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Crosslinked poly(ethylene glycol) (PEG)/sulfonated polyhedral oligosilsesquioxane (sPOSS) hybrid membranes for direct methanol fuel cell applications

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ABSTRACT

Organic–inorganic hybrid crosslinked membranes based on poly(ethylene glycol) (PEG) and sulfonated polyhedral oligomeric silsesquioxane (POSS-SO_3H) with urethane crosslinks were prepared as candidate materials for a proton exchange membrane for direct methanol fuel cells (DMFC). Infrared (FT-IR) spectroscopy and ion exchange capacity measurements for the hybrid revealed the POSS is incorporated as a part of the crosslinked network. We found that proton conductivity increased and methanol permeability decreased with increasing POSS content in the hybrid membrane. In particular, our hybrid membranes demonstrated proton conductivities comparable to that of Nafion 117 while exhibiting lower methanol permeability as compared to Nafion 117. We postulate that the polar sulfonic acid groups of the incorporated sPOSS cages assemble to provide ion conduction paths while the hydrophobic portions of the same sPOSS cages combine to form a barrier to methanol permeation of the hybrid membrane.

1. Introduction

Fuel cell technologies based on proton exchange membranes has received rapidly extensive attentions during the past decade, largely owing to the many advantages offered over existing energy technologies. Among various fuel cells, direct methanol fuel cells (DMFCs) employing polymer electrolyte membranes are considered to be the most attractive power sources for portable devices or transportation applications because it has high energy density at low operating temperature and its fuel can be handled easily and inexpensive [1]. The requirement for the polymer to be employed as electrolyte membranes for DMFC is the high proton conductivity and low methanol permeability. Nafion^{TM}, a perfluorinated ionomer, is the most commonly used polymer for electrolyte membrane for fuel cells. Despite its attractively high proton conductivity and chemical stability, Nafion^{TM} has the disadvantage of high cost and high methanol crossover. The high methanol permeability allows undesirable transport of methanol from the anode side of the fuel cell, through the membrane, and to the cathode side, a phenomenon known as methanol crossover. As a consequence, excessive methanol permeability of any polymer electrolyte membrane leads to an unacceptable decrease in cell performance [2–4].

To overcome these drawbacks, modification of Nafion or development of new materials have been proposed. Of the several approaches to develop new membranes for DMFC, crosslinked organic–inorganic hybrid membranes have been explored extensively because they have several advantages in providing physical barrier against methanol crossover with improved mechanical and thermal stability [5–15]. For example, Thangamuthu et al. synthesized the crosslinked PEG/SiO_2 hybrid membranes for DMFC applications through sol–gel process, and the network doped with 4-dodecylbenzene sulfonic acid was to provide the hybrid membrane with proton conducting behavior [12,13].

Recently, membranes based on polymer/polyhedral oligomeric silsesquioxane (POSS) hybrids are reported by several research groups [14–19]. POSS features a well-defined nanosized Si–O cage structure (Si_8O_{12}) with additional organic functional groups covalently bonded to each vertex Si on the cage. By adjusting the external organic functional groups, the POSS nanoparticles can be incorporated into various polymers by simple blending or chemical grafting to provide proton conducting behavior with high thermal and dimensional stability as well as with greatly lowered methanol permeability. We reported on the polyvinyl alcohol (PVA)/sulfonated POSS (sPOSS) hybrid membranes by crosslinking reaction, and found that it offer great potential for use as polymer electrolyte membranes for DMFC applications [14].

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In the present work, we prepared crosslinked hybrid membranes based on poly(ethylene glycol) (PEG) and the sPOSS with urethane linking structure, and the structure of the hybrids and their performance as a PEM in DMFC was investigated.

2. Experimental

2.1. Materials

The polyethylene glycol (PEG) used in this study (98–99% hydrolyzed, average $M_w = 4600$), polyisocyanate (Desmodur N3600, Bayer), and 4-hydroxybenzenesulfonic acid (65 wt% solution in water) were purchased from Sigma–Aldrich Chemical (Milwaukee, WI, USA). Sulfonated POSS (sPOSS), as shown in Fig. 1, was synthesized by reacting a POSS triepoxide (triglycidyl isobutyl POSS, EP 0423, Hybrid Plastics Co., USA) – a POSS bearing three glycidyl groups – with 3 equivalents of 4-hydroxybenzene sulfonic acid. The synthetic procedure was described in detail in previous paper [14].

2.2. Preparation of membrane

To prepare PEG/sPOSS hybrid membranes, PEG was completely dissolved in 20 mL acetonitrile at room temperature. Separately, sPOSS was dissolved in 10 mL acetonitrile with the aid of ultrasonication. The sPOSS solution was added to the PEG solution in an amount to yield PEG/sPOSS weight ratios of 80/20, 70/30, 60/40, or 50/50. The resulting clear solution was then stirred vigorously for 6 h, at which the blend solution was maintained as a clear solution. Polyisocyanate was added to PEG/sPOSS blend solution at a level of [OH]/[NCO] = 1/1.05 with a small amount of dibutyltin dilaurate as a catalyst for the formation of urethane linkage. The reaction mixture was stirred at room temperature for an additional 30 min, following which it was cast into a Teflon™ dish for drying at 70 °C for 6 h to induce urethane linking crosslinked structure. The crosslinked PEG/sPOSS films were next dried in a vacuum oven at room temperature for 48 h, followed by immersion in a large volume of acetonitrile for 24 h at 80 °C to extract unreacted PEG and sPOSS. Finally, the crosslinked and extracted samples were immersed in deionized water to remove acetonitrile, with the water being changed at least 3 times, followed by exhaustive drying under vacuum.

The chemical bonding within the membranes was examined using attenuated total reflectance infrared (ATR-IR) spectroscopy (Varian 800 FT-IR) with a wave number resolution of 4 cm^{-1} and range of 400–4000 cm^{-1}.

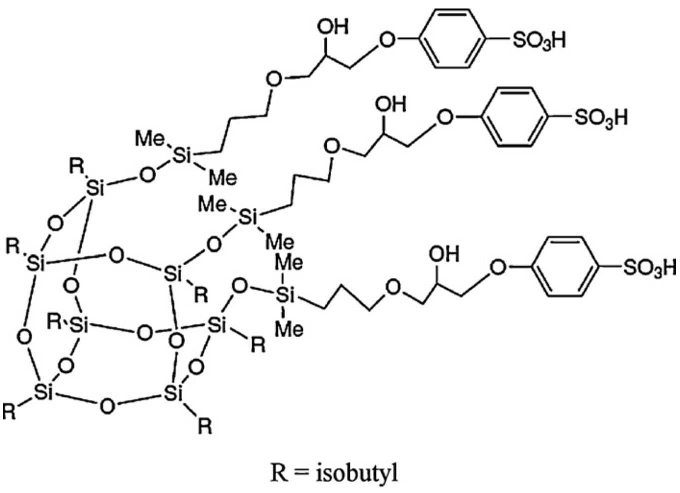

Fig. 1. Structure of sPOSS used in the study.

2.3. Water uptake

Samples for water swelling analysis were dried in vacuum at 40 °C for 48 h, and then cut into 2 cm × 2 cm squares, each sample then being weighed in the dry state before swelling in water at room temperature (20 °C). Afterwards, samples were immersed in deionized water for at least 24 h, dabbed for removal of surface water, and then immediately weighed. Water uptake was calculated by the following equation:

$$\text{Water uptake}\ (\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \tag{1}$$

2.4. Ion exchange capacity

The ion exchange capacity (IEC) was measured using the classical titration method. After immersing samples in distilled water, they were soaked in a large volume of 0.1 M HCl solution to fully protonate the acid functionalities. They were then washed with distilled water to remove excess HCl and equilibrated with 20 mL of 2 M NaCl solution for at least 24 h to effect ion exchange of Na^+ for H^+. Next, the remaining solution was then titrated with a 0.1 M NaOH solution using phenolphthalein as an indicator, allowing measurement of the number of ionizable groups within the sample; i.e., those groups that released protons into solution during ion exchange. The IEC value (in meq/g) is defined as milliequivalents of sulfonic groups per gram of dried sample, and obtained from the following equation:

$$\text{IEC} = \frac{M_{H^+}}{W_{\text{dry}}} \tag{2}$$

where M_{H^+} is milliequivalents of H^+ released during ion exchange and W_{dry} is the weight of dried membrane (g).

2.5. Proton conductivity

The proton conductivity of membranes was measured using the four-point probe technique at relative humidity 95%. The impedance of the membranes was measured using a HP 4192A LF Impedance Analyzer. The impedance analyzer was operated in galvanostatic mode with AC current amplitude of 0.1 mA over frequency range from 100 kHz to 0.1 Hz. Each sample was cut into strips that were approximately 1.0 cm wide and 4.0 cm long prior to being mounted on the cell. Measurements were carried out at various temperatures and the proton conductivity (σ) was obtained using the following relation:

$$\sigma = \frac{l}{RS} \tag{3}$$

where σ is the proton conductivity (S/cm), l is the distance between the electrodes used to measure the potential (cm), R is the measured impedance of membrane (Ω), and S is the cross-sectional area of the membrane (cm^2).

2.6. Methanol permeability

Methanol permeability of the membranes was determined using a diffusion cell described by Kim et al. [10]. This cell consists of two reservoirs of distinct composition (discussed below), each approximately 48 mL, partitioned by a vertical membrane. Each reservoir of the diffusion cell was slowly stirred during the experiment. Prior to apparatus assembly, the partitioning membranes were equilibrated in distilled water for at least 24 h. To drive methanol diffusion across the membranes, one reservoir contained a 2 M aqueous methanol solution while the other