GLASS MICROPOROUS FIBER/NANOPOROUS POLYTETRAFLUOROETHENE COMPOSITE MEMBRANES FOR HIGH EFFICIENT PHOSPHORIC ACID FUEL CELL

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Abstract. This paper reports a high efficient phosphoric acid fuel cell by employing a micro/nano composite proton exchange membrane incorporating glass microfiber (GMF) sealed by polytetrafluoroethylene (PTFE) nano-porous film. This multilayer membrane not only possesses both thermal and chemical stability at phosphoric acid fuel cell working temperature at 150~220℃ but also is cost effective. As a result, the inclusion of the high porosity and proton conductivity from glass microfiber and the prevention of phosphoric acid leakage from PTEF nano film can be achieved at the same time.The composite membrane maximum proton conductivity achieves 0.71 S/cm at 150 ℃ from AC impedance analysis, much higher than common phosphoric acid porous membranes For single cell test , The GMF fuel cell provides a 63.6mW/cm2 power density at 200mA/cm2 current density while GMF plus methanol treated PTFE (GMF+mPTFE) provides 59.2mW/cm2 power density at 160mA/cm2 current density for hydrogen and oxygen supply at 150 ℃. When we change the electrodes that are more suited for phosphoric acid fuel cell, the GMF+mPTFE single cell gets higher performance which achieve 296mW/cm2 power density at 900mA/cm2 current density for hydrogen and oxygen supply at 150 ℃.

1. Introduction

Phosphoric acid fuel cell (PAFC) belongs to medium temperature fuel cell. PAFC has many advantages, such as the power usage is enhance and supply often higher power density than PEMFC. PAFC operates at 150~220℃, so that the water produced in cathode vaporize rapidly, which simplify the water management design. Phosphoric acid has low vapor contents and good thermal stability at this temperature range (150~220℃). Liquid phosphoric acid play an important role in transporting protons which produced by hydrogen oxidation reaction from anode to cathode. Among many components in PAFC, the proton conductivity of the membrane is the most important part. Traditional Nafion will lose its moisture above 80℃, and the proton conductivity will decay. In the past decades, silicon carbide powders (SiC) were employed popularly as the matrix for containing phosphoric acid, for its high temperature endurance, mechanical integrity and resistant to phosphoric acid [1, 2]. However, the porosity is limited to 79~89% due to the space occupation of the power structure [3]. Therefore, this research introduce a way for improving the issue by using a composite proton exchange membrane. The micron pores (1-1.5 μm) of glass microfiber can provide higher (93%) porosity and better phosphoric acid possessing ability than those of SiC powder. However, the large opening of the membrane cannot effectively prevent the leakage of phosphoric acid to the reaction chamber [4]. Therefore, in this study, a 25μm thick PTFE thin film with nano pores (50-400 nm) with 70% porosity is employed to attach on the surface of glass microfiber in order to prevent phosphoric acid leakage, shown in Figure 1. (a). This composite proton exchange membrane not only possesses both thermal and chemical stability at phosphoric acid fuel cell's working temperature at 150~220℃ but also is cost effective. As a result, the inclusion of the high porosity and proton conductivity from glass microfiber and the prevention of phosphoric acid leakage from PTEF nano film can be achieved at the same time. And morphology as the schematic shown in Figure 1. (b).

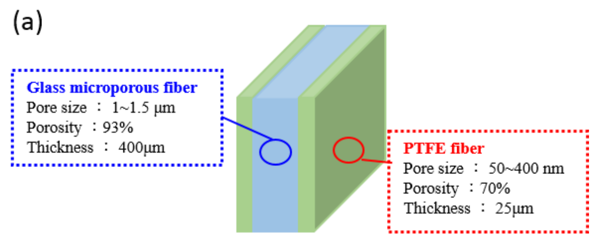

Figure 1. (a) GMF and PTFE composite membrane

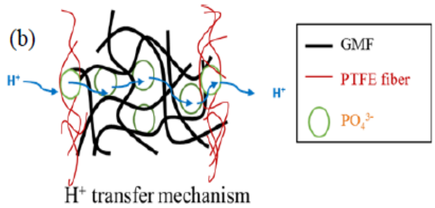

Figure 1. (b) composite membrane's proton transfer mechanism

2. Experimental

2.1 Preparation of composite membrane

Before assembling the two films together, we put PTFE in methanol or ethanol for 15 minutes with ultrasonic vibration as hydrophilic treatment [5], so that PTFE fiber can be fully loaded with phosphoric acid. After the treatment, put the methanol treated PTFE (mPTFE) into 85% phosphoric acid immediately for 20 minutes in room temperature to absorb phosphoric acid. Meanwhile, glass microfiber is soaks in 150℃ 85% phosphoric acid for 20 min to load phosphoric acid fully. After GMF and PTFE preparation, attach the two kinds of thin films together to form the three stacks composite film.

2.2 Preparation of the electrodes

Carbon clothes (CC) is used as the gas diffusion layer of phosphoric acid fuel cell. To prepare the electrodes, catalyst ink containing 20% Pt/XC72 carbon with 35 wt% PTFE as binder was sprayed on carbon cloth. Until the Pt loading reaches 1mg/cm^2, the electrodes was heated at 120℃ for 1 hour to evaporate solvent and sintered to melt the binder. Before the single cell test, the electrodes was soaked in 150℃ 85% phosphoric acid for 24 hours to enhance proton conductivity. Moreover, a PDMS ring is put around the membrane electrode assembly (MEA) to prevent phosphoric acid leakage, Shown in Figure 2.

2.3Analyses

AC impedance measurement is applied to measure the proton conductivity of the composite membrane. Also, a long term test is done to observe the durability of the membrane. Single cell test is applied to measure the performance of the MEA. The MEA consists of anode, cathode and GMF sealed with mPTFE which is filled with phosphoric acid. The cell was assembled at 5kgf·cm by cold press. Anode was supplied by H_2 at 100 sccm and cathode by O_2 at 100 sccm.

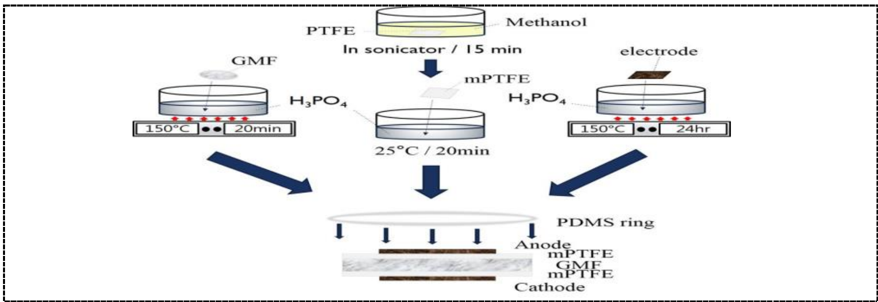

Figure 2. The preparation process illustrate of PTFE/GMF/electrodes

2. Results and discussion

3.1 AC impedance analysis

AC impedance test after assembling the three films together, we employed through-plane test to measure membrane proton conductivity in different temperature condition. Compare three data the red line is GMF, the blue line is GMF plus PTFE after methanol treatment (GMF+mPTFE), and the black line is Nafion117[R] with x-raid is Temperature and y-raid is proton conductivity , Nafion117[R] is a commercial proton exchange membrane , when test condition at 85 ℃ and 98% relative humidity that has maximum proton conductivity 6.5×10^{-2} S/cm, GMF has maximum proton conductivity 7.3×10^{-1} S/cm at 150 ℃ . The proton conductivity decreases with mPTFE + GMF Composite membranes, because of that structure increased a lot of resistance, shown in Figure 3.Although the proton conductivity decreases, The maximum proton conductivity of the composite membrane achieves high level 7.15×10^{-1} S/cm at 150 ℃, which is much higher than those of common phosphoric acid porous membranes ($\sim10^{-2}$ S/cm at 150 ℃)[6]. GMFB and GMFB+mPTFE composite proton conductivity compare, the experiment lasted for one hour, we can see only GMFB proton conductivity decreases 73%, while GMFB+PTFE composite membranes proton conductivity only decreases 21%.The results confirm that mPTFE nano porous is useful for preventing the phosphoric acid leakage, shown in Figure 4

*3.2 S*ingle cell test

The GMF fuel cell provides a 63.6mW/cm^2 power density at 200mA/cm^2 current density while GMF plus methanol treated PTFE (GMF+mPTFE) provides 59.2mW/cm^2 power density at 160mA/cm^2 current density for hydrogen and oxygen supply at 150 ℃(Fig.5). From comparison with OCV, the nanoporous PTFE membrane is effectively preventing the fuel crossover from performance of the 60% higher OCV at 0.8 volt with similar power density (~59.2 mW/cm^2). When we change the electrodes that are more suited for phosphoric acid fuel cell, the GMF+mPTFE single cell gets higher performance which achieve 296mW/cm^2 power density at 900mA/cm^2 current density for hydrogen and oxygen supply at 150 ℃(Fig.6).

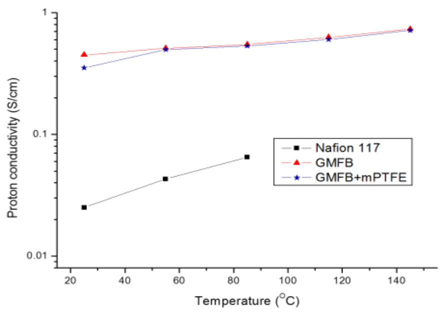

Figure 3.
Proton conductivity comparison among Nafion117,GMFB, and GMFB+mPTFE membranes at working temperatures

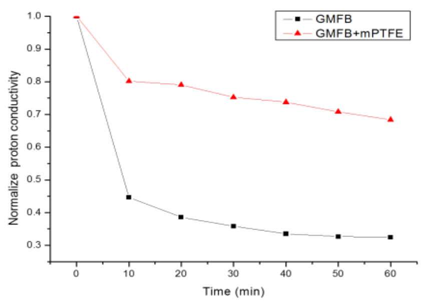

Figure 4.
Long-time test of Proton conductivity for GMFB and GMFB+mPTFE. (■)GMF and (▲) GMFB+mPTFE.

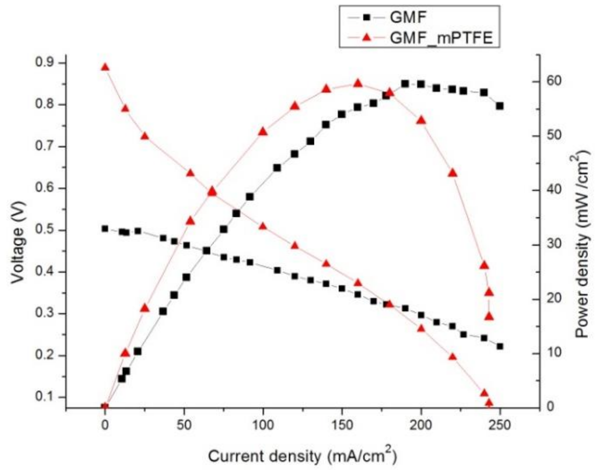

Figure 5.
Current density and power density of a single phosphoric acid fuel cell prepared (■) GMF and (▲) GMF+mPTFE.

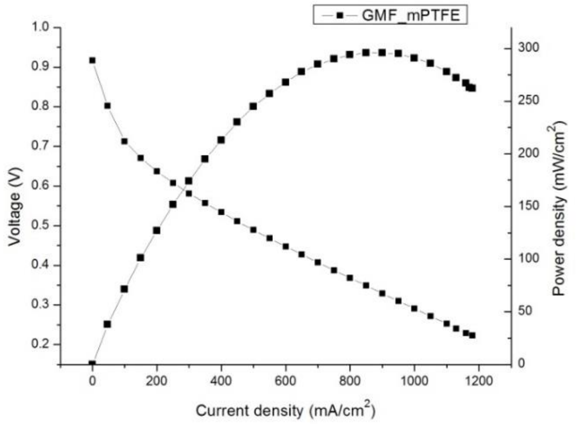

Figure 6.
Current density and power density of a single phosphoric acid fuel cell prepared by GMF+mPTFE

4. Conclusion
As a result, mPTFE+GMFB composite membranes can be achieved high porosity and proton conductivity from glass microfiber and PTEF nano film can be prevention of phosphoric acid leakage and 60% higher open circuit voltage (OCV) was obtained by employing this composite membrane. By AC impedance of the composite membrane, the proton conductivity of the composite membrane achieves 0.71 S/cm at 150 ℃. By the long term test, mPTFE is useful to prevent phosphoric acid leakage. By single cell test, the best performance of GMF+mPTFE composite membrane with proper electrodes, supplied with pure hydrogen and oxygen, achieve 296mW/cm^2 power density at 900mA/cm^2 current density at 150℃.

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