

Rapid communication

Supercritical CO₂ assisted synthesis of highly selective nafion–zeolite nanocomposite membranes for direct methanol fuel cells

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Abstract

We report the synthesis of nafion–zeolite (Fe-silicalite-1) nanocomposite membranes using either a supercritical CO₂ pre-treatment followed by impregnation with zeolite nanoparticles or *in situ* synthesis of Fe-silicalite-1 inside the pores of nafion membrane. The effects of the supercritical CO₂ activation and the size of embedded zeolite particles on the proton conductivity and methanol permeability of composite membranes are observed. In selected cases, the membranes exhibit extremely low methanol permeability and high selectivity (defined as proton conductivity/methanol permeability ratio).

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1. Introduction

Nafion based films are of interest as proton-conducting membranes in direct methanol fuel cells (DMFC). However, unmodified nafion membranes generally possess high methanol permeability, which makes them unsuitable in the current generation of commercial fuel cells. One approach to reduce methanol permeability is to incorporate nanoparticles of highly acidic inorganic materials into nafion membranes (thus making composites) [1–7]. The high surface acidity of incorporated nanomaterials, allows high proton conductivity to be achieved in the composite membranes, whilst blockage of the pores by the particles, reduces methanol transport.

The sol–gel syntheses of inorganic phases (SiO₂, TiO₂, ZrO₂) inside the pores of nafion membranes has previously been reported as an effective modification route to achieve high selectivities [7–10]. Zeolites are also of interest as modifiers in nafion membranes due to their inherent narrow pore size distribu-

tions, high surface acidity and high water uptake [11]. However, natural zeolites (like, montmorillonite [12,13], chabazite and clinoptilite [13–15]) and commercial zeolites (like, FAU and LTA [16]) do not allow control of pore structure, surface acidity and zeolite particle size, in the process of composite membrane synthesis. As such parameters play a crucial role in the transport properties of nafion–zeolite composites, it could be advantageous if any synthesis methods allowed some control over the inorganic particle properties.

Supercritical CO₂ treatments have been used to assist in the synthesis of hybrid styrene-nafion membranes [17] as well as for controlled foaming of polymer membranes [18,19]. Supercritical carbon dioxide is essentially single phase, consisted in compressed carbon dioxide which is above its critical temperature ($T_c = 31.8^\circ\text{C}$) and pressure ($P_c = 73.8\text{ MPa}$) [20]. Under such conditions, CO₂ has properties between those of a liquid and a gas. Supercritical CO₂ has been used in a range of materials related applications, particularly in foaming and in emulsion templating [20–22].

In this work, we report the methanol transport properties of several nafion-composite membranes incorporating micro- and nanosized particles of zeolite (Fe-silicalite-1), amorphous silica and *in situ* crystallized Fe-silicalite-1, and compared them to an unmodified commercial nafion-115 membrane. In the prepara-

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tion of these composites, supercritical carbon dioxide (sc-CO₂) treatment of some of the membranes was used prior to incorporation of the inorganic phase. Two methods of deposition of zeolites such as deposition from colloid or suspension solution and direct *in situ* synthesis inside the pores of nafion membrane were used. Very low methanol permeability was achieved for composite membranes that were prepared using a colloidal intercalation route (from colloidal Fe-silicalite-1 as well as silica solution) and from *in situ* synthesis of Fe-silicalite-1 inside the pores of nafion membrane.

2. Experimental

2.1. Synthesis of Fe-silicalite-1

Fe-silicalite-1 was synthesized via a hydrothermal reaction in a 50 ml stainless steel autoclave according to method slightly modified to that reported elsewhere [23]. Tetraethoxysilane, tetrapropylammonium hydroxide, deionized water and iron(III) nitrate pentahydrate were mixed at molar ratio of 1:0.4:20:0.019 and left for crystallization in autoclave at temperature 150 °C for 30 and 12 h to obtain Fe-silicalite-1 suspension ($d_{\text{particles}} > 1 \mu\text{m}$) and colloid ($d_{\text{particles}} \approx 0.1 \mu\text{m}$), respectively. The suspension obtained was then converted into H-form by treating with ammonium hydroxide, followed by filtering, drying, calcinating and suspending in distilled water. The as prepared colloid was used without any treatment. According to the XRD analysis performed by HZG-4 analyzer with Cu K α radiation at 2θ range of 5–50°, samples structures were typical for ZSM-5 zeolite.

2.2. Supercritical CO₂ treatment

A typical experimental set up was as follows. The membranes were loaded into the stirred Parr reactor (450 ml volume), which was filled with CO₂ at 50 Bar by withdrawal cylinder. The temperature was then raised to 45 °C and the pressure in the vessel was increased using a chilled syringe pump (Isco 100D model). At the end, the pressure was released gradually over 15 min for each experiment.

2.3. Preparation of nafion–zeolite composite membranes

Prior to impregnation, pure nafion-115 membranes were treated in 2 M H₂O₂, 1 M H₂SO₄, and distilled water, respectively, in order to remove organic impurities and increase protonic conductivity. Each treatment step was carried out at 80 °C for 1 h. Furthermore, selected membranes (hereafter denoted as sc-naf-) were additionally treated in supercritical CO₂ at 45 °C and 13.1–13.8 MPa for 2 h. Inorganic modifications of all nafion-115 membranes were performed by the following four methods: (1) immersing in as-synthesized Fe-silicalite-1 colloid solution at room temperature for 24 h under intensive stirring (samples sc-naf-coll and naf-coll); (2) immersing in as-synthesized Fe-silicalite-1 suspension solution at the same conditions, followed by drying (sample sc-naf-susp); (3) *in situ* synthesis of Fe-silicalite-1 nanoparticles inside the pores membrane (sample sc-naf-zeol); (4) immersing in pre-silicalite

sol (sample sc-naf-sol). All thus prepared composite membranes were then consequently treated by H₂O₂, H₂SO₄ and deionised water at 80 °C for 1 h per step.

2.4. Methanol permeability

Methanol permeability was determined at 50 °C using pervaporation cell. One part of the cell is flushed by 1 M methanol–water solution, while the other part is blown by pure air at variable velocity. The flux of methanol into gas phase was measured by chromatographic method and plotted against the air velocity. The region where the value of methanol flux into gas phase does not depend upon the air velocity, which means that all methanol molecules passed through membrane are discharged, was obtained and taken for calculation of methanol permeability.

2.5. Proton conductivity

Proton conductivity was measured at room temperature using two-electrode scheme. Stainless steel electrodes are 1.5 mm in diameter. Before measurements membranes were immersed in distilled water for 2 days. The resistivity was obtained by impedance spectroscopy in the 100 kHz–10 MHz frequencies region using the low-frequency signal generator and oscilloscope. The difference of the simple mean of resistivities of one- and two-layer of membrane were taken.

2.6. Water uptake

Membranes were swelled in distilled water for one day, followed by weighing. After this procedure membranes were dried for 1 day in exsiccator over sodium hydroxide powder, followed by another weighing. Water uptake was determined by the difference between the weights of dry and swelled membranes. Such a method does not produce any structure changes of nafion and was checked to give the same results as that of drying in oven at 80 °C.

3. Results and discussion

The characteristics of synthesized composite membranes and virgin commercial nafion-115 membrane are listed in Table 1.

Methanol permeability of the pure nafion membrane equals to $2.5 \times 10^{-6} \text{ cm}^2/\text{s}$, which is in agreement with the literature data (1.7×10^{-6} to $7.3 \times 10^{-6} \text{ cm}^2/\text{s}$) [6,7,24–26]. Its proton conductivity was measured at 61 mSm/cm which is also in agreement with the range reported in the literature (13–95.3 mS/cm) [6,26–28]. Treatment of a pure nafion membrane in supercritical CO₂ (sample sc-naf) resulted in a pronounced decrease of both the methanol permeability (80% that of pure nafion) and proton conductivity (to 57% of the value for pure nafion). This is in line with the reduction of water uptake from 25 to 16%. Impregnation of the non-activated nafion membrane with colloidal Fe-silicalite-1 (sample naf-coll), leads to a three-fold reduction of both methanol permeability and proton conductivity. However, the selectivity of such a composite is still close

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