

Decrease in hydrogen crossover through membrane of polymer electrolyte membrane fuel cells at the initial stages of an acceleration stress test

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Abstract—An acceleration stress test (AST) was performed to evaluate the durability of a polymer membrane in a polymer electrolyte membrane fuel cell (PEMFC) for 500 hours. Previous studies have shown that hydrogen crossover measured by linear sweep voltammetry (LSV) increases when the polymer membrane deteriorates in the AST process. On the other hand, hydrogen crossover of the membrane often decreases in the early stages of the AST test. To investigate the cause of this phenomenon, we analyzed the MEA operated for 50 hours using the AST method (OCV, RH 30% and 90 °C). Cyclic voltammetry and transmission electron showed that the electrochemical surface area (ECSA) decreased due to the growth of electrode catalyst particles and that the hydrogen crossover current density measured by LSV could be reduced. Fourier transform infrared spectroscopy and thermogravimetric/differential thermal analysis showed that -S-O-S- crosslinking occurred in the polymer after the 50 hour AST. Gas chromatography showed that the hydrogen permeability was decreased by -S-O-S- crosslinking. The reduction of the hydrogen crossover current density measured by LSV in the early stages of AST could be caused by both reduction of the electrochemical surface area of the electrode catalyst and -S-O-S- crosslinking.

Keywords: PEMFC, Membrane, Degradation, Hydrogen Crossover, Linear Sweep Voltammetry, Accelerated Stress Test, Cross Linking

INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFC) are widely regarded as a power source because of the high energy conversion efficiency and environmental friendliness. However, their commercialization has been delayed due to their short lifetime and high price [1,2]. PEMFCs, which require a lifetime of 5,000 to 40,000 hours depending on the application, have failed to meet this criterion due to the degradation of the components of the membrane and electrode assembly (MEA) during long-term operation [3-9].

Enhanced durability of the polymer membrane is very important for extending the lifetime of a PEMFC. The degradation that shortens the lifetime of the electrolyte membrane is classified largely into chemical/electrochemical, thermal and mechanical degradation [3]. Chemical/electrochemical degradation refers to the degradation of the membrane due to the attack of radicals/hydrogen peroxide generated in the cell against the membrane [10]. To shorten the evaluation time of the membrane durability, a degradation accelerating method (acceleration stress test, AST) is used. The AST of the United States Department of Energy (DOE) measures the membrane durability of chemical/electrochemical by measuring hydrogen crossover current density by linear sweep voltammetry (LSV) after 500 hours of operation at OCV, 30% of relative humidity (RH) and 90 °C [11].

The membrane's chemical stability test of the DOE requires 500 hours of test time, even in the acceleration method, and it is affected by the electrode because it is evaluated in the membrane and electrode assembly (MEA) state. Therefore, the Fenton reaction, which can evaluate the durability of the membrane in a short time only with the polymer membrane out of the cell, has been applied widely to an evaluation of the chemical durability of membranes [12-18]. In the Fenton reaction, hydrogen peroxide reacts with metal ions to generate oxygen radicals, which deteriorate the electrolyte membrane. In the OCV holding process of the cell (AST of DOE), oxygen radicals and hydrogen peroxide are generated in a similar manner, so that the cause of membrane degradation can be said to be the same. Although many studies have attempted to deteriorate membranes by the Fenton reaction, it is difficult to obtain reproducible results [12-18].

The hydrogen permeability of the polymer membrane is generally increased due to degradation of the polymer membrane during the accelerated degradation test, but hydrogen permeability is sometimes decreased at the early stages of the acceleration degradation test [19-21]. When the polymer membrane deteriorates, the hydrogen permeability increases, but the opposite phenomenon occurs at the beginning of AST. Jeong et al. [21] reported that electrode deterioration also occurred at the beginning of AST and the active area of the electrode decreased, resulting in a decrease in hydrogen permeability measured by LSV. Qiao et al. [22] reported that S-O-S crosslinking occurs when the membrane degrades due to the oxidation of H₂O₂ out of the cell, and the diffusion coefficient of hydrogen decreases. These phenomena are related to the decrease in

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hydrogen permeability in early stages of AST. We examined the cause of the decrease in hydrogen permeability through the membrane at the initial stages of the membrane degradation acceleration test.

EXPERIMENTAL

1. Single Cell Operation and Accelerated Stress Test

PEMFC cell tests were performed in a 25 cm² single cell. This cell was assembled with commercial MEA (with a perfluor sulfonic acid membrane), GDL, Teflon gaskets, bipolar plates, and end plates installed in a fuel cell test station (C&L Co.).

Before the ASTs, the fuel cell was activated by constant voltage (CV) cycling, which was dropped repeatedly from 0.9 V to 0.4 V at 0.05 V intervals for 10 seconds and kept at 0.4 V for 5 min. The ASTs were performed in hydrogen and air at the OCV, 90 °C and 30% relative humidity. Membrane degradation after the AST was evaluated by measuring the hydrogen crossover. Hydrogen crossover was determined electrochemically by LSV [11]. Hydrogen and nitrogen gases were fed into the anode and cathode at 40 and 200 ml/min, respectively, at atmospheric pressure and 80 °C. The voltage from 0 to 0.5 V was swept at a scan rate of 1.0 mV/sec using a potentiostat (Solatron, SI 1287) during LSV.

Degradation of the polymer membrane out of the cell occurred via the Fenton reaction. The Fenton reaction was carried out in 20% hydrogen peroxide and a 10 ppm Fe²⁺ ion solution at 80 °C for 24 hours.

2. Analysis

Hydrogen crossover was measured directly by gas chromatography (GC, SIMADZU, GC-4B) equipped with a thermal conductivity detector (TCD) and a molecular sieve column (5A F-3847, 3.0 m, 3.0 mm ID). The vent gas from the cathode outlet was passed through a chiller circulating ethanol at 3 °C to remove the moisture from the gas, which then flowed to the gas chromatograph. Fourier transform infrared (FT-IR, Nicolet iS5 FTIR) spectroscopy was performed in the range of 400-4,000 cm⁻¹. The FT-IR spectra were measured using an ATR device equipped with a 1.8 mm diamond window. Pt particles in the electrode were observed by transmission electron microscopy (TEM, JEM-2010, JEOL, Ltd.) at an accelerating voltage of 200 kV. For TEM analysis, the catalysts were scraped off the carbon cloth of the tested MEA and placed into vials containing ethanol and then agitated ultrasonically for 5 min to form a suspension. The generation of radicals in the membrane and electrode assembly was measured using electron spin resonance (ESR, JEOL, JESFA200) spectroscopy [23]. Thermal analysis was performed using thermogravimetric/differential thermal analysis (TG/DTA, Nano Technology, Inc. TG/DTA 6200 and DSC 6200, SII). The samples (5-10 mg) were heated from 25 to 600 °C at a heating rate of 10 °C min⁻¹ with an inert N₂ gas purge.

RESULT AND DISCUSSION

1. The Decrease in Hydrogen Crossover After AST

The membrane was degraded by the electrochemical degradation accelerating protocol of the DOE [11]. That is, the MEA was deteriorated for 50 hours under the OCV, RH 30% and 90 °C operation conditions. The hydrogen crossover current density (HCCD) before and after degradation was measured by LSV, as shown in

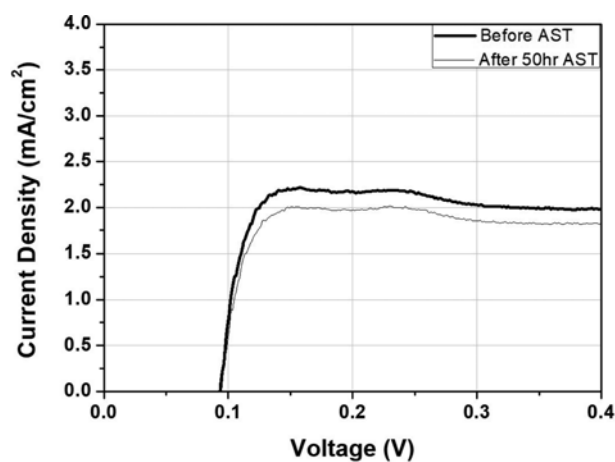


Fig. 1. Comparison of hydrogen crossover current density measured by linear sweep voltammetry before and after 50 hr acceleration stress test.

Fig. 1. HCCD decreased from 2.10 mA/cm² to 1.94 mA/cm², i.e., HCCD decreased by 7.6% after AST operation. Generally, the hydrogen permeability should increase if the polymer membrane deteriorates [4]. Measurements of hydrogen permeability by LSV can be influenced by changes in the electrode during the AST because the HCCD measured by LSV is the current generated by oxidizing the permeated hydrogen at the cathode electrode [21]. Therefore, the hydrogen permeability before and after degradation was measured by gas chromatography (GC), which can measure the hydrogen permeability directly without influencing the electrode [Fig. 2]. At the cathode, the initial hydrogen concentration decreased from 930 ppm to 903 ppm after the AST. The hydrogen permeability by GC showed a 2.9% decrease after membrane degradation. The change in hydrogen permeability according to GC was attributed to only the change in the membrane state.

2. Effect of Electrode Degradation on the Hydrogen Crossover Current Density

The hydrogen crossover measured by LSV reflects the changes

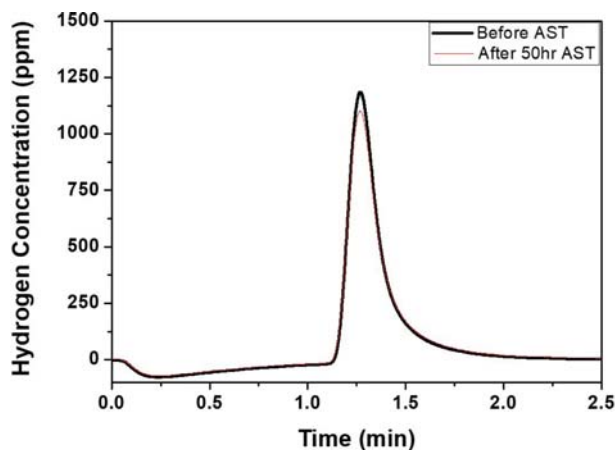


Fig. 2. Comparison of hydrogen crossover concentration measured by gas chromatograph before and after 50 hr acceleration stress test.

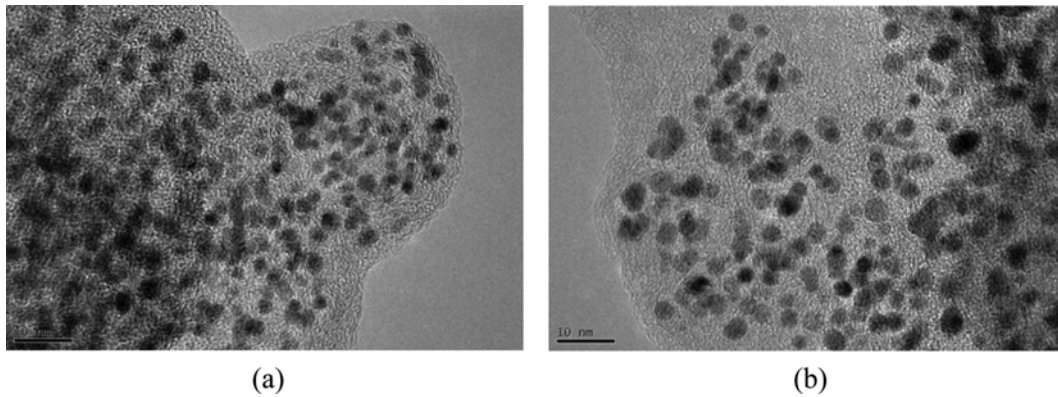


Fig. 3. Transmission electron microscopy image of platinum particles in cathode (a) before AST, (b) after 50 hr acceleration stress test.

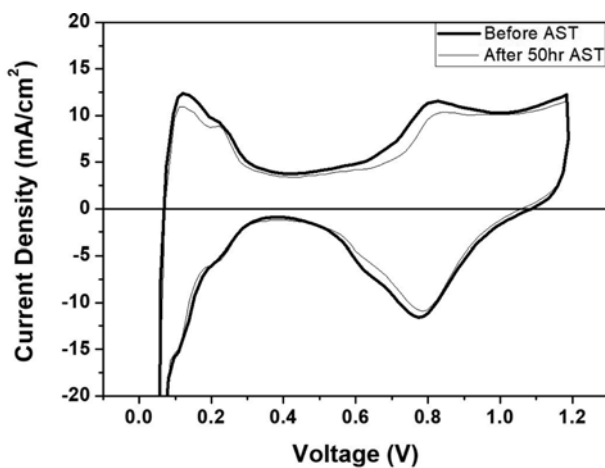


Fig. 4. Variation of cyclo-voltammery before and after 50 hr acceleration stress test.

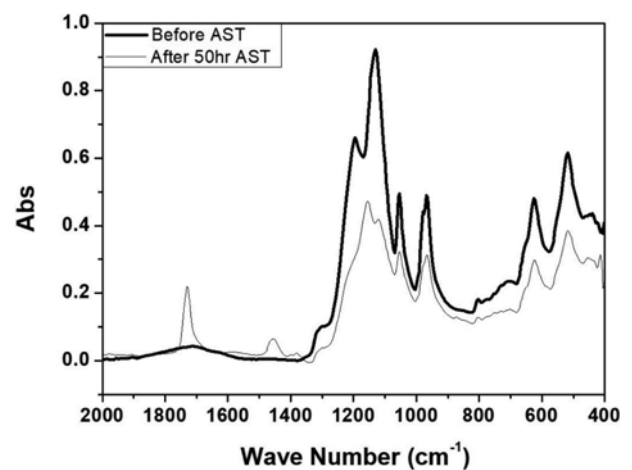


Fig. 5. IR spectra of PFSA membrane before and after 50 hours acceleration stress test.

in both the membrane and electrode catalyst. When the Pt particles become larger due to electrode degradation, the electrochemical surface area (ECSA) decreases and hydrogen crossover measured by LSV also decreases [24]. This is because the decrease in ECSA reduces the oxidation rate of the hydrogen that reaches the cathode. To ascertain the change in Pt particle size with the degradation of the electrode, the Pt catalyst particle size before and after degradation was analyzed by TEM, as shown in Fig. 3. After 50 hours of degradation, the Pt particle size increased slightly from 2–4 nm to 3–5 nm. Fig. 4 presents the CV data of the MEA before and after the AST; ECSA decreased by 13.2%. The decrease in hydrogen crossover measured by LSV was 2.9% due to the membrane change in 7.6%; the remainder was due to the increase in catalyst particle size.

3. Chemical Change of the Polymer Membrane After the AST

After 50 hours of AST, FT-IR analysis of membranes was used to determine the cause of the decreased hydrogen permeability associated with the changes in polymer membranes. Figs. 5, 6 present the FT-IR spectra of the membrane before and after 50 hours of degradation. The peak at $1,450\text{ cm}^{-1}$, which was not observed before degradation, occurred after degradation. This peak was assigned to the S-O-S crosslink peak first discovered by Qiao et al. [22] after 22 days hydrogen peroxide contact of the Nafion mem-

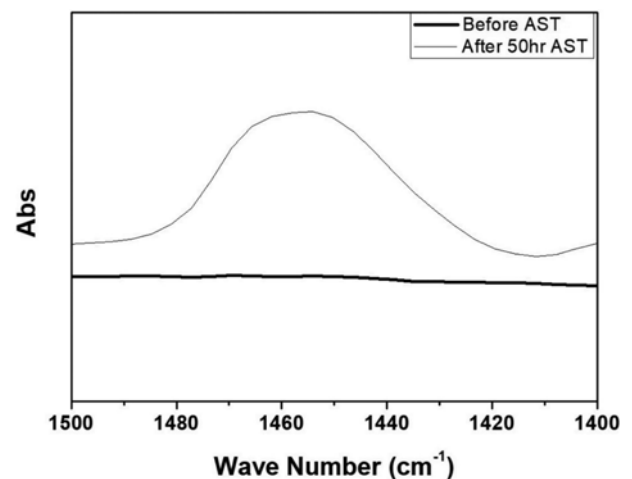


Fig. 6. Extended IR spectra of PFSA membrane between $1,500$ and $1,400\text{ cm}^{-1}$ before and after 50 hours AST.

brane out of the cell. The S-O-S peak clearly appeared after 50 hours of the AST in the cell. The SO_3^- ion peak near $1,060\text{ cm}^{-1}$ remained after the AST and some of the SO_3^- became an S-O-S link [25,26]. Qiao et al. [22] reported that an S-O-S crosslink was formed be-

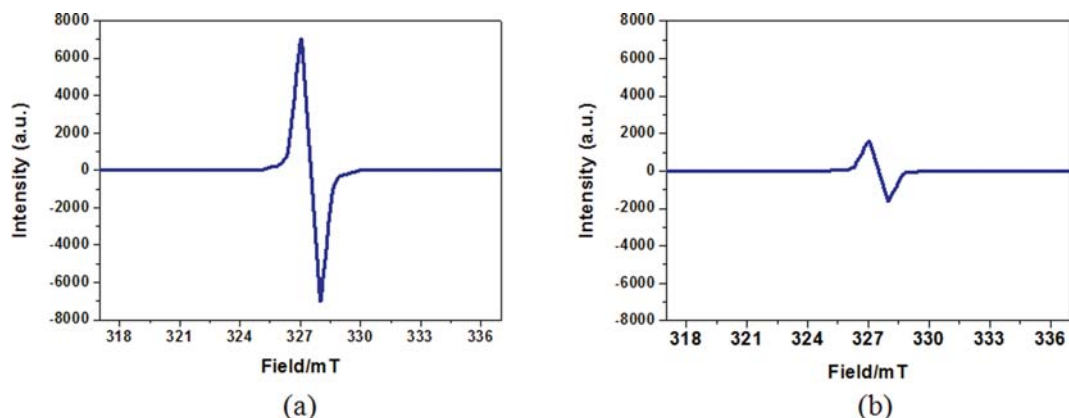


Fig. 7. Electron spin resonance spectra of carbons in electrode contacting membrane (a) anode side, (b) cathode side.

tween two side groups of hydrophilic clusters due to the hydrogen peroxide oxidation effect. The S-O-S crosslink was confirmed at the beginning of OCV holding degradation, and it is considered that S-O-S crosslinking is the cause of the decrease in hydrogen permeability due to membrane changes at the beginning of AST.

The degradation of the polymer membrane is caused mainly by oxygen radicals generated in the PEMFC driving condition [27,28]. Therefore, ESR analysis of the membrane after degradation was performed to determine if oxygen radicals occurred during AST. Oxygen radicals are difficult to analyze, and the amount of carbon radicals generated by oxygen radicals was measured [29]. Fig. 7 presents the results of ESR analysis of the anode and cathode electrodes. More radicals were generated at the anode side. The location of membrane degradation differed according to the various studies, which showed that considerable membrane degradation occurred at the anode side [30,31] and cathode side [32,33]. The results of this study are consistent with studies of more degradation at the anode side in the membrane [30,31].

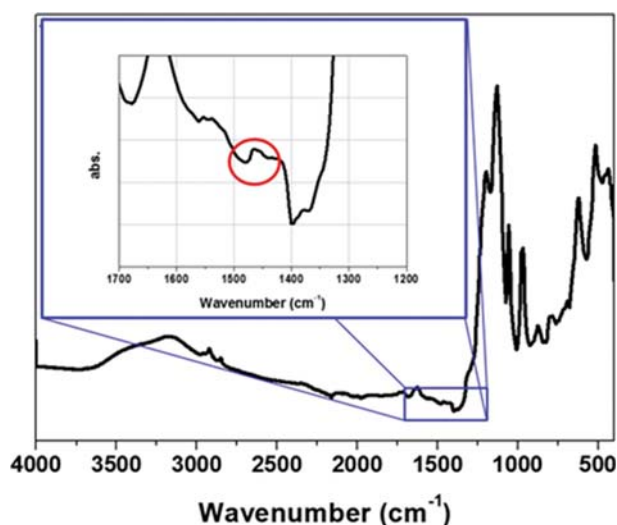
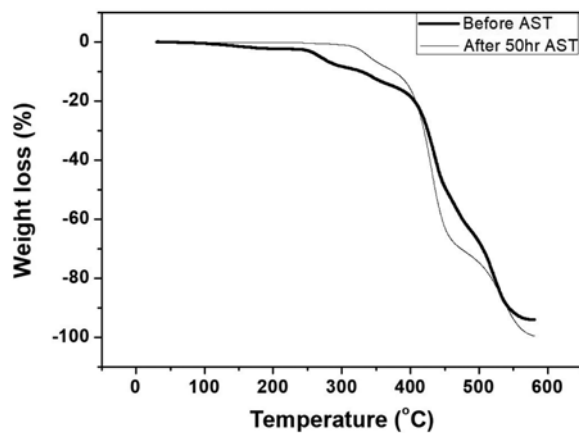
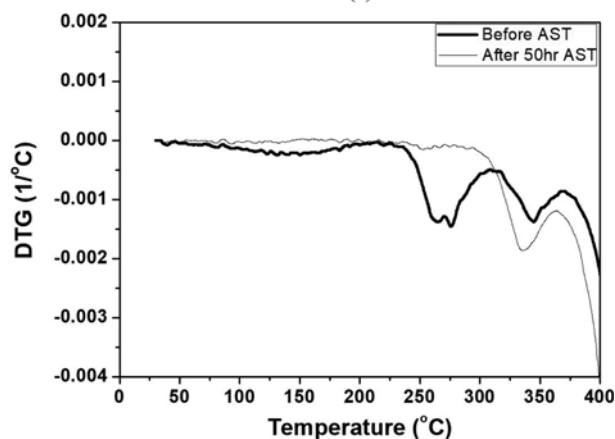


Fig. 8. Extended IR spectra of PFSA membrane between 1,700 and 1,200 cm^{-1} after Fenton reaction in hydrogen peroxide 20% and 10 ppm Fe^{2+} ion solution at 80 $^{\circ}\text{C}$ for 24 hours.

To confirm the occurrence of S-O-S crosslinking by radicals, the Nafion membrane was deteriorated by the Fenton reaction as a radical generation out of the PEMFC cell. Fig. 8 presents the FT-IR spectra of the Nafion membrane after 1 day of the Fenton reaction. S-O-S peaks weakly appeared at $1,460\text{ cm}^{-1}$, as in the cell



(a)



(b)

Fig. 9. Thermogravimetry analysis profile of membrane before and after AST (a), Differential thermogravimetry profile of membrane before and after AST (b).

experiments. The S-O-S crosslink occurred after 22 days of a reaction with hydrogen peroxide [22], but it occurred only in one day with the Fenton reaction. Because hydrogen peroxide is also present in the Fenton solution, the S-O-S peak can be seen by hydrogen peroxide during the Fenton reaction, but the peak occurred by radicals in such a short time. In addition, the S-O-S peak that occurred after AST in the cell within two days was also due to oxygen radicals, not hydrogen peroxide.

4. TG Analysis Before and After AST

Fig. 9 shows the TG/DTA results of the membranes before and after the AST. As in other studies, water is removed first, followed by degradation of the sulfonic acid group, and then by breaking of the PTFE main chain [22,34-37]. From 75 °C to 250 °C, the weight loss was attributed to water loss. The temperature at which the sulfonic acid group is pyrolyzed in the PFSA membrane is at least 275 °C [36,37], and the degraded membrane is decomposed at a lower temperature of 258 °C. This is because the S-O-S crosslink begins to decompose at lower temperatures than that needed for C-S and C-O-C bonds [36]. The non-degraded membranes decreased in weight by SO₂ decomposition at 330 °C, but the S-O-S cross-linked membranes lost weight due to S-O-S decomposition at approximately 75 °C below this temperature. As shown in the DTG graph, the part remaining in the degraded membrane without crosslinking decomposed to show a weight reduction at 341 °C.

CONCLUSION

The decrease in hydrogen crossover in the early stages of an electrochemical accelerated degradation test was studied. After 50 hours of the AST, the particle size of the platinum particles of the electrode increased and the active area of the electrode decreased. As a result, the hydrogen crossover current density measured by LSV decreased. GC also showed a decrease in hydrogen crossover, which was not influenced by the electrode. That is, the hydrogen permeability was decreased due to the problems of the measurement method, but the hydrogen permeability was decreased by the change in polymer membrane. The chemical change in the polymer membrane after 50 hours of AST was -S-O-S- crosslink formation, which was not observed before degradation. The generation of -S-O-S- by contact with hydrogen peroxide took a long time, but this could be shortened by radicals in the Fenton reaction.

TGA confirmed that the temperature at which SO₃⁻ was decomposed to SO₂ was lowered due to -S-O-S- crosslinking. The reduction of the hydrogen crossover current density measured by LSV at the beginning of AST of PEMFC MEA was confirmed by the reduction of the active of the electrode catalyst and the generation of -S-O-S- crosslinking in this work.

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REFERENCES

1. M. L. Perry and T. F. Fuller, *J. Electrochem. Soc.*, **149**(7), S59 (2002).

2. J. Kurtz, H. Dinh, G. Saur and C. Ainscough, DOE 2017 Annual Merit Review, Washington, DC, June 8 (2017).
3. M. P. Rodgers, L. J. Bonville, H. R. Kunz, D. K. Slattery and J. M. Fenton, *Chem. Rev.*, **112**, 6075 (2012).
4. D. P. Wilkinson and J. St-Pierre, *Handbook of Fuel Cell: Fundamentals Technology and Applications*, Vol. 3, Wiley, Chichester, England, 611 (2003).
5. S. D. Knights, K. M. Colbow, J. St-Pierre and D. P. Wilkinson, *J. Power Sources*, **127**, 127 (2004).
6. Z. Luo, D. Li, H. Tang, M. Pan and R. Ruan, *Int. J. Hydrogen Energy*, **31**, 1838 (2006).
7. A. Pozio, R. F. Silva, M. D. Francesco and L. Giorgi, *Electrochim. Acta*, **48**, 1543 (2003).
8. S. Chen, H. A. Gasteiger, K. Hayakawa, T. Tada and Y. Shao-Horn, *J. Electrochem. Soc.*, **157**, A82 (2010).
9. D. E. Curtin, R. D. Lousenberg, T. J. Henry, P. C. Tangeman and M. E. Tisack, *J. Power Sources*, **131**, 41 (2004).
10. A. Collier, H. Wang, X. Yaun, J. Zhang and D. P. Wilson, *Int. J. Hydrogen Energy*, **31**, 1838 (2006).
11. DOE Fuel Cell Technologies Office, 2016 Multi-Year Research, Development and Demonstration Plan, Protocols for Testing PEM Fuel Cells and Fuel Cell Components, Page 3.4-46 (2016).
12. H. Wang, M. Tang and D. Pan, *Int. J. Hydrogen Energy*, **33**(9), 2283 (2008).
13. T. Kinumoto, M. Inaba, Y. Nakayama, K. Ogata, R. Umebayashi and A. Takaka, *J. Power Sources*, **158**(2), 1222 (2006).
14. J. Healy, C. Hayden, T. Xie, K. Olson, R. Waldo and M. Brundage, *Fuel Cells*, **5**(2), 302 (2005).
15. B. P. Pearman, N. Mohajeri, D. K. Slattery, M. D. Hampton, S. Seal and D. A. Cullen, *Polym. Degrad. Stab.*, **98**(9), 1766 (2013).
16. J. Hao, Y. Jiang, X. Gao, F. Xie, Z. Shao and B. Yi, *J. Membr. Sci.*, **522**(15), 23 (2017).
17. H. Zhu, S. Pei, J. Tang, H. Li, L. Wang, W. Yuan and Y. Zhang, *J. Membr. Sci.*, **432**, 66 (2013).
18. Z. Chang, H. Yan, J. Tian, H. Pan and H. Pu, *Polym. Degrad. Stab.*, **138**, 98 (2017).
19. W. Liu, K. Ruth and G. Rusch, *J. New Mater. Mater. Electrochem. Syst.*, **4**, 227 (2001).
20. B. Kieitz, J. Kolde, S. Priester, C. Baczkowski and M. Crum, *ECS Trans.*, **41**(1), 1521 (2011).
21. J. J. Jeong, J. H. Jeong, S. H. Kim, B. K. Ahn, J. J. Ko and K. P. Park, *Korean Chem. Eng. Res.*, **52**(4), 425 (2014).
22. J. Qiao, M. Saito, K. Hayamizu and T. Okada, *J. Electrochem. Soc.*, **153**(6), A967 (2006).
23. E. Endoh, S. Terazono, H. Widjaja and Y. Takimoto, *Electrochem., Solid-State Lett.*, **7**(7), A209 (2004).
24. J. H. Song, S. H. Kim, B. K. Ahn, J. J. Ko and K. P. Park, *Korean Chem. Eng. Res.*, **51**(1), 68 (2013).
25. Z. Liang, W. Chen, J. Liu, S. Wang, Z. Zhou, W. Li, G. Sun and Q. Xin, *J. Membr. Sci.*, **233**, 39 (2004).
26. M. Ludvigsson, J. Lindgren and J. Tegenfeldt, *Electrochim. Acta*, **45**(14), 2267 (2000).
27. F. D. Cons, *ECS Trans.*, **16**(2), 235 (2008).
28. M. Danilczuk, F. D. Cons and S. Schlick, *J. Phys. Chem., B*, **113**, 8031 (2009).
29. E. Endoh, S. Terazono, H. Widjaja and Y. Takimoto, *Electrochem.*

- Solid-State Lett.*, **7**, 145 (2004).
30. N. Ohguri, A. Y. Nosaka and Y. Nosaka, *J. Power Sources*, **195**, 4647 (2010).
31. W. Liu and D. Zuckerbrod, *J. Electrochem. Soc.*, **152**, A1165 (2005).
32. S. Kundu, M. W. Fowler, L. C. Simon, R. Abouatallah and N. Beydokhti, *J. Power Sources*, **183**, 619 (2008).
33. L. Zhang and S. Mukerjee, *J. Electrochem. Soc.*, **153**, A1062 (2006).
34. S. R. Samms, S. Wasmus and R. F. Savinell, *J. Electrochem. Soc.*, **143**(5), 1498 (1996).
35. S. H. Almeida and Y. Kawano, *J. Therm. Anal. Calorim.*, **58**, 569 (1999).
36. H. J. Lee, M. K. Cho and Y. Y. Jo, *Polym. Degrad. Stab.*, **97**, 1010 (2012).
37. Q. Deng, C. A. Wilkie, R. B. Moore and K. A. Mauritz, *J. Appl. Polym. Sci.*, **68**, 747 (1998).