

Effects of curing condition of solution cast Nafion® membranes on PEMFC performance

Singaram Vengatesan, Eunae Cho[†], Hyoung-Juhn Kim, and Tae-Hoon Lim

Fuel Cell Research Center, Korea Institute of Science and Technology,
39-1 Hawolgok-dong, Sungbuk-gu, Seoul 136-791, Korea
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Abstract—To study the feasibility of applying solution-cast membranes to polymer electrolyte membrane fuel cells (PEMFCs), single cells prepared with solution-cast membranes were tested. The solution cast membranes were fabricated from a commercial Nafion solution under various conditions. Effects of annealing temperature on characteristics of the solution-cast membranes were investigated by measuring water uptake and ionic conductivity of the membranes. Performance of the single cells using the prepared solution cast membranes was evaluated in terms of i-V curves, Nyquist plots, and H₂ crossover current density. Based on the results, solution-cast membranes were fabricated by being cured at 150 °C for different hours to examine effects of curing time on cell performance. Finally, durability of solution-cast membranes was investigated with operating the single cells for 1,000 hr.

Key words: Solution-cast Membrane, Polymer Electrolyte Membrane Fuel Cell, Curing Temperature, Curing Time, Performance

INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFCs) are considered as prominent energy sources for electric vehicle propulsion and applications that require clean, quiet and portable power [1]. Nafion, a perfluorosulfonic acid membrane, is still considered to be one of the best proton-conducting electrolytes for the PEMFCs. Nafion has a strong perfluoroethylene backbone with flexible side chains of perfluorinated vinyl ethers terminated by sulfonic acid group. Properties of Nafion membrane mainly depend on its microstructure. The superselectivity of Nafion for proton conduction and its chemical and thermal stability are attributed to the structure [2]. Numerous studies have been conducted on the microstructure of Nafion during the past 30 years [3]. Most of the studies showed that the microstructure of Nafion consists of three regions: hydrophobic fluorocarbon backbone, hydrophilic ionic clusters of sulfonic acid groups, and interfacial region [4]. The hydrophilic ionic clusters of sulfonic acid groups present in the Nafion membrane can adopt a spherical structure of inverted micelles about 4 nm in diameter [5]. The water absorbed by Nafion membrane is incorporated into the ionic clusters of the sulfonic acid group and the water content in hydrated Nafion membrane can vary up to 22 molecules of water per sulfonic acid group [6]. Nafion membrane has many desirable properties as a proton-conducting electrolyte, such as high mechanical strength and dimensional stability, good chemical stability as well as high proton conductivity under high-humidity conditions [7]. However, the membrane has poor ionic conductivity at low humidity and/or elevated temperatures [8], which limits the possibility of operating fuel cells at these conditions. Also, there is increasing demand for thin membranes which can reduce the cost and ohmic resistance of the fuel cells and for an alternative preparation method for membrane-electrode assembly (MEA) to improve the fuel cell perfor-

mance [9].

Solution casting method is widely used to prepare membranes from their ionomer dispersions with the advantages that thickness of membranes can be easily controlled in a wide range and the prepared membranes could be further processed to meet the fuel cell requirements. However, there are some disadvantages of the solution casting method that the cold cast films are generally mechanically weak, susceptible to crack formation and soluble in many polar solvents, especially in water at room temperature [10]. Thus, membrane processed at low temperatures could not be desirable for fuel cell applications. To overcome these problems, usually the cast films were heat processed either in a solvent with high or low boiling temperature [2,10,11]. Generally, the annealed films undergo morphological changes when heated above the glass transition temperature ($T_g=109$ °C for protonated Nafion) leading to improvement of mechanical stability of the membrane. This phenomenon was clearly explained by Zook et al. [2] by observing that cold cast Nafion films have a micellar configuration with the sulfonic acid groups on the outside and tetrafluoroethylene backbone inside of the micelle; by the heat treatment, the micelle structure was changed into an inverted micelle with the sulfonates on the interior. These polar sulfonic acid groups form a cluster network inside the structure. The improvement in mechanical properties by thermal treatments could be ascribed to the thermal conversion of the micellar structure of cold cast membranes to an inverted micellar structure. It was also found that curing Nafion at high temperatures imparted reduction in solubility, apparently by increasing the crystallinity of the polymer, and decreased gas permeability. These suggest that the curing procedure may seal pinholes or cracks present in the Nafion membrane, in addition to increasing crystallinity of Nafion [10-13].

Although, many authors have studied the physical-chemical properties of recast and heat processed cast membranes, none of them reported their application in fuel cell conditions. Recently Curtin et al. [9] reported the fuel cell performance of solution-cast membranes. However, there was limited information about the casting conditions.

[†]To whom correspondence should be addressed.
E-mail: eacho@kist.re.kr

To develop a solution-cast membrane for PEMFC applications, in this study, influences of curing condition on properties and PEMFC performance of cast membranes were examined by measuring physical-chemical properties such as ionic conductivity and water uptake of the membranes and fuel cell performance. To evaluate fuel cell performance, i-V characteristics, impedance spectroscopy and linear sweep voltammetry were measured. Finally, the long-term stability of these cast membranes was studied by operating the single cells for 1,000 h at a constant load.

EXPERIMENTAL

1. Preparation of Solution Cast Membranes

The solution-cast membranes with thickness of about 50 μm were prepared from 20 wt% commercial Nafion solution (DuPont Fluoroproducts) with EW 1100 on a glass plate and dried at ambient condition for 48 h, followed by curing at an elevated temperature in a vacuum chamber. As the annealed films undergo morphological changes when heated above the glass transition temperature ($T_g = 109^\circ\text{C}$ for protonated Nafion), all the curing temperatures in this study were chosen to be above T_g of Nafion. Then the membranes were immersed in de-ionized water and taken off from the glass plate. Finally, they were immersed in boiling in 5% H_2O_2 +0.5 M H_2SO_4 solution and de-ionized water, for 1 h, respectively, to obtain acid form of the membranes. Then, the membranes were stored in de-ionized water. The membrane thickness was measured in dry state by using a digital screw gauge (Mitutoyo). For durability test, cast membranes with thickness of about 85 μm were prepared from 20 wt% Nafion solution and dried at 70°C overnight, followed by curing at 150°C for 6 h in a vacuum chamber.

To measure water uptake, the prepared membranes were cut ($3 \times 3 \text{ cm}^2$) and immersed in de-ionized water for 24 h. Then, the membrane samples were taken out and water was removed from the membrane surface carefully with a tissue paper and immediately weighed with a digital balance (W_1). To measure dry weight (W_2) of the membrane, the membrane was dried in an oven at 60°C for 3 h and in a vacuum chamber containing desiccator of P_2O_5 for 1 week and then weighed. The water uptake of the membrane was calculated as follows:

$$\% \text{ Water uptake} = \frac{W_1 - W_2}{W_2} \times 100$$

To measure ionic conductivity of the prepared membranes, a four point probe conductivity cell as described in ref. [7] was used. Membrane samples were cut into 1 cm width and 4 cm length and immersed in de-ionized water for 24 h prior to mounting on the cell. After mounting the membrane, the conductivity cell was immersed in de-ionized water at 25°C and the conductivity was measured with a Zahner IM6 electrochemical impedance analyzer in a galvanostatic mode with ac current amplitude of 1 mA over a frequency range from 1 Hz to 5 MHz.

2. Preparation of Membrane Electrode Assemblies (MEAs)

The catalyst inks for the electrodes were prepared by using 40 wt% Pt/C (E-Tek Inc.), 5 wt% Nafion solution (Dupont Fluoroproducts), and isopropyl alcohol (Baker analyzed HPLC grade reagent). Then the ink was sprayed on the prepared cast membrane with Pt loading of 0.3 and 0.4 mg cm^{-2} for anode and cathode, respectively.

Then the catalyst-coated membrane (CCM) was dried in an oven at 60°C for 12 h. For comparison, MEA with commercial Nafion 112 membrane was prepared by the same method.

3. Single Cell Tests

Single cells were assembled with prepared CCM, gas diffusion media, Teflon gaskets and graphite blocks. For all single cell tests, humidified hydrogen and air were fed to the anode and cathode, respectively, with flow rate of 400, 1,200 cc min^{-1} under ambient pressure. Temperatures of the cell, anode saturator, and cathode saturator were maintained at 80, 80 and 68°C , respectively, for all the tests. Performance of the cell was evaluated by measuring i-V characteristics by using an electric load (Daegil Electronics, EL 500P).

Impedance of the single cells was estimated by measuring AC impedance spectroscopy with a frequency response analyzer (Zahner Electric IM6) in potentiostatic mode at 0.8 V with amplitude of 5 mV over a frequency range from 10 mHz to 10 KHz.

The H_2 crossover current density through the MEA was measured by using linear sweep voltammetric method at a steady state. The potential was swept from 0.05 V to 0.6 V.

4. Durability Test

To examine the durability of the prepared membranes and effects of membrane hydration on cell performance as a function of operation hour, a single cell was fabricated with a thinner solution cast membrane ($\sim 85 \mu\text{m}$ in thickness) to improve durability over normal cast membranes ($\sim 50 \mu\text{m}$ in thickness), and i-V characteristics, impedance and H_2 crossover current density were measured periodically for 1,000 h.

RESULTS AND DISCUSSION

The thickness of all the solution-cast membranes prepared for single cell test and durability test was measured to be $52 \pm 3 \mu\text{m}$ and $85 \pm 3 \mu\text{m}$, respectively (thickness of commercial Nafion 112 membrane was $51 \pm 1 \mu\text{m}$).

1. Effects of Curing Temperature on Cell Performance

To examine effects of curing temperature of cast membranes on their characteristics and fuel cell performance, cast membranes were prepared by being cured at different temperatures (120 – 165°C) for 6 h. Table 1 shows water uptake and ionic conductivity of the prepared cast membranes. As curing temperature increased, water uptake of the cast membranes was lowered, probably due to an increase in crystallinity of the membrane [13]. In addition to the increased crystallinity, as curing temperature increased, the ionic clusters in Nafion ionomer could shrink, resulting in reduction of the cluster size. Ionic conductivity of the cast membranes was higher than that of commercial Nafion 112 membrane since well-defined

Table 1. Effects of curing temperature on ionic conductivity and water uptake of the cast membranes

Membrane	Curing temperature ($^\circ\text{C}$)	Ionic conductivity (S/cm)	Water uptake (%)
Cast membrane	120	0.133	35.45
Cast membrane	135	0.130	32.98
Cast membrane	150	0.137	29.26
Cast membrane	165	0.122	27.94
Nafion 112	-	0.115	33.48

ionic clusters could be formed in the cast membranes while being cured at a high temperature and the well defined ionic cluster channels could facilitate the proton migration through the membranes. On the other hand, ionic conductivity of the cast membranes did not exhibit a relationship with curing temperature; the cast membrane cured at 150 °C showed the highest ionic conductivity.

Fig. 1 shows performance of single cells by using the prepared cast membranes cured at different temperatures for 6 h. Single cells using the cast membranes and Nafion 112 membrane exhibited almost similar performance. The single cell using the cast membrane cured at 150 °C showed slightly higher performance than the others, which could be attributed to the higher proton conductivity of the membrane as revealed in Table 1.

To examine effects of curing temperature on the electrochemical characteristics of the single cells using the cast membranes, AC im-

pedance spectroscopy was measured. Fig. 2 shows Nyquist plots for the single cells fabricated with the prepared cast membranes and Nafion 112. The applied cell voltages were IR-corrected. The Nyquist plots shown in Fig. 2 are semi-circular; the left point of intersection with the x-axis corresponds to the ohmic resistance and the diameter of the semi-circle to the charge transfer resistance. In the AC impedance measurement, oxygen electrode served as the working electrode and hydrogen electrode as the counter electrode. The counter electrode also served as the reference with its negligible over-potential for the hydrogen oxidation or evolution reaction [14]. Thus, the charge transfer resistance obtained through the AC impedance study primarily could be attributed to the oxygen reduction reaction. As shown in Fig. 2, ohmic resistance of the single cells was almost the same, while charge transfer resistance of the single cells using the cast membranes was lower than that of the single cell using Nafion 112. Charge transfer resistance exhibits no tendency with curing temperature, as observed for ionic conductivity in Table 1.

Generally, curing a cast membrane at a higher temperature reduces gas permeability through the membrane by sealing the pinholes which could be formed during the membrane casting process [10]. Fig. 3 shows H_2 crossover behavior for the single cells from using the prepared cast membranes and Nafion 112 membrane. It clearly shows that H_2 crossover current density decreased as the curing temperature increased, which could be attributed to an increase in crystallinity of the membrane as curing temperature increased and hence, a decrease in gas permeability. Crossover of all the cast membranes was higher than that of Nafion 112 since they were home-made and possibly contained defects.

2. Effect of Curing Time on Cell Performance

From the results presented in Figs. 1-3, among the cast membranes, the one that cured at 150 °C exhibited the best performance. Thus, to examine effects of curing time on cell performance, cast membranes were prepared by curing for different hours at 150 °C. Fig. 4 shows the single cell performance of the prepared cast membranes. There was significant improvement in performance as the

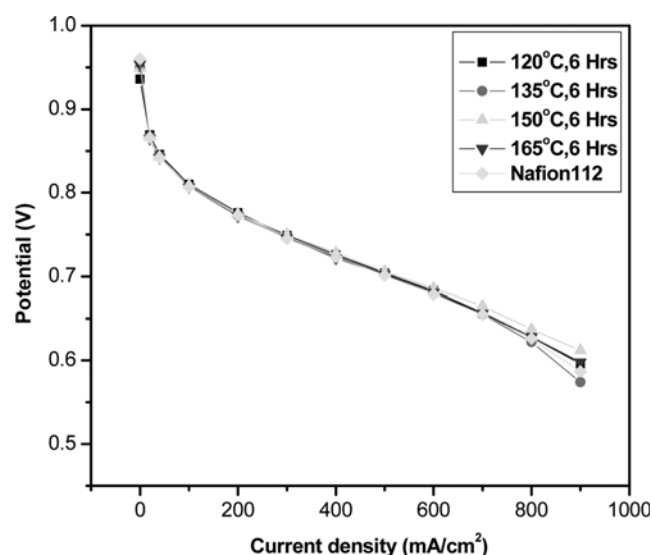


Fig. 1. Effects of curing temperature on performance of the single cells fabricated with the prepared cast membranes.

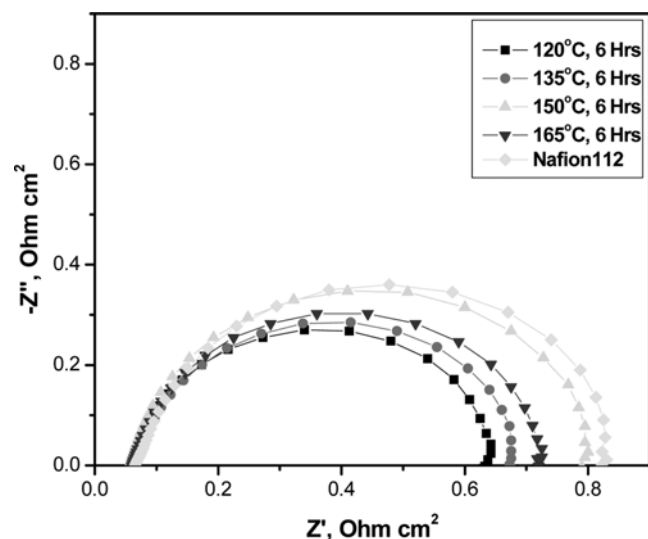


Fig. 2. Effects of curing temperature on Nyquist plots for the single cells fabricated with the prepared cast membranes.

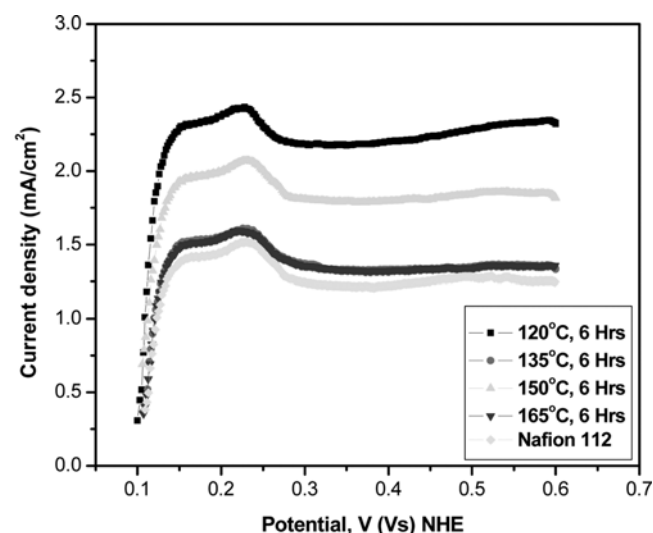


Fig. 3. Effects of curing temperature on H_2 crossover current for the single cells fabricated with the prepared cast membranes (Scan rate=2 mV s⁻¹, H_2 /air flow rate=400/1,200 cc min⁻¹).

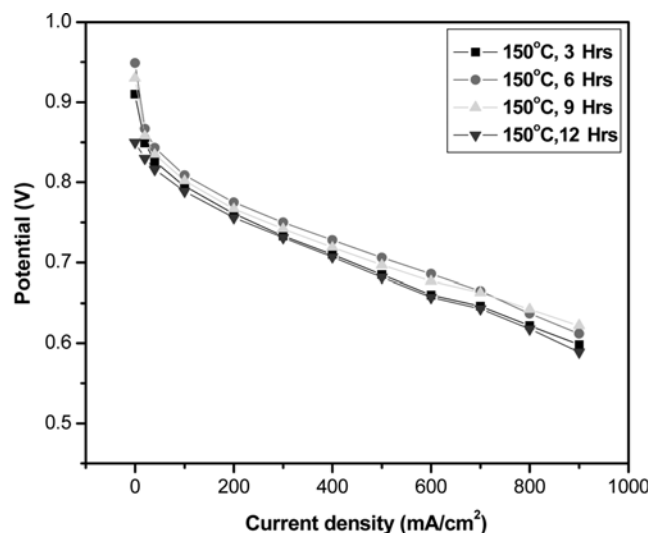


Fig. 4. Effects of curing time on performance of the single cells fabricated with the prepared cast membranes.

curing time increased from 3 to 6 h, probably due to formation of well-defined polar clusters during the longer curing time. However, a further increase in curing time from 6 to 9 and 12 h reduced the cell performance. Even though curing membrane for longer than 6 h would produce highly crystalline and mechanically stable membrane, ionic cluster could shrink, resulting in lower ionic conductivity of cast membrane and lower cell performance.

Fig. 5 shows Nyquist plots for the single cells using the cast membranes cured for different hours. It reveals that ohmic resistance of the single cells was almost the same, whereas charge transfer resistance slightly decreased as curing time increased. Curing a membrane for longer time produces migration of sulfonic acid group from bulk to surface of the membrane; this in turn may reduce the charge transfer resistance between membrane and catalyst layer [15].

Fig. 6 shows H_2 crossover current density for the single cells by

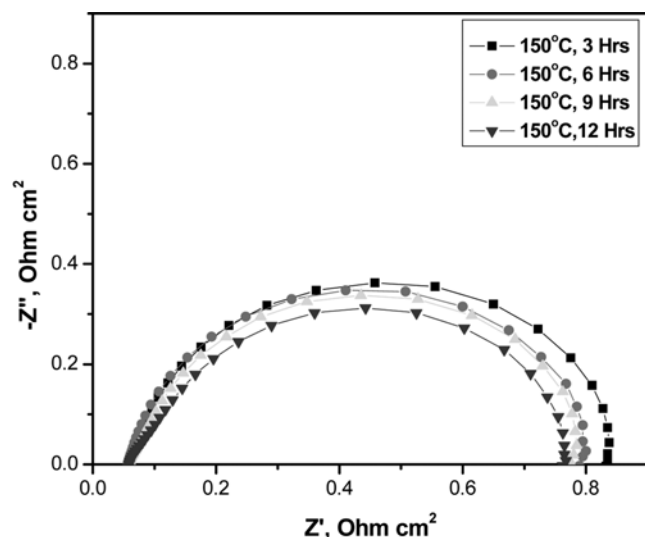


Fig. 5. Effects of curing time on Nyquist plots for the single cells fabricated with the prepared cast membranes.

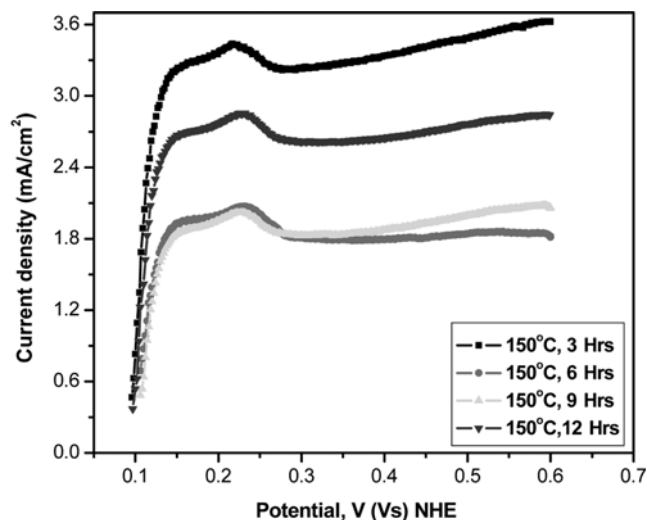


Fig. 6. Effects of curing time on H_2 crossover current for the single cells fabricated with the prepared cast membranes (Scan rate = 2 mV s^{-1} , H_2 /air flow rate = $400/1,200 \text{ cc min}^{-1}$).

using the prepared cast membranes. With increasing curing time, crossover current density decreased because longer curing produces a mechanically stable and crystalline membrane.

3. Durability Test

According to St- Pierre et al. [16], water plays a crucial role in cell performance and ultimately has influence on lifetime and degradation state of PEMFC membranes. To elucidate this phenomenon, single cell was operated for 1,000 h by using a solution-cast membrane prepared in a dry condition as described above.

Fig. 7 shows i-V curves measured for the single cell at different operating hours. It is clearly seen that the cell performance improved slightly up to 500 h due to increase in water content in the membrane and in proton conductivity. After 500 h, the cell performance decreased gradually up to 700 h, and then significantly dropped. This could be correlated with an increase in H_2 crossover through

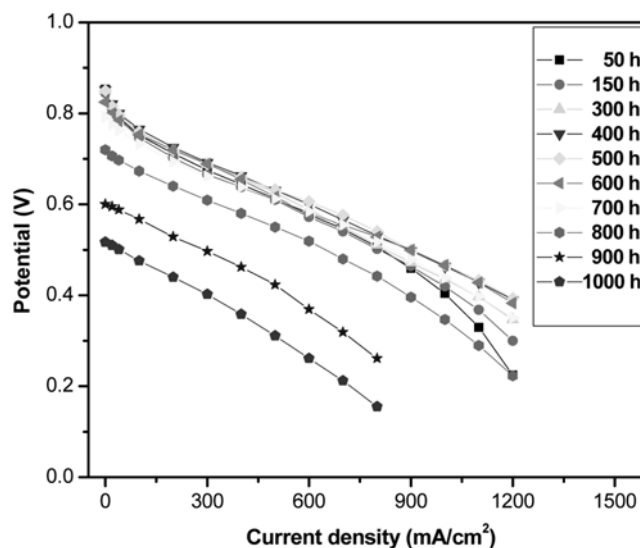


Fig. 7. Effects of operating time on performance of the single cell fabricated with the cast membrane cured at 150°C for 6 h.

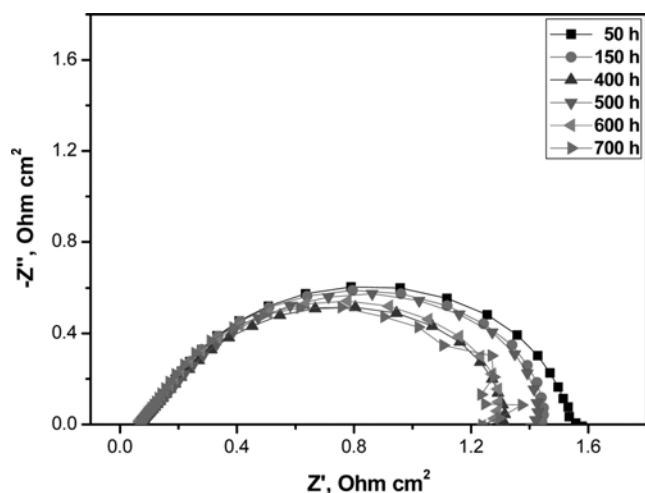


Fig. 8. Effects of operating time on Nyquist plot for the single cell fabricated with the cast membrane cured at 150 °C for 6 h.

the membrane as presented below.

Nyquist plots for the single cell were measured at different operating hours and presented in Fig. 8. After 700 h, AC impedance could not be measured since open circuit voltage (OCV) was lowered below the impedance measurement voltage (0.8 V). Ohmic resistance was almost the same, while charge transfer resistance decreased with increasing operating time even though the cell performance was lowered. This could be attributed to the lower over-potential for the impedance measurement. In other words, the impedance was measured at the same potential (0.8 V) for all the operating time although the open circuit potential was lowered as the operating times increased as shown in Fig. 7. Since charge transfer resistance exponentially depends on over-potential (difference between equilibrium potential and applied potential), it decreased with operating time as revealed in Fig. 8.

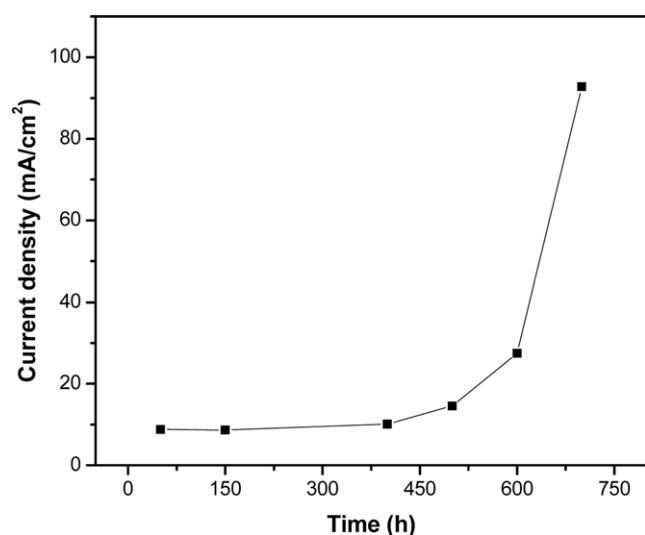


Fig. 9. Effects of operating time on H₂ crossover current density for the single cell fabricated with the cast membrane cured at 150 °C for 6 h.

H₂ crossover current density of cast membrane measured at different operating hours was taken as a current density at 0.4 V as presented in Fig. 9. It shows that the crossover current density slightly increases with operation time up to 600 h and then abruptly at 700 h. After that, H₂ crossover current density could not be measured since the current exceeded the maximum current measurement limit of the equipment. These results imply that the cast membrane exhibits high cross over and substantial degradation, which could be possibly causing membrane thinning and/or pinhole formation. Therefore, for application of the cast membrane to fuel cells, proper processes need to be developed to improve durability by preventing membrane thinning and/or pinhole formation.

CONCLUSIONS

Solution-cast membranes were prepared from commercial Nafion solution under various curing conditions. As curing temperature increased at a fixed curing time, water uptake of cast membrane decreased, while ionic conductivity of all the cast membranes was almost similar and higher than commercial Nafion 112 membrane. Performance, ohmic resistance, and charge transfer resistance of the single cells using the cast membrane were comparable to those of the single cell using the commercial Nafion 112 membrane. However, H₂ crossover current density of cast membranes was higher than that of commercial Nafion 112 membrane, even though it decreased with curing temperature. Among the solution cast membranes cured for different hours at a fixed curing temperature of 150 °C, one that cured for 6 h exhibited the best performance.

Performance of the solution cast membrane was abruptly lowered after 700 h mainly due to an increase in H₂ crossover current density. Even though the solution-cast membranes exhibited poor durability and high H₂ crossover current density, taking into consideration that the solution-cast membranes used in this study were home-made manually, the shortcomings would be overcome. All those results imply that the solution-cast membranes could be applied to fuel cells, leading to development of new fabrication techniques for membrane-electrode assemblies (MEAs).

REFERENCES

1. A. J. Appleby and F. R. Foulkes, *Fuel cell handbook*, Van Nostrand Reinhold, New York (1989).
2. L. A. Zook and J. Leddy, *Anal. Chem.*, **68**, 3793 (1996).
3. C. H. Wirquin, *J. Membr. Sci.*, **120**, 1 (1996).
4. T. D. Gierke and W. S. Hsu, in A. Eisenberg and H. L. Yeager Eds., *Perfluorinated Ionomer Membranes*, ACS Symposium Series 180, American Chemical Society, Washington DC (1982).
5. S. H. de Almeida and Y. Kawano, *J. Therm. Anal. Calorim.*, **58**, 569 (1999).
6. T. A. Zawodzinski, C. Derouin, S. Radzinski, R. J. Sherman, V. T. Smith, T. E. Springer and S. Gottesfeld, *J. Electrochem. Soc.*, **140**, 1041 (1993).
7. J. J. Sumner, S. E. Creager, J. J. Ma and D. D. DesMarteau, *J. Electrochem. Soc.*, **145**, 107 (1998).
8. T. A. Zawodzinski, Jr., T. E. Springer, J. Davey, R. Jestel, C. Lopez, J. Valerio and S. Gottesfeld, *J. Electrochem. Soc.*, **140**, 1981 (1993).
9. D. E. Curtin, R. D. Lousenberg, T. J. Henry, P. C. Tangeman and

- M. E. Tisack, *J. Power Sources*, **131**, 41 (2004).
10. G. Gebel, P. Albert and M. Pineri, *Macromolecules*, **20**, 1425 (1987).
11. M. Laporta, M. Pegoraro and L. Zanderighi, *Macromol. Mater. Eng.*, **282**, 22 (2000).
12. Z. Fan and D. J. Harrison, *Anal. Chem.*, **64**, 1304 (1992).
13. H. Y. Jung, K. Y. Cho, Y. M. Lee, J. K. Park, J. H. Choi and Y. E. Sung, *J. Power Sources*, **163**, 952 (2007).
14. X. Cheng, B. Yi, M. Han, J. Zhang, Y. Qiao and J. Yu, *J. Power Sources*, **79**, 75 (1999).
15. Z. Liang, W. Chen, J. Liu, S. Wang, Z. Zhou, W. Li, G. Sun and Q. Xin, *J. Membrane Science*, **233**, 39 (2004).
16. J. St-Pierre, D. P. Wilkinson, S. Knights and M. L. Bos, *J. New Mat. Electrochem. Syst.*, **3**, 99 (2000).