Study on the Nafion-impregnated polycarbonate composite membranes which were formed under supercritical CO_2 for PEMFCs

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1. Introduction

Fuel cells are long-term stable power sources not necessarily requiring electric charging or discharging and very promising power sources for electric vehicles (EVs) to be replaced combustion engines using hydrocarbon fuel in the future. The advantages of polymer electrolyte fuel cell (PEFC) which is strongly applied to EVs are a high power output convenience for fuel supply and long life time etc [2]. However, high cost is needed to manufacture PEFC stacks, which has restricted their commercialization for EVs.

In this work, polycarbonate membranes with various porosities were prepared by phase inversion with supercritical CO_2. Supercritical CO_2 was used as a non-solvent instead of water. Advantages of this method are getting higher porosity and homogeneous membranes, and eliminating more PEG (poly ethylene glycol) which was used to form pores in the films. Composite membranes were prepared by impregnating Nafion solution as ionomer in the porous polycarbonate membranes. The chemical and physicalproperties of porous polycarbonate membranes were examined. After impregnating of Nafion into membranes, ion conductivity, gas permeability and other properties were investigated.

2. Experimental

Polycarbonate and PEG was dissolved in the organic solvent with the ratio of PC: PEG = 7:1 and 9:1 respectively, and then surfactant was added with 0.24wt. % of PEG. Reasonable amount of the polymer solution was poured on prepared PEN (Poly Ethylene Naphthalate) film and cast with desired thickness. After drying the membrane at the room temperature, the dried membrane was placed in the membrane formation chamber. The experimental apparatus for supercritical CO_2 is shown in Fig. 1. After the temperature of the chamber was reached to the desired temperature, CO_2 was injected into the chamber until the pressure was reached at desired pressure. The pressure was regulated by the back pressure regulator. This experience was performed with parameters such as temperatures and pressures to find out the optimum condition for formation of membranes.

Before being impregnated, porous PC membranes was placed in the prepared vacuum filtation equipment and 5% Nafion solution was inhaled in the membranes. Nafion solution was impregnated into the porous polycarbonate membranes formed with supercritical CO_2 by immersing membranes in Nafion solution for 3h, and then dried at 60℃ for 3h and then additional thermal treatment was given after impregnating and drying process.

3. Results and discussion

3.1 Chemical and physical properties of polycarbonate membranes

Fig.2 shows the surface and cross section images of polycarbonate membranes that were formed in supercritical fluid. The pores in polycarbonate membranes were clearly shown and they looked like bubbles connected each other in mixed ratio of 7:3 but pores was rarely observed in the ratio of 9:1. The more PEG is contained, the more pores it gets. However, membranes are wicker. Hence 7:3 was the reasonable ratio to form membranes. The thickness of membranes was averagely 10-20m and the pore size was 1-3m. To get optimum conditions to form membranes, the experiment was performed by various temperatures, pressures and times. As shown in Fig.3, PEG was eliminated mostly at 150bar. As pressure was increased, elimination of PEG was increased, however, over 150bar, it would rather be decreased.

3.2. Impregnation of Nafion solution

Table 1 shows the equilibrium impregnated amounts of Nafion solution in the porous PC membranes. As shown in Fig.1, pores were rarely observed in the mixed ratio 9:1. It means that it is most impossible to infiltrate Nafion solution into the inside of that kind of membranes. The membrane with mixed ratio of 7:3 was more absorbed Nafion solution than that with 9:1 because it had more pores and path which solution passed through.

3.3. Water uptake

The diffusion of protons through the polymer electrolyte is directly related to the extention of the hydration of membranes. The absorption of water in pure polycarbonate is very small. However, As Nafion solution is impregnated into the membrane. The water uptake starts to increase.

One of the commercial membranes for fuel cells, Nafion 115 used for comparison in this work usually has 33.7% of water uptake. Water uptake depends on how much Nafion solution is loaded on the membranes. The one with mixed ratio 9:1 absorbed 15% of its weight and the other one did 34% of its weight like Nafion 115. The water uptake of membranes dried at room temperature is also twice as much as that of the membrane dried at elevated temperature [4, 5].

3.4. Gas permeability

Gas permeability was measured to check the presence of pinholes or pores in the Nafion-impregnated composite membranes. The upstream pressure difference was from 1 to 5 atm and a bubble flow meter was located at the gas outlet to record the gas permeating rate.

All membranes that were used in this work didn't have any holes or pores.

3.5. Dimensional stability

Dimensional changes were measured before and after the membranes took up waters. PC composite membranes didn't show any dimensional changes but Nafion 115 expanded 28.8 % of its initial size. We could see that the PC composite membranes were more stable in dimension.

3.6. Tensile properties

PC is known for rigid and quite hard polymer. Therefore, as shown in Table 2, initial PC membranes showed higher tensile strength and lower elongation that commercial membrane but they were by far weaker that initial PC membranes after heat treatment. It might be suggested that both high heat treatment temperature and sulfone in Nafion solution effected on rigidness of PC membranes.

3.7. Ionic conductivity and conductance

Composite membranes usually have lower ionic conductivity than commercial membranes because polymer membrane used as a substrate works as a resistant.

Ionic conductivity was measured at room temperature and as we expected, the PC composite membranes showed lower value. Particularly, the composite membrane with increasing mixed ratio had much lower. It is presumed because Nafion solution didn't impregnateinto the inside of the membrane but remained on the surface. Even though ionic conductivity was lower, It should be applicable to PEMFCs due to higher conductance depending on the thickness of membranes.

4. Conclusions

Membranes formed with supercritical CO_2 showed different behavior in accordance with the amount of PEG which was added to form pores in membranes. The ratio of PC and PEG, 7:3 was optimum for composite membranes for fuel cells. Measurement of the gas permeability revealed that all the pores of the composite membranes were blocked like the commercial membrane, Nafion 115 and they absorbed as much water as Nafion 115 did. When Nafion 115 took up water, it showed dimensional change expanding 28.8% of its initial size but the composite membranes didn't expand at all. The composite membrane with the ratio of PC and PEG, 7:3 had lower ionic conductivity but higher conductance due to the thinner thickness.

Thinking over PC composite membranes with these characteristics, it is quite sure that this membrane is feasible for PEMFCs but serious problem still remains, which we have to overcome. The PC composite membranes were weaker than commercial membranes and especially, after heat treatment, they become much weaker. So it couldn't be guaranteed any durability and long lifetime during performing. If this problem was settled down, we could see this kind of membranes in the field of fuel cells and strongly effect on cost down.

Acknowledgement

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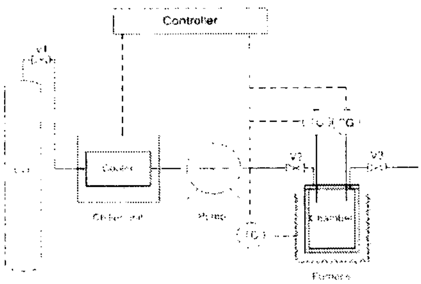


Fig. 1. Experimental apparatus. V. valve; PG. Pressure gauge; TC. Thermo couple.

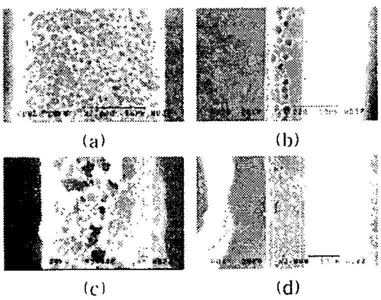
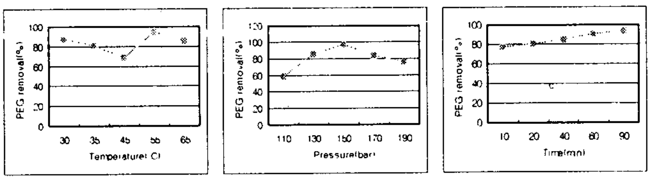


Fig. 2. Cross sectional SEM images (a) PC membrane with the ratio of PC and PEG, 7:3 formed at 150bar, 55C, (b) PC membrane with 9:1 formed 150bar, 55C, (c) Nafion impregnated PC membrane PC:PEG-7:3 (d) Nafion impregnated membrane PC:PEG-9:1



(a) (b) (c)

Fig. 3. Effecs of various operational Temperature, Pressure and residual Time on PEG removal (a) Effect of temperature, (b) Effect of pressure and (c) Effect of time

Table 1. Impregnation amount of Nafion solution in each of PC membranes

Type of membranes \ Item	Film thickness (㎛)	Film thickness after impregnateion (㎛)	Imprregnated Nafion amount (㎎/㎠)
PC composite membrane(EW-1100) with the ratio of 7:3	15	42.3	3.5
PC composite membrane(EW-1100) with the ratio of 9:1	18	45	1.3

Table 2. The electrochemical and physical properties of electrolyte membranes

Types of membranes \ Items	Ionic conductivity (S/cm)	Conductance (S/㎠)	Water uptake (%)	Dimensional stability (%)	Tensile properties (Mpa)	Elongation (%)	Gas permieability (GPU)
PC membrane with the ratio of 7:3	·	·	·	·	37.27	3.40	none
PC membrane with the ratio of 9:1	·	·	·	·	70.22	6.75	57.3
Nafion 115 (EW-1100)	0.105	6.7	33.7	28.8	15.04	532	none
PC composite membrane (EW-1100) with the ratio of 7:3	0.061	15.25	47.1	0	13.83	3.55	none
PC composite membrane (EW-1100) with the ratio of 9:1	0.006	1.02	15	0	28.44	6.90	none

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