

Phosphoric Acid-doped SDF-F/poly(VI-co-MPS)/PTFE Membrane for a High Temperature Proton Exchange Membrane Fuel Cell

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Sulfonated poly(fluorinated arylene ether)s (SDF-F)/poly[(*N*-vinylimidazole)-co-(3-methacryloxypropyl-trimethoxysilane)] (poly(VI-co-MPS))/poly(tetrafluoroethylene) (PTFE) is prepared for a high temperature proton exchange membrane fuel cell (PEMFC). The reaction of the membrane with phosphoric acid forms silicate phosphor, as a chemically bound proton carrier, in the membrane. Thus-formed silicate phosphor, nitrogen in the imidazole ring, and physically bound phosphoric acid act as proton carriers in the membrane. The physico-chemical and electrochemical properties of the membrane are investigated by various analytical tools. The phosphoric acid uptake and proton conductivity of the SDF-F/poly(VI-co-MPS)/PTFE membrane are higher than those of SDF-F/PVI/PTFE. The power densities of cells with SDF-F/poly(VI-co-MPS)/PTFE membranes at 0.6 V are 286, 302, and 320 mW cm⁻² at 150, 170, and 190 °C, respectively. Overall, the SDF-F/poly(VI-co-MPS)/PTFE membrane is one of the candidates for anhydrous HT-PEMFCs with enhanced mechanical strength and improved cell performance.

Key Words : High-temperature PEMFCs, Proton conducting membrane, Acid-doped membrane, Anhydrous condition

Introduction

A proton exchange membrane fuel cell (PEMFC) has been considered as one of the most promising clean energy production systems and as a suitable primary power source for transportation and stationary applications due to its major advantages such as high efficiency, high energy density, etc.¹⁻⁶ The commercial application of PEMFC, however, has been limited by some issues such as cost, performance, and stability.¹⁻⁶ Currently, the typical PEMFC uses perfluoro-sulfonic acid (PFSA) polymer membranes, for instance Nafion and its derivatives.¹⁻⁶ Even though PFSA polymer membranes have demonstrated good performance and stability below 90 °C, it still has several obstacles, such as high cost and low proton conductivity and poor performance under elevated temperature conditions.^{2,4-6}

PEMFCs operated under high temperature and anhydrous conditions provide valuable advantages⁷ including high tolerance to impurities in the fuels, such as CO and hydrocarbon, reduction of the amount of noble metal catalyst on the electrode due to fast reaction kinetics, and construction of compact system without external humidifiers. Thus, the development of new PEM membranes for anhydrous, high temperature operation has been extensively studied.^{1,6,8,9} In our previous study,⁴ we proposed a novel membrane for high-temperature PEMFCs, H₃PO₄-doped sulfonated poly(fluorinated arylene ether)s (SDF-F)/poly(*N*-vinylimidazole) (PVI) membrane which is less expensive and more durable in phosphoric acid. The thermal stability and conductivity (~2.85 × 10⁻² S cm⁻¹) of the membrane were comparable to

those of PBI.⁸ These PVI-series membranes, however, have poor mechanical properties after the reaction with phosphoric acid.⁴

In the present study, we prepared SDF-F/poly[(*N*-vinylimidazole)-co-(3-methacryloxypropyl-trimethoxysilane)]-(poly(VI-co-MPS))/PTFE membrane which is doped with phosphoric acid to form silicate phosphor as a proton carrier. We used porous poly(tetrafluoroethylene) (PTFE) as a reinforcement material to improve its mechanical properties and tensile strength. The prepared membrane was characterized by various analytical tools. Single cell test for SDF-F/poly(VI-co-MPS)/PTFE membrane was carried out at 150, 170, and 190 °C to examine the cell performance by measuring cell voltage degradation and phosphoric acid loss.

Experimental

Preparation of Blending Membrane and MEA. The synthesis of SDF-F was performed according to the procedure described in our previous publication.³ The prepared SDF-F (1.00 g) was dissolved in VI (4.23 g, 0.045 mol) and MPS (1.22 g, 0.005 mol) with azobisisobutyronitrile (AIBN) as an initiator for the polymerization of VI and MPS. The initial homogeneous mixture of SDF-F, VI, and MPS converts to a viscous solution during the polymerization process. The viscous solution was placed on a side of porous PTFE film (~10 μm thickness), and then it was pressed at 100 kgf cm⁻². Then, the other side of PTFE film was treated by the same procedure. Subsequently, it was hot-pressed (40 kgf cm⁻²) at 130 °C for 1 hour. The prepared SDF-F/

poly(VI-co-MPS)/PTFE membrane was immersed into the phosphoric acid solution saturated by an excess amount of phosphorous pentoxide (P_2O_5) at 100 °C for 48 hours. The prepared membrane was sandwiched in between two commercial Pt/C electrodes (E-TEK, Pt loading = 0.5 mg cm^{-2}), and the membrane electrode assembly (MEA) was hot-pressed (40 kgf cm^{-2}) at 130 °C for 5 minutes. The detailed procedure was described elsewhere.⁴

Physical and Electrochemical Characterizations. The thermal stability of the membrane was investigated by thermogravimetric analysis (TGA, TA Instruments, SDT 2960). A ramping speed was 10 °C min^{-1} over the temperature range of 25–800 °C under a nitrogen atmosphere. The phosphoric acid uptake of the membranes was determined by measuring the difference of masses before and after immersing them into phosphoric acid. The chemical structure was identified by Fourier transform-infrared spectroscopy (FT-IR, Nicolet 380). The morphology and the elemental distribution of the prepared membrane were investigated by field emission-scanning electron microscopy (FE-SEM, Hitachi S-4300) and energy dispersive spectroscopy (EDS, Horiba EX-200) coupled with SEM. Electrochemical impedance spectroscopy (EIS) was carried out to measure the proton conductivity using a two probe technique^{3,4} with IM6 impedance analyzer (Zahner elektrik Co.). Impedance spectra were taken after an appropriate equilibrium period in the frequency range of 10 mHz to 10 kHz with AC perturbation of 5 mV. The single cell tests were performed at 150, 170, and 190 °C without any external humidification. The both electrodes were initially purged by dry nitrogen gas (flow rate = 80 $cm^3 min^{-1}$) for 12 hours. Then, the main experiments were performed with H_2 and O_2 (flow rate = 80 $cm^3 min^{-1}$) introduced into the anode and the cathode, respectively. To determine the amount of phosphoric acid loss, two stainless steel bottles were connected to gas outlets to collect the exhausted water during the experiment. The concentration of phosphoric acid in the exhausted water was analyzed by an ordinary pH meter.

Results and Discussion

Characterization. After the preparation of polymer membranes, the formation of copolymer was examined by infrared spectroscopy. Figure 1 shows the infrared spectra of poly MPS (PMPS), poly VI (PVI), poly(VI-co-MPS), and phosphoric acid-doped poly(VI-co-MPS). The obtained IR spectra of PMPS and PVI are corresponding to the previous publications.^{10–18} The IR spectrum of PMPS shows its characteristic vibrational features at 2841 (C–H stretching in OCH_3), 1729 (C=O stretching), 1460 (CH_2 bending), 1085 (Si–O–C asymmetric stretching), and 980 cm^{-1} (Si–O–Si bending).^{10–14} Interestingly, the IR spectrum of PMPS does not show the vibrational feature at 1637 cm^{-1} , which is assigned to C=C stretching, and the absence of monomeric C=C stretching feature indicates the formation of polymerized MPS. For PVI, the vibrational features were observed at 1497 (C–C and C=N (ring) stretching), 1227 (C–H (ring) in-plane bending and C–N (ring) stretching), and 915 cm^{-1}

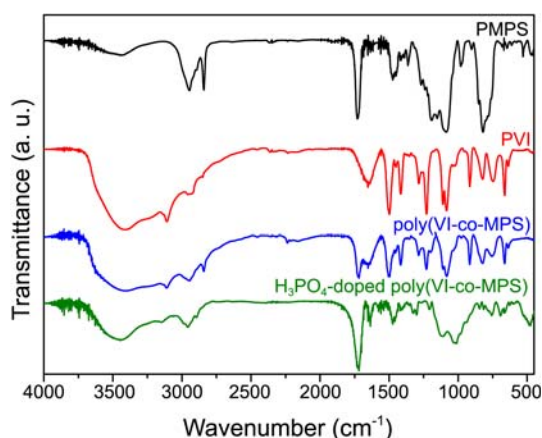


Figure 1. The FT-IR spectra for (a) PMPS, (b) PVI and (c) poly(VI-co-MPS), and (d) H_3PO_4 -doped poly(VI-co-MPS).

(ring deformation) which are in good agreement with previous literatures.^{15–18} The IR spectrum of poly(VI-co-MPS) shows the combined features of those of PMPS and PVI. However, the doping of phosphoric acid into poly(VI-co-MPS) causes significant change in IR spectrum. The frequency regions of 1250–800 and $\sim 500 cm^{-1}$ which were assigned the main absorption bands of phosphoric acid and/or phosphates.^{8,19} Specifically, the broad absorption band at $\sim 1020 cm^{-1}$ is attributed to the presence of Si–O–P bond, and other one at $\sim 1120 cm^{-1}$ with a shoulder at $\sim 1170 cm^{-1}$ is originating from the asymmetric stretching of PO_2 in PO_4 group.^{5,19,20} The result of IR unambiguously shows that silicate phosphor is formed by the reaction between the phosphoric acid and the silane group in MPS.

For the operation of a high temperature PEMFC, the membranes should have a good thermal stability. Otherwise, the cell operation at high temperature may give damages to membranes that cause critical problems such as mass flow and voltage drop. The thermal stability of prepared membranes was investigated by TGA. Figure 2 shows TGA results of SDF-F/poly(VI-co-MPS) and SDF-F/poly(VI-co-MPS)/PTFE membranes. The weight loss below 100 °C is mainly due to the loss of water. Then, the significant weight loss at 300–

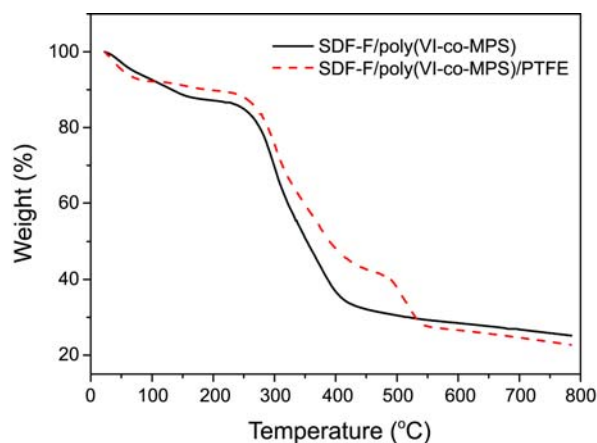


Figure 2. The TGA data of SDF-F/Poly(VI-co-MPS) blend membrane and SDF-F/Poly(VI-co-MPS)/PTFE blend membrane.

400 °C is attributed to the elimination of sulfonyl group in SDF-F⁴ and the degradation of VI rings^{17,18} and MPS.^{21,22} The thermal degradation temperature of PTFE is ~500 °C corresponding to the previous result.⁴ Hence, the onset temperature for the degradation of SDF-F/poly(VI-co-MPS)/PTFE membrane is higher than 250 °C. It is indicated that the prepared membrane demonstrates a good thermal stability enough to endure the high temperature operation (150-200 °C).

The high proton conductivity can be achieved by the addition of proton carriers, such as a heteropoly acid.^{23,24} In this study, in order to obtain a good proton conductivity, SDF-F/poly(VI-co-MPS)/PTFE membrane was reacted with phosphoric acid since it acts as a proton carrier.²⁵ As a result, through the reaction of the silane groups in MPS with phosphoric acid, the silicate phosphor was formed as shown in Figure 1. Thus-formed silicate phosphor and the physically adsorbed phosphoric acid affect the proton conductivity. Phosphoric acid uptake of SDF-F/poly(VI-co-MPS)/PTFE membrane was 561%. On the other hand, the phosphoric acid uptake of SDF-F/PVI/PTFE membrane (~400%⁴) was lower than that of SDF-F/poly(VI-co-MPS)/PTFE.

The morphology of the membrane and distribution of Si and P in the membrane were investigated by SEM-EDS. Figure 3 shows SEM and EDS images for the cross-section of SDF-F/poly(VI-co-MPS)/PTFE membrane. Figures 3(a)

and (c) show the morphologies of the membranes after drying at 120 °C and after subsequent reaction with phosphoric acid for 48 hours, respectively. Prior to and after soaking the membrane in phosphoric acid, the thicknesses of the membrane were 66 and 172 μm, respectively. Figure 3(b) shows the distribution of Si of dried membrane shown in Figure 3(a), and it indicates that SDF-F/poly(VI-co-MPS) was perfectly impregnated in porous PTFE layer. Figure 3(d) shows P mapping image of phosphoric acid-doped membrane shown in Figure 3(c) which indicates the homogeneous distribution of P in the membrane after immersing the membrane into phosphoric acid. It is evident that the SDF-F and poly(VI-co-MPS) was blended homogeneously and the phosphoric acid is doped well throughout the SDF-F/poly(VI-co-MPS)/PTFE membrane.

Electrochemical Properties. The proton conductivity of the phosphoric acid-doped SDF-F/poly(VI-co-MPS)/PTFE membrane was investigated using electrochemical impedance spectroscopy in the frequency range of 10 mHz - 10 kHz at 150-190 °C. The proton conductivity was determined from the intercept of bulk resistance at high frequency in Nyquist plot. The detailed procedure is described elsewhere.⁴ At 150 °C, the proton conductivity of the membrane is $6.01 \times 10^{-2} \text{ S cm}^{-1}$ which is much higher than that of SDF-F/PVI/PTFE membrane ($2.20 \times 10^{-2} \text{ S cm}^{-1}$ at 150 °C⁴). The conductivities at 170 and 190 °C are 7.28×10^{-2} and $7.68 \times 10^{-2} \text{ S cm}^{-1}$,

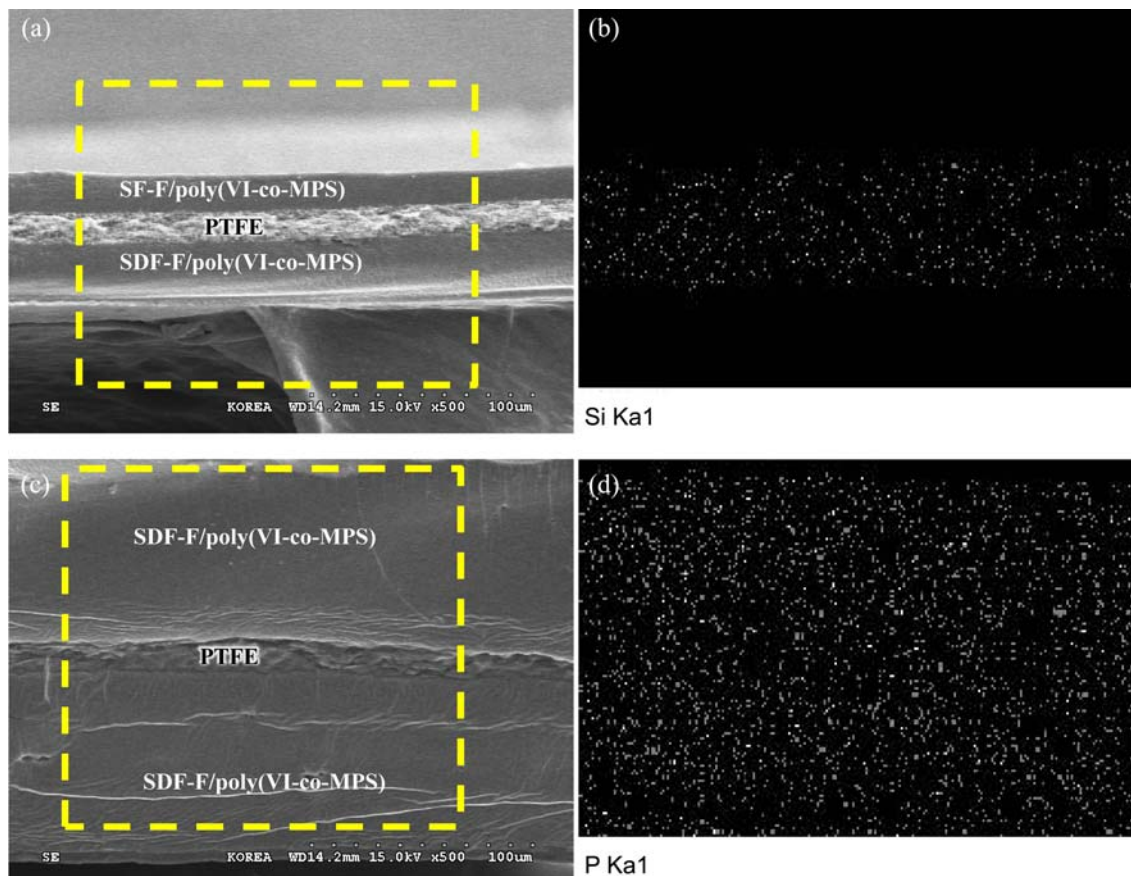


Figure 3. SEM images of the cross section of the SDF-F/Poly(VI-co-MPS)/PTFE blend membrane (a) before soaking, (b) Si mapping image of (a), SDF-F/Poly(VI-co-MPS)/PTFE blend membrane (c) after soaking in phosphoric acid, and (d) P mapping image of (c).

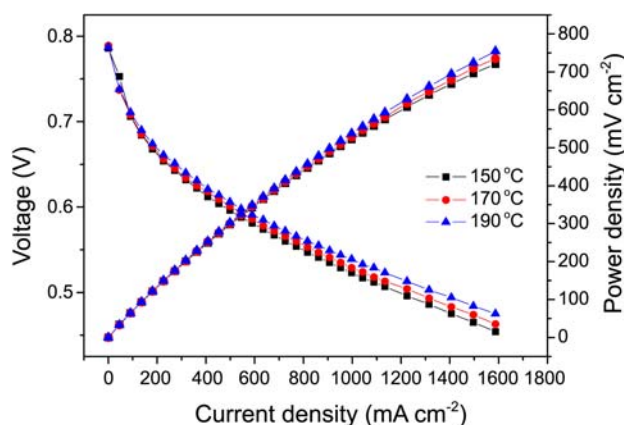


Figure 4. Current density vs. voltage and power density of the single cell operation with the SDF-F/Poly(VI-co-MPS)/PTFE blend membrane using hydrogen and oxygen gas (flow rate 80 cm³ min⁻¹) with no external humidification under ambient pressure at various temperature; (■) 150 °C, (●) 170 °C, and (▲) 190 °C.

respectively. From the Arrhenius plot, the activation energy of proton conduction in this membrane is determined to 10.06 kJ/mol. This activation energy is lower than and/or comparable to that of phosphoric acid-doped PBI membrane.²⁶ The better proton conductivity of phosphoric acid-doped SDF-F/poly(VI-co-MPS)/PTFE membrane than that of SDF-F/PVI/PTFE is originating from the formation of silicate phosphor and high phosphoric acid uptake in the membrane because silicate phosphor and/or phosphoric acid can act as proton carriers. Moreover, due to the characteristics of acid-doped membrane that the conductivity proportionally increases with the doping level of phosphoric acid at constant temperature, phosphoric acid-doped SDF-F/poly(VI-co-MPS)/PTFE membrane with higher phosphoric acid uptake have better conductivity than SDF-F/PVI/PTFE at the same temperature. In this membrane, the high proton conductivity can be obtained with amphoteric acid as an active dopant because the amphoteric acids give associated anions which are able to act as both donors and acceptors in proton transfer.^{24,27}

The performance of the membrane was investigated by measuring current density and voltage of a single cell. The single cell test was performed at 150, 170, and 190 °C without any external humidification. Figure 4 represents the single cell performance as a function of operating temperature. The current density at constant voltage increases with an increase in the temperature. This is a typical phenomenon of an acid-doped membrane since the rate of reaction on the electrode and the proton conductivity of membrane are enhanced as the cell temperature increases.^{28,29} The power densities of SDF-F/poly(VI-co-MPS)/PTFE membrane at 0.60 V were 286, 302, and 320 mW cm⁻² at 150, 170, and 190 °C, respectively. This power density of SDF-F/poly(VI-co-MPS)/PTFE membrane is higher than that of SDF-F/PVI/PTFE membrane (263.5 mW cm⁻² at the temperature of 150 °C⁴).

The durability of the SDF-F/poly(VI-co-MPS)/PTFE membrane was examined at 190 °C under the same condition as the single cell test, and a control experiment was performed with SDF-F/PVI/PTFE membrane. Figure 5 shows the cell

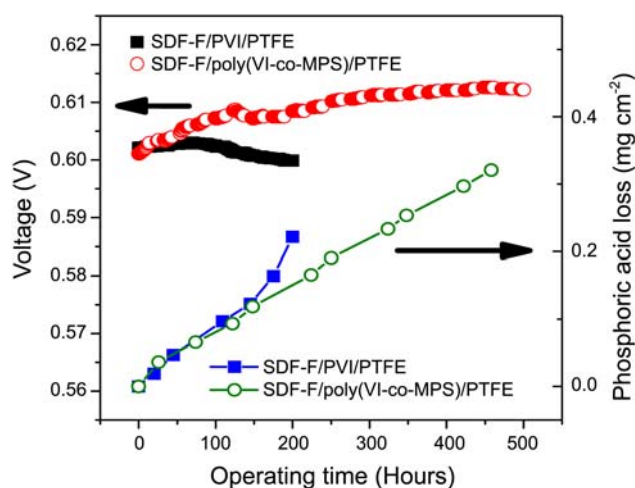


Figure 5. Voltage and phosphoric acid loss during long-term operation for SDF-F/PVI/PTFE and SDF-F/Poly(VI-co-MPS)/PTFE blend membrane fuel cell operated at 190 °C with hydrogen and oxygen gas under steady-state operating conditions.

voltage and the amount of phosphoric acid loss from the membrane as a function of operating time. The cell voltage and phosphoric acid loss of SDF-F/PVI/PTFE and SDF-F/poly(VI-co-MPS)/PTFE membranes were monitored at the fixed current densities of 470 and 533 mA cm⁻², respectively. For the SDF-F/PVI/PTFE membrane, even though the voltage drop was not observed for 0-70 hours, we observed the reduction of cell voltage after 70 hours. The rates of voltage drop and phosphoric acid loss were 11 μV h⁻¹ and 1.11 × 10⁻³ mg cm⁻² h⁻¹, respectively. On the other hand, for SDF-F/poly(VI-co-MPS)/PTFE membrane, the voltage drop was not observed for 500 hours. Interestingly, the voltage increases from 0.601 to 0.612 V during the durability test, even if the loss of phosphoric acid from the membrane was observed. The rate of phosphoric acid loss was 7.4 × 10⁻⁴ mg cm⁻² h⁻¹ which is much lower than that of SDF-F/PVI/PTFE membrane. The phosphoric acid loss is the main problem in degradation of H₃PO₄-doped polymer membrane.³⁰ Interestingly, even though the phosphoric acid was continuously leaked from SDF-F/poly(VI-co-MPS)/PTFE membrane, the voltage drop was not observed in the present study. Because the membrane initially contains excess amount of phosphoric acid which is the weakly (physically) bound phosphoric acid, the initial loss rate of phosphoric acid measured by pH of the exhausted water should be higher than the average value. It is reported that the concentration of phosphoric acid in the exhausted water for the acid-doped PBI membrane³¹ was initially high. After a certain time, however, the loss rate decreases and is much lower than initial value.³¹ Moreover, due to the reduction of the concentration of phosphoric acid in the membrane with increasing operating time, the flux of phosphoric acid leaked from the membrane should also decrease according to Fick's law. In fact, considering the formation of carbonates in the exhausted water from atmospheric CO₂, the initial rate of phosphoric acid loss (7.4 × 10⁻⁴ mg cm⁻² h⁻¹) is over-estimated. Therefore, the reaction of SDF-F/poly(VI-co-MPS)/PTFE membrane with phosphoric acid forms silicate

phosphor, as a chemically bound proton carrier, in the membrane. The existence of silicate phosphor in the membrane increases its proton conductivity and improves the cell performance.

Conclusion

We successfully prepared phosphoric acid-doped sulfonated poly(fluorinated arylene ether)s (SDF-F)/poly[(*N*-vinylimidazole)-co-(3-methacryloxypropyl-trimethoxysilane)] (poly(VI-co-MPS))/PTFE as a polymer electrolyte membrane for high temperature PEMFC and investigated the membrane with various analytical tools. The chemical structure of prepared membrane was confirmed by FT-IR. SDF-F/poly(VI-co-MPS)/PTFE membrane shows a better thermal stability with respect to PVI-series membranes and homogeneous distribution of Si and P after the reaction with phosphoric acid. The membrane has higher phosphoric acid uptake (561%) and proton conductivity (6.01×10^{-2} - 7.68×10^{-2} S cm⁻¹ at 150-190 °C) with respect to SDF-F/PVI/PTFE. For the single cell test (cell voltage = 0.6 V), power density was 320 mW cm⁻² at 190 °C, and it shows stable performances. For steady-state fuel cell operation at 190 °C, the phosphoric acid loss rate from the SDF-F/poly(VI-co-MPS)/PTFE blend membranes was 7.4×10^{-4} mg cm⁻² h⁻¹. These experimental results show that the SDF-F/poly(VI-co-MPS)/PTFE membranes has a good proton conductivity, stability, and high cell performance for high temperature operation. The SDF-F/poly(VI-co-MPS)/PTFE blend membranes can be a promising as the proton conducting electrolyte for the PEMFCs working at the high temperatures (150-190 °C).

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