

높은 이온교환능력을 가지는 버미큘라이트와 술폰화된 폴리아릴렌에테르술폰으로 제조된 복합막의 연료전지 적용을 위한 특성평가

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Characterization of Composite Membranes Made from Sulfonated Poly(arylene ether sulfone) and Vermiculite with High Cation Exchange Capacity for DMFC Applications

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요 약: 본 연구에서는 용액 캐스팅법을 이용하여 각기 다른 함량의 VMT가 첨가된 SPAES/VMT 복합막이 제조되었다. SPAES 매트릭스 내의 VMT입자 분산은 전자주사현미경으로 관찰된 평균분포에 의해 확인되었다. 1 wt%보다 적은 함량을 포함한 복합막은 고분자 매트릭스 내에 좋은 분산성을 나타내어 막의 상부층과 하부층에 매끈한 표면을 가졌다. 복합막의 함수율은 온도가 증가함에 따라 급격하게 증가되었으며 VMT는 높은 이온교환능력으로 인하여 강한 수분친화도를 가짐으로 인해 높은 모든 흡착된 수분은 bound water인 것으로 확인하였다. VMT의 함량이 1 wt%보다 적게 첨가된 복합막에서 증가된 이온전도도와 낮아진 메탄올 투과도를 확인할 수 있었다. 모든 복합막 중에서 SPAES/VMT 1.0 wt% 복합막은 선택도 측면에서 가장 뛰어난 연료전지 성능을 가졌으며 Nafion 112과 비교하여 두배 이상 우수한 값을 나타내었다. 이것은 SPAES/VMT 1.0 wt% 복합막이 직접메탄올 연료전지의 구동을 위한 가장 우수한 조건이 될것이라 사료된다.

Abstract: In this study, polymer composite membranes based on sulfonated poly(arylene ether sulfone) (SPAES) were prepared using a solution casting method with different amount of vermiculite (VMT) content. The dispersion of VMT particles in the SPAES matrix was confirmed by means of a scanning electron microscopy observation. The composite membrane containing less than 1 wt% of VMT has a smooth skin on the top and bottom, which means there is a good dispersion of VMT in the matrix. The water uptake of the composite membranes gradually increases as the temperature increases, and the results confirm that all the adsorbed water is bound water because VMT has a strong water affinity on account of its high cation exchange value. A composite membrane with a VMT content of less than 1 wt% increases the proton conductivity and reduces the methanol permeability. Of all the composite membranes, the membrane SPAES/VMT 1.0 has the best fuel cell performance in terms of membrane selectivity. The performance value of SPAES/VMT 1.0 is double that of Nafion 112, which suggests that SPAES/VMT1.0 could be an excellent candidate for direct methanol fuel cells.

Keywords: DMFC, vermiculite, proton conductivity, methanol permeability, composite membrane

1. Introduction

Direct methanol fuel cells (DMFCs) are especially

attractive for potable power applications due to their high energy density at low operating temperatures and use a liquid fuel [1,2]. To be used in DMFC systems, membranes must have an adequate level of proton con-

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Table 1. The standard CEC values (at pH of 7) [9].

Clay minerals	CEC (meq./100 g)
Kaolinite	3~15
Halloysite 2H ₂ O	5~10
Halloysite 4H ₂ O	40~50
Montmorillonite-group	70~100
Illite	10~40
Vermiculite	100~150
Chlorite	10~40
Glauconite	11~20 +
Palygorskite-group	20-30
Allophane	~70

ductivity as well as limited methanol transport capabilities. Methanol that is transported across the membrane must be able to react at the cathode without producing electricity. This methanol transport causes not only low fuel utilization, but also loss of performance by a mixed potential effect [3]. Nafion membranes, which have good chemical and thermal resistance and high proton conductivity, are commonly used as electrolytes. However, their high methanol crossover is a major drawback in DMFC applications. This limitation is associated with the Nafion microstructure: that is, the interconnected ionic domains strongly enhance the high level of proton conductivity but simultaneously accelerate the diffusion of methanol [1,4]. Some researchers have endeavored to reduce the methanol permeability through the polymer electrolyte membrane. To that end, they have used inorganic materials to produce a tortuous pathway for methanol molecules. Organic-inorganic hybrid membranes have the potential to enhance the hydration and water retention properties at high temperatures. In addition, layered silicates, such as montmorillonite (MMT), have an attractive hydrophilic property and good level of thermal stability; and the modification of layered silicate have also been studied in order to improve their proton conductivity [5-7]. Lee *et al.* prepared Nafion/

sulfonated MMT composite membranes for DMFCs. They found that these composite membranes compared favorably with a pristine Nafion membrane: specifically, the composite membranes displayed a dramatic decrease in the methanol and water permeability and slight decrease in proton conductivity [1]. Galiano *et al.* used Nafion/sulfonated laponite composite membranes for proton exchange membrane fuel cells. They found that the water retention properties were enhanced when the plasma activation modified the hydrophilic layered silicate and the surface. A membrane-electron assembly (MEA) with composite membranes is better than a Nafion membrane at a high operating temperature [6]. In our previous work, we incorporated natural and organic modified MMT was incorporated in a poly(styrene-*b*-ethylene/butylene-*b*-styrene) copolymer to reduce the methanol permeability. Hydrophilic natural MMT has a high level of proton conductivity and a low level of methanol permeability [7].

Vermiculite (VMT) has a high cation exchange capacity (CEC) due to the substitution of its main cations, namely Si⁴⁺ and Al³⁺. The substitution leads to a net negative surface charge that is compensated by an interlayer of exchangeable hydrated cations (Ca²⁺, Mg²⁺, Cu²⁺, Na⁺, and H⁺) [8]. VMT can be dispersed in water in the same manner as MMT but its platelets have a much higher aspect ratio and CEC. Table 1, which shows the standard CEC values reported by Carroll, indicates that VMT has the highest CEC of the various clay minerals [9].

In this study, the sulfonated poly(arylene ether sulfone) (SPAES)/VMT composite membranes were prepared using a solution casting method. The incorporation of hydrophilic VMT was expected to improve the water retention ability of polymer composite membranes. Moreover, its relatively high CEC and aspect ratio were expected to provide a tortuous pathway for methanol molecules without any significant loss of proton conductivity. The optimum VMT content in the SPAES matrix was examined with respect to fuel cell performance and membrane stability.

2. Experimental

2.1. Materials

The 4,4'-Dichlorodiphenylsulfone (DCDPS) and 4,4'-biphenol (BP) as the aromatic halide and diol, respectively, purchased from Tokyo Kasei (Tokyo, Japan) were recrystallized in isopropyl alcohol (IPA) and dried in a vacuum oven for a minimum of 12 h at 120°C. Fuming sulfuric acid (28% free SO₃; Aldrich, South Korea) was used to convert the DCDPS to 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS; yield: 91.4%). Sodium chloride (NaCl), sodium hydroxide (NaOH), toluene (C₆H₅CH₃), potassium carbonate (K₂CO₃), and dimethyl acetamide (DMAc) were obtained from Aldrich (South Korea) and were used as received. *N*-methylpyrrolidone (NMP; Aldrich, South Korea) was used as a solvent.

VMT, which was obtained from G.biotech Co. Ltd (South Korea), had a large heterogeneous grain size (in the range of 2 mm to 1 cm). An agate ball mill at the Korea research institute of chemical technology was used to grind the VMT to a particle size fraction of less than 100 μm.

2.2. Preparation of SPAES/VMT Composite Membranes

The SPAES was synthesized by using direct copolymerization of sodium-salted DCDPS, DCDPS, and BP in accordance with previously reported methods [10-13]. The degree of sulfonation of the prepared SPAES was controlled to 50%, and its inherent viscosity was approximately 1.5 dL/g. VMT particles were dispersed in NMP with a sonicator for 1h. The VMT content in the mixture was varied (0.5, 1, 2, and 4 wt%) on the basis of the SPAES. The SPAES was dissolved in the same solvent to obtain a 5 wt% solution. The dispersed VMT mixtures were added to a homogenous 5 wt% SPAES solution and stirred for 12 h at room temperature. The solution was cast on a silicon rubber guided glass plate. The level glass plate was stored inside a fume hood and dried slowly as the temperature was increased to 80°C using an IR ramp. The thick-

ness of all cast membranes was approximately 80 μm. The membranes were acidified in a 1 M H₂SO₄ boiling solution for 3 h, and then washed in boiling deionized water for 1 h. The SPAES/VMT composite membranes are referred to as SPAES/VMT#, where # indicates the VMT content.

2.3. Characterization

A cross-section of the membrane was observed by means of a field emission scanning electron microscope system (FE-SEM, Philips XL30 S FEG, Netherlands). The water uptake (%) of the SPAES composite membranes was measured in terms of the weight difference of a dry sample and a hydrated sample at temperatures of 25, 40, 60 and 80°C. The water state inside the hydrated membrane was determined with a differential scanning calorimeter (DSC; DSC Q20, TA Instruments, USA) at a heating rate of 10°C/min. The content of free water (%) was calculated by dividing the endothermic peak, which was derived from the fusion enthalpy of water in the temperature range of -30 to 30°C by the endothermic heat fusion of pure water, 335 J/g.

The mechanical stability of the membrane was evaluated by means of a dynamic mechanical analyzer (DMA; DMA Q800, TA Instruments, USA). The membranes were cut into 0.5 cm × 3 cm sections and examined at a rate of 1 N/min to 18 N under an isothermal condition at 25°C. The proton conductivities of the membranes were tested at various temperatures and humidities using a complex impedance analyzer (SP-300; BioLogic, France) over a frequency range of 100 mHz to 1 MHz. The composite membrane was fixed in a four-point probe cell, which consisted of four platinum wire outer current-carrying electrodes. The conductivity was calculated using the following equation:

$$\sigma = \frac{L}{R \cdot A} \quad (1)$$

where σ is the proton conductivity (in S/cm), L is the distance between the Pt electrodes (in cm), A is the

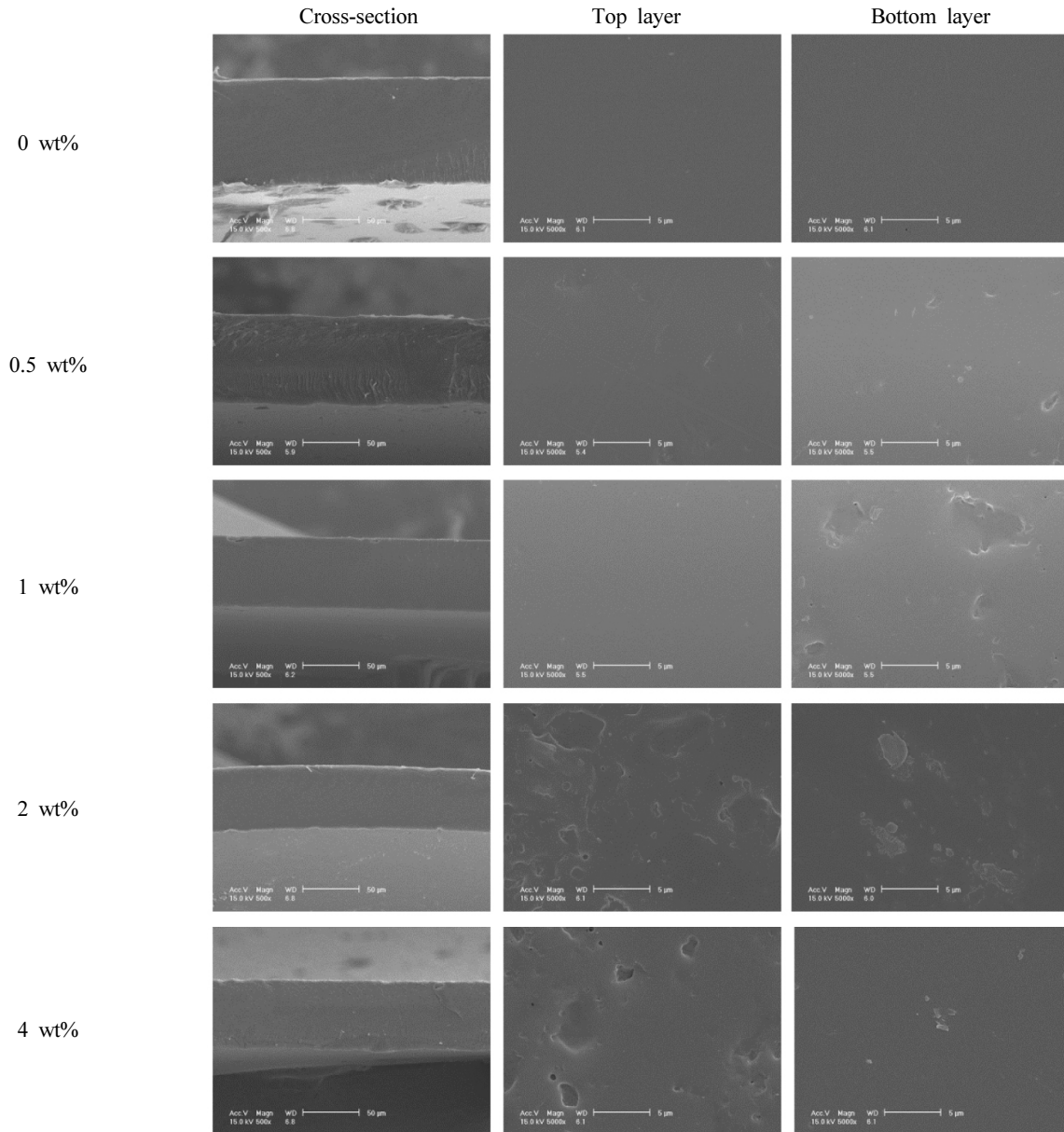


Fig. 1. SEM images of the cross-section (500 \times), top side and bottom side (5,000 \times) for the SPAES and SPAES/VMT composite membranes with different amount of VMT content.

membrane cross-sectional area (in cm^2), and R is the membrane resistance (in Ω). The methanol permeability was measured at room temperature by means of a two-chamber diffusion cell method. One chamber (80 mL) contained a 10 M (34 wt%) methanol solution and the other chamber (80 mL) was filled with deionized water. The methanol concentration was periodically recorded with a GC-M600D gas chromatograph

(Younglin Co. South Korea) equipped with a thermal conductivity detector (TCD) and a PoraPack Q 80/100 packed column. Using a predetermined standard curve, a membrane's methanol permeability was calculated from the linear interpolation of the permeate-side cell methanol concentration C_B , versus time, t . The slope of the graph can be written as $(t)/t_0 = \alpha$. The methanol permeability can be calculated as follows:

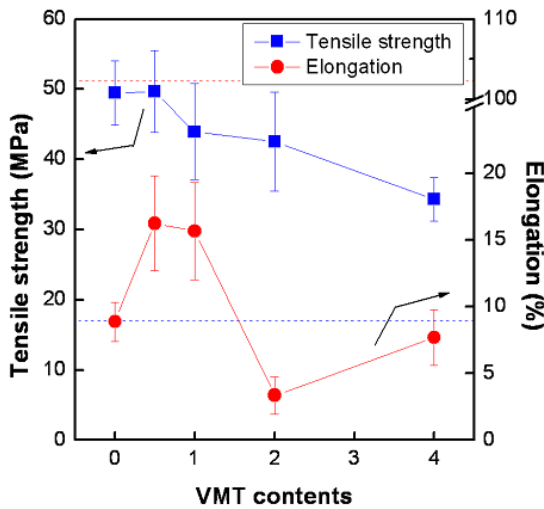


Fig. 2. Mechanical properties of the SPAES and SPAES/VMT composite membranes with different amount of VMT content.

$$P = \alpha \times \frac{V_B \cdot L}{A \cdot C_A} \quad (2)$$

where V_B is the volume of the water compartment, C_B is the concentration of methanol in the permeate compartment at time, t , A is the membrane effective area, and L is the membrane thickness.

3. Results and Discussion

3.1. Dispersion of Vermiculite Particles

SPAES/VMT composite membranes containing various amounts of VMT were prepared by a solution casting method. Although the VMT particles are well dispersed and swollen in NMP, the aggregation of VMT in the polymer matrix must be confirmed on account of the possible gravity-induced VMT accumulation at the bottom during the fabrication of the membrane. The dispersion of VMT particles in the SPAES matrix was observed with a FE-SEM at $500 \times$ and $5,000 \times$ magnifications of a membrane cross-section and top and bottom. Fig. 1 shows that the VMT in the SPAES matrix is highly compatible and homogenous until the addition of 1 wt% of VMT, representing very smooth surface morphologies. When the VMT

content exceeds 2 wt%, partially aggregated VMT and its detachment in the SPAES matrix can be observed at the top and bottom.

3.2. Mechanical Properties

A proton conducting membrane with excellent mechanical strength is required to operate for a long lifetime in DMFCs. The mechanical properties, including the tensile strength and elongation at break, were measured at room temperature with a DMA and the results are presented in Fig. 2. A comparison of a SPAES membrane and Nafion 112 membrane shows a huge difference in the values of the tensile strength and elongation. The SPAES membrane has a high tensile strength of approximately 50 MPa and low elongation of less than 10%, whereas the Nafion 112 membrane has relatively low tensile strength of 18 MPa and high elongation of more than 100%. These results indicate that the SPAES membrane is brittle and stiff whereas the Nafion 112 is soft and flexible.

The SPAES/VMT0.5 membrane has a maximum tensile strength of 50 MPa and an elongation at break value of 17%. The SPAES/VMT1 membrane has a slightly weaker tensile strength in slightly decreased, but an elongation at break value is higher than that of the other composite membranes, possibly due to the dispersion or exfoliation of the VMT layers [5]. However, when the VMT content exceeds 2 wt%, there is a significant decline in both tensile strength and elongation. The aggregation of VMT particles in the SPAES matrix appears to make the membrane more brittle and fragile. Therefore, SPAES/VMT composite membranes with less than 1 wt% VMT can be excellent candidates for long-term application in DMFC systems.

3.3. Water Uptake and State

Fig. 3 shows the results of the membrane stability in relation to the water uptake at different temperatures of the SPAES and SPAES/VMT composite membranes. The water uptake of SPAES membrane at room temperature is higher than that of the composite membranes. However, when the temperature of the water is

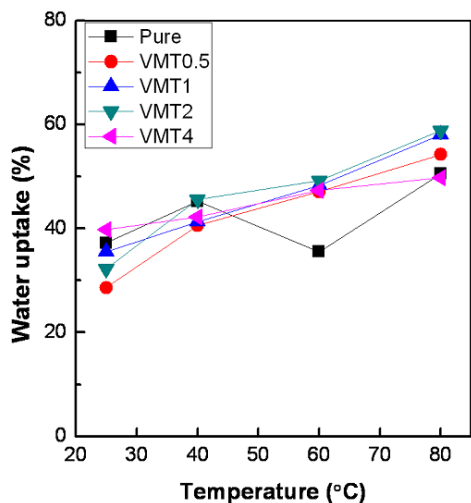


Fig. 3. Water uptakes of the SPAES and SPAES/VMT composite membranes containing different amount of VMT content at various temperatures.

increased to 80°C, the composite membranes adsorb a higher amount of water than the SPAES membrane because VMT particles have a high water affinity. As a result, the composite membranes have a higher water uptake at the high temperature of 80°C.

The state of water absorbed in a membrane is an important parameter that affects the proton conductivity and methanol permeability. Our previous studies on fuel cell membranes were focused on the water state of a proton conducting membrane so that we could understand how the water state affects the fuel cell performance [7]. However, this study is the first in which the DSC failed to detect the amount of free water (the endothermic peak around 0°C). After several repetitions of the experiments, we concluded that all the water absorbed in VMT composite membranes is bound by the strong interaction of water molecules with the exchange cations and surface layers. The strong water sorption in the SPAES/VMT composite membranes can be explained as follows: all the structural sites in the interlayer spaces are filled with water molecules and with all the possible water-cation, water-surface oxygen atoms, and water-water bonds that can be confirmed for a particular level of hydration [14,15]. The general water adsorption ability of the expended VMT is re-

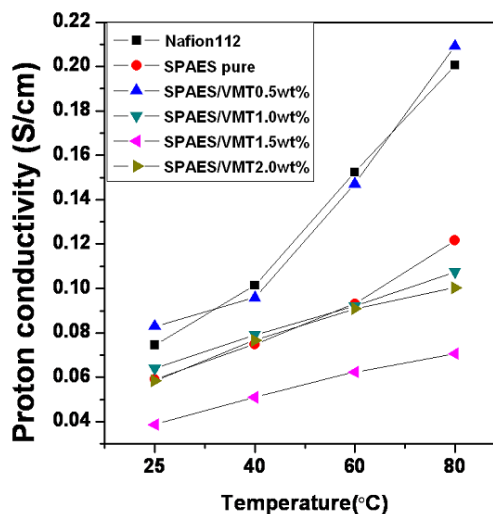


Fig. 4. Proton conductivities of the Nafion 112 (dotted line), SPAES, and SPAES/VMT composites containing different amount of VMT content at various temperatures.

portedly in the weight range of 200% to 325% and in the volume range of 20 to 50% [16].

3.4. Proton Conductivity

The proton conductivity of the membranes was measured in terms of the membrane resistance using an AC impedance. Fig. 4 shows that for all membranes the proton conductivity increases as the temperature increases. Of all the SPAES/VMT composite membranes, the SPAES/VMT 0.5 membrane has the highest proton conductivity at all temperatures. Interestingly, the proton conductivity soars as the temperature of the SPAES/VMT 0.5 membrane increases; in this case, the SPAES/VMT 0.5 membrane has an even higher proton conductivity (0.21 S/cm) than that of the Nafion 112 (0.20 S/cm). This might be due to the combined effect of two factors. Firstly, it has the better water retention at high temperatures, which in turn can be attributed to the strong hygroscopic property of VMT. And, secondly, it has strong barrier properties (which prevent the transport of protons from the anode to the cathode) because the VMT particles in the SPAES matrix are well dispersed [16-18]. However, the proton conductivity of the composite membranes gradually declines when the VMT content exceeds 2 wt%. The re-

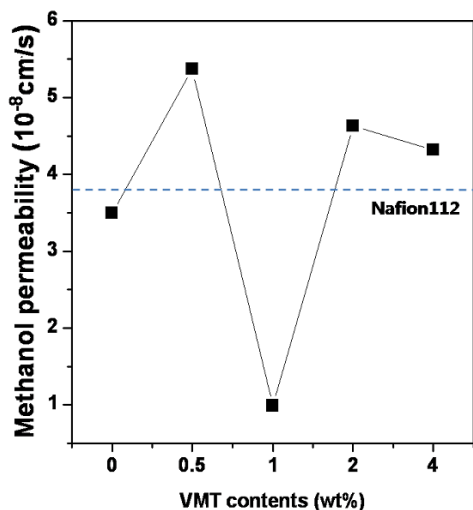


Fig. 5. Methanol permeabilities of the Nafion 112 (dotted line), SPAES, and SPAES/VMT composite membranes with different amount of VMT content.

sults in Fig. 1 confirm that when the VMT content exceeds 2 wt% aggregation occurs in the SPAES matrix and the transfer of protons in the membrane is restricted [19]. In conclusion, when the VMT content is less than 1 wt%, the proton conductivity is improved by the strong hydroscopic property and the good dispersibility of the VMT particles.

3.5. Methanol Permeability

Fig. 5 shows the methanol permeability of the SPAES membrane and the SPAES/VMT composite membranes with different amount of VMT content. The SPAES/VMT composite membranes have less methanol permeability than the SPAES membrane if the VMT content is less than 1 wt%. This result is related to the fact that the barrier properties of the VMT layers are strengthened by the creation of a tortuous pathway that retards the permeation of methanol molecules through the SPAES matrix. When the membrane has a VMT content of 2%, the methanol permeability dramatically increases most likely on account of the aggregation of VMT particles, which produces a partially defected morphology in the membrane. We concluded therefore that the dispersion of a clay layer can significantly reduce the methanol permeability because it controls the

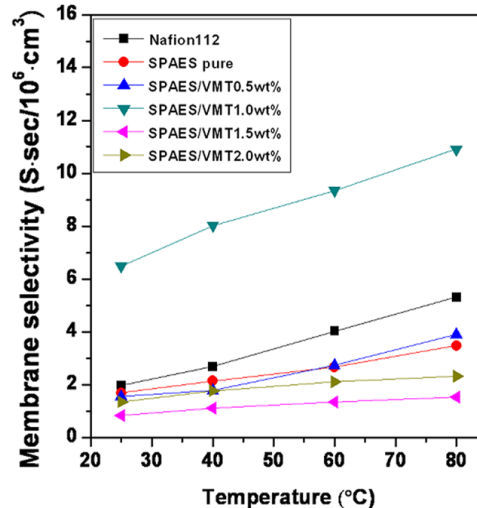


Fig. 6. Membrane selectivities of the Nafion 112 (dotted line), SPAES, and SPAES/VMT composite membranes with different amount of VMT content at various temperatures.

distance of the methanol transport pathway through the exfoliated layers. Our results confirm that a VMT particle content of 1 wt% is the most effective proportion in terms of methanol permeability; this proportion yields the lowest methanol permeation of $0.99 \times 10^{-8} \text{ m}^2/\text{s}$ with well dispersed particles in the membrane.

3.6. Membrane Selectivity

Membrane selectivity is a commonly accepted means of evaluating membrane performance in terms of proton conductivity and methanol permeability [20,21]. For the SPAES membrane and the SPAES/VMT composite membranes, we defined membrane selectivity as the ratio of proton conductivity to methanol permeability. Fig. 6 shows the membrane selectivity of the SPAES membrane and SPAES/VMT composite membranes for different amount of VMT content at various temperatures. The synergistic effect of increasing the proton conductivity and decreasing the methanol permeability improves the overall fuel cell performance of SPAES/VMT composite membranes with a VMT content less than 1 wt%. Note that the SPAES/VMT composite membrane with a VMT content of 1 wt% has the best performance; in fact, its performance is two

times greater than that of the Nafion 112 membrane.

4. Conclusion

VMT has potential as a barrier material for methanol transport due to its layered silicate structure and high hydroscopic property. SPAES/VMT membranes with different amount of VMT content were prepared via a solution casting method. The dispersion of VMT into SPAES matrix was measured by means of a SEM observation of a cross-section and top and bottom of the composite membranes. Good VMT dispersion was found in composite membranes with a VMT content of less than 1 wt%. Composite membranes with a VMT content in excess of 2 wt% have a partially aggregated portion or depressions on the top and bottom of the membranes. These results correlate well with the mechanical properties of the composite membranes. The mechanical properties of the membrane with a VMT content of less than 1 wt% appear to be enhanced on account of the better dispersion or exfoliation. In contrast, the composite membrane with a VMT content of more than 2 wt% has significantly weaker mechanical strength due to partial aggregation. The water uptake of the SPAES membrane and the SPAES/VMT composite membranes gradually increases as the temperature increases; and the gradient of increase is sharper in composite membranes with a high VMT content. This outcome may be due to the fact that the high CEC of VMT gives it a strong hydroscopic property. The highest proton conductivity was obtained with the SPAES/VMT 0.5 membrane on account of its strong water adsorption ability and good dispersion of VMT. The lowest methanol permeability was found in the SPAES/VMT 1 membrane because the exfoliated or dispersed layers of VMT form a tortuous pathway for methanol molecules. A composite membrane with a VMT content of less than 1 wt% has a high proton conductivity and a low methanol permeability. These factors work together to improve the fuel cell performance. Thus, this type of membrane is highly suitable for DMFC applications.

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