



Short communication

Nafion[®]/bio-functionalized montmorillonite nanohybrids as novel polyelectrolyte membranes for direct methanol fuel cells

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ABSTRACT

Polyelectrolyte membranes based on Nafion[®] and bio-functionalized montmorillonite (BMMT) with chitosan biopolymer, as polycationic intercalant were fabricated by solvent casting method. X-ray diffraction analysis confirmed the exfoliated structure of clay. Methanol permeability results revealed that the presence of 10 wt% BMMT in synthesized nanohybrid membranes can reduce the permeability to $5.72 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ in comparison with 2.00×10^{-6} for that of Nafion[®] 117. However proton conductivity of nanohybrids was decreasing with increasing BMMT loading, but obtained values were indicating the lower sacrificing of conductivity in comparison with membranes based on unmodified MMT. According to selectivity parameter, membranes containing 2 wt% of BMMT showed optimum properties. It was suggested that improvement of transportation properties could be due to the electrostatic interaction between amino groups of chitosan and Nafion[®] sulfone groups. Considering the suitable thermal stability, low methanol crossover and appropriate proton conductivity properties, Nafion[®]/BMMT nanohybrid membranes, could be proposed as novel polyelectrolytes for direct methanol fuel cell application.

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1. Introduction

Fuel cell is considered as one promising green, reliable and highly efficient power generation technology in 21st century [1,2]. Among the various types of fuel cells, direct methanol fuel cells (DMFCs) due to their low weight, high energy density, simple design, low emission and the ease of handling their liquid fuel, are suitable for portable electronic devices and transportation applications.

The key part of DMFCs is proton exchange membrane (PEM). The role of PEM is to provide proton conduction from the anode to the cathode and indeed it acts as an effective separator of the anode (methanol) and cathode (oxygen) reactants. In such an application, perfluorosulfonic polymers show optimal characteristics as solid electrolytes for polymeric electrolyte fuel cells [3]. The most common and commercialized member of this family of polymers is Nafion[®], which is supplied by DuPont. This unique polymer fulfills mechanical strength and chemical/thermal stability as well as high proton conductivity. In spite of these desirable properties,

high methanol crossover and high cost are its critical limitations for DMFCs commercialization [4,5]. Therefore, to reach high performance membranes, methanol permeability should be reduced. In this respect, it is suggested a remarkable reduction of methanol permeability could be achieved by modifying the size of the proton transport nanochannels, developing new types of ionomers and introducing tortuous pathways [6,7]. It is proposed that tortuous pathways could be made by dispersing inorganic fillers. The exfoliation of layered silicate nanosheets in the polymer matrices can provide high barrier properties and improve thermal and mechanical properties [8,9]. The most common nanoclay which is used to prepare polymeric nanocomposite is montmorillonite (MMT) [10].

In recent years, different methods have been used to improve Nafion[®] performance. Lee and coworkers fabricated a composite polyelectrolyte based on Nafion[®] and perfluorinated sulfonic acid functionalized MMT and reported an enhancement in proton to methanol selectivity of nanocomposite polyelectrolytes containing modified MMT [6,11]. They showed that using these sulfonated MMT not only decrease the methanol permeability, but also retain the proton conductivity of membranes. Furthermore, it has been investigated that mixing of negatively charged Nafion[®] and positively charged polyelectrolytes leads to the formation of a complex and miscibility enhancement. Created electrostatic interaction could lead to improvement of transport properties, moderate

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swelling, high thermal stabilities and improve mechanical properties [12,13]. Considering two mentioned phenomena, the aim of this research is to combine these two effective mechanisms. So, we used functionalized MMT with a positively charged polymer which could form a polyelectrolyte nanohybrid with Nafion®.

In current study, at first montmorillonite was functionalized with chitosan polycationic biopolymer as Bio-modified MMT (BMMT) and then nanohybrids with different loading weights of BMMT were fabricated. Obtained results of this novel nanohybrid membrane were compared with unfunctionalized MMT. According to our knowledge, to date, this class of polyelectrolyte complexes has not been studied as a candidate for DMFC applications.

2. Experimental

2.1. Materials

Chitosan (molecular weight 280,000 g mol⁻¹, degree of deacetylation 83%) was supplied by Fluka. Acetic acid and methanol were obtained from Merck. All other analytical-grade reagents from commercial sources were used without further purification. K-10 montmorillonite clay was purchased from Fluka and used as unfunctionalized MMT. Deionized water (purified with Milipore™) was used in this work. Nafion® 5 wt% solution in water and low molecular weight alcohols was acquired from E.I. DuPont de Nemours Company for membrane formation. Nafion® 117 membranes, from DuPont were used for comparison of properties.

2.2. Modification process of MMT

Modification of MMT with chitosan was carried out according to previously reported method [14]. Briefly, 1 g of MMT was dispersed in 50 mL of deionized water and certain amount of chitosan was separately dissolved in 1% (v/v) acetic acid aqueous solution. Both mixtures were then poured in an Erlenmeyer flask. The prepared mixture was stirred at 60 °C for 48 h. After the heating treatment, the mixture was centrifuged, and then washed with acetic acid solution and water. The product was dried in an air circulating oven at 60 °C for 6 h. It was ground and kept in glass capped bottle for further usage.

2.3. Membrane preparation

BMMT at various loadings (1.0, 2.0, 3.0, 5.0 and 10.0 wt%) was suspended in Nafion® solution at 25 °C and stirred for 2.5 h. The resultant mixture was ultra-sonicated for five successive 30 min intervals and concentrated in a rotary evaporator. The viscose solution was casted on Petri dishes and incubated at 25 °C for one night and then dried at 70 °C for 8–10 h. Finally, fabricated membranes were annealed at 120 °C overnight. Similar procedure was carried out to prepare membranes based on Nafion®/unfunctionalized MMT. Subsequently, prepared membranes were modified according to following procedure: At first, all membranes were boiled in hydrogen peroxide (3 vol%, for 30 min), washed several times with deionized water and boiled for 1 h in deionized water. Membranes were then boiled in sulfuric acid (0.5 molar) for another hour and washed several times with deionized water. The neat Nafion® membranes were modified by the same modification procedure.

2.4. Characterization

2.4.1. X-Ray diffraction

Dispersion of MMT particles in the membranes were detected by XRD (SIEMENS XRD-D5000 diffractometer, Cu-K α). The scanning diffraction angle, 2θ , was less than 15°.

2.4.2. Thermogravimetry analysis

The degradation process and the thermal stability of the MMT, BMMT and obtained nanohybrid membranes were investigated by TGA (Perkin-Elmer Pyris1). The approximately 10–20 mg of fully dried samples were characterized with a heating rate of 10 °C min⁻¹.

2.4.3. Proton conductivity

The conductivity was calculated from $\sigma = LR^{-1}A^{-1}$ equation, where, L is the membrane thickness, A is the cross sectional area of the membrane sample and R is the resistance [15]. In this study, the conductivities were measured using membranes with the same relative humidity (RH), which was fixed for all samples. The conductivity cell was set into the humidity chamber at 25 °C and 95%RH for at least 3 h before the measurement.

2.4.4. Methanol permeability

The methanol diffusion coefficient was measured via a two-compartment glass diffusion cells. Methanol solution was placed on one side of the diffusion cell (cell A) and pure water was placed on the other side (cell B). Cell A was filled with a solution of methanol (10 wt%) in deionized water. The solution in each compartment was continuously stirred to ensure uniformity. The concentration of the methanol in cell B was measured by gas chromatography. The methanol diffusion coefficient was determined using following equation:

$$P = \frac{1}{C_A} \left(\frac{\Delta C_{B(t)}}{\Delta t} \right) \left(\frac{LV_B}{A} \right)$$

where P is the methanol diffusion permeability of the membrane (cm² s⁻¹), C_A is the concentration of methanol in cell A (mol L⁻¹), $\Delta C_B/\Delta t$ is the slope of the molar concentration variation of methanol in the cell B as a function of time (mol L⁻¹ s), V_B is the volume of each diffusion reservoir (cm³), A is the membrane area (cm²) and L is thickness of the membrane (cm) [8].

3. Results and discussion

As is well-known, polymer–clay nanocomposites are materials of increasing interest due to their desirable functional features. Nanoclays are usually intercalated to increase their interlayer region [16]. Although scarcely applied, positively charged polymers can be intercalated in nanoclays following cationic exchange reactions. Thanks to the cationic nature of chitosan in acidic media, this biopolymer also appears as an excellent candidate for intercalation in Na⁺–MMT via cationic exchange processes [17]. In present research, MMT with negative surface charges was modified with chitosan cationic polysaccharide, as a macromolecular intercalant. Amino groups of chitosan in acidic solution convert to cationic form of –NH₃⁺ which is necessary for the cation exchange reaction [14].

The XRD patterns and schematic microstructures of unmodified montmorillonite, modified montmorillonite with chitosan biopolymer (BMMT) and nanohybrid based on Nafion®/BMMT are illustrated in Fig. 1. As shown, the interlayer distance between clay layers for unmodified MMT was recorded to be 12.34 Å (2θ 7.15°) (Fig. 1(i)). It was increased to 15.78 Å (2θ 5.59°) for the MMT modified with chitosan polycation (Fig. 1(ii)). This enhancement of interlayer distance in clay structure was due to the entrance of chitosan chains into gallery spaces. The intercalation of the polymer chains usually increases the interlayer spacing of nanoclay. In an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers [18]. As seen in Fig. 1(iii), when BMMT mixes with Nafion® chains, the crystalline

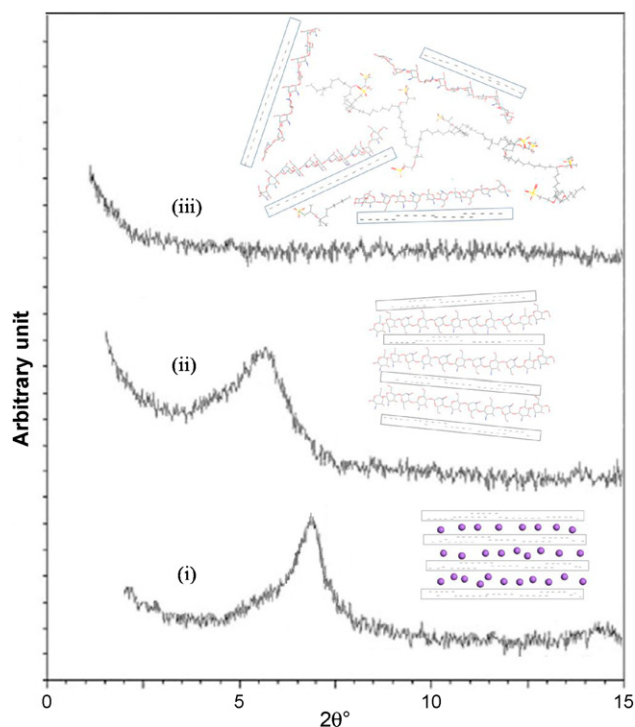


Fig. 1. XRD patterns and schematic microstructures of unmodified MMT (i); bio-modified MMT (BMMT) (ii) and Nafion®/BMMT nanohybrids (iii).

peak almost disappears. The possible exfoliated microstructure of synthesized nanohybrid is shown schematically in Fig. 1(iii).

PEMs may need to exhibit fast proton transport at high temperatures for better performance in fuel cell applications. The thermal stability and decomposition behavior of the PEMs were studied by thermogravimetry analysis (TGA). The thermograms of unmodified montmorillonite, bio-modified montmorillonite with chitosan (BMMT), Nafion® 117 and Nafion®/BMMT nanohybrid membranes are plotted in Fig. 2. It can be seen that BMMT starts to lose weight by increasing temperature to higher than 220°C in comparison with unmodified MMT (Fig. 2(a)). This observation could be explained with the decomposition initiation of chitosan intercalant chains. As displayed in Fig. 2(b), Nafion® nanohybrid membrane has shown a three-step degradation pattern. The weight loss curve of nanohy-

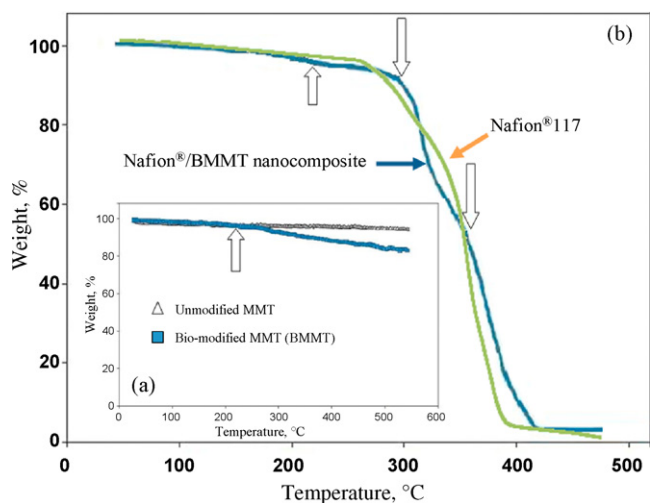


Fig. 2. TGA thermograms of (a) MMT and BMMT, (b) Nafion® 117 and Nafion®/2 wt% of BMMT nanohybrid membrane.

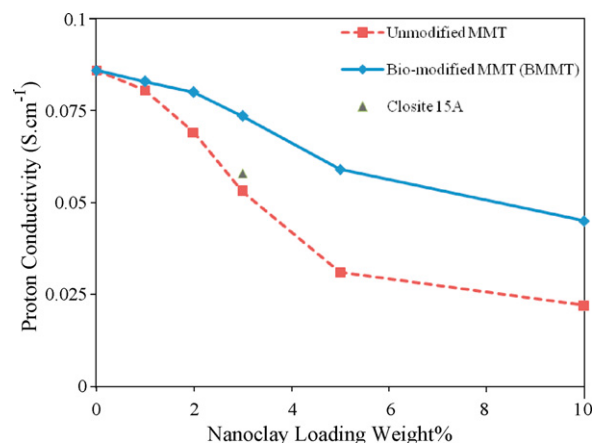


Fig. 3. Proton conductivity as a function of nanoclay loading weights for membranes based on Nafion®/MMT and Nafion®/BMMT at completely humidified state.

brid shows a slight falling region at about 220°C . This could be related to chitosan degradation as same as BMMT thermogram. The second degradation step starts at about 300°C which could be attributed to the decomposition of the Nafion® sulfonic side chains [19]. Finally a sharp decreasing region occurs after 360°C due to the degradation of PTFE backbone of the Nafion® polymer. A similar decomposition behavior is observed for Nafion® 117, except the chitosan decomposition step.

The proton conductivity behaviors of fabricated nanocomposites with different MMT and BMMT loading weights are compared in Fig. 3. As shown, the proton conduction of both kinds of nanocomposite membranes is decreasing with increasing filler loading weight. This emphasizes the effect of small particles, such as nanoclays, in separating polymer chains from each other and consequently decreasing proton conductivity. On the other hand, in the presence of filler, SO_3^- groups in the polymer chains were decreased per unit volume. From the proton conductivity comparison of Nafion®/MMT and Nafion®/BMMT nanocomposite in Fig. 3, the higher proton transporting ability of Nafion®/BMMT could be understood.

Polycationic chitosan chains were used as a macromolecular intercalating agent for functionalization of montmorillonite. Since chitosan contains both hydroxyl and amino groups, two kinds of interaction could be expectable between chitosan and Nafion®, which are (i) electrostatic interaction between ammonium ion ($-\text{NH}_3^+$) of chitosan and sulfone groups ($-\text{SO}_3^-$) of Nafion® and (ii) hydrogen bonding between Nafion® sulfone groups and hydroxyl groups of chitosan. Due to these kinds of interactions, chitosan molecules could be considered as coupling agent in nanocomposite structure. But, it should be noticed, due to the presence of protonated amine groups, chitosan itself exhibits conductivity [13] and is able to enhance the hydrophilicity of the fabricated nanohybrid. Therefore, in present application, chitosan plays the role of a functional compatibilizer.

As mentioned, solution casting technique, which is a common method to induce the exfoliation process, has been employed to prepare nanohybrid membranes. So, we could expect that the exfoliation process take place in a proper way. On the other hand, the delamination of nanosheets is less difficult in low content of nanoclay. Nonetheless, even in low content of nanoclays, still a remarkable difference could be observed between proton conductivity of BMMT nanohybrid membranes compared with MMT nanocomposites. Despite this, there might still be a little disparity in exfoliation extent which could be due to the functionalization of the MMT with chitosan. Hence, to eliminate the effect of gallery space on the exfoliation, the proton conductivity results of organi-

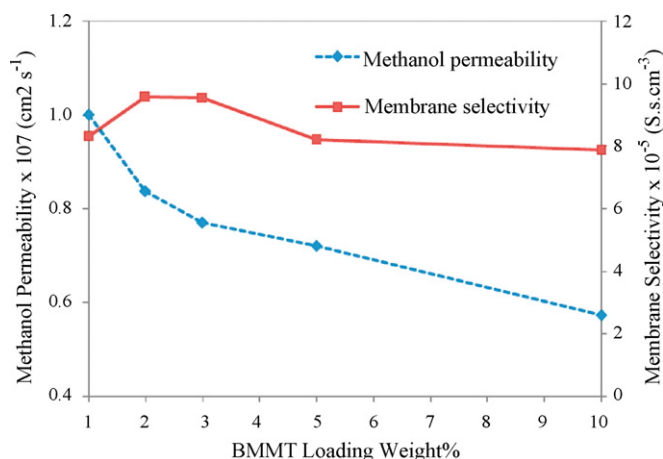


Fig. 4. Methanol permeability and membrane selectivity of Nafion®/BMMT nanohybrids at different BMMT loading weights.

cally treated montmorillonite (Cloisite® 15A, were purchased from Southern Clay Products, Inc.) at 3 wt% were measured and displayed in Fig. 3. Cloisite® 15A is a kind of commercial clay, which is treated by inserting low molecular weight alkylammonium inside their structural sheets. As seen, the proton conductivity values for MMT, Cloisite® 15A and BMMT at 3 wt% of loading were 0.053, 0.058 and 0.0735 S cm⁻¹, respectively.

As illustrated in Fig. 4, permeability results clearly demonstrate the methanol crossover has been decreased effectively thanks to the addition of BMMT. The reduction of permeability arises from the longer diffusive pathway in the presence of filler. The presence of impermeable nanosheets introduces a tortuous pathway for a diffusing penetrant.

Since the proton conductivity is a crucial property of fuel cell membranes, it should not be sacrificed in order to reduce methanol permeability. So, in the current research, we have been trying to preserve the proton conduction of membranes as much as possible and reduce the methanol crossover at the same time. This observation may be because of the ionic interaction between amino groups of chitosan intercalant chains and sulfonic side chains of Nafion®. Zhang et al. [12] have shown that interaction between negatively charged Nafion® and positively charged polybenzimidazole leads to the formation of a complex, and miscibility enhancement which could result improvement of transport properties. In present study, this hypothesis was proved by lower reduction in proton conductivity of polycation contained nanohybrids (BMMT), but through electrostatic interaction. Furthermore, in conventional nanocomposites the weak interfacial interaction between macromolecular chains and nanoparticles could cause the formation of nanovoids, which is not preferred to access the minimized methanol permeability. But, here the intercalated chitosan chains may have been acted as surface coupling agent. Permeability results showed that the presence of 10 wt% BMMT in synthesized nanohybrid membranes can reduce the permeability to $5.72 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ in comparison with $2.00 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for that of Nafion® 117.

Proton conductivity and methanol permeability are the two transport properties that determine DMFC performance. The presence of BMMT has a beneficial influence on methanol permeability

and the opposite effect on proton conductivity. For identification of the optimum composition, the membrane selectivity parameter (ratio of proton conductivity to methanol permeability) of Nafion®/BMMT nanohybrid membranes at various BMMT loadings was calculated and shown in Fig. 4. The higher selectivity value leads to a better membrane performance. As illustrated, the maximum selectivity appears at 2.0 wt% of BMMT loading. The nanohybrid membranes at this composition showed good proton conductivity (up to 0.08 S cm⁻¹), low methanol permeability (down to $8.37 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) and good processability. It could be concluded that modification of MMT with positively charged polyelectrolyte could cause better miscibility with perfluorosulfonic polymers and lead to selectivity improvement.

4. Conclusion

In current study, novel nanohybrid polyelectrolyte membranes based on functionalized montmorillonite and Nafion® have been investigated. MMT was functionalized with chitosan biopolymer and assigned as bio-modified montmorillonite. XRD patterns of Nafion®/BMMT nanohybrids membranes were featureless, indicative of the disordered and exfoliated structure of clay. Conductivity and permeability characterization of synthesized nanohybrid membranes revealed that the presence of BMMT has led to drastic reduction of methanol crossover and lower loss of conductivity properties in comparison with unmodified nanocomposite membranes with similar composition. It is proposed that observed performance enhancement could be due to ionic interaction between functional groups of chitosan polycation and negatively charged Nafion® moieties. Nafion®/BMMT nanohybrid membranes, due to their high proton conductivity, low methanol permeability and suitable thermal stability, could be considered as promising polyelectrolyte membranes for DMFC applications.

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