Pt-ZrP membrane을 이용한 자기가습형 연료전지에 관한 연구

김재일, 손동훈, 이한규, 이태희
연세대학교 공과대학 화학공학화

A Study of Self-Humidifying PEMFC Using Pt-ZrP Membrane

Jae-il Kim, Dong-hoon Son, Han-kyu Lee, Tae-hee Lee
Department of Chemical EngineeringYonsei University

Introduction

Water management in electrolytes is one of the complicated problems to be overcome. So far, water content in PEMs has been managed indirectly by humidifying reactant gas. External humidification of the reactant gas is a burden for the fuel cell system. It requires a gas humidification subsystem that adds to the weight. For examples, commercial stacks with stack integrated gas humidification systems (DeNora, Italy, 5 kW stack and Ballard Power Systems, Canada, 5 kW stacks), the humidification section accounts for about 20% of the stack weight. Furthermore, the humidifiedreactant gas transports latent heat caused by water vaporization into the cell, which has to be removed by the cooling system. Therefore, this method makes the system complicate and lower the cell's energy efficiency because of the large latent heat. This also has difficulty responding to a quick start-up due to a large heat capacity of water reservoir. In this study, we report on PEMFC, which do not require external humidification. Pt-Nafion composite membrane was fabricated for self-humidifying PEMFCs by equilibrium impregnation reduction method. Water is produced by the crossover of hydrogen and oxygen on Pt particles in the membrane. The generated water can fully hydrate the membrane, resulting in stable operation of PEMFCs without any external humidification. But there is a decrease of fuel cell performance due to poor proton conductivity as the cell temperature was increased. Zirconium phosphate hydrate (ZrP, $Zr(HPO_4)H_2O$ for form and $Zr(PO_4)(H_2PO_4)_32H_2O$ for form) have features of increasing conductivity using high proton mobility on the surface of ZrP particles and good water retention. So we fabricate Pt-Zirconium phosphate Nafion composite membrane in order to improve water retention properties at increased cell temperature.

Experimental

In this experimental, E-Tek electrode were used. The average Pt loading in the electrode is 0.4 mg/cm^2. Prior to preparation of the membrane-electrode assembly, the electrodes were impregnated with Nafion solution. The membrane was Nafion 112(thickness : 50 µm) These were cleaned by being immersed in boiling 3% H_2O_2 for 1 hour, and then in boiled 1 mole H_2SO_4 for 1 hour. The membrane was then rinsed in boiling de-ionized water for 1 hour and the procedure was repeated at least twice to remove the sulfuric acid completely.

In the Equilibrium Impregnation Reduction, the membrane was equilibrated for 24 hr with a solution of 0.5 mM $Pt(NH_3)_4Cl_2$(Aldrich). After impregnation, the membrane was exposed to a solution 1.0 M $NaBH_4$ at pH 13(NaOH) that varied from 5 min to 60 min. After reaction, the membrane was boiled in a solution of 1 M H_2SO_4 and in distilled water to exchange sodium ions with hydrogen ions in the membrane. Zirconium phosphate was incorporated into Pt-Nafion membrane via an ion exchange reaction involving Zr^{4+} ions followed by immersion of the membrane in H_3PO_4. For this purpose, the membrane were first swollen in a boiling methanol-water solution (1:1 vol) and dipped in a zirconyl chloride (Aldrich) solution that varied from 0.1 M to 2 M for several hours at 80℃. The membranes were then rinsed in water to remove excess solution and finally placed in 1 M phosphoric acid overnight at 80℃. As a result, an insoluble zirconium phosphate was formed in-situ and entrapped in the nanopores of the Pt-Nafion membrane. The membranes were repeatedly rinsed in de-ionized water to remove excess acid. After completing the membrane and the electrode treatment, they were assembled and hot pressed at 120℃ and 3 Metric ton for 3 minutes. The operating temperature was 30, 40, and 50℃ and the pressure of cell was 1 atm.

Result and Discussion

At first, we examined the dependence of reduction time using equilibrium impregnation reduction method on cell performance and the dependence of cell operation temperature. Figure 1 and figure 2 shows the effect of reduction time using equilibrium reduction method. The best reduction time was 5 minutes. Figure 3 shows the effect of cell temperature on the cell performance. As the cell temperature was raised, cell performance was decreased. We assumed that cell temperature over 30℃ was too high to keep hydrating the membrane without external water support.

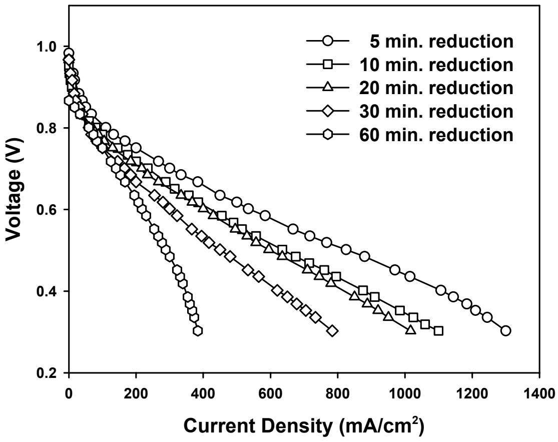

Figure 1. Effect of the Pt loading on cell performance.

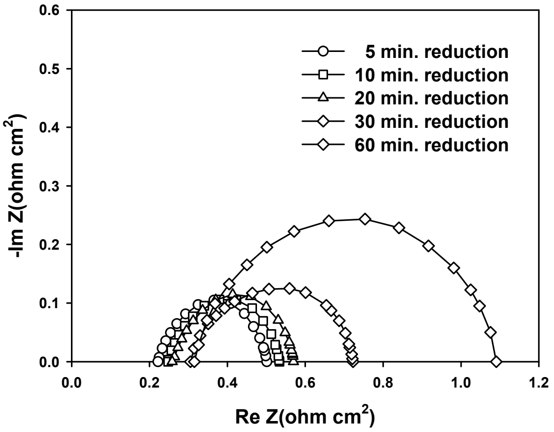

Figure 2. Nyquist plot with different Pt loading.

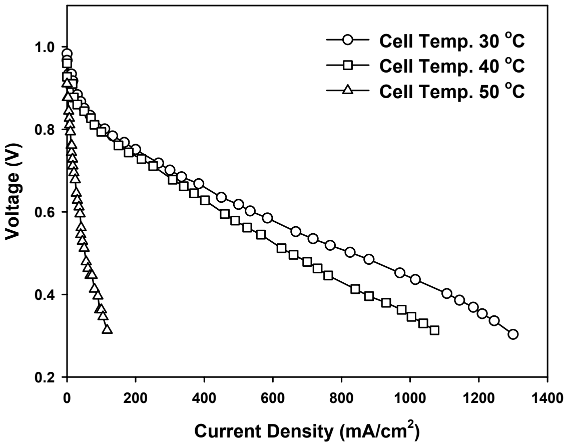

Figure 3. Effect of cell temperature (reduction time 5min)

The cross-sections of composite Pt-ZrP composite membranes were analyzed using SEM-EDS mapping. Figure 4 shows that reduction time was longer than 5 minutes, Pt particles coagulate during the chemical reduction process and eventually covered the membrane surface. Pt particles on the surface of membrane hinder the crossover of H_2 and O_2. So Pt particles in the membrane did not generate enough water to hydrate membrane.

Table 1 shows the amount of Pt in the membrane using ICP analysis. Figure 5 shows that the Pt-ZrP composite membranes have a uniform distribution of zirconium phosphate throughout the cross-section of the membrane.

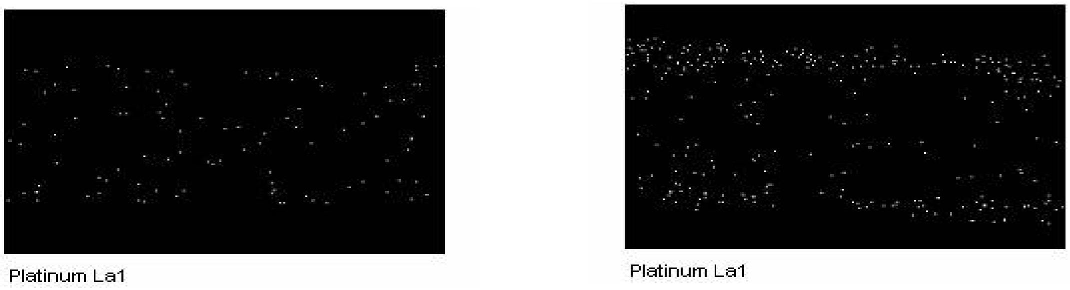

Figure 4. SEM-EDS mapping of Pt distribution along the cross section of Pt-ZrP membrane. reduction time 5 min(left), 60 min.(right).

Table 1. Amount of Pt in the Nafion membrane when reduction time 5min and 60 min

Reduction time	5 min	60 min
Pt amount	0.0638 mg/cm3	16.944 g/cm3

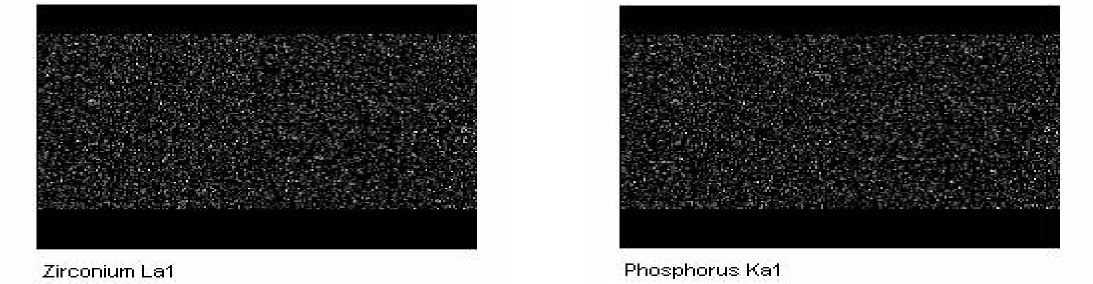

Figure 5. SEM-EDS mapping of P, Zr distribution along the cross section of Pt-ZrP membrane.

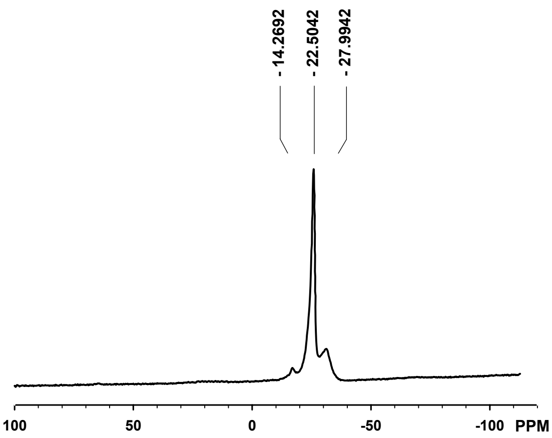

Figure 6. ^{31}P MAS-NMR of Pt-ZrP composite Nafion membrane

^{31}P MAS-NMR shown in Figure 6, confirmed that more than one type of phosphate was present in the composite membrane. The intensity signal at -22 ppm(HPO_4^{2-}) is associated with the form of ZrP, while the two smaller signals on either side of it, at -14 ppm($H_2PO_4^-$) and -28 ppm(PO_4^{3-}) are characteristic of the form. We examined the dependence of the cell operating temperature and zirconyl chloride amount on cell performance.

While the amount of ZrP was not important factor on cell performance at 30℃(figure 7, 8), the amount of ZrP played a roll in cell performance at 50℃ (figure 9, 10). Until the amount of zirconyl chloride reached to 1 M, the amount of ZrP was increased with zirconyl chloride. So the water retained by ZrP was increased in the membrane.

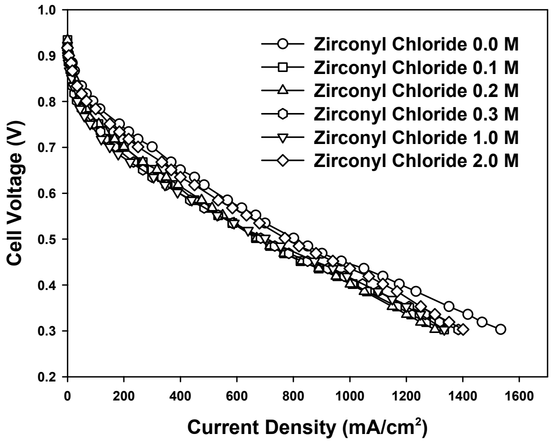

Figure 7. Performance of different zirconyl chloride.

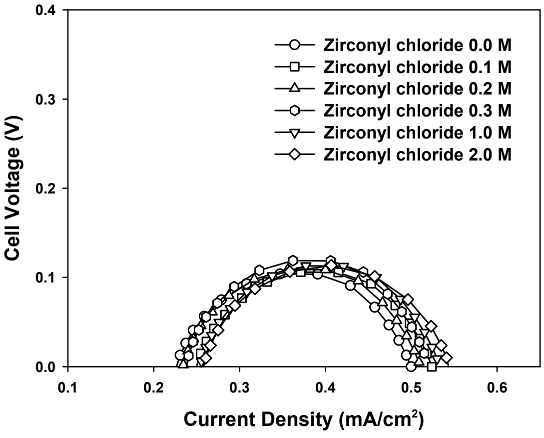

Figure 8. Nyquist plot with different zirconyl chloride.

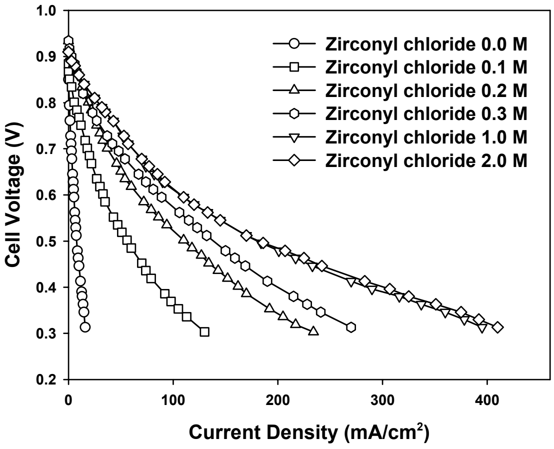

Figure 9. Performance of different zirconyl chloride

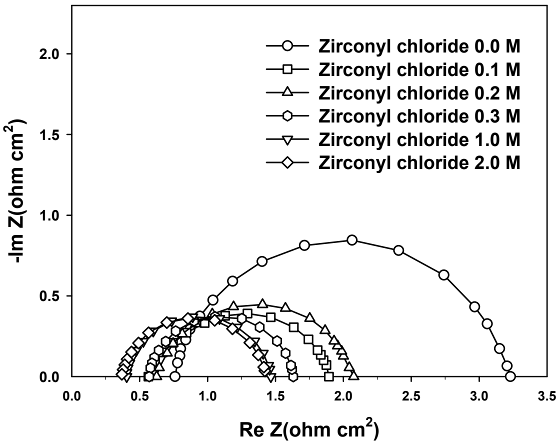

Figure 10. Nyquist plot with different zirconyl chloride

When amount of zirconyl chloride was more than 1 M, the cell performance was similar to using 1 M. Table 2 shows that amount of ZrP particles were the same in the membrane, 1 M and 2 M of zirconyl chloride.

Table 2. Weight gain for ZrP particles in the membrane

Amount of zirconyl chloride (M)	0.1 M	0.2 M	0.3 M	1 M	2 M
Weight gain percent (%)	2.375 %	4.301 %	7.895 %	12.558 %	12.501 %

CONCLUSION

We developed and compared Pt-ZrP membranes. The results were :

1. Performance of fuel cells with Pt-ZrP membranes indicated that PEM fuel cell could be operated without subsystem of humidification
2. Impregnated Pt, ZrP particles are well distributed.
3. Proper reduction time of equilibrium impregnation reduction method was 5 minutes.
4. More than 1 M of zirconyl chloride had not effect on the amount of ZrP particles.

ACKNOWLEDGEMENTS

This work was supported by Korea Research Foundation Grant.
(KRF-2001-A1008-2001-005-E00030)

REFERENCES

1. Masahiro Watanabe, "Self-Humidifying Polymer Electrolyte Membranes for Fuel Cells," J. Electochem. Soc., Vol. 143, No. 12, pp. 3847-3852, December. 1996.
2. Masahiro Watanabe, "Analyses of Self-Humidification and Suppression of Gas Crossover in Pt-Dispersed Polymer Electrolyte Membranes for Fuel Cells," J. Electrochem. Soc., Vol. 145, No. 4, pp. 1137-1141, April. 1998.
3. Felix N. Bchi, "Operating Proton Exchange Membrane Fuel Cells Without External Humidification of the Reactant Gases," J. Electrochem. Soc., Vol. 144, No. 8, pp. 2767-2772, August. 1997.
4. C.Yang, "Approaches and Technical Challenges to High Temperature Operation of Proton Exchange Membrane Fuel Cells,"J. Power Sources, Vol. 103, pp. 1-9, May. 2001.