



Electrochemical investigation of sulfonated poly(ether ether ketone)/clay nanocomposite membranes for moderate temperature fuel cell applications

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ARTICLE INFO

Article history:

Received 18 July 2009

Received in revised form

11 November 2009

Accepted 20 November 2009

Available online 27 November 2009

Keywords:

Sulfonated poly(ether ether ketone)

Polymer–clay nanocomposites

Direct methanol fuel cells

Electrochemical performance

Moderate temperature

ABSTRACT

In the present study, polyelectrolyte membranes based on partially sulfonated poly(ether ether ketone) (sPEEK) with various degrees of sulfonation are prepared. The optimum degree of sulfonation is determined according to the transport properties and hydrolytic stability of the membranes. Subsequently, various amounts of the organically modified montmorillonite (MMT) are introduced into the sPEEK matrices via the solution intercalation technique. The proton conductivity and methanol permeability measurements of the fabricated composite membranes reveal a high proton to methanol selectivity, even at elevated temperatures. Membrane based on sPEEK and 1 wt% of MMT, as the optimum nanoclay composition, exhibits a high selectivity and power density at the concentrated methanol feed. Moreover, it is found that the optimum nanocomposite membrane not only provides higher performance compared to the neat sPEEK and Nafion[®] 117 membranes, but also exhibits a high open circuit voltage (OCV) at the elevated methanol concentration. Owing to the high proton conductivity, reduced methanol permeability, high power density, convenient processability and low cost, sPEEK/MMT nanocomposite membranes could be considered as the alternative membranes for moderate temperature direct methanol fuel cell applications.

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1. Introduction

Fuel cells are considered as the convertor of chemical energy to electricity with reduced pollution and environmental impacts [1]. Direct methanol fuel cells (DMFCs) possess several advantages over the other types of fuel cells like hydrogen-fed polymer electrolyte membrane fuel cells in the field of portable electronics and transportation usages. Methanol as a fuel produce a high power density per unit mass (6 kW h kg^{-1}) and can be handled and stored conveniently. However, the present DMFC technology encounter two major limitations; first, the poor oxidation kinetics of the fuel and second, the permeation of the methanol across the proton exchange membrane (PEM), which results in the depolarization of the cell, reduction in fuel efficiency and decreased open circuit voltage (OCV) [2–4].

The current standard PEM used in DMFCs is Nafion[®] 117. The Nafion[®] membranes present high proton conductivity at optimal water contents as well as thermal and chemical long-term stability in oxidative conditions [5]. However, Nafion[®] 117 suffers from high methanol permeability of about $2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 25°C and 2 M methanol feed, which increases at higher temperatures [6]. Hence, current researches concerned with DMFCs are focused on the development of replacement membranes to attain higher proton conductivity at higher temperatures, support an adequate water balance and reduced methanol permeation rate [7]. Over the past years, researchers have been investigating different methodologies to achieve such goals, including synthesizing new polymers with non-fluorinated backbones [8–11], sulfonation of different polymers and also incorporation of various inorganic fillers into polymeric matrices, such as montmorillonite, titanium dioxide, zirconium phosphate, silica and zeolite [12–19].

Polymer nanocomposites are hybrid systems comprising high surface area nanostructured particles [20]. The unique characteristics of polymer–clay nanocomposites arise from nanoscale dispersion of clay layers into the polymeric matrix, which strongly relies on the interfacial properties. From a morphological point of

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view, exfoliated polymer–clay nanocomposites rather than intercalated nanocomposites are considered as the ideal structures for high-performance nanocomposites [21,22].

Among non-fluorinated hydrocarbons, poly(ether ether ketone) (PEEK), because of its lower preparation cost, good film forming properties, and also chemical, thermal and mechanical stability, was shown to be promising for fuel cell applications. In different studies, sulfonation process is employed as an effective method to introduce sulfonate groups into the polymer structure to increase negative functionalities and consequently improve proton conductivity [14–17,23–27]. The reduced hydrophobic/hydrophilic nano-phase separation of sulfonated poly(ether ketone)s in comparison with perfluorosulfonic polymers results in less interconnected hydrophilic domains and consequently reduced electro-osmotic drag as well as the permeation coefficient, which are advantageous for DMFC applications [9]. The authors have recently reported the preparation and characterization of the sulfonated PEEK/organically modified montmorillonite (MMT) nanocomposites as the proton-exchange membranes for DMFC applications [14]. In this regard, commercially available organically modified MMT was selected in the present research to prepare high-performance, cost-effective and easy to prepare hydrocarbon based nanocomposite membranes to achieve reduced methanol permeability and higher open circuit voltage (OCV). Subsequently the temperature dependency of the proton conductivity and methanol permeability properties as well as the fuel cell performance of the fabricated membranes was investigated to evaluate the SPEEK/MMT membranes for moderate DMFC applications.

2. Experimental

2.1. Materials and methods

Sulfonation process of PEEK (PolyScience, Inc., USA) carried out according to the previously reported procedure [14,16]. Sulfonated PEEK samples with various Degrees of sulfonation were dissolved in *N,N*-dimethylacetamide (DMAc, Merck Chemical Co., Germany) and stirred for 24 h. Organically modified montmorillonite clay (Cloisite™ 15A) was purchased from Southern Clay Products Inc. (USA). MMT was suspended in DMAc at room temperature, stirred for 2 h, ultra-sonicated for another hour and mixed with the SPEEK solutions. The obtained mixtures were ultra-sonicated for half an hour, stirred for 8 h at 80 °C and then concentrated. The resultant viscous suspensions were cast on glass plates, incubated at room temperature for one night, 70 °C for 8–10 h and 120 °C overnight. The membranes were boiled in 3 wt% hydrogen peroxide (Merck Chemical Co., Germany) for half an hour, then washed and boiled in deionized water. Membranes were boiled again in 1 M sulfuric acid for half an hour, and washed several times with deionized water.

Nafion® 5 wt% solution in water and low molecular weight alcohols was acquired from E.I. DuPont de Nemours Company for membrane electrode assembly preparation. Nafion® 117 membranes, from E.I. DuPont Co. were used for the comparison of data.

2.2. Preparation of membrane electrode assembly (MEA)

The electrodes were prepared by catalyst decaling and painting technique [11,14–17]. Pt-black and Pt/Ru black were used as catalysts for the anode and cathode, respectively. They were mixed with a 5 wt% Nafion® solution in isopropanol and several drops of glycerol (as the suspension/painting agent). The suspension was brushed directly (4 mg cm⁻²) onto the dry membranes, and hot-pressed at 120 °C for 90 s to increase the contact area between the catalyst layer and membranes. Finally, the prepared MEAs were boiled in a dilute acidic solution.

2.3. Characterization methods

The degree of sulfonation (DS), ion exchange capacity (IEC) and water uptake measurements were performed in accordance with the previous reports [14–17]. The proton conductivity of hydrated membranes was measured at room temperature via the AC impedance method. Impedance measurements were made using a Solartron Interface 1260 gain phase analyzer, over the frequency range of 1 Hz to 10 kHz. The conductivity was calculated through the equation of $\sigma = L/(RA)$, where L is the membrane thickness, A is the cross-sectional area of the membrane and R is the resistance.

The conductivity measurements have been performed using BT-112 Conductivity Cell, BekkTech LLC. This Conductivity Cell has been designed for an in-plane, 4-point probe measurement to obtain the bulk conductivity of membranes. The conductivity of the membranes was measured at the relative humidity (RH) of 95%, which was fixed for all samples. To get an insight into the temperature dependency of proton conductivities, conductivity measurements were also performed in the temperature range of 25–80 °C in the current research. The conductivity cell was set into the humidity chamber (Espec SH-2) at 95%RH and 25 °C and for at least 3 h before the measurement. Subsequently, the temperature was raised and the conductivity data at higher temperatures were collected.

The methanol permeability was measured using 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). The solution in each compartment was continuously stirred to ensure homogeneity. Then, the concentration of the methanol in cell B was measured by gas chromatography method. The methanol permeability was determined as follows:

$$C_{B(t)} = \frac{A}{V_B} \frac{DK}{L} C(t - t_0) \quad (1)$$

where, $C_{B(t)}$ is the concentration of methanol in cell B (in mol L⁻¹), DK is the methanol permeability (in cm² s⁻¹), C is the concentration of methanol in cell A (in mol L⁻¹), V_B is the diffusion reservoir volume (in cm³), A is the membrane area (in cm²) and L is thickness of the membrane (in cm). To evaluate the membranes at elevated temperature, methanol permeability measurements have also been performed at 50 and 70 °C.

DMFC performance tests of the manufactured membranes were investigated using a laboratory single cell DMFC. The cell was made from four 316 stainless steel (end plates and flow fields), two carbon papers (gas diffusion layers, GDL, TGP-H-120 Toray) and a membrane electrode assembly. Silicon rubber was used to seal the internal sections. Single cell performance was evaluated at two different methanol concentrations: 1 and 5 M. Methanol was fed to the anode side at 20 psi back pressure for 1 h. Oxygen was introduced at the cathode side with gradual pressure increase to 20 psi, and the cell was allowed to run for half an hour before collecting polarization curves. All single cell tests were conducted three times, and the results are presented as the average data.

3. Results and discussion

Sulfonation is a process of introducing sulfonate groups into the polymer chains in order to increase negative charges for better proton conductivity. Hence, poor proton conductivity of PEEK has been improved through the sulfonation reaction in this study. It has been proposed that the PEEK structure is sulfonated by reaction with concentrated sulfuric acid [26] or chlorosulfonic acid [28]. Since sulfonation with chlorosulfonic acid may lead to chemical degradation of polymer chain, sulfuric acid was used in the present research. The sulfonation rate and the extent of sulfonation in the presence

Table 1
Obtained physical properties of the sPEEK at room temperature.

Degree of sulfonation (%)	Reaction time (h) ^a	Membrane thickness (μm) ^a	Ion exchange capacity (mequiv. g^{-1}) ^b	Water uptake (%) ^b	Proton conductivity (S cm^{-1}) ^b	Methanol permeability $\times 10^7$ ($\text{cm}^2 \text{s}^{-1}$)	Membrane selectivity (S s cm^{-3}) ^c
41	30	103	1.2	23	0.011	2.68	34268
43	35	100	1.27	24.5	0.012	2.81	34783
49	50	97	1.42	28.1	0.0157	3.11	34889
62	70	110	1.7	40.5	0.0194	5.5	35273
69	90	114	1.88	47	0.023	6.8	34074
70	95	110	1.93	48	0.024	6.9	33333
82	110	107	2.2	75	0.032	10.7	31683
89	120	130	2.38	Soluble	–	–	–

^a These results are mean value of at least three trials for each sample and standard variation not exceeded 10%.

^b Results from our previous study [14].

^c Proton conductivity to methanol permeability ratio.

of sulfuric acid could be controlled by varying the reaction time and temperature. The data for PEEK sulfonation at various substitution degrees with sulfuric acid has been reported in the previous study [14] and the obtained results are summarized in Table 1. By increasing the time of sulfonation reaction, ion-exchange capacity, degree of sulfonation and water uptake are increased to almost 2.4 (mequiv. g^{-1}), 90% and 75%, respectively. Introducing the sulfonate groups in the PEEK structure reduces its crystallinity and increases its solubility in polar solvent. As seen in Table 1, the water uptake or the ability of imbibing large amount of water as well as the proton conductivity of the membranes have an increasing trend. Increasing the sulfonation degree has a beneficial influence on proton conductivity but undesirable effect on methanol permeability. So, the selectivity which is defined as the ratio of proton conductivity (as the desirable property) to methanol permeability (as the undesirable property) is often used to assess the contribution of both transport properties and decide on the optimum degree of sulfonation [14–19]. Membrane selectivity values of the sPEEK membranes at various sulfonation degrees are calculated and reported in Table 1. An improvement in membrane selectivity has been achieved due to the presence of sulfonate groups on polymer backbone. The maximum (optimal) selectivity parameter in the current system was measured to be 35,273 S s cm^{-3} , which was observed at 62% of sulfonation degree.

The ratio of the mole number of water molecules to the fixed-charged sulfonate groups, denoted as lambda (λ), was calculated from Eq. (2):

$$\lambda = \frac{WU}{IEC \times M_{\text{water}}} \quad (2)$$

where WU , IEC and M_{water} are the water uptake, ion exchange capacity and molecular weight of water (18 g mol^{-1}), respectively. In fact, the average number of water molecules per sulfonic acid groups (λ) shows how many water molecules could be bound to the ionic groups of sPEEK. The hydration of polyelectrolytes and the proton conduction across the membranes is often described as λ . Here, it was found that λ is enhanced by increasing the degree of sulfonation and reach to about 19 water molecules per $-\text{SO}_3\text{H}$ group in the case of sPEEK with 82% of sulfonation. Fig. 1 shows that the proton conductivity and methanol permeability of the sPEEK membranes are highly related to the value of λ .

The effect of sulfonation degree on proton conductivity of sPEEK membranes at different temperatures has been shown in Fig. 2(a). The conductivity is increasing gradually as more sulfonic acid groups introduced to the polymer and eventually reach $3.2 \times 10^{-2} \text{ S cm}^{-1}$ for the 82% of sulfonation at 25°C . In fact, the high ionic conductivity at elevated sulfonation level might be attributed to the more interconnection of swollen ionic domains of the membrane to form a three-dimensional network structure and facilitate proton conduction.

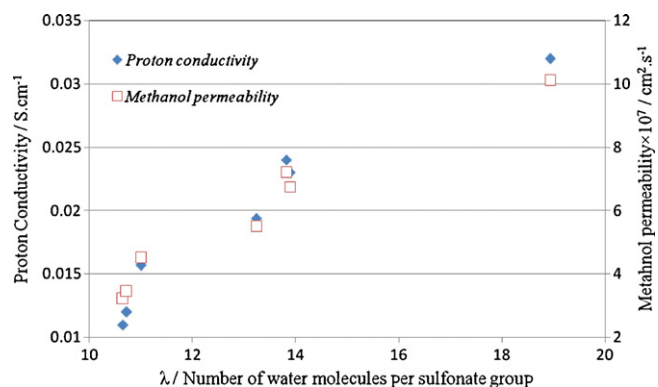


Fig. 1. The relationship between the average number of water molecules per fixed sulfonic acid groups, proton conductivity and methanol permeability of different sPEEK membranes.

PEMs may need to provide rapid proton transport at high temperatures. Fig. 2(b) is an Arrhenius plot of conductivity as a function of temperature in the range of $25\text{--}80^\circ\text{C}$ for sulfonated membranes. As seen, proton conductivity is improving with increasing temperature. The dissociation constants of acids increase at elevated temperature, as the ion contents in the sPEEK polymers increases [29]. All the membrane samples exhibited positive temperature–conductivity dependency, which suggests a thermally activated process. The relationship between conductivity and temperature is basically consistent with the Arrhenius equation, $\sigma = \sigma_0 \exp(-E_a/RT)$, where σ is the proton conductivity (in S cm^{-1}), σ_0 is a pre-exponential factors, E_a is the activation energy of proton conduction (in kJ mol^{-1}), R is the universal gas constant ($8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (in K). The activation energy of proton conduction can be calculated from the Arrhenius equation. The inset to Fig. 2(b) provides a comparison of the activation energy values for sulfonated samples. Higher activation energy is observed in the membranes with lower degree of sulfonation. Since the presence of sulfonate groups creates more reachable routes for protons transportation, activation energies decrease. Moreover, when the degree of sulfonation is increased to a sufficient level, the ionic domains become more interconnected and simultaneously overcome the diffusion limitations and allow the ionic conductivity to reach its maximum value [9].

Besides the high proton conductivity and low methanol permeability, the membranes used in DMFCs should also possess good hydrolytic stability. In the present study, the hydrolysis stability of the sPEEK membranes was evaluated through measurement of proton conductivity before and after soaking membranes in 90°C water for 15 days. Li et al. [28] have reported that ignorable change of proton conductivity after such test condition corresponds to an acceptable hydrolytic stability. The prepared sPEEK membranes

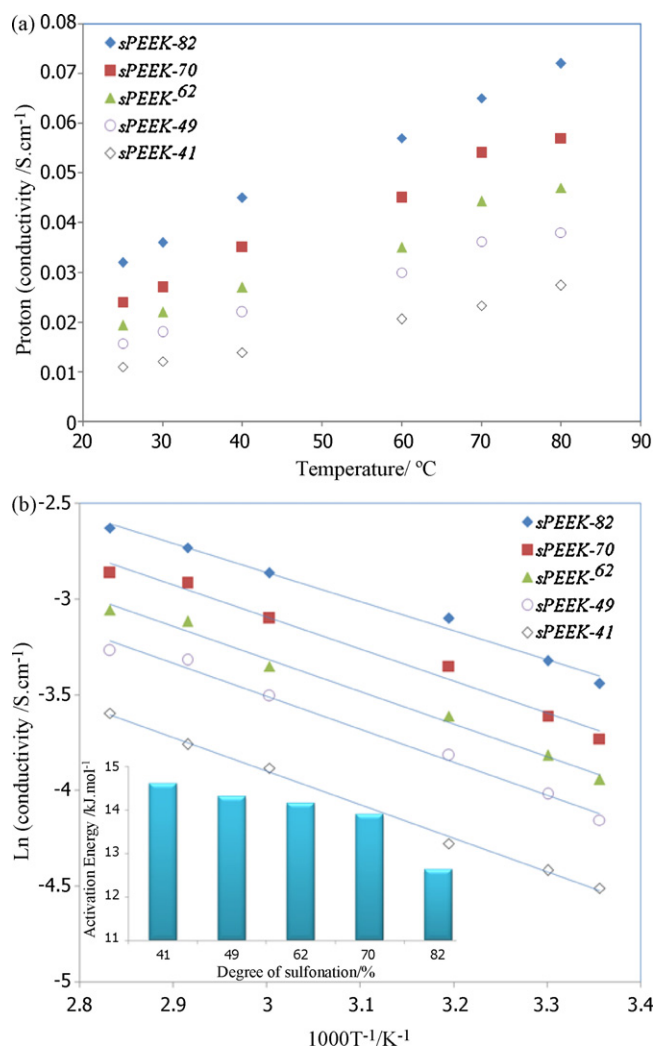


Fig. 2. Proton conductivity of the sPEEK membranes at different temperatures (a). Arrhenius plot of conductivity as a function of temperature in the range of 25–80 °C (b), the inset shows the activation energy values for sulfonated samples.

with sulfonation degree of more than 70% showed more than 10% alteration in proton conductivity. Such conductivity variation may be related to partially decomposition of the sulfonic acid groups in aqueous environment. However, sPEEK sample with 62% of sulfonation showed negligible change in proton conductivity. The same results have been reported previously for sPEEK membranes with a degree of sulfonation above 60% are not suitable for DMFC appli-

cations [29]. Considering its acceptable proton conductivity, low activation energy, and dimensional stability in aqueous environments, 62% was selected as the optimum degree of sulfonation.

After determining the optimum sulfonation degree, various loading weights of MMT were incorporated into the sPEEK-62 matrices. Table 2 summarizes the proton conductivity, methanol permeability and membrane selectivity of the fabricated nanocomposite membranes in comparison with recast Nafion® with the same thickness and Nafion® 117 membranes. On the basis of obtained results, the maximum membrane selectivity is achieved at 1.0 wt% of nanoclay content with the corresponding values of $1.73 \times 10^{-2} \text{ S cm}^{-1}$ and $2.05 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for proton conductivity and methanol permeability at 25 °C, respectively. The inclusion of MMT into the sPEEK matrices affects both the conductivity and permeability properties. In general, incorporation of the silicate layers into the polyelectrolytes restricts the accessible nanometric channels for migration of polar molecules such as hydrogen ions, water and methanol molecules [18]. Nonetheless, at low MMT loading of 1.0 wt% both the adequate proton conductivity and low methanol crossover have been fulfilled.

The ion conductivity of the nanocomposite membranes at different temperatures is shown in Fig. 3(a). From the comparison of Fig. 2(a) with Fig. 3(a), it could be found that the proton conductivity of nanocomposite membranes is lower than neat sPEEK-62 membrane and decreases sequentially by increasing the content of inorganic filler. As mentioned before, the reduction in conductivity is attributed to the fact that MMT layers baffle proton transport due to increased tortuosity of proton transfer routes. As illustrated in Fig. 3(a), the proton conductivity at all compositions of MMT is improving remarkably with increasing temperature. The Arrhenius plot for the nanocomposites is also depicted in Fig. 3(b), and indicates the positive temperature–conductivity relationships for all nanocomposites as for unfilled sPEEK samples. The inset to Fig. 3(b) provides a comparison between the activation energy of neat and filled sPEEK membranes. The activation energy of proton conduction for nanocomposite membranes is higher than that of for sPEEK-62 sample. Although the activation energy is rising with increasing nanofiller content, but at 1.0 wt% of MMT the activation energy is comparable with pristine sPEEK.

Generally, the proton migration across the ionomers could occur through two known mechanisms of hopping and vehicle [30]. In the former mechanism, hydrated proton jumps to the lone electrons pair of neighboring water molecule and in the latter, proton in the form of hydronium transports with solvent molecules in hydrophilic domains. For hopping mechanism, the activation energy of proton conduction has been reported to be around 14–40 kJ mol^{-1} [31]. On the other hand, in Nafion® membranes with the activation energy of about 9 kJ mol^{-1} both proton migration mechanisms have been commonly accepted

Table 2

Transport properties of sPEEK/MMT nanocomposite membranes in comparison with recast Nafion® and Nafion® 117 membranes.

Sample	MMT loading weight (%)	Membrane thickness (μm) ^a	Proton conductivity (S cm^{-1}) ^{b,c}	Methanol permeability $\times 10^7$ ($\text{cm}^2 \text{ s}^{-1}$) ^{b,c}	Membrane selectivity (S s cm^{-3}) ^{b,d}
sPEEK/MMT-0 wt%	0.0	110	0.0194	5.50	35273
sPEEK/MMT-0.5 wt%	0.5	95	0.0187	2.24	83482
sPEEK/MMT-1.0 wt%	1.0	100	0.0173	2.05	84390
sPEEK/MMT-1.50 wt%	1.5	97	0.014	2.00	70000
sPEEK/MMT-3.0 wt%	3.0	101	0.0088	1.75	50286
sPEEK/MMT-5.0 wt%	5.0	98	0.007	0.92	76087
sPEEK/MMT-10.0 wt%	10.0	94	0.0009	0.45	20000
Recast Nafion®	–	105	0.0844	21.73	38840
Nafion® 117	–	180	0.081	20.00	40500

^a These results are mean value of at least three trials for each sample and standard variation not exceeded 10%.

^b Results from our previous study [14].

^c Measured at 25 °C.

^d The ratio of proton conductivity to methanol permeability.

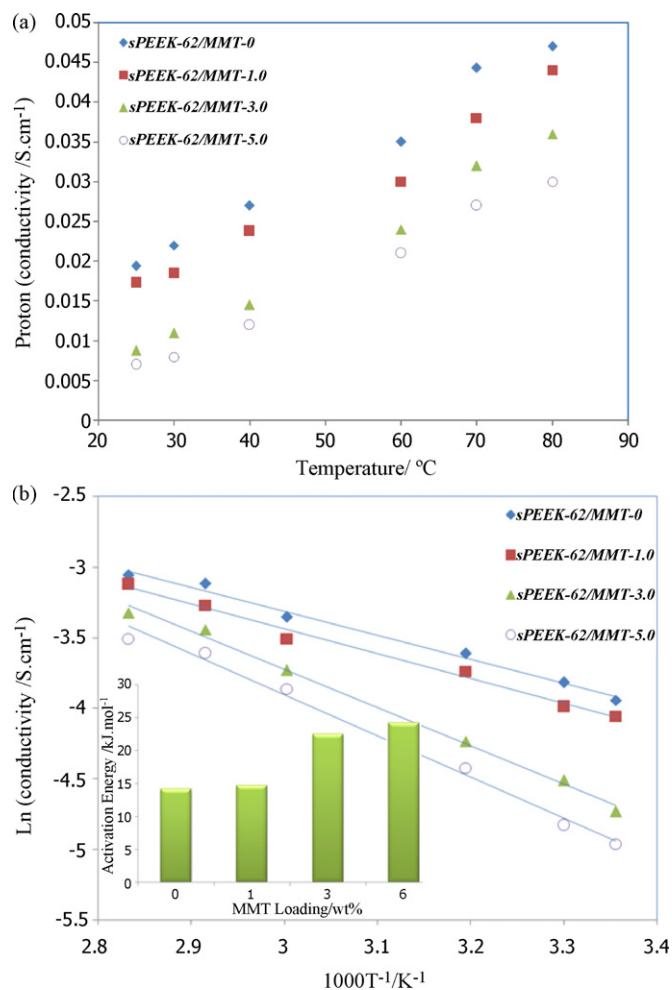


Fig. 3. Proton conductivity of the sPEEK based nanocomposite membranes at elevated temperatures (a). Arrhenius plot of conductivity as a function of temperature (b), the inset shows the activation energy values for of the nanocomposite samples.

to exist [29]. Therefore, on the basis of activation energy of sPEEK-62/MMT-1.0 wt% nanocomposite membrane, it could be suggested that the proton migration might have occurred via both the mechanisms and primarily by the vehicular mechanism. The relatively higher activation energy of prepared nanocomposite membranes compared to Nafion[®] membranes could be interpreted with the lower ionic phase separation and the rigid microstructure of PEEK's backbone which lead to narrower proton channels and a highly branched structure.

The methanol permeability of neat sPEEK and sPEEK-62/MMT-1.0 wt% membranes at three temperatures is displayed in Fig. 4(a). As seen, the methanol permeability is increased with increasing temperature and nanocomposite membrane shows lower permeability compared to pristine sulfonated polymer. The noteworthy point of Fig. 4(a) is the considerable difference between permeability values at elevated temperature, which reveals the better performance of the nanocomposite membrane at higher temperatures.

The relationship between permeability and temperature was found to be in a good agreement with the Arrhenius equation (Fig. 4(b)). In this case, σ , σ_0 and E_a are replaced by P , P_0 and $E_{a,MeOH}$, which P is the methanol permeability (in cm² s⁻¹), P_0 is a pre-exponential factor and $E_{a,MeOH}$ is the activation energy of methanol permeability (in kJ mol⁻¹). As shown in the inset to Fig. 4(b), the nanocomposite membrane exhibits notably higher activation energy for methanol permeation. In general, the narrower proton

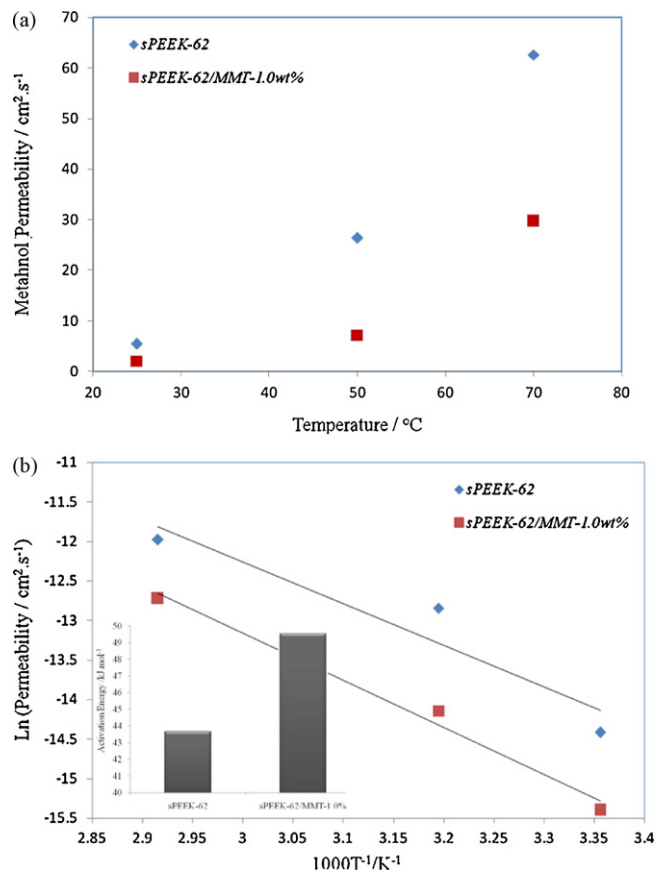


Fig. 4. Methanol permeability of neat and MMT filled sPEEK membranes at 25, 50 and 70 °C in normal (a) and Arrhenius format (b). In (c) the effect of MMT incorporation on the activation energy of methanol permeation ($E_{a,MeOH,NC}$) is illustrated.

channels and lower electro-osmotic drag in sPEEK matrices prevent the crossover of methanol [26]. In addition, in the case of nanocomposite membrane the dispersion of silicate nanosheets restricts the migration of methanol molecules. The presence of MMT provides a drastic reduction of permeability even at higher temperatures. It could be expected that this favorable barrier properties lead to an improved DMFC performance at elevated temperatures.

On the basis of proton conductivity and methanol permeability properties, it could be understood that the inclusion of MMT has reduced both transport characteristics of the sPEEK matrices, which has been also reported in the previous studies [14–18]. In this regard, the sulfonation of the montmorillonite has been proposed to maintain the proton conductivity of the corresponding sPEEK nanocomposite membranes. Although the functionalization of montmorillonite could mitigate its side effects on conductivity, but it leads to the enhancement of methanol permeation concurrently [29]. In the present research, a commercially available organically modified MMT has been employed to not only provide the exfoliation of MMT sheets within the sPEEK matrix thanks to the enhanced gallery spaces [14], but also achieve low cost ion exchange membranes with beneficial barrier properties and improved performance for DMFC applications, which will be discussed later.

Proton conductivity and methanol permeability are the two transport properties of a polyelectrolyte membrane, which determine its electrochemical performance. The higher selectivity value leads to a better membrane performance in practical condition. For temperature dependency investigation of transport properties, the membrane selectivity values of sPEEK-62/MMT-1.0 wt% as well as neat sPEEK membranes have been shown in Fig. 5. As could be seen, the maximum selectivity is achieved at room temperature for

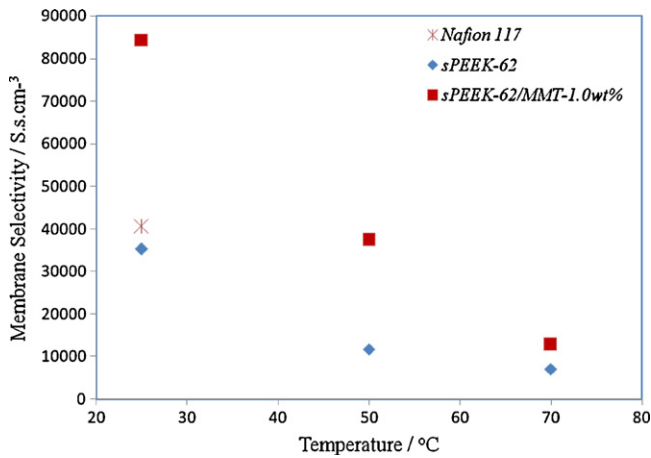


Fig. 5. Temperature dependency of membrane selectivity parameter of sPEEK-62/MMT-1.0 wt% and neat sPEEK membranes.

both membranes. Such an observation originates from the favorable influence of increasing temperature on proton conductivity and its greater adverse effect on methanol permeability. Nanocomposite membranes are shown to be more selective than unfilled sPEEK in the whole range of temperatures. Moreover, if we consider the tunability feature of such ionomers thanks to a variety of possible compositions, related potential applications as DMFC membranes are expectable.

The electrochemical evaluation of manufactured nanocomposite was carried out by means of a single cell DMFC. The performance

test was carried out using two different methanol concentrations of 1 and 5 M at 70 °C. As exhibited in Fig. 6(a) and (b), the current densities for the sPEEK-62/MMT-1.0 wt% and Nafion® 117 membranes were measured to be 35 and 67 mA cm⁻² (at a potential of 0.5 V and 1 M methanol concentration) and 76 and 71 mA cm⁻² (at a 0.5 V potential and 5 M methanol concentration), respectively. The power density of the nanocomposite membranes and Nafion® 117 were obtained to be 18 and 33.5 mW cm⁻² (at potential of 0.5 V and 1 M methanol concentration) and 38 and 35.5 mW cm⁻² (at 0.5 V potential and 5 M methanol concentration), respectively. The results reveal the superior electrochemical behavior of the nanocomposite membrane at the concentrated methanol feed in comparison with Nafion® 117.

The open circuit voltage (OCV) for neat sPEEK, sPEEK-62/MMT-1.0 wt% and Nafion® 117 membranes were measured to be 0.682, 0.686 and 0.68 for 1 M methanol, and 0.675, 0.69 and 0.665 for 5 M methanol, respectively (Fig. 6(c)). The OCV for the nanocomposite membranes is higher than reference sPEEK and Nafion® 117 membranes at both methanol concentrations, which such difference become more obvious at elevated methanol concentration. OCV is closely related to the methanol permeation and it increases when the methanol crossover is decreased. Methanol crossover hinders oxygen reduction at the anode and consequently leads to a drastic decrease in the OCV. The higher OCV clearly indicates that the incorporated MMT into sPEEK membrane significantly decreases the rate of methanol crossover, as is consistent with methanol permeability results (Fig. 4).

The maximum current density of the sPEEK-62/MMT-1.0 wt% membrane reaches 772 mA cm⁻² compared to 448 mA cm⁻² for

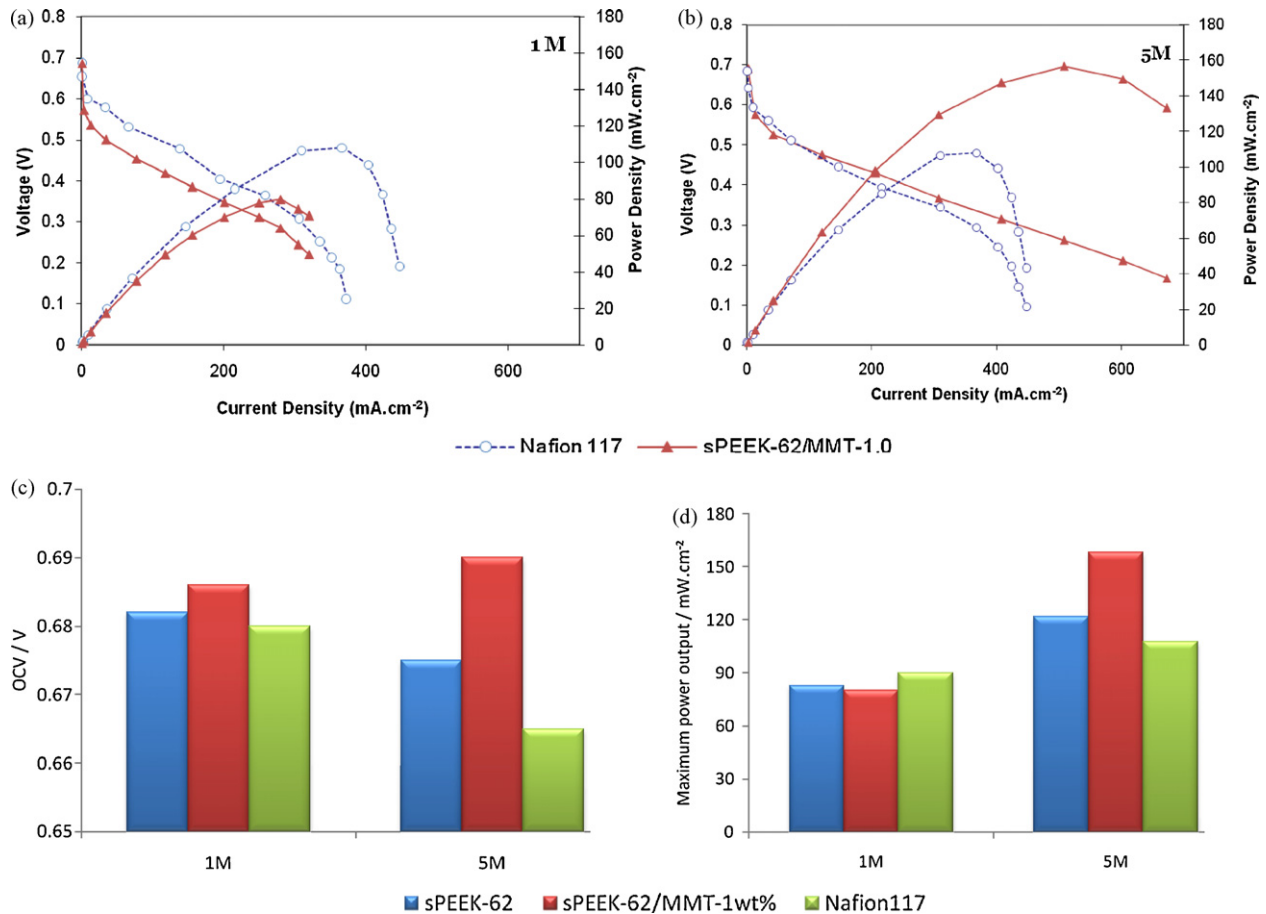


Fig. 6. DMFC performance test at 70 °C, V-I and P-I for sPEEK-62/MMT-1.0 wt% nanocomposite membrane compared to Nafion® 117 at 1 M (a) and 5 M methanol feed (b). OCV (c) and maximum power density output (d) for neat sPEEK, sPEEK/MMT and Nafion® 117 membranes.

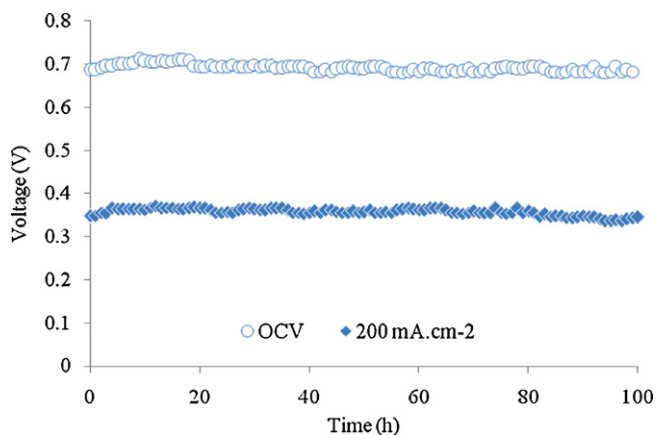


Fig. 7. Endurance testing of MEAs comprising sPEEK-62/MMT-1.0 wt% nanocomposite membrane at 70 °C and 1 M methanol feed. The (○) and (◆) symbols correspond to the open circuit voltage (OCV) and voltage at constant current of 200 mA cm⁻², respectively.

Nafion[®] 117. The electro-osmotic contribution, which depends on the methanol concentration of the feed solution, becomes more important when the electric current increases. The maximum power density of the nanocomposite membrane was measured to be as high as 158 mW cm⁻², whereas the highest power density output of the reference sPEEK and Nafion[®] 117 membranes at the same methanol concentration of 5 M obtained as 122 and 108 mW cm⁻², respectively (Fig. 6(d)). Accordingly, the sPEEK-62/MMT-1.0 wt% membrane supplies over 29.5% more power output than unmodified sPEEK and 46.3% more power output than Nafion[®] 117 at 70 °C. The remarkable improvement in proton to methanol selectivity of the nanocomposite membranes comparing with unfilled sPEEK and Nafion[®] were reflected by the improved fuel cell performance of the MMT filled membrane.

In order to evaluate the long-term stability and performance of the prepared nanocomposite membrane at the fuel cell operational condition, the endurance testing of the fabricated MEAs comprising sPEEK-62/MMT-1.0 wt% membrane was performed at 70 °C and 1 M methanol solution feed continuously for 100 h. In this respect, the output voltage at a constant current of 200 mA cm⁻² and open current voltage (OCV) of the DMFC single cell were measured and the obtained results have been shown in Fig. 7. As seen, the performance curves in Fig. 7 have two trends; during the first 12 h, the voltage of the single cell increases from 0.3475 to 0.382 V with a rate of 2 mV h⁻¹. Such an observation may be attributed to the activation of electrocatalyst and decrease in the internal resistance of the single cell [32]. In the following stage, the voltage of the single cell decreases to 0.3473 V at 80 h with a decline rate of 4 mV h⁻¹.

In a similar manner, two regions also can be recognized in OCV data, a rising stage at the beginning and then it levels off. According to the endurance testing results, a little or no decline in performance was observed during 100 h, which is related to a suppressed methanol crossover using the sPEEK based nanocomposite membrane. By considering the steady performance curves of the DMFC single cell, it is expectable that the durability and stability of the nanocomposite membranes to be suitable for methanol fuel cell at moderate temperature operational conditions.

4. Conclusion

Sulfonated poly(ether ether ketone) (sPEEK) with different degrees of sulfonation were prepared and the optimum sul-

fonation degree was determined based on transport properties, hydrolytic stability of the membranes. Subsequently, a series of nanocomposite membranes based on the optimum sPEEK sample and organically treated montmorillonite (MMT) were prepared. The nanocomposite membranes showed higher proton conductivity and membrane selectivity at elevated temperatures. The membrane selectivity of the sPEEK/MMT nanocomposite was comparable to that of for Nafion[®] 117 as long as the MMT loading was less than 10 wt%. 1.0 wt% MMT filled membranes showed a high selectivity and power density at the concentrated 5 M methanol feed. The nanocomposite membrane provided the highest performance in comparison with the cells based on neat sPEEK and Nafion[®] 117. In addition, it was turned out that sPEEK-62/MMT-1.0 wt% membrane is able to provide 46.3% more power output than Nafion[®] 117 at 70 °C. Besides, nanocomposite exhibited a high open circuit voltage at higher methanol concentration. Owing to the favorable properties of high proton conductivity, low methanol permeability, high power density, ease of preparation and low cost, sPEEK-62/MMT-1.0 wt% nanocomposite membrane could be considered as a promising polyelectrolyte for moderate temperature DMFC applications.

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