



A composite membrane based on PTFE and solid poly (mixed acid $(\text{PMo}_{12}\text{O}_{40})_X\text{-(PO-OH)}_Y$) for high-temperature fuel cells

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Abstract

A novel high-temperature proton exchange membrane (PEM) (PTFE/ $(\text{PMo}_{12}\text{O}_{40})_X\text{-(PO-OH)}_Y$ composite membranes) was prepared by impregnating mixed acid into the porous PTFE membrane. The porous PTFE membrane serves as the support structure of the membrane, and $(\text{PMo}_{12}\text{O}_{40})_X\text{-(PO-OH)}_Y$ sol is used as the proton conductor. The solid poly acid $(\text{PMo}_{12}\text{O}_{40})_X\text{-(PO-OH)}_Y$ exhibits a proton conductivity of 0.025 S cm^{-1} at $180 \text{ }^\circ\text{C}$, and the PTFE/ $(\text{PMo}_{12}\text{O}_{40})_X\text{-(PO-OH)}_Y$ membrane presents a good proton conductivity (0.02 S cm^{-1}) when the relative humidity is below 0.5% and temperature is $180 \text{ }^\circ\text{C}$. Besides, the PTFE/ $(\text{PMo}_{12}\text{O}_{40})_X\text{-(PO-OH)}_Y$ membrane performs moderate property as tested in hydrogen fuel cells. SEM and EDX reveal that the structure of $(\text{PMo}_{12}\text{O}_{40})_X\text{-(PO-OH)}_Y$ gel is uniformly distributed in the pores of PTFE, which enhanced the proton conductivity of the composite membranes.

Keywords PTFE · $(\text{PMo}_{12}\text{O}_{40})_X\text{-(PO-OH)}_Y$ · High-temperature · PEMFC · Proton conductivity

Introduction

With the intensification of energy and environmental issues, people's demand for efficient and pollution-free energy is more urgent. Fuel cells have been recognized as one of the most promising energy conversion devices in the past few decades. Proton exchange membrane fuel cells (PEMFCs) attract people's attention due to its high power density, pollution-free, and portable characteristics, and they are considered efficient power supplies for portable equipment, electric vehicles, and integrated cogeneration systems [1–6]. Compared with PEMFCs under the traditional working temperature ($T < 80 \text{ }^\circ\text{C}$), high-temperature ($T > 100 \text{ }^\circ\text{C}$) PEMFC (HT-PEMFC) is more attractive because of some advantages, such as higher catalyst activity, high tolerance of impurity (such as CO), simple hydrothermal management system, and high heat recovery [7–9].

Nowadays, PEMFC technology relies on perfluorosulfone (PFSA) polymer membranes (such as Nafion) as proton-conducting materials [10]. And the Nafion membranes are

the leading and the most successful electrolytes used in PEMFCs, but the transfer of PEMFC protons in Nafion membranes must rely on liquid water. However, the Nafion membranes start dehydrating when the temperature is high, resulting in a sharp decrease in proton conductivity, so the Nafion membranes do not apply to HT-PEMFCs. Therefore, the key to the development of HT-PEMFC is to find a proton exchange membrane with high proton conductivity and high thermal stability. And some progress has been made, such as the water retention of Nafion can be improved by doping zirconium phosphate (ZrP), SiO_2 , and others [11–15], but Nafion's cost makes commercialization extremely expensive. Hence, many nanopore polymers have aroused people's interest and begun to be widely explored in HT-PEMFCs. [16] Among them, the polybenzimidazole (PBI) membrane was most commonly used. But the PBI membrane itself cannot transfer protons and electrons. It obtains proton conductivity by doping phosphoric acid, but excess acid reduces the mechanical strength and lifetime of the PBI membrane. [17–24] To solve this problem, the researchers increased the mechanical strength of the membranes by filling the nano-ion into the pores of the PBI, including SiO_2 [25] and sulfophenylated TiO_2 [26], but the synthesis process was very cumbersome. Besides, other membranes such as polyacrylamide (PAM) backbone [27] and polyvinyl alcohol (PVA)-based components [28] were also used. These membranes exhibited

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relatively low proton conductivity. In recent years, studies have found that porous PTFE can improve the mechanical strength of the membrane, and the polymer composite membrane prepared based on PTFE has high proton conductivity and thermal stability. For example, Park et al. [29] directly mixed PTFE and ZrP and then pressed them into composite membranes; zirconium phosphate increased the proton conductivity from PTFE 10^{-13} to 2.2×10^{-3} S cm^{-1} . Based on this, Al-Othman et al. [30] added glycerol (GLY) to the synthesis of ZrP/PTFE to obtain a membrane with a conductivity of approximately 0.02–0.045 S cm^{-1} ; and then, Al-Othman et al. [31] prepared the modified Si–ZrP/PTFE/GLY membrane and S–ZrP/PTFE/GLY, and the addition of silicic acid increased proton conductivity. Recently, Al-Othman et al. [32] studied the proton conductivity of phosphotungstic acid (PWA) to ZrP/PTFE/GLY membrane and they found proton conductivity decreases when PWA was added to the ZrP/PTFE/GLY membrane. This may be that the addition of PWA has no positive effect on the modification of ZrP so that the PWA-ZrP/PTFE/GLY membrane has a proton conductivity of 0.003 S cm^{-1} . In these studies, the ZrP is used as a proton conductor to settle in the pores of PTFE, and the addition of silicic acid/sulfuric acid/phosphoric acid is to change the diameter of ZrP. However, we want to explore the effect of solid polymer acid on proton conductivity, and now, reports on solid polymer acid as proton conductors are rare.

Herein, in our current work, we have synthesized a new membrane type of high-temperature PEMFC, which uses the porous PTFE membrane as a support structure. In the pores of the PTFE membranes, $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ sol is used as a proton conductor to prepare a proton exchange membrane with high temperature, thereby combining the advantages of PEMFC and PAFC. The composite membrane has good mechanical strength and high proton conductivity, and the performance of the membrane is evaluated in a hydrogen fuel cell test.

Experiment

Composite membrane preparation

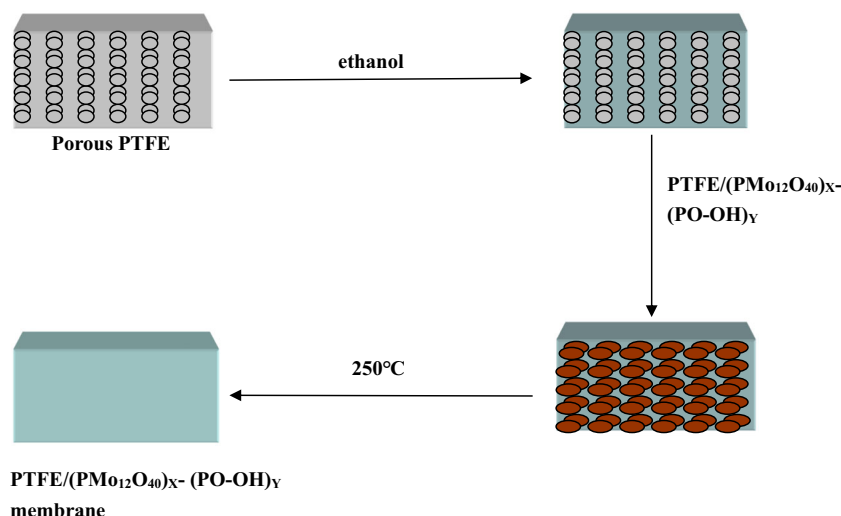
The PTFE/ $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ membrane was prepared according to the procedure shown in Scheme 1. First, the porous polytetrafluoroethylene membrane was immersed in the mixed solution of H_2SO_4 (98 wt.% aqueous solution, purchased from Sigma-Aldrich) and H_2O_2 (30 wt.% aqueous solution, purchased from Sigma-Aldrich) with a mass ratio of 7:3 and soaked for 1 h at 80 °C for surface activation, and then rinsed with plenty of water. Then, it was immersed in a mixed solution having 1.0 mol/L NaOH (Sigma-Aldrich reagent grade), H_2O_2 (30 wt.% aqueous solution), and pure water with a mass ratio of 1:1:5, and soaked for 30 min at 70 °C to carry out further purification and rinsed with plenty of water. All chemicals are used directly without further treatment.

Next, the solid poly (mixed acid $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$) and $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ /PTFE membrane was prepared as follows. First, 1.0 g of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (Sigma-Aldrich reagent grade) inorganic powder was dispersed in $\text{CH}_3\text{CH}_2\text{OH}$ (Sigma-Aldrich), and then 3 g of H_3PO_4 (85 wt.% solution, Sigma-Aldrich) was added, and after stirring for 4 h at 70 °C, a mixed solution was obtained. The mixed solution was heated at 250 °C for 7 h to obtain the solid polymer acid $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$. The treated PTFE membrane was immersed in the mixed acid solution obtained in the above step, and then dried at 250 °C for 7 h to get the $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ /PTFE membrane.

Characterization

The proton conductivity was measured by electrochemical impedance spectroscopy (EIS) four-probe method with the equipment (Parstat, 2273) and the frequency range from 1 to

Scheme 1 General procedure for the fabrication of a PTFE/ $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ composite membrane



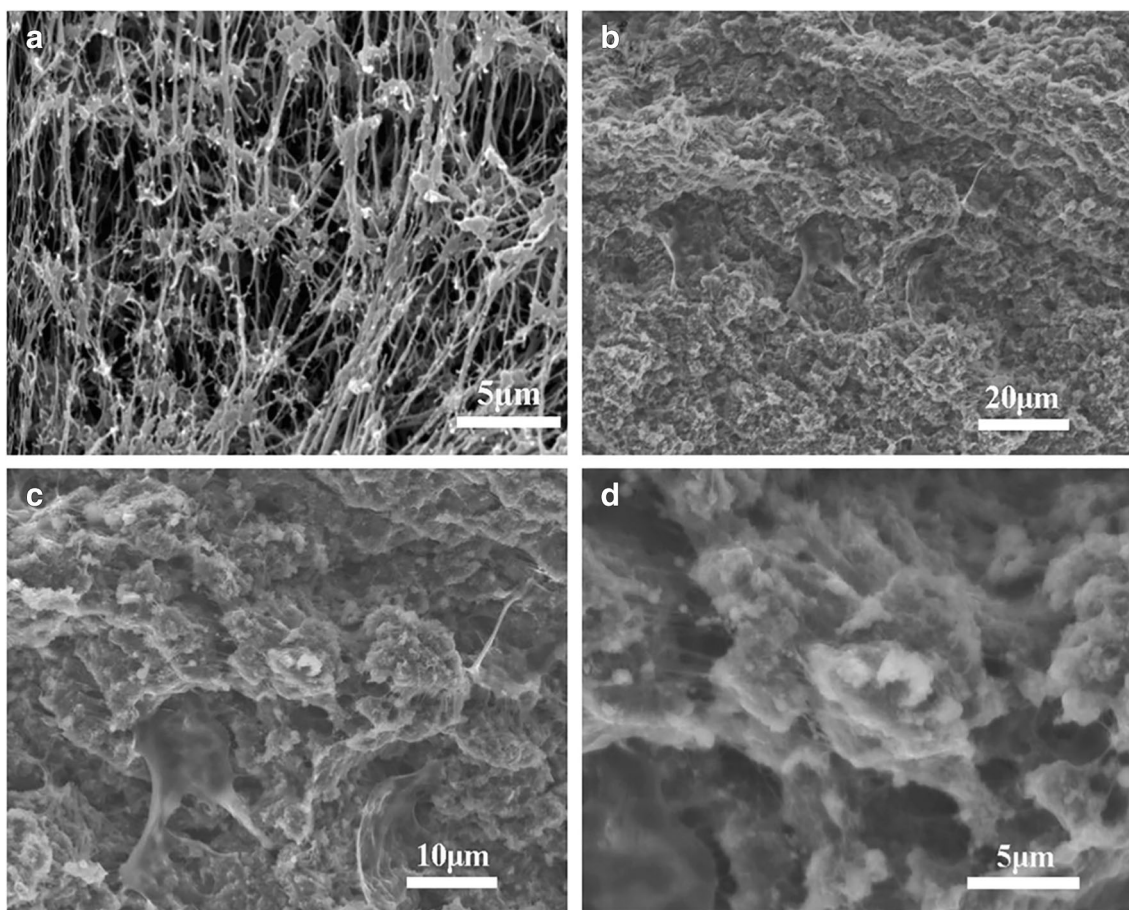


Fig. 1 SEM images from the surface of the PTFE (a) and the cross section of PTFE/(PMO₁₂O₄₀)_x-(PO-OH)_y composite membrane (b, c, d)

20 kHz. Then, the proton conductivity (σ) is calculated by the formula $\sigma = L/RA$, where L and A are the thickness and effective area of the membrane, respectively, and R is the high frequency intercept of the impedance curve using the real axis on the complex impedance plane.

The membrane details were observed by SEM (JEOL JSM-5300lv) and analyzed by semi-quantitative EDX.

Membrane electrode assembly

At 150 °C and the pressure of 0.1 ton cm⁻², the anode and cathode were hot pressed to the doping membranes for 10 min to prepare the membrane electrode assembly (MEA). The catalyst ink was prepared by the mixing the carbon-based catalyst (60% Pt on Vulcan XC-72, eTek Inc.) and PBI in DMAC (5%, w/w) and PVDF (1%, w/w) solutions for 12 h. And then, the ink was dropped to a carbon paper carrier covered with a carbon gas diffusion layer (eTek) to prepare electrodes.

Fuel cell test

The MEA (of the active cross section area of 1 cm²) was sandwiched between two high-density graphite blocks

impregnated with phenolic resin, and then parallel gas flow channels were processed thereon. Using H₂ and O₂ for cell testing, the gas flow rate used was about 40 times higher than the stoichiometric requirement for the maximum current obtained from the cell test. Tube electric heaters were installed in the graphite block to achieve the required temperature.

Results and discussion

SEM observation and morphological study of composite membrane

Figure 1 exhibits the SEM of the surface and the cross section of the PTFE/(PMO₁₂O₄₀)_x-(PO-OH)_y composite membrane. Figure 1a shows the result of electron microscopy after × 5000 magnification of the PTFE surface. It presents the surface of PTFE is coarse, loose, and porous. Figure 1b and c present that the plate-like material is formed and the PTFE skeleton was covered. Figure 1c is the result of further magnifying the surface of the PTFE/(PMO₁₂O₄₀)_x-(PO-OH)_y by 5000, exhibiting that the pores are densely packed and significantly smaller compared with those of the PTFE in Fig. 1a. This is

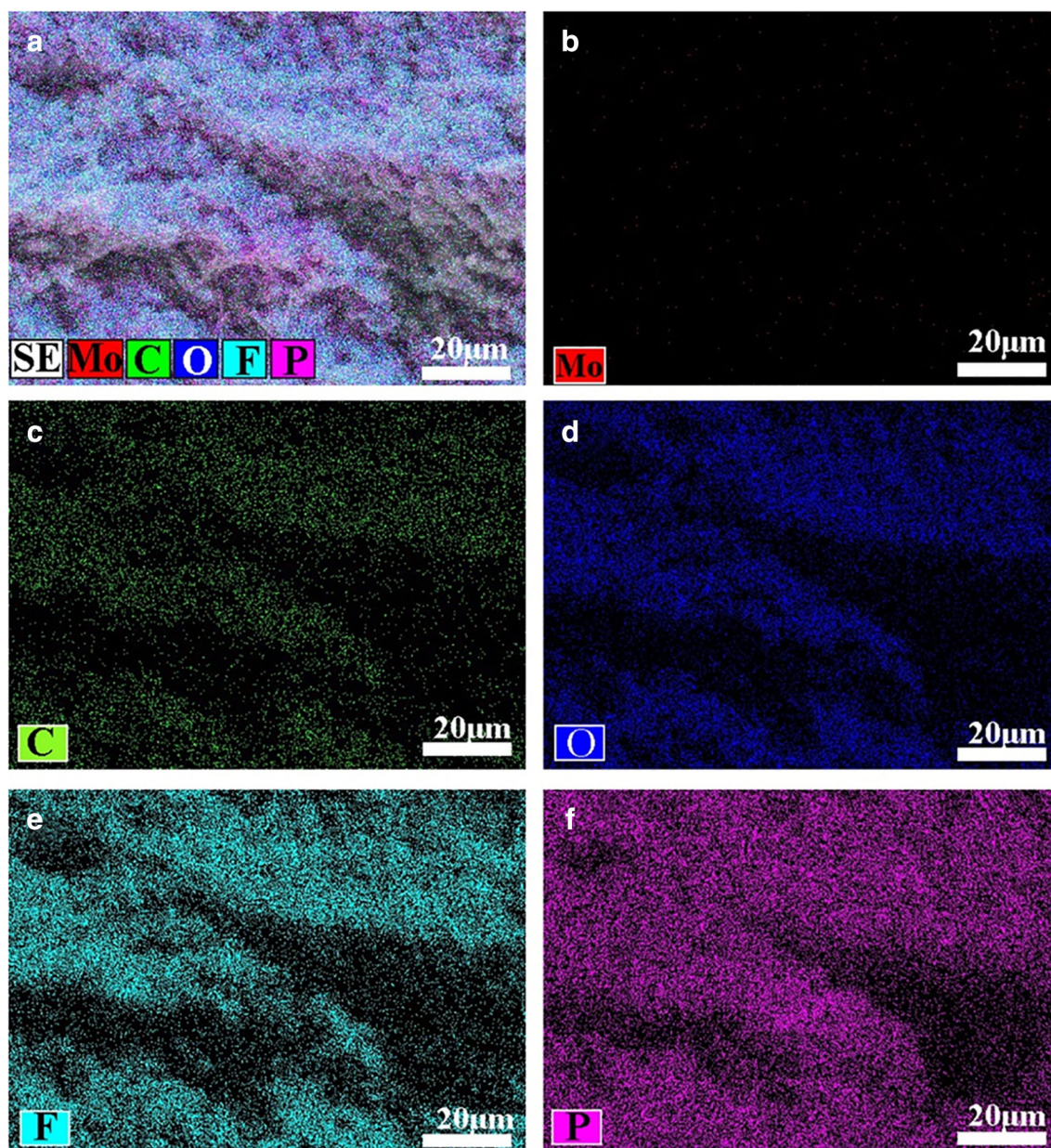


Fig. 2 All the elements (a) (Mo (b), C (c), O (d), F (e), P (f)) in the cross section of PTFE/(PMo₁₂O₄₀)_x-(PO-OH)_y composite membrane

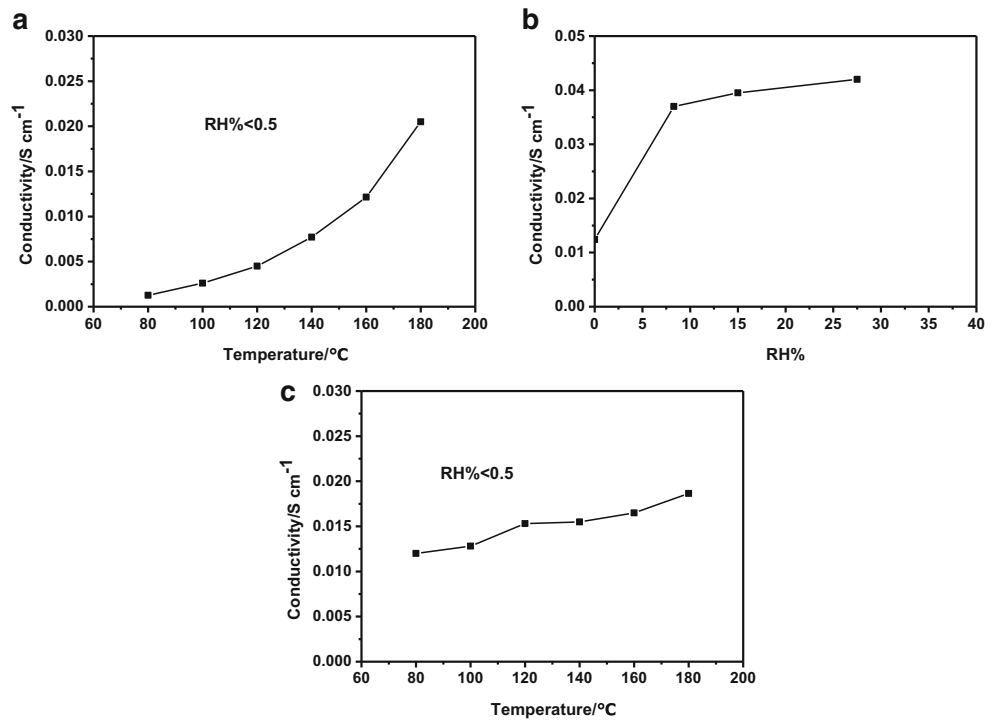
because during the experiment, small particles of poly acid (PMo₁₂O₄₀)_x-(PO-OH)_y enter the pores of PTFE and form sol clusters in the pores. All sol clusters are joined together and cohered to PTFE polymer. The distribution of the total elements of the cross section of the (PMo₁₂O₄₀)_x-(PO-OH)_y composite membrane in Fig. 2a also confirms the tight connection between the poly acid clusters and PTFE pores, and it delivers the dispersion density of P and Mo is much higher than that of F and C, and the elements of P, Mo, F, and C are homogeneously distributed, indicating a good dispersion of the (PMo₁₂O₄₀)_x-(PO-OH)_y cluster in the pores of PTFE. The pores of PTFE are densely packed by sol, which can prevent the gas cross between the anode and the cathode of

the fuel cell. On the other hand, part of the pores of PTFE/(PMo₁₂O₄₀)_x-(PO-OH)_y provides space for the flow of reactants and product after the catalyst is added [31].

Proton conductivity of PTFE/(PMo₁₂O₄₀)_x-(PO-OH)_y membrane

Figure 3a shows the influence of temperature on proton conductivity of (PMo₁₂O₄₀)_x-(PO-OH)_y solid acid. As can be seen from Fig. 3a, (PMo₁₂O₄₀)_x-(PO-OH)_y produces a high proton conductivity (0.025 S cm⁻¹) with the temperature from 80 °C increased to 180 °C. The effect of RH on proton conductivity of (PMo₁₂O₄₀)_x-(PO-OH)_y is shown in Fig. 3b. It exhibits that the

Fig. 3 Proton conductivity of $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ at different temperatures, $\text{RH} < 0.5$ (a); at different relative humidities at $160\text{ }^\circ\text{C}$ (b). Proton conductivity of PTFE/ $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ membrane with the thickness $50\text{ }\mu\text{m}$ at different temperatures, $\text{RH} < 0.5$ (c)



proton conductivity increases greatly with the relative humidity, when the RH% is in the range of 0.5 to 8.5. However, when the RH% exceeds 8.5, the proton conductivity tends to be flat and between 0.04 and approximately 0.045 S cm^{-1} . This is because the phosphomolybdic acid (PMo) itself is hydrophilic, and as the relative humidity increases, the water content increases. Besides, the phosphoric acid used in the experiment also contains water, and Ganapathy et al. [33] have reported that heteropoly acids have a high proton mobility in the hydrated state. All in all, the solid acid $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ prepared has great potential as proton conductors.

Figure 3c presents the proton conductivity of PTFE/ $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ membrane. The proton conductivity is about 25–50% higher than that of $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ solid acids shown in Fig. 3a, when the temperature is $80\text{--}160\text{ }^\circ\text{C}$. And at $180\text{ }^\circ\text{C}$, the proton conductivity of PTFE/ $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ membrane is 0.02 S cm^{-1} , and it presents great potential in the application of high-temperature proton exchange fuel cell. The enhancement of proton conductivity of PTFE/ $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ composite membrane at high temperature can be attributed to the following reasons: during the preparation of composite membrane, the addition of heteropoly acid increases the number of OH^- groups and provides more jumping paths for protons; phosphomolybdic acid connects with phosphate clusters, which may create new proton transport pathways; phosphomolybdic acid is a hydrophilic inorganic material, and the connection of $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ to PTFE may improve water absorption and increase the amount of water molecules in the composite membranes and increase their conduction path; and then, as seen in SEM, plate-like solid acids $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ are filling the PTFE holes, leading to an increase in the total surface area and therefore the proton conductivity.

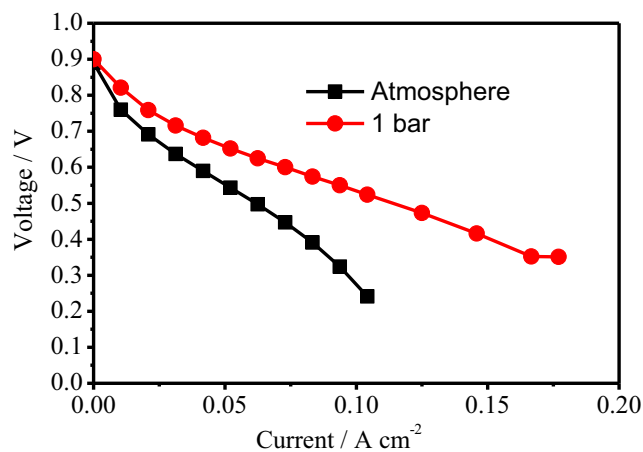


Fig. 4 Cell voltage, current density polarization curves of a PEMFC with a PTFE/ $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ membrane, operated at $160\text{ }^\circ\text{C}$; $\text{H}_2, \text{O}_2\text{:Pt/C (60%):PVDF:PBI} = 230\text{:7:12}$. Black circle, 1 bar overpressure; black square, atmospheric pressure

Fuel cell performance

Figure 4 indicates the performance of the fuel cell with the PTFE/ $(\text{PMo}_{12}\text{O}_{40})_x\text{-(PO-OH)}_y$ composite membrane of $70\text{ }\mu\text{m}$ thickness. The cell voltage shows a notable loss of polarization voltage; for example, when the battery voltage is 0.4 V , the current

density is only 200 mA cm^{-2} . The reason for the relatively poor performance of the fuel cell is that the structure of the catalyst layer is poor, and the catalyst layer is a simple PVDF-bonded carbon having no proton conductor. By optimizing the catalyst layer structure, including the proton-conducting composite, the performance of the current composite membrane fuel cells can be improved, and this is also the direction we need to work next.

Conclusion

A high-temperature proton-conductive membrane was made using porous PTFE membrane as a supporting structure and $(\text{PMo}_{12}\text{O}_{40})_X\text{-(PO-OH)}_Y$ as a proton conductor. The PTFE/ $(\text{PMo}_{12}\text{O}_{40})_X\text{-(PO-OH)}_Y$ membrane has good proton conductivity of 0.02 S cm^{-1} when the RH is under 0.5% and the temperature is $180 \text{ }^\circ\text{C}$. The membrane exhibited modest voltage performance when tested in hydrogen fuel cells, which was partly due to the preparation method of the catalyst layer, and this is what the next work needs to improve. However, the PTFE/ $(\text{PMo}_{12}\text{O}_{40})_X\text{-(PO-OH)}_Y$ composite membrane still has great potential in the application of high-temperature PEMFCs.

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