J Mater Sci (2009) 44:3674–3681
DOI 10.1007/s10853-009-3490-z

Long-term performance of polyetheretherketone-based polymer electrolyte membrane in fuel cells at 95 °C

**Jinhua Chen · Maolin Zhai · Masaharu Asano ·
Ling Huang · Yasunari Maekawa**

Received: 28 January 2009 / Accepted: 11 April 2009 / Published online: 25 April 2009

Abstract A poly(styrenesulfonic acid)-grafted polyetheretherketone (ssPEEK) polymer electrolyte membrane was developed by radiation grafting of ethyl styrenesulfonate (ETSS) onto PEEK film and subsequent hydrolysis. The long-term durability of the ssPEEK electrolyte membrane was tested in a fuel cell at 95 °C, during which it exhibited a lifetime of more than 1000 h and a slow voltage degradation of 18 μV h^{-1} at a current density of 0.3 A cm^{-2}. After durability test, the catalyst layers were analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM); the polymer electrolyte membrane was investigated by determining the change in thickness, proton conductivity, and amounts of sulfonic acid groups. It was concluded that the degradation of performance in fuel cell was due to the thermal aging of the hydrocarbon polymer electrolyte membrane being exposed to the electrochemical environment with the pure oxygen acting as the oxidant gas, as well as the Nafion-based catalyst layer being subjected to high temperature for a long time, where the Pt catalyst was aggregated and sintered.

Introduction

Operation of automotive polymer electrolyte membrane fuel cells (PEMFCs) at high temperature is highly desired since the electrochemical reaction efficiency and CO tolerance will be enhanced, and the water and heat management of the fuel cell system will be simplified [1–3]. The Nafion membranes now being used have demonstrated stable performance for more than 60,000 h in a cell at temperatures below 80 °C, but above this temperature their lifetime drastically decreased, and is rarely longer than 1,000 h [3–5]. Therefore, new polymer electrolyte membranes have to be developed for the high temperature PEMFCs. At present, a modified perfluorosulfonic acid composite membrane developed by Asahi Glass Co., Ltd., Japan has been confirmed to be durable for more than 6,000 h in a cell at 120 °C [6]. On the other hand, the phosphoric acid-doped poly(benzimidazole) membranes were reported to be durable for more than 6,000 h in a cell at temperatures above 160 °C [7]. However, problems such as high cost and low temperature performance need to be solved before these materials can be used in commercial products.

Attachment of sulfonic acid groups to thermally stable aromatic polymers is an attractive method to develop an inexpensive polymer electrolyte membrane for PEMFCs which enables operation in a wide temperature window [8]. These aromatic polymers can be given high proton conductivity either by introducing sulfonic acid groups onto aromatic rings through sulfonation or by direct polymerization of the sulfonated monomers. Among membranes prepared in these ways, sulfonated polyimide, sulfonated polyarylenethersulfone (sPES), and sulfonated polyetheretherketone (sPEEK) have received particular attention over the last few years [8–16]. For example, one sPES, namely

---

J. Chen (✉) · M. Zhai · M. Asano · Y. Maekawa
Environment and Industrial Materials Research Division, Japan Atomic Energy Agency (JAEA), 1233 Watanuki-machi, Takasaki, Gunma 370-1292, Japan
e-mail: chen.jinhua@jaea.go.jp

M. Zhai · L. Huang
College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

BPSH-35, was reported to be durable in a cell at 100 °C for more than 500 h [11–13]. It was also confirmed that blend and hybrid membranes containing sPEEK have a long lifetime of more than 300 h in a cell at temperatures above 90 °C [4, 12].

We are developing polymer electrolyte membranes by modifying existent commercial polymer films [15–18]. In our previous study, we developed a doubly crosslinked sPEEK membrane by radiation crosslinking and subsequent sulfonation of the PEEK films [15]. These crosslinked sPEEK membranes exhibited good properties comparable to Nafion membrane. More recently, to avoid the damage induced by the sulfonation, we made a PEEK-*g*-poly(styrenesulfonic acid) (ssPEEK) electrolyte membrane by ethyl styrenesulfonate (ETSS) grafting and subsequent hydrolysis [14]. Although the poly(styrenesulfonic acid) (PSSA) homopolymer membranes are not electrochemically stable and the fuel cell using the PSSA membranes exhibits poor performance [19, 20], the PSSA-grafted electrolyte membranes were reported to be quite stable and to be promising candidates for application in fuel cells [21–24]. For example, a long lifetime of about 4,000 h has been confirmed for the PSSA-grafted poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) electrolyte membrane-based fuel cell at the operating temperature of 80 °C [23]. On the other hand, we also found that the PSSA-grafted electrolyte membrane, ssPEEK membrane (43 μm in thickness), was durable in a fuel cell at 95 °C and 40 RH% for more than 250 h, the conditions under which the Nafion membrane drastically deteriorated [16].

In order to further enhance the lifetime, a thick ssPEEK membrane with a relatively low degree of grafting was prepared. The performance of a cell with this membrane, including the durability of the membrane, was tested at 95 °C. After the cell test, the used membrane as well as the cathode and anode were investigated to determine their degradation during fuel cells operation. Thus, the useful feedback was obtained for latter membrane development and fuel cell design.

Experimental part

Preparation of the polymer electrolyte membranes

Figure 1 shows the process for the ssPEEK polymer electrolyte membrane preparation and the chemical structures of polyetheretherketone (Vitrex PEEK, amorphous type), ethyl styrenesulfonate (ETSS, Tosoh, Japan), and divinylbenzene (DVB, Aldrich). The PEEK film was first immersed in a 20 wt% solution of DVB in dioxane at 50 °C for 24 h. After the DVB-treatment, it was confirmed that DVB was attached to the PEEK film at a ratio of about 8%. Subsequently, the DVB-treated PEEK film was γ-ray irradiated, and then immersed in a solution of ETSS in dioxane under argon at 80 °C for 24 h for grafting. Finally, the ETSS-grafted film was hydrolyzed in 95 °C water for 24 h to remove the ethyl groups. Thus, a PEEK-*g*-poly(styrenesulfonic acid) (ssPEEK) electrolyte membrane was obtained. The degree of grafting was defined as $(W_g - W_D)/W_D \times 100$, where W_D is the weight of the DVB-treated PEEK film, and W_g is the weight of the dry ssPEEK membrane.

Characterization of the polymer electrolyte membrane

Ion exchange capacity was determined by acid–base titration. The dried membrane in the protonic form (about 80 mg) was immersed in 20 ml of NaCl-saturated aqueous solution and equilibrated for 24 h. The solution was then titrated with 0.02 M NaOH solution. Based on the titration results, the ion exchange capacity was calculated. Water uptake was determined as follows. First, the membrane was immersed in distilled water for 24 h; then, the membrane

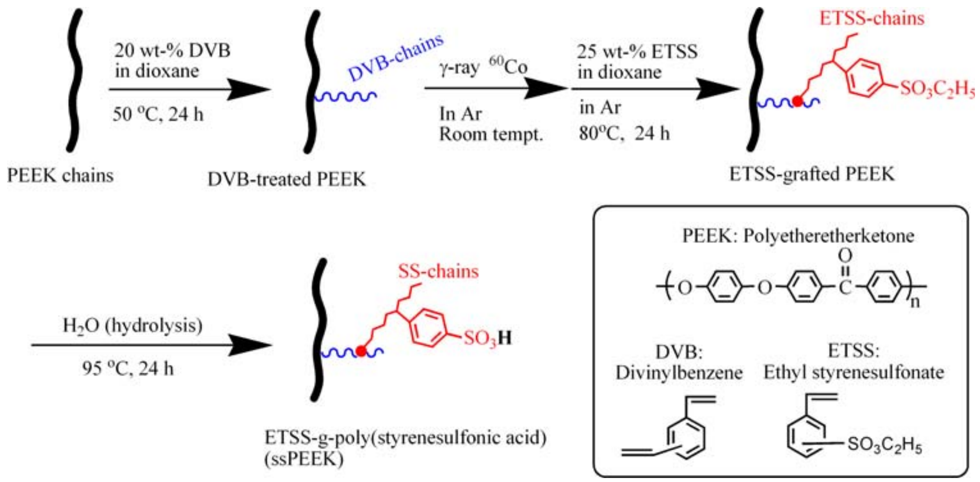


Fig. 1 Process for polymer electrolyte membrane preparation and the chemical structures of the PEEK base film and the DVB and ETSS monomers

was taken out and weighed after wiping off the excess surface water. The water uptake was calculated as $(W_{\mathrm{wet}} - W_{\mathrm{dry}})/W_{\mathrm{dry}} \times 100$, where W_{wet} and W_{dry} are the membrane weights in the wet and dry states, respectively. Proton conductivity was determined by impedance spectroscopy measurement using a Solartron 1269 analyzer with an AC perturbation of 10 mV. The samples were hydrated in water at 25 °C overnight before the measurement. The high frequency intercept on the real axis of the Nyquist plot was used to calculate the proton conductivity of the membrane [25, 26].

The mechanical property was determined according to ASTM D 882. Dumb-bell specimens were prepared and stored in temperature/humidity-controlled chamber at 23 °C and 70% relative humidity for 24 h prior to the test. The tensile tests were carried out using an STA-1150 universal testing instrument (A&D Co., Ltd., Japan) at a constant crosshead speed of 20 mm min^{-1}. For each sample, five or more specimens were used for the measurement.

MEA preparation and fuel cell test

A membrane/electrodes assembly (MEA) was prepared by hot-pressing the anode, membrane, and cathode (Pt loading 0.6 mg cm^{-2}) at 170 °C under 5 MPa for 1 min, and then under 10 MPa for 1 min. In our preliminary experiment, both Nafion and sulfonated PEEK (sPEEK) materials were used as binder in the catalyst layers. However, it was found that the performance of fuel cell using the sPEEK-based catalyst was quite lower than that of the Nafion-based catalyst [27]. Therefore, the Nafion solution was used as the binder for the preparation of catalyst layers. The MEA together with two PTFE gaskets were sandwiched in a 5 cm^2 fuel cell (Electrochem Inc.) for testing. During the cell test, pure hydrogen and oxygen gases were fed at a flow rate of 0.05 L min^{-1} each to the anode and cathode, respectively, under atmospheric pressure. The cell temperature was fixed at 95 °C, and the relative humidity of the fed gas was controlled by the humidifiers. For the durability test, the fuel cell was run by a computer program in a cycle of running for 0.6 h in the current density range of 0–0.6 A cm^{-2}, and then for 10 h fixed at 0.3 A cm^{-2}.

Analysis of fuel cell degradation

The membrane and the catalyst layers after the fuel cell test were investigated to determine the cell degradation. The residue sulfonic acid groups of the membrane on anode and cathode sides were analyzed by Fourier transform infrared (FT-IR) spectroscopy in the attenuated total reflection (ATR) mode. The catalyst layers were analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements.

Results and discussion

Preparation of the ssPEEK membranes

The ssPEEK membrane is a highly branched material, containing poly(styrenesulfonic acid) (SS) side chains, the PEEK backbones, and a small amount of DVB that provides strong interlinking between the SS and PEEK chains. The PEEK backbones maintain excellent properties in the ssPEEK membranes owing to there being no direct connection between the PEEK chains and the highly hydrophilic sulfonic acid groups [12]. On the other hand, the grafted SS side chains have a high density of sulfonic acid groups, which is favorable for forming ionic clusters for proton transport.

Ex situ properties of the ssPEEK membranes

Table 1 shows the ex situ properties of the ssPEEK membranes and the Nafion 212 membrane. As seen in Table 1, in spite of the high IEC, the ssPEEK membranes exhibit better mechanical strength than Nafion. The traditional sPEEK membranes with high IEC become highly swollen and even dissolve in water at high temperatures [8]. On the contrary, in our graft ssPEEK membranes, the water uptake is quite low, and changes slightly with

Table 1 Properties of the ssPEEK polymer electrolyte membranes

Membranes	Grafting (%)	IEC (mmol g^{-1})	Thickness (μm)	Water uptake (%)	Proton conductivity (mS cm^{-1})	Tensile properties at break	
						Strength (MPa)	Elongation (%)
F10[a]	66	2.16	96	43	59	87	179
D62[b]	87	2.53	43	61	62	81	167
Nafion 212	–	0.91	52	30	63	35	295

[a] F10 membrane prepared by grafting of 15 kGy-preirradiated 50-μm thick PEEK/DVB film in 15% ETSS solution at 80 °C for 73 h

[b] D62 membrane prepared by grafting of 30 kGy-preirradiated 25-μm thick PEEK/DVB film in 25% ETSS solution at 80 °C for 24 h

increase in temperature, thus exhibiting excellent dimensional stability. For instance, when the temperature was changed from 25 to 60 °C, the water uptake of the traditional sPEEK membrane (IEC, 1.65 mmol g^{-1}) increased from 38% to 96% [15], while the water uptake of the F10 ssPEEK membrane (2.16 mmol g^{-1}) increased only from 43% to 51%.

Current–voltage (*I–V*) performance of the ssPEEK membrane-based fuel cell

In our previous study [16], thin D62 ssPEEK electrolyte membranes with 87% degree of grafting were confirmed to be durable in a cell for more than 250 h at 95 °C and 40 RH%. However, the cell ultimately broke down due to crack damage of the membrane along the catalyst layer. In this study, a thick F10 ssPEEK membrane with a relatively low degree of grafting of 66% was used for the cell test.

The current–voltage (*I–V*) performance of the fuel cell using the thick F10 ssPEEK membrane at 95 °C and at different relative humidities ranging from 40 to 100 RH% is shown in Fig. 2. For comparison, the *I–V* performance of the thin D62 membrane-based fuel cell at 95 °C and 40 RH% is also presented. As expected, the *I–V* performance improves with increase in the relative humidity of the fed hydrogen/oxygen gases. This can be ascribed to the decrease in cell resistance with the increase in humidity. For instance, the resistance of the F10 membrane-based fuel cell decreased from 0.78 to 0.17 Ω cm^{-2} when the relative humidity increased from 40 to 100 RH%. On the other hand, the resistance of the fuel cell using the thin D62 membrane was 0.14 Ω cm^{-2} even at the low relative humidity of 40 RH%. Therefore, the thin D62 membrane-based fuel cell shows the best performance at the low humidity of 40 RH%.

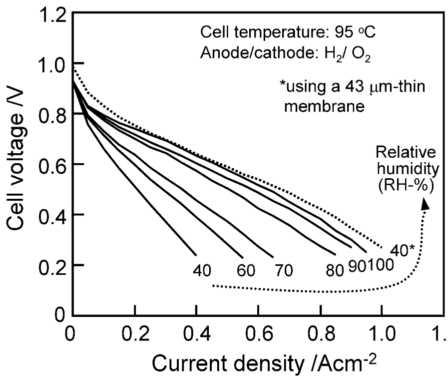


Fig. 2 *I–V* performances of the ssPEEK-based fuel cells at 95 °C and different relative humidity of the fed gases. *For comparison, the thin ssPEEK membrane-based fuel cell reported in our previous study is presented [16]

Long-term test of the ssPEEK membrane-based fuel cell

As seen in Fig. 2, the F10 membrane-based cell performance was little influenced by increase in the relative humidity above 80 RH%, but below this the cell performance decreased drastically. Therefore, the F10 membrane-based cell was operated at 95 °C and 80 RH% to test its long-term membrane durability, as shown in Fig. 3.

It is generally believed that the membrane degradation in fuel cells is due to the H_2O_2 generated by the oxygen crossover though the membrane [28]. In this study, the ex situ membrane durability was tested in a 3% H_2O_2 solution at 60 °C. Nafion was almost unchanged in the 3% H_2O_2 solution for more than 100 h, but the F10 ssPEEK membrane became brittle after 8 h and then cracked into powder-like pieces after 24 h. Even then, it was interesting to see that the F10 membrane-based cell could be stably run for more than 1025 h at the high temperature of 95 °C while the Nafion-based fuel cell fast deteriorated under such a condition [16]. The high durability of the ssPEEK membranes was attributed to its high thermal and mechanical stability as well as its low permeability of hydrogen and oxygen at high temperature [27].

As seen in Fig. 3, the degradation rate of open circuit voltage (OCV) was about 29 µV h^{-1}, and the voltage degradation with current density at 0.3 A cm^{-2} was about 18 µV h^{-1}. Such a slow degradation rate is believed to satisfy the requirement of automotive fuel cells [3]. Drastic degradation of the OCV and the cell voltage at 0.3 A cm^{-2} was observed after 980 and 1025 h, respectively.

However, with a re-start of the fuel cell after a 5-min drying treatment, the OCV almost returned to its the initial value, indicating that the gas crossover through the membrane had not yet significantly increased; the drastic decrease in OCV as well as in the cell voltage at 0.3 A cm^{-2} was mainly due to the degradation which occurred in the Nafion-based catalyst layer.

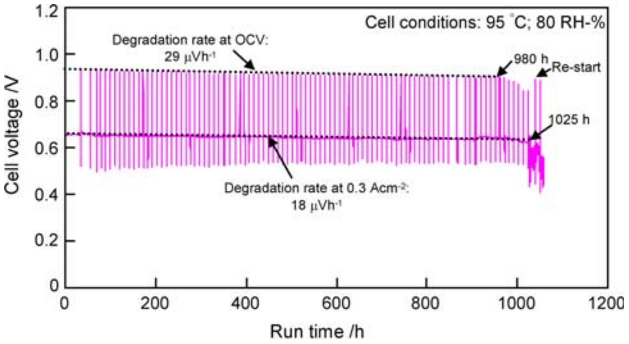
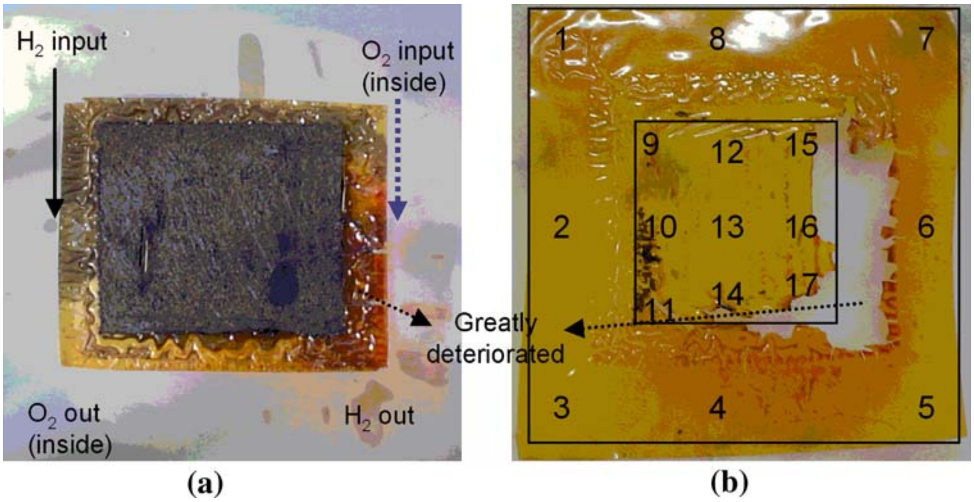


Fig. 3 Durability testing of the ssPEEK fuel cells at the conditions of 95 °C and 80 RH%. The cell was periodically run mainly with the program: at 0–0.6 A cm^{-2} for 0.6 h and then at 0.3 A cm^{-2} for 10 h

Fig. 4 The pictures of **a** MEA together with PTFE gasket and **b** the membrane after the durability test



After the durability test, the fuel cell was carefully taken apart. Figure 4a shows the photograph of the MEA with the white PTFE gasket covering it. The MEA was still intact, but the membrane around the active layers, especially near the cathode inlet was significantly aged, and was deeply yellowed. It is likely that this localized aging was due to the high oxygen concentration near the cathode inlet, indicating the lack of oxygen concentration uniformity in the cell and flow path configuration. In addition, the membrane between the active layer and PTFE gasket was directly exposed to the oxygen and hydrogen without any solid support. The cycling of swelling–shrinking of the membrane due to the poor water management in fuel cells will accelerate the membrane deterioration. The deteriorated part of the membrane near the cathode inlet was so brittle that it fell from the membrane when the MEA was being taken apart, as shown in Fig. 4b.

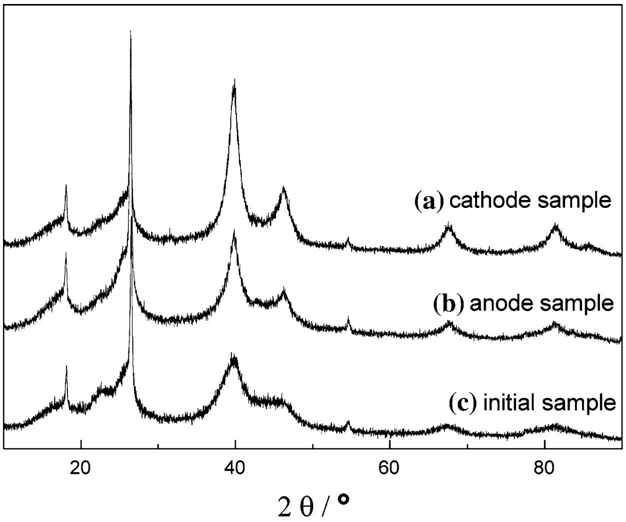


Fig. 5 XRD of the cathode (a) and anode (b) catalyst layer after long-term fuel cell test and the initial catalyst layer (c) before test

Analysis of the catalyst layer after durability test

The catalysts before and after use were investigated by XRD and TEM, as shown in Figs. 5 and 6, respectively. The size of the Pt particles was measured from the TEM imagines. The size distribution together with the average size of the Pt particles is also given in Fig. 6. In this study, although the ssPEEK was used as the new polymer electrolyte membrane, the binder in catalyst layer was the Nafion solution. The state of a Nafion-based catalyst layer after such a long and severe durability test (95 °C, 80 RH% for more than 1,000 h) has rarely been reported.

Through the XRD measurement and calculation by the Scherrer equation, as shown in Table 2, we found that the size of the Pt particles in the anode and cathode was 4.9 and 6.5 nm, respectively, while in a new MEA before any test, it was 2.6 nm. Therefore, the Pt particles aggregated significantly and were sintered during the cell durability test; this degradation was more severe on the cathode side. This Pt aggregation may be due to the corrosion of the carbon and the degradation of the Nafion binder [29, 30].

Similar Pt aggregation and sintering were also observed in the TEM images. In them, it is seen that some Pt particles on the cathode catalyst layer were dissociated from the carbon carrier. The average size calculated from TEM imaging was 3.1 nm for the catalyst before test, and were 3.9 and 5.4 nm for the anode and cathode after test, respectively.

Analysis of the ssPEEK membrane after durability test

The membrane was divided into 17 pieces, marked with numbers as shown in Fig. 4b, for thickness, proton conductivity, and FT-IR/ATR analyses. The results are shown in Fig. 7. The big square represents the whole membrane, and the small square at the center represents the active area

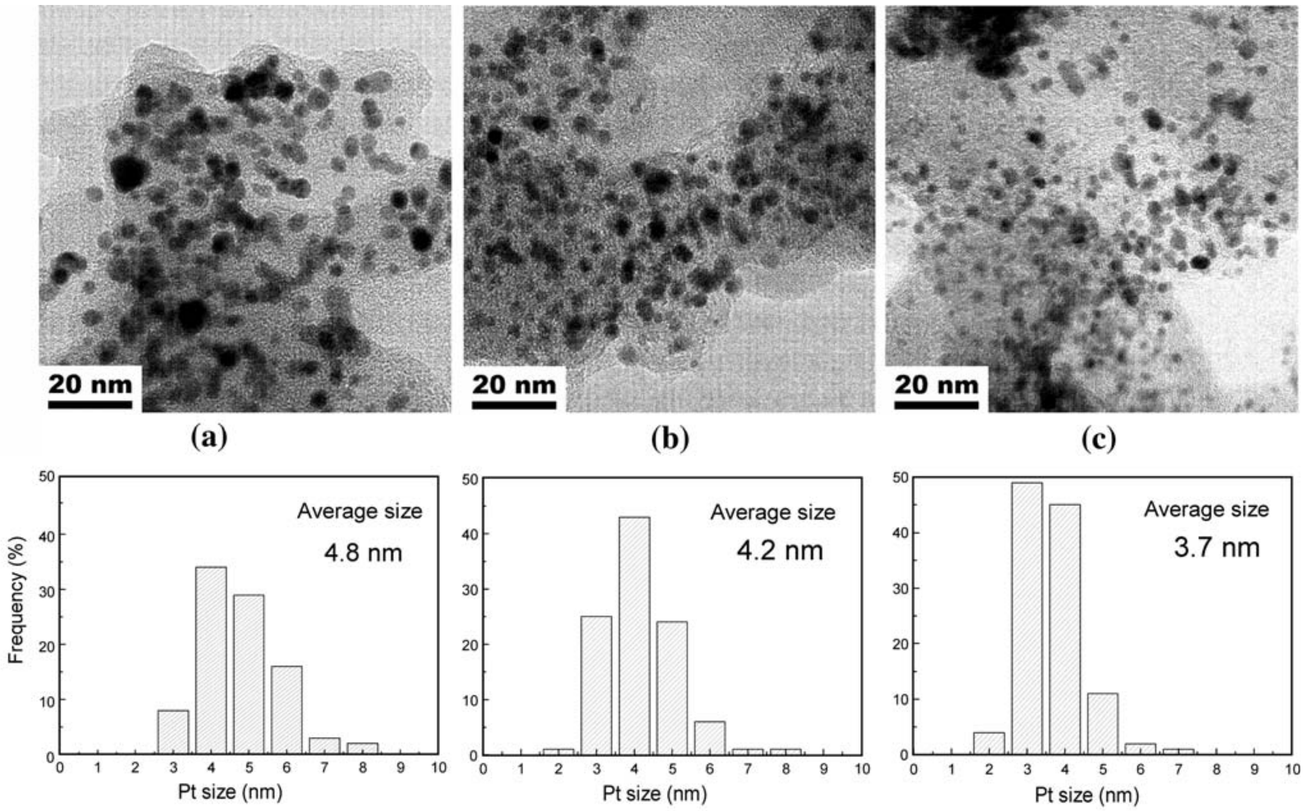


Fig. 6 TEM imagines and the corresponding Pt particle distribution diagrams of the cathode (**a**) and anode (**b**) catalyst layer after long-term fuel cell test and the initial catalyst layer (**c**) before test

Table 2 Average sizes (nm) of the Pt particles before and after durability test measured by XRD and TEM methods

Methods	Before test	After test	
		Anode	Cathode
XRD	2.6	4.9	6.5
TEM	3.1	3.9	5.4

that is covered by the catalyst layers. The dotted line indicates the destroyed part of the membrane. The initial thickness and proton conductivity were 96 μm and 59 mS cm^{-1}, respectively.

After the durability test, the thickness of the active area, especially near the cathode inlet, was somewhat decreased (Fig. 7a). On the other hand, as seen in Fig. 7b, the proton conductivity at the active area decreased to about one-third of the initial value. Even at the non-active area, the proton conductivity slightly decreased due to aging at a high temperature for a long time. During the test, the fuel cell stood on the platform. Obviously, the downside areas showed more serious degradation than the upside areas of the tested membrane. It was thought that the flooding of water occurring at the downside had accelerated the degradation of membrane.

The sulfonic acid groups of the membrane remaining after the durability test were investigated by FT-IR in the ATR mode. The ATR mode is a useful tool for the membrane analysis because only the membrane region within several micrometers of the surface is detected. The strength ratios of the characteristic absorptions of the sulfonic acid groups and PEEK chains at 1031 and 927 cm^{-1}, respectively, were used for analysis. From the FT-IR/ATR results, it can be found that both the active surface of the anode and the cathode lost about 20% of their sulfonic acid groups. The deterioration on the cathode side of the membrane was more severe than that on the anode side. However, although the membrane near the cathode inlet was very brittle, the number of sulfonic acid groups was not distinctly lower than that near the anode inlet. It was reflected that the membrane deterioration in the high temperature fuel cell was mainly due to the thermal oxidation aging of the PEEK substrate materials, resulting in the deeply colored and brittle region near the cathode inlet. In the future studies, more thermally stable materials, such as PBI and PI, should be considered as the base film materials for the development of long-term hydrocarbon durable polymer electrolyte membranes for high temperature PEMFCs.

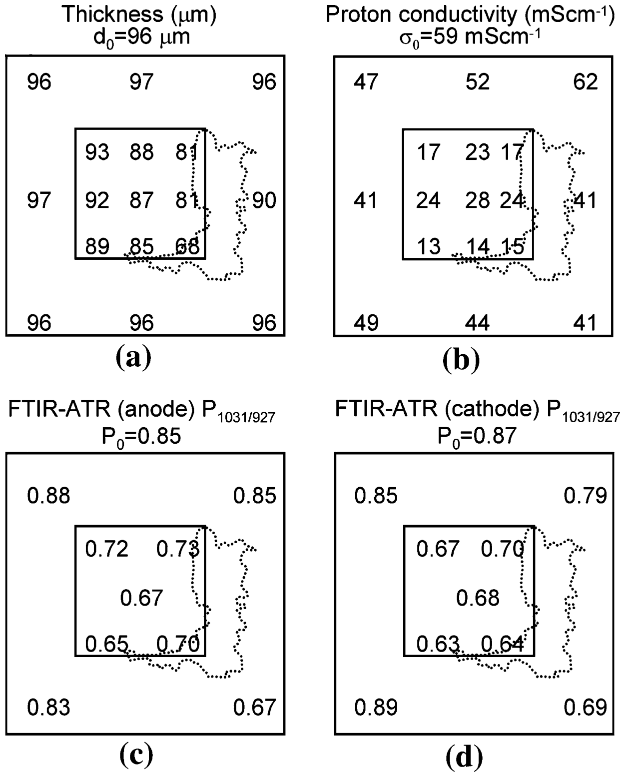


Fig. 7 The distribution of the thickness, proton conductivity, and relative values of sulfonic acid groups on anode and cathode sides (measured by FT-IR/ATR) of the ssPEEK membranes after cell durability test

Conclusions

A PEEK-based polymer electrolyte membrane was successfully prepared by grafting of ethyl styrenesulfonate (ETSS) onto DVB-treated PEEK films and subsequent hydrolysis of the ETSS graft chains to form SS chains. The ssPEEK membrane exhibited good proton conductivity similar to Nafion while its mechanical strength was quite better than Nafion.

The performance of the ssPEEK polymer electrolyte membrane-based fuel cell at a high temperature of 95 °C was little influenced by rises in the relative humidity above 80 RH%, but below this it decreased drastically. In addition, the ssPEEK polymer electrolyte membrane-based fuel cell can be stably run at 95 °C and 80 RH% for more than 1,000 h, exhibiting a very low voltage degradation of 18 $\mu V h^{-1}$ at a current density of 0.3 A cm^{-2}. This high membrane durability is ascribed to the excellent properties of the PEEK backbone, which maintain the high chemical and mechanical stability of the membrane, and to the well-constructed, ion-conductive, grafted side chains, which give the membrane high proton conductivity.

The polymer electrolyte membrane after the durability test near the cathode inlet was very brittle, and was deeply yellowed. In addition, the proton conductivity and amounts of sulfonic acid groups at the active area were lower than those at the non-active area of the membrane. Furthermore, the Pt particles in the catalyst layer aggregated and sintered during the cell durability test; this phenomenon was more severe on the cathode side. Therefore, the degradation in cell performance was due to the ssPEEK membrane thermal aging and the Pt aggregation. This problem can be somewhat mitigated by optimizing the MEA and flow path designs in order to avoid the local aging of the membrane at the edge of active region and near the inlet of the cathode.

References

1. Savadogo O (2004) J Power Sources 127:135
2. Li Q, He R, Jensen JO, Bjerrum J (2003) Chem Mater 15:4896
3. Wu J, Yuan XZ, Martin JJ, Wang H, Zhang J, Shen J, Wu S, Merida WA (2008) J Power Sources 184:104
4. Bi W, Fuller TF (2008) J Electrochem Soc 155:B215
5. Lakshmanan B, Huang W, Olmeijer D, Weidner JW (2003) Electrochem Solid State Lett 6:A282
6. Endoh E (2008) ECS Trans 12:41
7. Schmidt T, Baurmeister J (2008) J Power Sources 176:428
8. Roziere J, Jones DJ (2003) Annu Rev Mater Res 33:503
9. Zhang L, Mukerjee S (2006) J Electrochem Soc 153:A1062
10. Asano N, Aoki M, Suzuki S, Miyatake K, Uchida H, Watanabe M (2006) J Am Chem Soc 128:1762
11. Sethuraman VA, Weidner JW, Haug AT, Protsailo LV (2008) J Electrochem Soc 155:B119
12. Bauer B, Jones DJ, Rozière J, Tchicaya L, Alberti G, Casciola M, Massinelli L, Peraio A, Besse S, Ramunni E (2000) J New Mater Electrochem Syst 3:93
13. Wang F, Hickner M, Kim Y, Zawodzinski TA, McGrath JE (2002) J Membr Sci 197:231
14. Li W, Fu Y, Manthiram A, Guiver MD (2009) J Electrochem Soc 156:B258
15. Chen J, Maekawa Y, Asano M, Yoshida M (2007) Polymer 48:6002
16. Chen J, Asano M, Maekawa Y, Yoshida M (2008) J Membr Sci 319:1
17. Chen J, Asano M, Yamaki T, Yoshida M (2006) J Mater Sci 41:1289. doi:10.1007/s10853-005-2573-8
18. Septiani U, Chen J, Asano M, Maekawa Y, Yoshida M, Kubota H (2007) J Mater Sci 42:1330. doi:10.1007/s10853-006-1196-z
19. Prater K (1990) J Power Source 29:239
20. Yu J, Yi B, Xing D, Liu F, Chao Z, Fu Y, Zhang H (2003) Phys Chem Chem Phys 5:611
21. Li J, Matsuura A, Kakigi T, Miura T, Oshima A, Washio M (2006) J Power Sources 161:99
22. Büchi FN, Gupta B, Haas O, Scherer GG (1995) Electrochim Acta 40:345
23. Gubler L, Kuhn H, Schmidt TJ, Scherer GG, Brack HP, Simbeck K (2004) Fuel Cells 4:196
24. Kim BN, Lee DH, Han DH (2008) J Electrochem Soc 155:B680
25. Chen J, Asano M, Yamaki T, Yoshida M (2006) J Membr Sci 269:194
26. Chen J, Asano M, Yamaki T, Yoshida M (2006) J Power Sources 158:69

27. Ramani V, Swier S, Shaw MT, Weiss RA, Kunz HR, Fenton JM (2008) J Electrochem Soc 155:B532
28. Shao Y, Yin G, Wang Z, Gao Y (2007) J Power Sources 167:235
29. Aricò S, Stassi A, Modica E, Ornelas R, Gatto I, Passalacqua E, Antonucci V (2008) J Power Sources 178:525
30. Franco A, Gerard M (2008) J Electrochem Soc 155:B367