for higher proton conductivity. These results suggest that there is a potential for improvement in fuel cell performance using Nafion/KIT-6 composites.

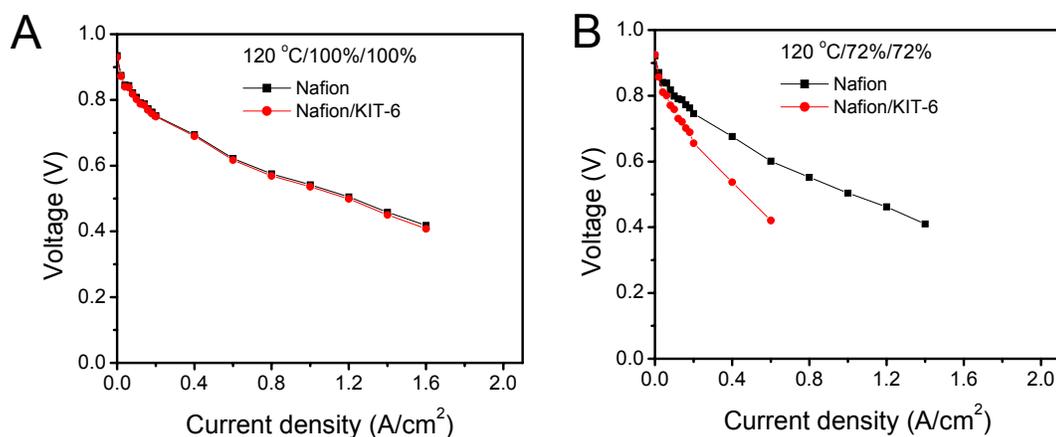


Figure 5. Polarization curves for the MEA made with Nafion membrane and Nafion/KIT-6 composite membrane. The cell temperature and humidifier temperature were maintained at (A) 120 °C and 120 °C; and (B) 120 °C and 110 °C respectively. Gas pressure at 3 atm.

Conclusions

The large mesoporous KIT-6 particles were synthesized and acid functionalized successfully. Nafion/KIT-6 composite membranes were prepared by casting method. The Nafion/KIT-6 composite membrane demonstrated little improved fuel cell performance to that of the Nafion membrane at 100% relative humidity (RH), however, it was much higher at low RH (72%). These results suggest that this new type of Nafion composite membrane may be successfully used as an improved proton exchange membrane in high temperature PEMFC.

Acknowledgment

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