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Mesostructured-aluminosilicate-Nafion hybrid membranes for direct methanol fuel cells

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ABSTRACT

Organic–inorganic hybrid membranes are prepared from Nafion and acid functionalized aluminosilicate with varying structures and surface areas. Acid-functionalized mesostructured aluminosilicate with cellular foam framework (Al-MSU-F type) of surface area 463 $m^2 g^{-1}$, acid-functionalized aluminosilicate molecular sieves (Al-HMS type) of surface area 651 $m^2 g^{-1}$ and acid-functionalized mesostructured aluminosilicate with hexagonal network (Al-MCM-41 type) of surface area 799 $m^2 g^{-1}$ have been employed as potential filler materials to form hybrid membranes with Nafion. The structural behavior, water uptake, ion-exchange capacity, proton conductivity and methanol permeability of the hybrid membranes are extensively investigated. Direct methanol fuel cells (DMFCs) with Al-HMS-Nafion and Al-MCM-41-Nafion hybrid membranes deliver respective peak power-densities of 170 mW cm^{-2} and 246 mW cm^{-2}, while a peak power-density of only 48 mW cm^{-2} is obtained for the DMFC employing pristine recast-Nafion membrane under identical operating conditions. The unique properties associated with hybrid membranes could be exclusively attributed to the presence of pendant sulfonic-acid groups in the filler materials, which provide proton-conducting pathways between the filler and matrix in the hybrid membranes, and facilitate proton transport with adequate balance between proton conductivity and methanol permeability.

1. Introduction

Direct methanol fuel cells (DMFCs) are being projected as one of the most attractive power sources for portable devices such as cellular phones, laptop computers and other personal digital-assistants [1–8]. However, methanol crossover from anode to cathode through the polymer electrolyte membrane in a DMFC results in parasitic loss of methanol fuel with consequent mixed-potential at the cathode that affects the fuel-cell voltage by 40–100 mV at a given current density [9–17]. Hence, designing suitable polymer electrolyte membranes to reduce methanol crossover is a subject of current R&D on DMFCs. At present, perfluorosulfonic acid membranes with a hydrophobic backbone and hydrophilic sulfonic acid pendant side chain, such as Nafion, are being widely used in DMFCs. However, Nafion membranes suffer from high methanol permeability due to the solvated protons through the water-filled ion-cluster channels [18,19]. To extend the performance of DMFCs, undesirable methanol crossover through the membrane electrolytes needs to be reduced whilst retaining their good proton conductivity and mechanical stability [20–22].

In the literature [23–38], several efforts have been expended to realize organic–inorganic composite membranes for DMFCs by incorporating silica [23–28], titania [29–31], zirconia [32–34], zeolites [35], and heteropolyacids [36–38], in the Nafion moiety. These composite membranes with inorganic fillers do restrict methanol crossover but their poor proton conductivity limits their acceptance in advanced DMFCs. Characteristics of Nafion-based hybrid membranes significantly differ with the nature of inorganic filler materials, namely their structural properties, composition and the method of impregnation to the host matrix. In the light of the foregoing, newer materials with advanced synthetic protocols for realizing suitable filler materials and their impregnation into Nafion matrix are highly desirable.

Aluminosilicates are proton conductors with strong Brønsted acidity even at elevated temperatures [39], they are quasi-solid electrolytes in which protons move along the hydrogen bonds [40]. Accordingly, the diffusion rate for protons in aluminosilicates is expected to be similar to the aqueous solutions. Furthermore, porous aluminosilicate materials have been found to be attractive due to their textural and surface features, namely highly ordered-structures, high surface-area, and wide pore-range/pore-size distribution [41–44]. Porous morphology of aluminosilicates

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facilitates specific ionic-interactions with the host matrix, and enhances water-uptake and other related properties of the composite membranes. Lavorgna et al. [45], studied transport properties of zeolite Na-X-Nafion membranes and demonstrated that their proton conductivity and selectivity can be significantly improved in relation to Nafion. It has been found that the size of Na-X zeolite particles plays a seminal role in the proton conductivity and methanol permeability. Chen et al. [46], also showed that Nafion-zeolite Beta composite membranes can be successfully used to improve the performance of DMFCs. These membrane electrolytes when tested in a DMFC with 1 M methanol feed exhibit higher power density than those with pristine Nafion-115 membranes.

The present study describes a rational choice for three different types of aluminosilicates, namely aluminosilicate mesostructured cellular foam framework Al-MSU-F, aluminosilicate molecular sieve Al-HMS, aluminosilicate with mesostructured hexagonal network Al-MCM-41, with varying structures and surface areas for incorporating in Nafion matrix to form a hybrid. Prior to their incorporation in the host matrix, these fillers are acid functionalized to provide continuous proton-conducting pathways between the filler and the matrix. To the best of our knowledge, such types of hybrid membranes are unique for its application in DMFCs. Interestingly, these hybrid membranes exhibit a significant reduction in methanol permeability and foster an enhancement in the performance of DMFCs.

2. Experimental

2.1. Materials

Aluminosilicate with mesostructured cellular foam framework, Al-MSU-F (particle size 300 nm), aluminosilicate molecular sieves, Al-HMS (particle size 0.74 μm), aluminosilicate with mesostructured hexagonal network MCM-41 (particle size 100 nm) were procured from Sigma–Aldrich. Nafion ionomer (5 wt.%) was procured from Du Pont. Sulfuric acid was procured from Merck, Germany. Toray TGP-H-120 was procured from E-tek (US). Vulcan XC 72R carbon was procured from Cabot Corporation (US). Pt–Ru (60 wt.% in 1:1 atomic ratio) and Pt/C (40 wt.% Pt on Vulcan XC-72R carbon) were obtained from Alfa Aesar (Johnson Matthey) Ltd. All chemicals were used as received. De-ionized water (18.4 MΩ cm) used for experiments was produced by a Millipore system.

2.2. Acid functionalization of aluminosilicates and fabrication of hybrid membranes

To create pendant sulfonic acid groups in the filler materials, acid functionalization was conducted separately with 1 g each of aluminosilicate materials in 100 mL aq. 0.5 M sulfuric acid solution in a round bottom flask. The solution was stirred continuously at 80 °C under reflux condition for 12 h. The products were recovered by filtration and washed copiously with de-ionized water until it reached neutral pH. The resulting powder was dried overnight at 80 °C. Acid functionalized aluminosilicate-Nafion hybrid membranes were prepared by solution-casting method. The required amount of aluminosilicate material was dispersed in 5 wt.% commercial Nafion solution (Du Pont) and the resultant admixture was ultra-sonicated for 30 min followed by mechanical stirring for 12 h. The admixture was then transferred to a Plexiglass plate and dried overnight at 70 °C under vacuum. For comparison, 5 wt.% Nafion solution was re-cast in a similar manner without any filler materials. Membranes thus formed were peeled by adding water followed by thermal treatment at 100 °C for 24 h to ensure their thermal stability. Thickness of all the finished membranes was ~170 μm.

2.3. Characterization

2.3.1. Physical and structural characterization

Textural and surface properties of aluminosilicates before and after functionalization were studied by N_2-physisorption and temperature-programmed desorption, respectively. Nitrogen adsorption–desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2020. Total surface area and pore volumes were determined using Brunauer–Emmett–Teller (BET) equation and the single-point method, respectively. Pore-size distribution (PSD) data were obtained by Barrett–Joyner–Halenda (BJH) method and the position of the maximum in PSD was taken as the average pore-diameter.

Al-MSU-F, Al-HMS and Al-MCM-41 before and after functionalization were examined under a 200 kV Tecnai-20 G2 transmission electron microscope (TEM) for determining pore size and structure. The samples were suspended in acetone with ultrasonic dispersion for 3 min. Subsequently, a drop of the suspension was deposited on a holey carbon grid followed by drying. TEM images for the samples were recorded both in the axial and perpendicular directions of the pores. Images were recorded with a Multiscan CCD Camera (Model 794, Gatan) using low-dose condition.

2.3.2. Proton-conductivity measurements

Proton-conductivity measurements were performed for the membranes using four-probe DC method [47]. In brief, four probes were placed on a flat surface of the membrane and the current was passed through two outer electrodes while the floating potential was measured across the inner pair. To prevent carrier injection, the membrane surface was mechanically lapped with machinable Teflon sheet and probes were kept in a closed glass-container. Proton-conductivity data for the membranes were measured under fully-humidified condition (100%) by keeping de-ionized water at the bottom of the test container and equilibrating it for ~24 h. Subsequently, conductivity measurements were carried out at 30 °C and 80 °C. The resistivity of the membranes was calculated from Eq. (1) following Valdes [48].

$$\rho_o = \frac{V}{I} \times 2\pi S \tag{1}$$

In Eq. (1), ρ_o is resistivity in Ω cm; V is the voltage in V; I is current in A and S is the probe distance in cm (0.2 cm-fixed).

Since the bottom surface was non-conducting, correction factor for the membranes was obtained from Eq. (2):

$$G_7\left(\frac{W}{S}\right) = \frac{2S}{W}\log_e 2 \tag{2}$$

In Eq. (2), W is the thickness of the membrane in cm.

Final resistivity of the membranes was obtained using Eq. (3):

$$\rho = \frac{\rho_o}{G_7(W/S)} \tag{3}$$

Proton conductivity of the membranes was obtained from Eq. (4):

$$\sigma = \frac{1}{\rho} \tag{4}$$

In Eq. (4), σ is the proton conductivity of the membrane in S cm^{-1} and ρ is corrected resistivity in Ω cm.

2.3.3. Water-uptake measurements

Water-uptake measurements were carried out for pristine recast-Nafion and aluminosilicate-Nafion hybrid membranes. Before subjecting the membranes to sorption, the membrane samples were dried at 100 °C for the removal of moisture. Dry membrane sample weights (W_o) were measured and equilibrated in de-ionized water for 24 h at room temperature. The membranes were surface blotted and sorbed membranes were weighed (W_∞).