

Proton-conducting composite membranes derived from sulfonated hydrocarbon and inorganic materials

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Abstract

Composite polymer membranes are prepared by embedding layered silicates such as Laponite and Montmorillonite (MMT) into sulfonated poly(ether ether ketone) (sPEEK) membranes for fuel-cell applications. Sulfonation of the polymer increased membrane hydrophilicity to give good proton conductivity. Layered silicates incorporated into polymer membranes help to reduce swelling significantly in hot water; they also help to decrease methanol permeability. These polymer/clay composite membranes show thermal stability to 240 °C and $(3\text{--}3.5) \times 10^{-3} \text{ S cm}^{-1}$ proton conductivity at room temperature. In addition, methanol cross-over is reduced without a serious reduction in the proton conductivity. In a single-cell test using hydrogen and oxygen, the prepared membranes give current densities that are between 70 and 80% of those with Nafion 115 membranes. As a result, for polymer electrolytes, sPEEK/clay composite membranes offer a low-cost alternative to perfluorinated membranes.

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1. Introduction

Fuel cells convert the chemical energy of fuel into electrical energy with high efficiency and low emission of pollutants. Consequently, fuel cells have been considered as promising alternative devices for energy conversion. Polymer electrolyte membrane fuel cells (PEMFCs), which employ polymer membranes as an electrolyte, are suitable for the mobile and domestic applications because they have a low operating temperature, do not suffer from leakage problems and have a fast start-up advantage.

Perfluorinated membranes from the DuPont, Dow and Asahi Chemical companies, which have been used exclusively for electrolyte membranes in PEMFCs, possess outstanding chemical and mechanical stability with a polymer backbone similar to polytetrafluoroethylene. These membranes also have high proton conductivity ($10^{-2} \text{ S cm}^{-1}$) due to the sulfonic acid group of the side chains, and perform excellently not only in PEMFCs but also in direct methanol fuel cells (DMFCs).

Besides these advantages, perfluorinated membranes may have two shortcomings: they are very expensive due to the toxic and complicated production process and show considerable methanol permeability in DMFCs. High methanol cross-over not only reduces fuel utilization efficiency, but also decreases the cathode performance [1]. These drawbacks have prompted research into alternative membranes based on partially perfluorinated ionomers and hydrocarbon polymer. For example, investigations have been conducted on aromatic polymers such as polyethersulfone (PSU), poly(ether ether ketone) (PEEK), polyphenylquinoxaline (PPQ) and polybenzimidazole (PBI) [2–4].

In this study, composite membranes from sulfonated hydrocarbon polymer and inorganic materials. In particular, PEEK is chosen because of its good mechanical properties. The thermal and chemical stability of PEEK are also good, and proton conductivity can be improved via sulfonation [5,6].

Both Laponite and Montmorillonite (Na-MMT) are well-known layered silicates composed of silica tetrahedral and alumina octahedral sheets. When polymers are mixed with these natural or synthetic inorganic materials, their properties are considerably improved. Due to its characteristics,

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polymer filler can increase the mechanical strength or impact resistance of these polymers and can reduce the permeability of gases such as oxygen and moisture [7]. The layered silicates materials embedded in a polymer matrix are expected to play a role in reducing methanol permeability and in preventing excessive swelling at high temperatures. In addition, the humidity in the membrane is expected to be maintained under various cell conditions.

2. Experimental

2.1. Preparation of polymer

PEEK (polyoxy-1,4-phenyleneoxy-1,4-phenylene-carbonyl-1,4-phenylene) was obtained in powder form from Aldrich and was used without any further purification. For the sulfonation of PEEK, 15 g of polymer was dissolved in 300 ml of concentrated (95%) sulfuric acid (H_2SO_4) and stirred at 50°C for a given time between 4 and 20 h. The polymer solution was poured into a large excess of ice water to precipitate the polymer. The precipitate was collected by filtration and washed vigorously with distilled water until the pH of the polymer became neutral. The polymer was then dried in an oven at 90°C for 12 h [8,9].

The degree of sulfonation (DS) or the ion-exchange capacity (IEC) was determined by a titration method. This involved soaking of 2 g of sulfonated polymer in a concentrated NaCl solution and heating at 60°C for 6 h. The solution was titrated with 0.1 M NaOH using phenolphthalein as an indicator.

2.2. Layered silicate materials

Sodium-Montmorillonite (Na^+ -MMT) and Laponite were supplied by the Southern Clay Co. and used as obtained with no further purification. Laponite ($\text{Na}_{0.7}^+[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{0.2}(\text{OH})_4]^{0.7-}$) is a synthetic product which is composed of six octahedral magnesium ions and two layers of four tetrahedral silicon atoms. The cation-exchange capacity of MMT is 95 meq. per 100 g.

2.3. Preparation of composite membranes

The sulfonated polymer was dissolved (10 wt.%) in dimethylacetamide (DMAc), and the inorganic materials were added to this solution. The mixture was stirred and treated in an ultrasonic bath for 1 h. The polymer solution was heated to evaporate most of the solvent, and was cast on a glass plate with a doctor blade. The cast membranes were dried at room temperature overnight and heated in a vacuum oven for 10 h at 100°C to remove the solvent. In addition, the prepared composite membranes were heated in 1 M sulfuric acid solution at 60°C for 6 h to substitute hydrogen ions for sodium ions in the layered silicate. The content of inorganic material in the composite membranes was 5–10 wt.%.

2.4. Water uptake of membranes

Polymer membranes were dried in a vacuum oven and weighted. They were then immersed in distilled water and heated at various temperatures for 6 h. After removing water from the membrane surface with absorbant paper, the membranes were weighted. The water uptake of the polymer membranes was calculated with reference to the weight of the dry polymer membrane, i.e. $(W_{\text{WET}}/W_{\text{DRY}} - 1) \times 100\%$.

2.5. Proton conductivity

The proton conductivity of the polymer membrane samples was measured by means of ac impedance spectroscopy over a frequency range of 5–10 MHz with a voltage of 10 mV, using a system based on a Solartron 1255 frequency response analyzer. A sample of the membrane ($2\text{ cm} \times 2\text{ cm}$) was placed in an open cell where it was clamped between two blocking platinum electrodes. Before the test, the membranes were dipped in water until sufficiently wet and compressed tightly between the blocking electrodes. The conductivity (σ) of the sample in the transverse direction was calculated from the impedance data, using the relation $\sigma = d/RS$ where d is the thickness of the sample, S the face area, and R is derived from the impedance data.

2.6. Methanol permeability

To determine the barrier properties of the membranes, measurements were made of the permeability of methanol in composite membranes and Nafion 115 membranes using the device shown in Fig. 1. The upper part of the permeation cell was filled with methanol. The methanol molecules diffuse along the concentration gradient through the membrane into the opposite compartment of the permeation cell. There, a constant nitrogen flow adjusted by a mass-flow controller (MFC), swept the molecules into the flame ionization detector of a gas chromatograph [10]. The permeation cell was placed in a temperature bath maintained at 40°C and the measuring area was 100 mm^2 .

2.7. Single-cell test (H_2 -PEMFC)

To remove the metallic impurities, the membranes were heated again in sulfuric acid at 60°C for 6 h and then washed repeatedly with distilled water. In addition, the treated membranes were repeatedly washed in hot water to remove the remaining sulfuric acid. The electrode and gas-diffusion layer were prepared by spraying methods. Twenty weight percent Pt/C (E-TEK) and 5 wt.% Nafion 115 solution were mixed with ethylene glycol and water. After being stirred overnight, the solution was sprayed on carbon paper that had been used for the gas-diffusion layer of the cell. The catalyst loading of the electrodes was 0.5 mg cm^{-2} and the area of electrodes was 9 cm^2 . The electrodes were then hot pressed to the membranes at 110°C and 70 kgf cm^{-2} for 3 min.

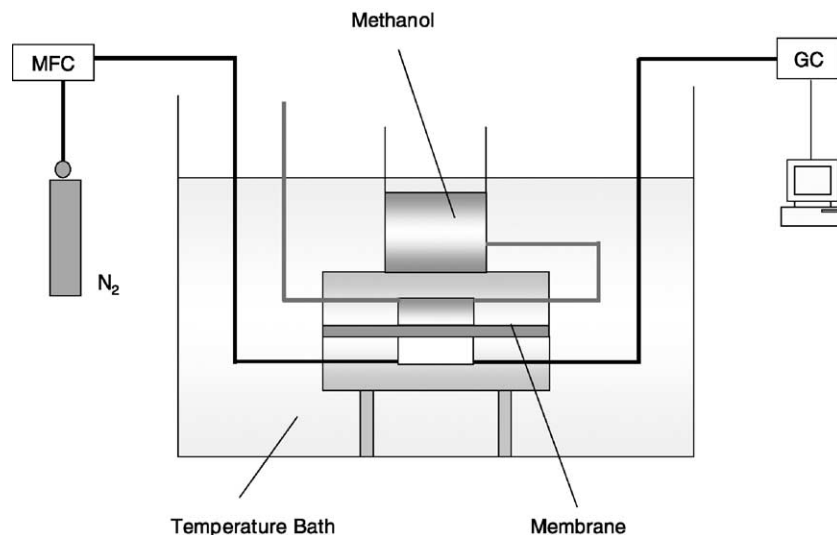


Fig. 1. Experimental set-up for measurement of methanol permeation.

The membrane and electrode assembly was positioned in a single-cell test fixture, and the single cell was installed in a fuel-cell test station. As shown in Fig. 2, the station is equipped with adequate controls for the potential, current density, temperature and pressure of the cell, and with mass-flow controllers for the gases. The performance of the single cell was evaluated between 50 and 80 °C under atmospheric conditions. Hydrogen gas and oxygen gas were supplied to the anode and cathode sides of the single cell, respectively. The utilization of hydrogen and oxygen was 70 and 40%, respectively. Furthermore, the reactant gas was fully humidified by passage through bubble-type chambers.

2.8. Other characterization methods

To analyze the thermal stability of the composite membranes, thermogravimetric analysis (TGA) was carried out using a DuPont 2200 thermal analysis station. Samples weighing about 10 mg were dried at 100 °C to remove any moisture and solvent, and then heated from 50 to 700 °C at a rate of 10 °C min⁻¹ in a nitrogen atmosphere.

The morphology of the composite membranes was investigated with a scanning electron microscope (SEM). Specimens for the SEM were prepared by freezing the dry membrane samples in liquid nitrogen and breaking them

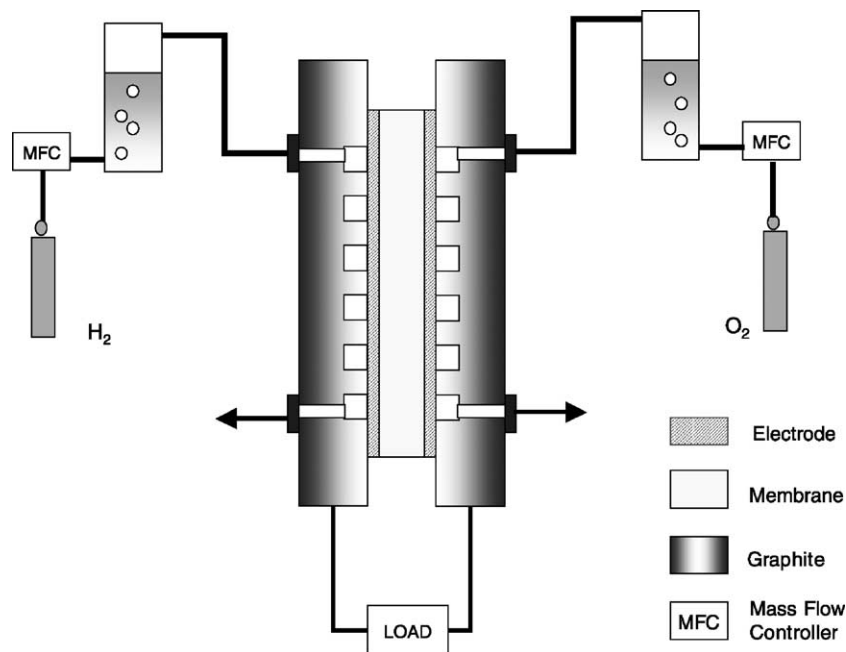


Fig. 2. Schematic diagram of H₂-O₂ PEFC test facility.

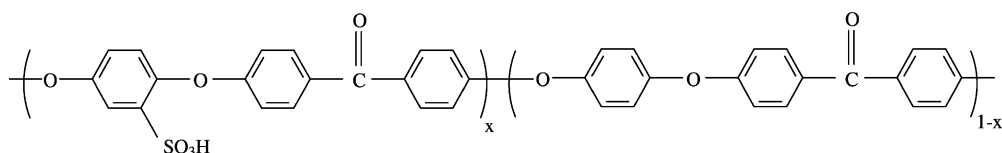


Fig. 3. Chemical structure of sulfonated PEEK.

to produce a cross-section. Fresh cross-sectional cryogenic fractures of the membranes were vacuum sputtered with a thin layer of gold before SEM examination.

3. Results and discussion

3.1. Sulfonation of PEEK

Sulfonation of PEEK was carried out using 95% H_2SO_4 to avoid degradation and a cross-linking reaction, which may occur with 100% H_2SO_4 or chlorosulfonic acid [11]. The sulfonation rate of PEEK with sulfuric acid is controlled by varying the reaction time and temperature. The sulfonation level is controlled in the range of 30–100%. The chemical structure of the sulfonated PEEK (sPEEK) is in Fig. 3. According to Bishop and co-worker [12] PEEK dissolved in H_2SO_4 does not undergo any molecular weight degradation even over long periods of time.

The physical and chemical properties of sulfonated PEEK depend on the degree of sulfonation, i.e. the concentration of sulfonic groups. Sulfonation modifies the chemical character of PEEK, reduces the crystallinity and consequently affects solubility. When the DS is lower than 40%, the sPEEK is soluble in strong H_2SO_4 , hot DMAc, and dimethyl sulfoxide; when the DS is above 50%, the sPEEK is soluble in the same solvent, even at room temperature; when there is a high DS (above 70%), the sPEEK is soluble in methanol and has poor chemical stability in hot water.

The ion-exchange capacity and the DS of the sPEEK are listed in Table 1 as a function of sulfonation time. It is observed that IEC increases continuously with reaction time. The sPEEK, which reacted for 10 h, has 1.7 meq. g^{-1} of IEC and shows proper solvent solubility, and so on. As a result, the sPEEK that was sulfonated for 10 h with 55–60% DS was selected for further studies. Various polymer/clay composite membranes were prepared, as shown in Table 2.

Table 1
Properties of sPEEK membrane according to degree of sulfonation

sPEEK	Temperature ($^{\circ}\text{C}$)	Time (h)	IEC (meq. g^{-1})	DS (%)	Solvent solubility	Chemical stability
sPEEK6h	50	6			–	
sPEEK8h	50	8	1.3	43	+	++
sPEEK10h	50	10	1.7	56	++	++
sPEEK15h	50	15	2.2	76	+++	–
sPEEK20h	50	20	3.0	113	+++	–

(+): good, (–): bad.

Table 2
Various composite membranes

Membrane	Components
sPEEK	Sulfonated PEEK (reaction time = 10 h)
sPEEK/Lapo5	Sulfonated PEEK + Laponite 5 wt.%
sPEEK/Lapo10	Sulfonated PEEK + Laponite 10 wt.%
SPEEK/MMT10	Sulfonated PEEK + MMT 10 wt.%

3.2. Water uptake

The main purpose of sulfonating aromatic PEEK is to increase its acidity and hydrophilicity because the presence of water is known to facilitate proton transfer and enhance the conductivity of solid electrolytes. The water uptake of the membranes increases with the DS and with water temperature. The water absorption of sPEEK membrane and various composite membranes was determined as a function of water temperature. As shown in Fig. 4, the sPEEK membrane undergoes 20–30% water absorption at 60°C . Above 70°C , however, the water content is between 100 and 400%. This extreme swelling of the membrane is crucial because the normal PEMFC operation temperature is between 70 and 80°C . The water uptake of a sPEEK/Lapo10 composite membrane displays a constant swelling between 20 and 50% up to 80°C . This very favorable result is obviously due to the cohesion of the polymer matrix and layered silicate. The clay embedded in the polymer matrix prohibits extreme swelling of the composite membranes.

3.3. Proton conductivity

Before measurement of the proton conductivity, the membranes were immersed in water for hydration. The proton conductivity of various composite membranes is shown in Table 3. By increasing the DS, the polymer becomes more hydrophilic and absorbs more water, which facilitates

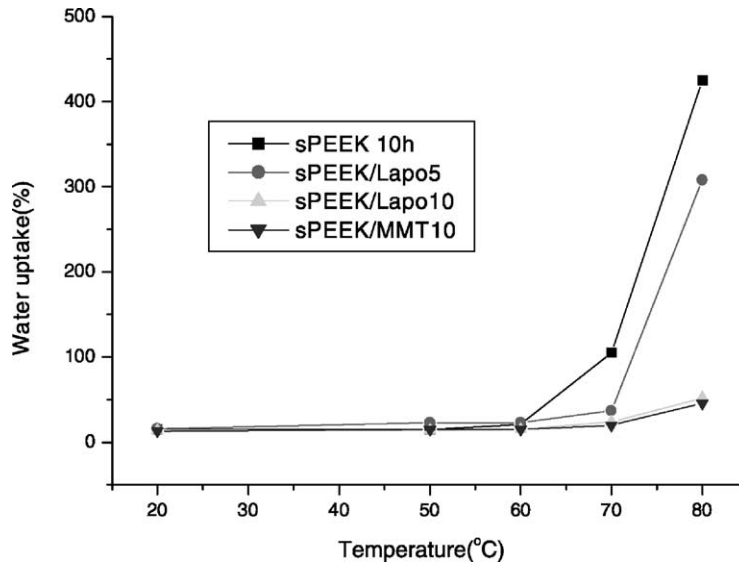


Fig. 4. Water uptake of sPEEK membranes as function of water temperature.

Table 3
Proton conductivity of composite membranes at room temperature

Membrane	Resistance (Ω)	Thickness (cm)	Conductivity ($\times 10^3$) (S cm ⁻¹)
Nafion 115	1.8	0.015	8.3
sPEEK	2.5	0.008	3.2
sPEEK/Lapo10	35	0.008	0.23
sPEEK/Lapo10/H ₂ SO ₄ ^a	2.7	0.008	3.0
sPEEK/MMT10/H ₂ SO ₄ ^a	3.7	0.010	2.7

^a Treated with 1 M H₂SO₄.

proton transport. Sulfonation raises the conductivity of the PEEK, not only by increasing the number of sulfonic groups (–SO₃H) but also by forming water-mediated pathways for protons.

In this study, the proton conductivity of the sPEEK membrane is 3.2×10^{-3} S cm⁻¹. Although this value is only one-third that of a Nafion 115 membrane under the same conditions, the thinness of the sPEEK membrane is expected to offset this shortcoming to some extent. The sPEEK/Lapo10 composite membrane shows a very low

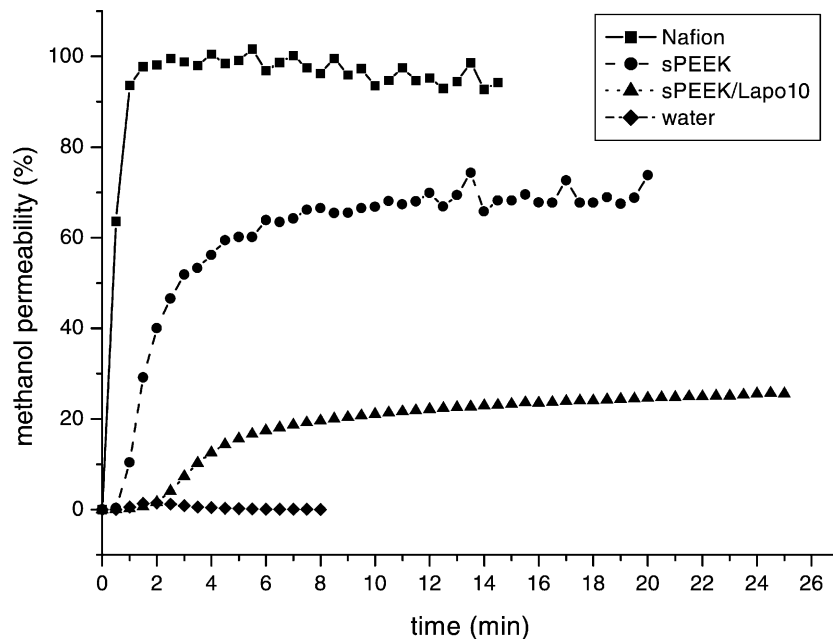


Fig. 5. Methanol permeability for Nafion 115 and composite membranes.

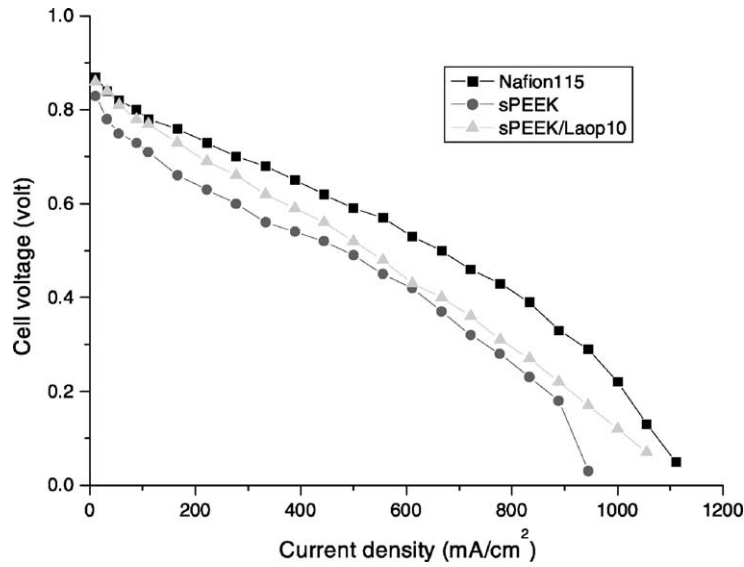


Fig. 6. Polarization curves for Nafion 115, sPEEK and sPEEK/Lap10 membranes in H₂-O₂ PEMFC (utilization of H₂: 70%; utilization of O₂: 40%; cell temperature: 60 °C).

proton conductivity of $0.12 \times 10^{-3} \text{ S cm}^{-1}$ because the clay dispersed in the polymer prohibits proton transport. After treatment in 1 M H₂SO₄ for 10 h, however, it recovers the proton conductivity of the primitive sPEEK membrane. Treatment with 1 M H₂SO₄ solution, which causes the sodium ions of the layered silicate to be substituted with hydrogen ions, is thought to facilitate proton movement.

3.4. Methanol permeability

The permeability of pure methanol through the membranes was investigated as a function of time. The relative methanol flux versus time for Nafion 115, sPEEK and

sPEEK/Lap10 composite membrane is shown in Fig. 5. The stationary methanol permeation rate decreases from 100% for Nafion 115 membrane to 25% for the sPEEK/Lap10 composite membrane. The sPEEK membrane displays a relative methanol permeability of 70%, and this barrier property is possibly due to the difference in microstructure between Nafion 115 and sPEEK membrane. The less-pronounced hydrophilic–hydrophobic separation of the sPEEK produces narrow channels and a highly branched structure [13]. The composite membrane with Laponite causes less methanol permeability because the micro-sized dispersion of the clay prevents methanol from transferring through the membrane.

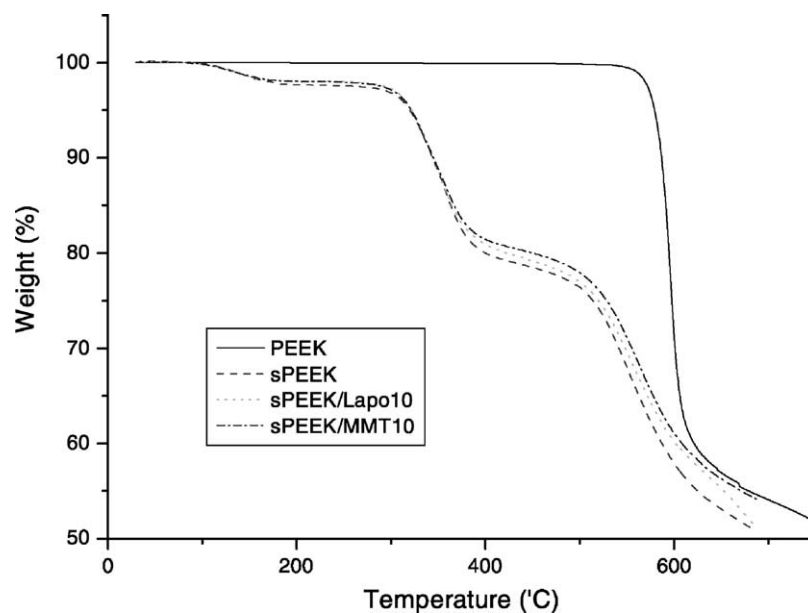


Fig. 7. TGA curves for PEEK, sPEEK and composite membranes.

Table 4
Effect of humidification on performance of various membranes (utilization of H₂: 70%; utilization of O₂: 40%)

Membrane	Cell temperature (°C)	Humid gas temperature (°C)	Temperature gap (°C)	Performance (V–A)
Nafion 115	60	80	20	0.6–3.3
	60	75	15	0.6–3.8
	60	70	10	0.6–4.4
	70	75	5	0.6–4.0
sPEEK	50	70	20	0.6–2.5
	50	65	15	0.6–2.5
	50	60	10	0.6–2.0
	50	55	5	0.6–0.9
	70	85	15	–
sPEEK/Lapo10	60	75	15	0.6–2.6
	60	70	10	0.6–2.7
	60	65	5	0.6–3.5
	70	70	0	0.6–3.0
	75	70	–5	–

3.5. Cell test

The sPEEK and sPEEK/Lapo10 composite membranes were applied in a H₂–O₂ PEMFC because sPEEK/Lapo10 composite membrane shows a stable property in the swelling test and has appropriate proton conductivity compared with the other prepared membranes. The polarization curves in the hydrogen–oxygen operation mode are shown in Fig. 6. The application of the prepared membranes yields promising results. Although the prepared membranes have lower proton conductivity than the Nafion 115 membrane, they perform comparably due to their thinness. When the Nafion 115 membrane produces 0.6 V–480 mA cm^{–2} in the polarization curve, the sPEEK and sPEEK/Lapo10 composite membranes yield 0.6 V–80 mA cm^{–2} and 0.6 V–370 mA cm^{–2}, respectively.

The curve for the sPEEK/Lapo10 membrane shows higher cell voltages than that of intrinsic sPEEK membrane, although both sPEEK and sPEEK/Lapo10 composite membranes have a similar proton conductivity of about 3×10^{-3} S cm^{–1} and a similar water uptake at a cell temperature of 60 °C. This result is thought to be due to the difference in their hydration state. The sPEEK/Lapo10 composite membrane yields a constant performance through broad humidification conditions. This performance is obviously due to the hydrophilic inorganic materials incorporated into the polymer matrix. These materials control the membrane swelling by easily absorbing moisture and by preventing water from drying up. On the other hand, sPEEK membrane is sensitive to the humidification condition of reactant gases. The membrane condition is prone to change into a flooding state or a dry state with cell conditions and these inappropriate membrane states deteriorate cell performance. In other words, the membranes are very sensitive to humidification conditions, such as humidification temperature and cell temperature.

The sPEEK/Lapo10 composite membrane also performed well above 70 °C, because of its dimensional stability in the swelling test. Nevertheless, sPEEK membrane cannot

be used above 70 °C because it is susceptible to extreme swelling and dries out easily.

The effects of the above humidification conditions and temperatures on cell performance are summarized in Table 4. At this point, however, only short-term fuel-cell tests on these membranes have been performed (maximum 100 h). Furthermore, the production process for the membrane–electrode assembly (MEA) is not yet optimized for the prepared membranes; thus, there is still potential to improve the PEMFC performance.

3.6. Thermal stability and morphology

Polymer electrolyte membranes that exhibit fast proton transport at an elevated temperature are required for PEMFCs. The thermal stability of the polymer electrolyte membranes was studied by heating samples in TGA. The resulting data for the PEEK, sPEEK and sPEEK/clay composite membranes are displayed in Fig. 7. The thermal decomposition temperature (T_d) of the membrane is a function of sulfonation. The PEEK polymer powder displays thermal stability up to 500 °C, but the sPEEK and sPEEK composite membranes lose 20% of their original weight above 250 °C. According to Rikukawa and Sanui [14], this initial weight loss in sPEEK membranes is due to thermal decomposition by desulfonation [14]. Our results suggest, however, that these hydrocarbon polymer membranes have adequate thermal properties for application in fuel cells because their thermal decomposition is detected above 230 °C.

4. Conclusions

In this study, a series of composite membranes has been prepared by incorporating Laponite and MMT into a partially-sulfonated PEEK polymer. The sPEEK/Laponite composite membrane exhibits $(3–3.5) \times 10^{-3}$ S cm^{–1} proton conductivity at room temperature and maintain thermal and chemical stability despite their thinness (60 μm). A

study of the water uptake of the sPEEK/Lap010 composite membrane has shown only 20–30% constant swelling up to 80 °C due to the cohesion of the clay and polymer matrix. In addition, because the clay embedded with the polymer matrix prevents methanol transport, the methanol permeability of the composite membrane is reduced to 25% compared with that of the Nafion 115 membrane.

In a single-cell test, the sPEEK/Lap010 composite membrane performs well compared with the Nafion 115 membrane. Furthermore, in spite of its thinness, the sPEEK/Lap010 composite membrane is relatively insensitive to the humidification condition of reactant gases in comparison with intrinsic sPEEK membranes. Moreover, due to low methanol permeability, the composite membrane is expected to yield a good result when examined in a DMFC.

Finally, due to their low-cost, constant water uptake and low methanol permeability, sPEEK/clay composite membranes may be considered for use in PEMFCs as alternatives to perfluorinated membranes.

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