Short communication

Sulfonated poly(fluorinated arylene ether)s/poly(*N*-vinylimidazole) blend polymer and PTFE layered membrane for operating PEMFC at high temperature

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Abstract

We prepared a novel phosphoric acid-doped sulfonated poly(fluorinated arylene ether)s/poly(*N*-vinylimidazole) blend polymer and poly(tetrafluoroethylene) (PTFE) layered membrane. The thermal and electrochemical properties of the new layered membrane were investigated by thermogravimetric analysis (TGA), electrochemical impedance spectroscopy (EIS), as well as the performance of its membrane electrode assembly (MEA). The morphology of membrane was observed with field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS). The fabricated membrane shows good mechanical property comparable to PBI membrane. The conductivity of new layered membrane was similar to that of polybenzimidazole (PBI) at high temperature. The single cell test showed that new PTFE layered membrane had a good performance over 150 °C. The PTFE layered membrane can be an alternative approach for PEMFC applications at high temperature.
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Keywords: High-temperature PEMFCs; PTFE layered membranes; Poly(fluorinated arylene ether)s; Poly(*N*-vinylimidazole)

1. Introduction

Fuel cells offer a highly efficient, environmentally friendly clean energy, not limited by the Carnot Cycle. Especially, polymer electrolyte membrane fuel cells (PEMFCs) are receiving more attention in the past few years because of their abilities as transportation application and power generators for both stationary and mobile [1]. Conventional PEMFC generally operates using Du Pont's perfluorosulfonic acid (PFSA) polymer membranes (e.g. Nafion®) as the electrolyte [2,3]. PFSA membranes perform well under hydrated conditions, below 90 °C. Unfortunately, Nafion® has instability, poor proton conductivity, and even degrades in low humidity at high temperatures above the boiling temperature of water [4–9].

High-temperature working PEMFC have certain advantages: (1) high tolerance to fuel impurities, especially significant quantities of carbon monoxide (>1% CO at 150 °C), (2) effective heat management, (3) increase of the cathode kinetic reaction rate, (4) elimination of cathode flooding, (5) no additional pressure requires, and (6) performance relatively independent of humidity [10].

In order to achieve higher operating temperatures, many new modified membranes have been studied in recent years. Among them, poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] (polybenzimidazole, PBI) and poly(2,5-benzimidazole) (ABPBI) are most promising membranes for high temperature. These membranes are less expensive than Nafion®, no humidification in PEMFC application, and working temperature reaches almost 200 °C. However, the cost of PBI is still high and ABPBI membranes ($\eta_{inh} = 2.4 \, dl \, g^{-1}$) were completely dissolved in concentrated 85% phosphoric acid [11].

We have also tried to synthesis novel membrane which is less expensive and more durable in phosphoric acid for high-temperature operation. We fabricated acid-doped sulfonated poly(fluorinated arylene ether)s (SDF-F)/poly(*N*-vinylimidazole) (PVI) blend membrane, which had good thermal stability and were insoluble in 100% phosphoric acid. The conductivity ($\sim 2.85 \times 10^{-2} \, S \, cm^{-1}$) of this membrane was comparable to that of PBI, but the mechanical strength was not good [12].

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In the present study, we prepared new proton exchange membrane with good mechanical property using PTFE film as a low cost, porous supporting material and sulfonated poly(fluorinated arylene ether)s (SDF-F)/poly(*N*-vinylimidazole) (PVI) blend polymer. The acid/base polymer with porous PTFE film layered membrane was impregnated in phosphoric acid solution with excess phosphorous oxide. Recent research reports have shown that porous PTFE-based composite membranes were prepared by impregnating Nafion® or PBI in order to reduce cost or to increase mechanical strength. Porous PTFE film used is chemically inert, suitable for use throughout the entire pH range, and withstand high temperature. In addition, it is dimensionally stable, soft and conformable, and high-tensile strength [13].

In this paper, we report the preparation of new polymer electrolyte membrane using sulfonated poly(fluorinated arylene ether)s/poly(*N*-vinylimidazole) blend membrane and PTFE film. The mechanical strength was measured by tensile strength. The characteristics of new membrane were observed by TGA and FE-SEM/EDS. The mechanical strength and thermal stability were improved by using PTFE film compared to sulfonated poly(fluorinated arylene ether)s/poly(*N*-vinylimidazole) blend membrane. The cell performance of the reinforced membrane with PTFE film was tested to determine whether the membrane was suitable for application in PEMFC at high temperatures. This phosphoric acid-doped membrane shows similar cell performance compared to PBI and ABPBI from 150 to 190 °C.

2. Experimental

2.1. Materials

The synthesis of poly(fluorinated arylene ether)s was from *N,N*-decafluorobiphenyl (Aldrich Chemical Co., 99%, DF) and 4,4′-(hexafluoro-isopropylidene)diphenol (Aldrich Chemical Co., 97%, F) using potassium carbonate (Junsei Chemical Co.) as a catalyst and *N,N*-dimethylacetamide (Junsei Chemical Co., DMAc) as a solvent. Sulfonated poly(fluorinated arylene ether)s were obtained from poly(fluorinated arylene ether)s (DF-F) in chloroform (Daejung Chemicals & Metals Co.) and fuming sulfuric acid (Aldrich Chemical Co., 20% fumed). Poly(*N*-vinylimidazole) was prepared by 1-vinylimidazole (Aldrich Chemical Co., VI) and purificated azobisisobutyronitrile (AIBN) as thermal initiator.

A GORE-TEX GR® STYLE R SHEET GASKETING (W.L. Gore & Associates Inc.) was used as a supporting material for composite membrane. Phosphoric acid and phosphorous oxide (Junsei Chemical Co.) were used as received.

2.2. Preparation of membranes

2.2.1. Synthesis of sulfonated poly(fluorinated arylene ether)s (SDF-F) membrane

The sulfonated poly(fluorinated arylene ether)s (SDF-F) was obtained according to the procedure described in our previous paper [14–16]. 0.01 mol of decafluorobiphenyl (DF) and 0.01 mol of 4,4′-(hexafluoro-isopropylidene)diphenol (F) were mixed with *N,N*-dimethylacetamide (DMAc), followed by adding 0.03 mol of potassium carbonate as a catalyst, and then heated up to 120 °C. After 1 h of stirring and heating, the mixture was poured into deionized water containing 1 wt% acetic acid to precipitate the polymer. The polymer was subsequently washed several times until the pH reached neutral, in order to remove excess potassium carbonate and acetic acid. Poly(fluorinated arylene ether)s (DF-F), white polymer, was obtained after drying in vacuum oven at 120 °C for 24 h.

Dried DF-F was dissolved in chloroform and then 9.8 ml of fuming sulfuric acid (20% fumed) was added drop by drop over 10 min using glass syringe. The reaction mixture was vigorously stirred for 2 h at room temperature. The sulfonated poly(fluorinated arylene ether) (SDF-F) was precipitated in water, washed until the pH reached neutral, and then vacuum evaporated to remove excess chloroform. The light yellowish polymer was obtained after drying in vacuum oven at 120 °C for 24 h. The SDF-F was dissolved in ethanol and the film cast on Teflon plate overnight. The size and thickness of membranes were controlled by the diameter of the plates and the weight of SDF-F.

2.2.2. Preparation of sulfonated poly(fluorinated arylene ether)s and N-vinylimidazole mixture

The synthesized SDF-F film was dissolved in *N*-vinylimidazole (VI), in the weight ratio of 1/4, with 0.5 wt% azobisisobutyronitrile (AIBN) as a thermal initiator for further polymerization of VI. The SDF-F membrane mixed homogeneously with VI resulting in viscous solution.

2.2.3. Preparation of acid-doped sulfonated poly(fluorinated arylene ether)s and poly(N-vinylimidazole)/PTFE layered membranes

The mixture of SDF-F membrane and VI solution was placed on the one side of thin and porous PTFE film (approximately 15 μm thicknesses), and then pressed at 100 kgf in order to spread uniformly on the film. The other side of PTFE film was treated as the same procedure. Then, the SDF-F/PVI solution was applied on both side of porous PTFE and pressed at 100 kgf to obtain more homogenous impregnated film. This sandwiched SDF-F and VI solution/PTFE film/SDF-F and VI solution was hot-pressed at 40 kgf at 130 °C for 1 h, resulting in polymerization of VI and dehydration. The layered membrane was dried at 120 °C for 24 h.

The SDF-F/PVI and PTFE layered membrane was soaked in phosphorous oxide saturated phosphoric acid solution at room temperature for 48 h. The saturated phosphoric acid was prepared by adding excess phosphorous oxide to 85% phosphoric acid. Phosphorous oxide was used to remove the trace of water in phosphoric acid.

2.3. Physical and chemical characterization of membranes

2.3.1. Phosphoric acid uptake

Phosphoric acid uptake of the SDF-F/PVI and PTFE layered membranes were measured by immersing in phosphoric acid

with excess phosphorous oxide at room temperature. They were left in the phosphoric acid for 48 h in order to reach total saturation. Then, the membranes were taken out from the phosphoric acid baths, wiped with filter papers, and then dried until the weight was constant.

The weight gain due to phosphoric acid was obtained by comparing the weight change before and after acid doping. The acid uptake was calculated according to the following equation:

$$\text{phosphoric acid uptake}\,(\%) = W(\%) = \frac{W_1 - W_0}{W_0} \times 100$$

where W_1 and W_0 refer to the weight of acid-doped membranes and the pure membranes, respectively.

2.3.2. Thermal stability

Thermogravimetric analyzer (TGA) was performed on each membrane using a SDT 2960 (TA Instruments, New Castle, DE) to investigate the thermal properties of the membrane. A scan rate of $10\,°C\,min^{-1}$ was applied over the temperature range of $25–800\,°C$ under a nitrogen atmosphere.

2.3.3. SEM morphology and EDS mapping

The morphology of membranes was studied using a field emission scanning electron microscope (FE-SEM, Hitachi S-4300, Hitachi Science Systems Ltd., Japan) at an acceleration voltage of 25 kV. Element mapping was performed with an energy dispersive spectroscopy (EDS, Horiba EX-200, Horiba Ltd., Kyoto, Japan) coupled with SEM. The use of EDS enabled us to evaluate the distribution of P through the cross-section of the SDF-F/PVI and PTFE layered membrane.

2.3.4. Mechanical property

The mechanical properties of membranes were measured by means of tensile strength, i.e., the ultimate tensile strength when the sample was broken. Tensile strength was measured according to the ASTM-1708 standard method using tensile testing machine (UTM INSTRON 4465, INSTRON) at room temperature.

The membranes were cut into rectangular strips, held in between the holders of the machine, and stretched with the load speed of $1\,mm\,min^{-1}$. The dimensions of the acid-doped layered membranes were 50 mm in length, 15 mm in width, and 0.2 mm in thickness. The values of tensile strain were obtained right before tearing the membranes.

2.3.5. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) for conductivity measurements was carried out in situ by means of a two-probe techniques with an IM6 impedance analyzer (Zahner elektrik Co.).

Proton conductivity of the membranes was measured from impedance data taken after an appropriate equilibrium period, at the frequency range of 10 mHz to 10 kHz with ac perturbation of 5 mV using an impedance analyzer. The conductivity (σ) was

Table 1
The percentages of phosphoric acid uptake and thickness changes of the SDF-F/PVI and PTFE layered membranes at room temperature

Membrane	Thickness before soaking in phosphoric acid (μm)	ΔThickness (μm)	Phosphoric acid uptake (%)
a	46	67	330
b	42	77	333
c	53	89	379
d	67	121	406
e	99	142	461
f	70	146	466

Weight ratio of the SDF-F and VI is 1/4.

determined from the following equation:

$$\sigma = \frac{a}{SR_b}$$

The conductivity (σ) was calculated from the bulk resistance (R_b) obtained from the x-axis intercept of the semicircle at the high-frequency point in Nyquist plot. Here, a is the thickness of the electrolyte and S is the surface area of the membrane.

2.4. Membrane electrode assembly (MEA) fabrication and single cell test

2.4.1. Membrane electrode assembly

The electrodes for anode and cathode were used as commercially available carbon cloths containing $0.4\,mg\,cm^{-2}$ of Pt catalysts (E-TEK) loading. The area of the electrode is $2.6\,cm \times 2.6\,cm$. The both electrodes were impregnated with the 5 M H_3PO_4/ethanol (1:7 v/v) by brushing, and then dried in oven for 5 min at $120\,°C$. The two Kapton film® (35 μm thickness, $6.5\,cm \times 6.5\,cm$) were used to press uniformly, which has square-shaped hole ($2.3\,cm \times 2.3\,cm$) in the middle. The size of membrane is $4.5\,cm \times 4.5\,cm$.
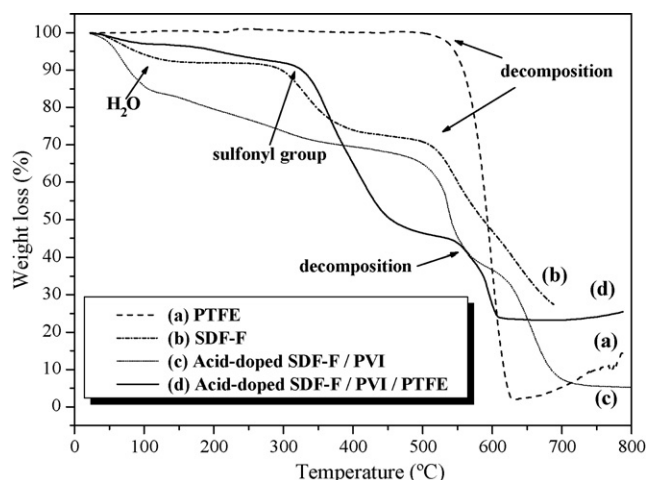

Fig. 1. TGA curves of (a) the PTFE film (without phosphoric acid), (b) the SDF-F membrane (without phosphoric acid), (c) phosphoric acid-doped SDF-F/PVI blend membrane, and (d) phosphoric acid-doped SDF-F/PVI and PTFE layered membrane under nitrogen atmosphere; $10\,°C\,min^{-1}$ scan rate, and the temperature range of $25–800\,°C$.

Finally, membrane electrode assembly (MEA) was prepared by sandwiching the electrode/Kapton film®/membrane/Kapton film®/electrode, and then hot-pressed at the pressure of 30 kgf at 110 °C for 5 min.

2.4.2. Single cell test

The MEA were coupled with gas-sealing gaskets and placed in a single cell test station. The anode and cathode was supplied with hydrogen and oxygen, respectively, with a flow of 80 cm³ min⁻¹ under ambient pressure. The cell was operated at the temperatures of 150, 170 and 190 °C without external humidification.

The single cell performances were characterized by polarization curves which were obtained using an electronic loader by varying the current. The voltage–current density curves were obtained by using a multimeter (Keithley 2000) and an electronic loader (DaeGil electronic load EL-200P). The flow rates of the gases were controlled by using a mass flow controller (MFC).

3. Results and discussion

3.1. Phosphoric acid uptake

In order to reach high-conductivity values, the new SDF-F/PVI and PTFE layered membranes were impregnated in phosphoric acid with excess phosphorous oxide to remove the trace of water.

Phosphoric acid uptake of the SDF-F/PVI and PTFE layered membrane was measured approximately 300–400% at the range of thickness 42–99 μm. The thickness of membranes was controlled by the amount of SDF-F/PVI polymer. Table 1 presented the phosphoric acid uptake dependent on membrane thickness change at room temperature. Thicker membrane shows higher
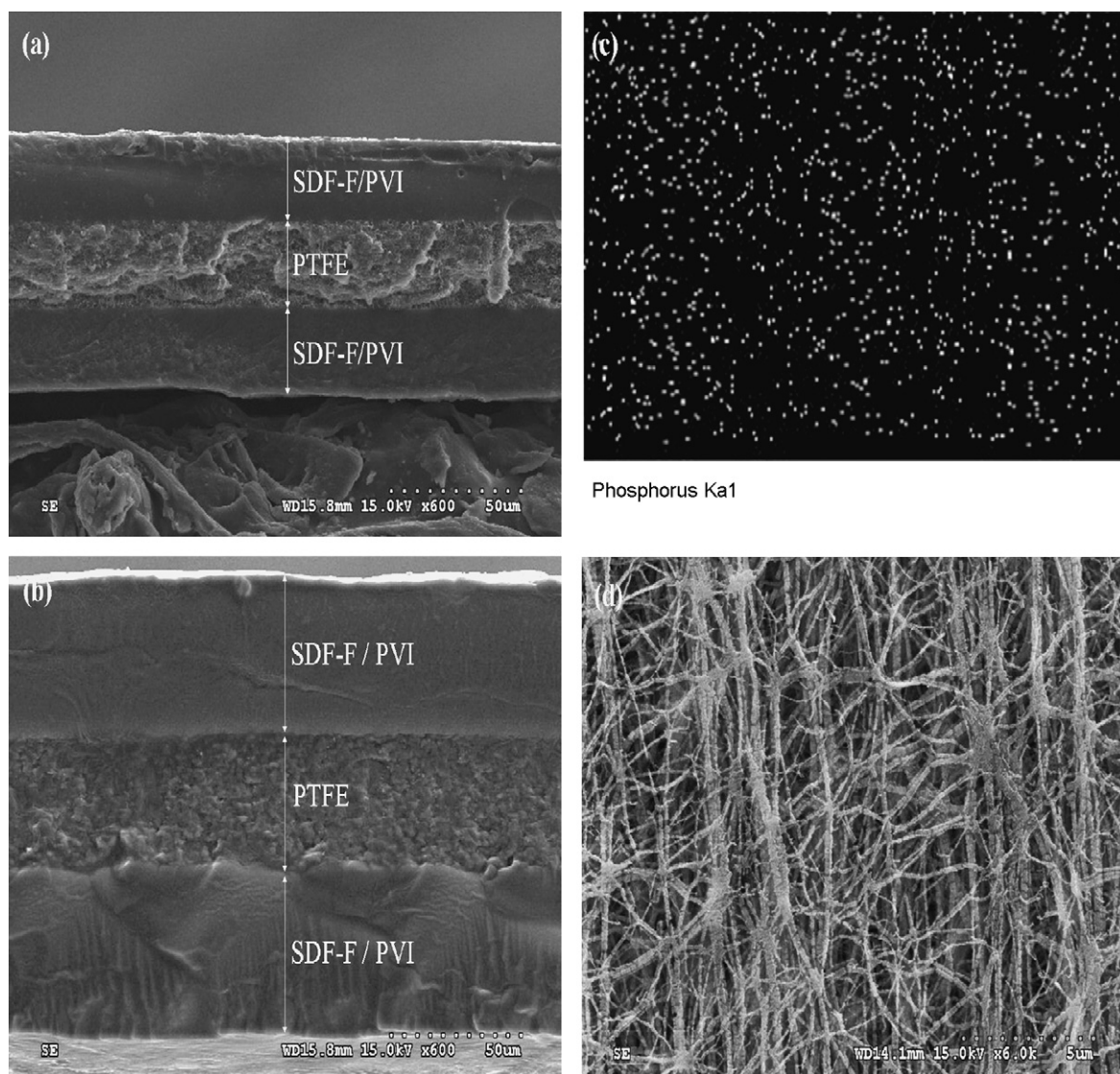

Fig. 2. SEM images of the cross-section of the SDF-F/PVI and PTFE layered membrane (a) before soaking, (b) after soaking in phosphoric acid, (c) P mapping image of (b), and (d) SEM image of the surface of the PTFE film.

phosphoric acid uptake than thinner membrane. This result indicated that the phosphoric acid uptake increased as the amount of SDF-F/PVI polymer increased.

3.2. Thermal analysis

For the operation of high temperature, the membranes should have a good thermal stability; otherwise the high-temperature cell operation gives damages to membranes, which can cause mass flow and voltage drops. Fig. 1 shows thermogravimetric analyses of SDF-F, acid-doped SDF-F/PVI membrane, PTFE film, and acid-doped SDF-F/PVI and PTFE layered membrane. The weight loss at temperatures below 200 °C was due to the loss of water (curves (b–d)). The thermal degradation temperature of all the membranes was 500–600 °C (curves (a–d)). The weight loss at 350–400 °C was due to the elimination of sulfonic acid group of SDF-F (curves (b–d)). The weight losses around 200–300 °C of the acid-doped SDF-F/PVI membrane (curve (c)), and the acid-doped SDF-F/PVI and PTFE layered membrane (curve (d)) is due to the resin water from the reaction of phosphoric acid to pyrophosphoric acid, as investigated by Samms et al. [17]. The degradation temperature about 350 °C for acid-doped SDF-F/PVI and PTFE membrane is much higher than the working temperature. The new membrane has a good thermal property enough to endure the high-temperature operation.

3.3. SEM morphology and EDS mapping

The morphology and distribution of P element in the layered membrane was observed by SEM and EDS. Fig. 2 shows SEM images (a and b) and EDS (P mapping) (c) of the cross-section of SDF-F/PVI and PTFE layered membrane, and SEM images (d) of the surface microstructure of PTFE film.

Fig. 2(a) and (b) shows the membranes prepared by drying in oven at 120 °C and by soaking in phosphoric acid for 48 h, respectively. The layers between SDF-F/PVI membrane and PTFE were observed, and they were well attached each other. As shown in Fig. 2(d), thin porous PTFE film consisted of fibers and knots [18]. It indicates that phosphoric acid solution can be impregnated well in new layered membrane. After soaking in phosphoric acid, the thickness of the membrane increased significantly. EDS mapping in Fig. 2(c) demonstrates the distribution of P through the cross-section of the layered membrane. The element of P has uniformly distributed and well doped throughout the acid-doped SDF-F/PVI and PTFE layered membrane.

3.4. Mechanical property

Table 2 summarized the tensile strength for the SDF-F/PVI and PTFE layered membrane after soaking in phosphoric acid. This result shows that the mechanical strength of the SDF-F/PVI and PTFE layered membrane (containing ∼400% H_3PO_4) shows similar to that of PBI membrane [1]. The new layered membrane was improved by reinforcing the mechanical strength with a porous PTFE supporting film. Therefore, it is reasonable that the new PTFE layered membranes are strong enough to be used in PEMFCs.

Table 2
The conductivity and mechanical strength of the PTFE layered SDF-F/PVI (180 μm thickness, containing ∼400% H_3PO_4) and the PBI (containing 500–600% H_3PO_4) membranes

Membrane	Conductivity (S cm^{-1})	Tensile strength after soaking in phosphoric acid (MPa)
SDF-F/PVI/PTFE	2.20×10^{-2}	12.30–13.10
PBI	$2.5–4.6 \times 10^{-2}$ [19,20]	12.55–14.40 [1]

3.5. Conductivity

The proton conductivities of acid-doped layered membrane were obtained by measuring the impedance using an IM6 impedance spectrometer with frequency range 10 mHz to 10 kHz at 150 °C. The data was measured using the in situ method at ambient pressure. The proton conductivity was calculated to 2.20×10^{-2} S cm^{-1} at 150 °C. The conductivity of the SDF-F/PVI and PTFE layered membranes (180 μm thickness, ∼400% H_3PO_4-doped) at 150 °C is comparable to that of PBI
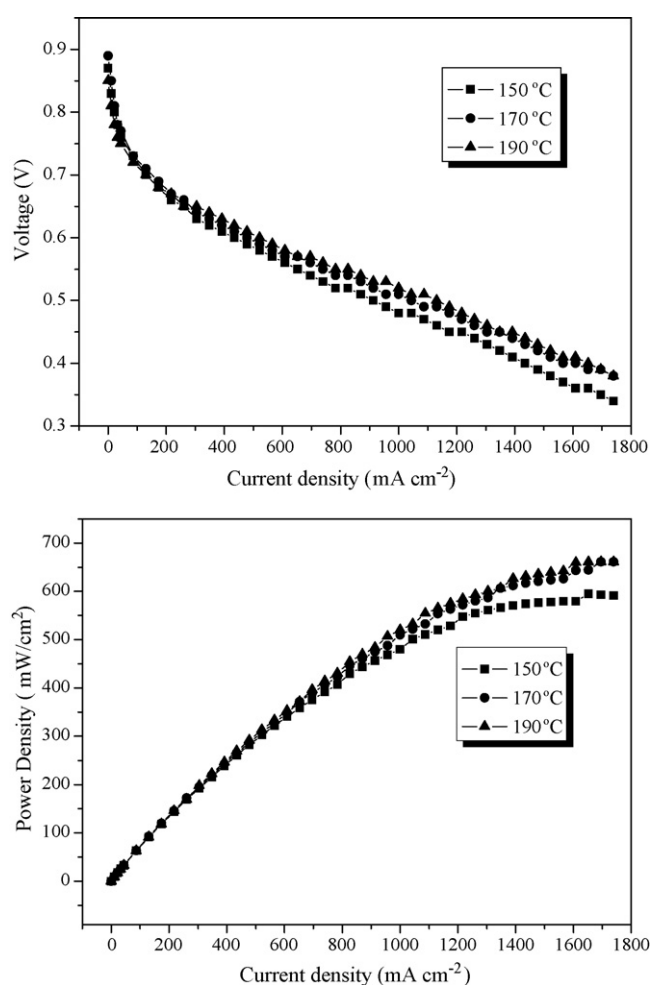

Fig. 3. Current density vs. voltage and power density of the single cell operation with the SDF-F/PVI and PTFE layered membrane using hydrogen and oxygen gas (flow rate 80 cm^3 min^{-1}) with no external humidification under ambient pressure at various temperature: (■) 150 °C, (●) 170 °C, and (▲) 190 °C.
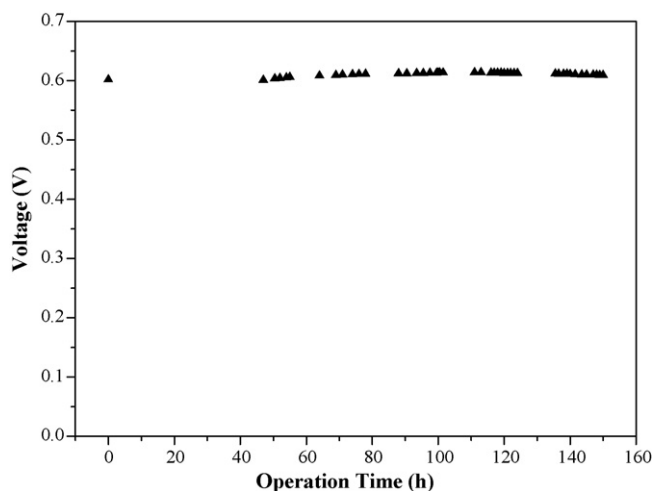
Fig. 4. The durability test of acid-doped SDF-F/PVI and PTFE layered membrane under the ambient pressure; hydrogen and oxygen flow rate of $80\,cm^3\,min^{-1}$ without external humidification for 150 h. The operation temperature and current density were fixed to 190 °C and 150 mA cm^{-2}, respectively.

membrane. It is reported that the conductivity values for the PBI membranes ranged from $2.50 \times 10^{-2}\,S\,cm^{-1}$ at 130 °C (280 mol% H_3PO_4) to $4.60 \times 10^{-2}\,S\,cm^{-1}$ at 160 °C (450 mol% H_3PO_4) [19,20].

3.6. Single cell performance and durability test

Fig. 3 presented the cell potential (V) versus current density (i) of single cell prepared with SDF-F/PVI and PTFE layered membrane (containing ~400% H_3PO_4) as a function of temperature. The single cell operated at 150, 170, and 190 °C using hydrogen and oxygen gas with no external humidification at ambient pressure. The power density was obtained to be 263.5 mW cm^{-2} at the temperature of 150 °C, 292.2 mW cm^{-2} at 170 °C, and 317.0 mW cm^{-2} at 190 °C with the potential of 0.6 V. As shown in Fig. 3, an increase in the operational temperature from 150 to 190 °C improves the cell performance. The maximum power density increased with temperature from 150 to 170 °C. However, the maximum power density at 190 °C is nearly same as that at 170 °C. At 190 °C, a loss of phosphoric acid may take place.

The cell performance versus time is shown in Fig. 4. The durability test of phosphoric acid-doped SDF-F/PVI and PTFE layered membrane was performed for 150 h under hydrogen and oxygen flow rate of $80\,cm^3\,min^{-1}$ at 190 °C. The cell voltage was monitored with fixed current density (150 mA cm^{-2}) for 150 h. The decrease of cell voltage was not observed during 150 h of continuous operation at 150 mA cm^{-2}. Therefore, we believed that this new layered membranes are good enough for high-temperature PEMFC operation.

4. Conclusions

We prepared the acid-doped sulfonated poly(fluorinated arylene ether)s (SDF-F)/poly(N-vinylimidazole) (PVI) and PTFE layered membranes as electrolyte for high-temperature PEMFC

operation. The new layered membranes have good mechanical strength by using a porous PTFE film. The EDS P mapping of cross-section shows uniform distribution of phosphoric acid. The PTFE layered membrane has high-proton conductivity of $2.20 \times 10^{-2}\,S\,cm^{-1}$ at 150 °C without external humidification. This value is comparable to that of PBI. The single cell test was performed under hydrogen and oxygen flow rate of $80\,cm^3\,min^{-1}$ at the temperature 150–190 °C without external humidification. The power density was 317 mW cm^{-2} at a cell voltage of 0.6 V and temperature of 190 °C. The new SDF-F/PVI and PTFE layered membranes show stable performances for 150 h. The experimental results show that the new layered type membrane has good proton conductivity, mechanical property, and high-cell performance for high-temperature operation. Therefore, it is concluded that new layered membrane can be a very promising candidate for high-temperature applications to PEMFCs.

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