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Durability of MEA Prepared with PFA-g-PSSA Membrane for Direct Methanol Fuel Cell

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1 Introduction

The direct methanol fuel cell (DMFC) is considered as a promising power source for portable multifunctional electronic devices and light-duty vehicles. The long-term stability of membrane materials for membrane electrode assemblies (MEAs) is of significant concern due to the degradation of cell components. The prepared sulfonic acid membranes with radiation-induced grafting method are potential substitutes for their corresponding commercial fuel cell membranes. The poly(tetrafluoroethylene-co-perfluorovinylether) (PFA) films as a polymer substrate with thermal, chemical and mechanical stabilities is used in this work. To evaluate long-term stability of the prepared MEA with radiation-grafted membrane (PFA-PSSA) for DMFC, the single cell is tested for 2000 h in a galvanostatic mode at a constant current density of 150 mA/cm^2 at 60 ^{o}C. During the long-term test, the changes in the cell performance are analyzed by the polarization curves, impedance spectra, the voltage and the output power of cell for roughly time intervals of 500 h.

2 Experimental

The polymer membrane was prepared by the simultaneous polymerization of styrene onto PFA films. Poly(tetrafluoroethylene-co-perfluorovinylether)-grafted-polystyrene sulfonic acid (PFA-g-PSSA) membranes were prepared by radiation-induced grafting method using a simultaneous irradiation technique of styrene onto PFA films with thickness of 50 μm and a subsequent sulfonation in a chlorosulfonic acid/dichloroethane mixture.

PtRu/C (HiSPEC 12100, Johnson Matthey) and Pt/C (HiSPEC 13100, Johnson Matthey) catalysts are used as the catalysts for anode and cathode, respectively. The Pt loading was 2 mg/cm^2 for the electrodes and the active area of the MEA was 9 cm^2. The MEA using PF50-SS50 membrane was fabricated by hot pressing method at 150 ^{o}C with a pressing pressure of 50 kg/cm^2 for 1 min (PFx-SSy: x = thickness of PFA film, y = DOG (degree of grafting) of polystyrene)

For long-term performance test of the MEA, a 1.0 M methanol solution (1.3 cc/min) and air (200 cc/min) were fed in the anode and cathode electrodes, respectively. The long-term performance test was carried out at a constant current density of 150 mA/cm^2 (1.35 A) for 2000 h at the temperature of 60 ^{o}C .

3 Results

SEM photographs of the cross-section of the PFA-g-PSSA films are shown in Figure 1. The thickness of PFA-g-PSSA films increased from 64 μm to 81 μm as increased the DOG of the membrane from 30 % to 80 % as shown in Fig 1. The enlarged images of Figure 1(a), 1(b)

and 1(c) are shown in Figure 1(d), 1(e) and 1(f). These SEM results confirm the incorporation of polystyrene in the pores of PFA films.

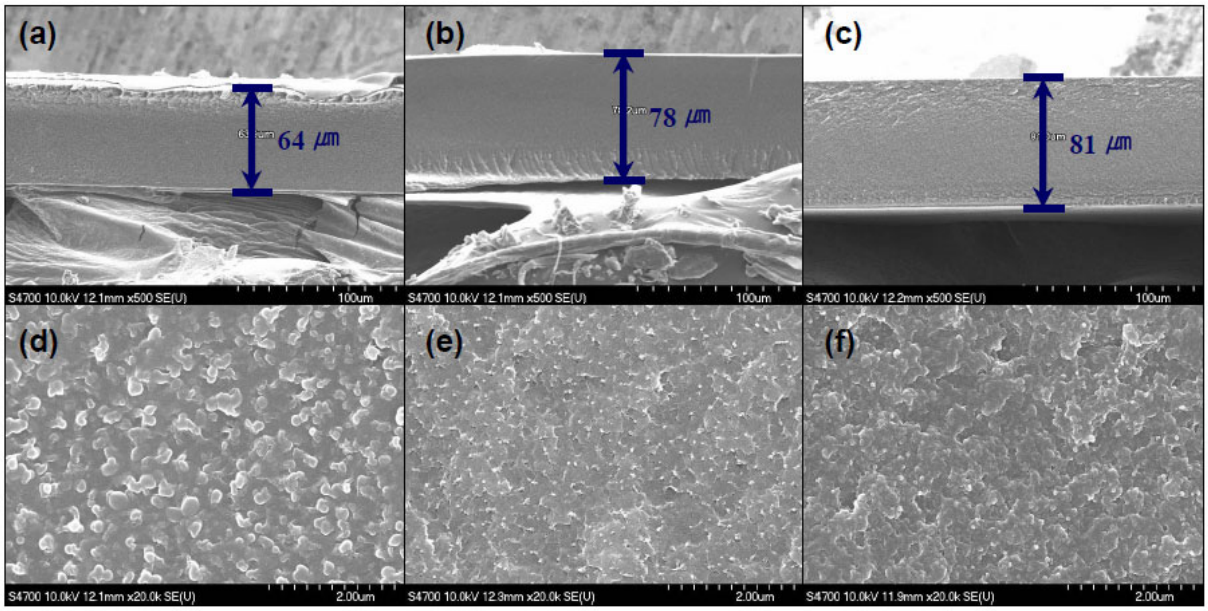

Figure 1: SEM images of the cross-section of the radiation-grafted membranes: (a, d) PF50-SS30, (b, e) PF50-SS50, (c, f) PF50-SS80.

Figure 2 shows the polarization curves of the single cells with the radiation-grafted membranes (PF50-SS30, PF50-SS50 and PF50-SS80). The power densities of the cells with the PF50-SS30, PF50-SS50 and PF50-SS80 membranes were 113, 123 and 118 mW/cm^2, respectively, at a constant cell voltage of 0.4 V. In addition, the ohmic resistance of single cell were 0.109, 0.104, and 0.105 Ωcm^2, respectively. The cell with PF50-SS50 membrane shows the highest cell performance than the other cells.

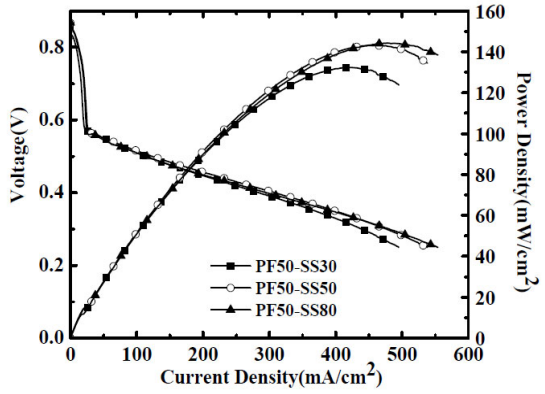

Figure 2: Polarization curves of the single cells with PFA-g-PSSA membranes at 60 °C.

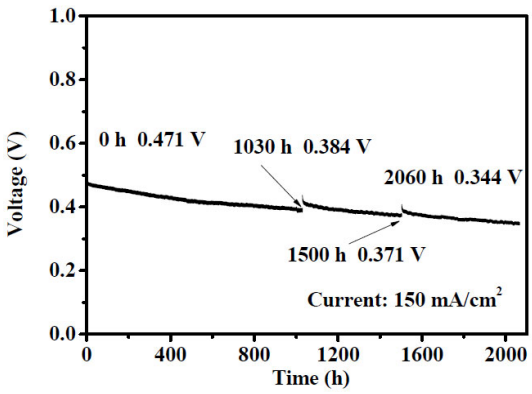

Figure 3: Long-term performance of a single cell based on the PF50-SS50 membrane at 60 °C.

Figure 3 shows the long-term performance of the cell based on the PF50-SS50 membrane for 2000 h at constant current density of 150 mA/cm^2 and 60 ^{o}C. At the beginning of the test, the cell provides 0.471 V (70mW/cm^2) of cell voltage and the cell voltage drop to 0.344 V (51.6 mW/cm^2) after 2000 h operation. The observed power density loss over the 2000 h period is about 26.2% (70 mW/cm^2 → 51.6 mW/cm^2). The decay rate of the cell voltage during 2000 h operation was determined to be about 61.6 μV/h.

In order to evaluate for MEA degradation, polarization curves were measured before and after the long-term test as shown in Figure 4. The initial peak power density of single cell was 143 mW/cm^2, and after preformed long-term test for 2000 h, the peck power density reduced to 86 mW/m^2.

Figure 5 shows the impedance spectra of the single cell at 0.4 V during the long-term test. The impedance arc increases with decreasing polarization due to increase charge-transfer resistance. On the impedance analysis results, the ohmic resistance of single cell increased from 0.101 to 0.103 Ωcm^2 after long-term operation.

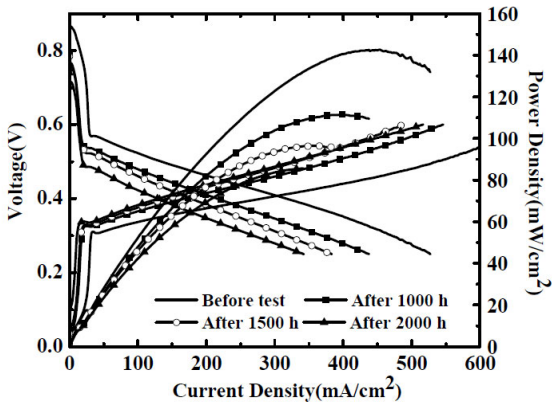

Figure 4: Polarization and power density curves of the cells before and during long-term test.

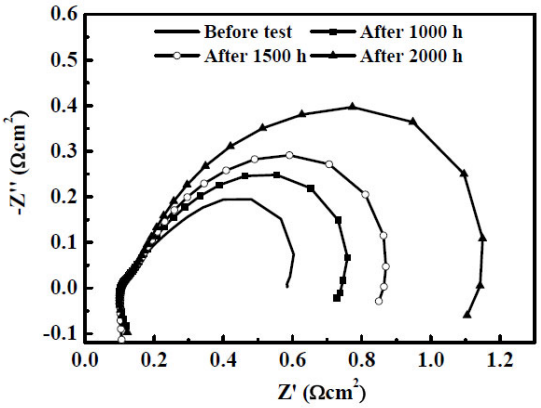

Figure 5: Impedance spectra of the cell according to polarization.

Figure 6 illustrates the powder X-ray diffraction (XRD) patterns of the anode and cathode catalysts. The XRD patterns exhibited primarily an intense diffraction peak (002) at 2θ = 26^o for carbon in the carbon paper. The characteristic peaks corresponding to Pt (111), (200) and (220) were identified from Pt and PtRu catalysts. These peaks indicated that Pt was present in the face-centered cubic (fcc) structure and the Pt (220) peak was selected to calculate the particle size of catalyst.

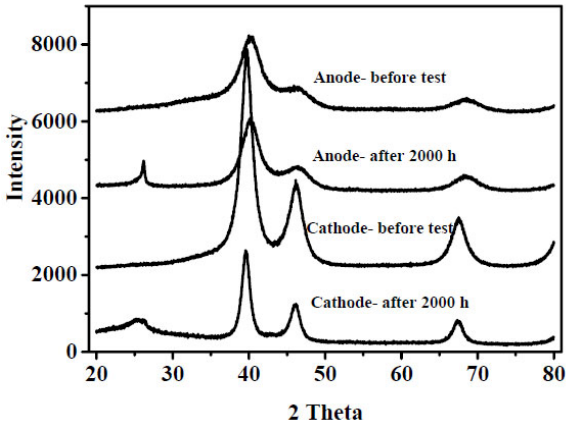

Figure 6: XRD patterns of the anode and cathode catalysts before and after long time test.

The mean particle sizes of the catalysts are summarized in Table 1. The change of particle size of the cathode and anode catalysts varied in the range of 0.5 nm and 2.0 nm, respectively. All the particle size of catalysts increased after long-term performance test and the particle size of the cathode catalyst increased much higher than the anode catalyst.

Table 1: Mean particle size of the catalysts calculated from XRD.

	Anode		Cathode	
	Before test	After 2000 h	Before test	After 2000 h
Particle size (μm)	2.0	2.5	4.1	6.1

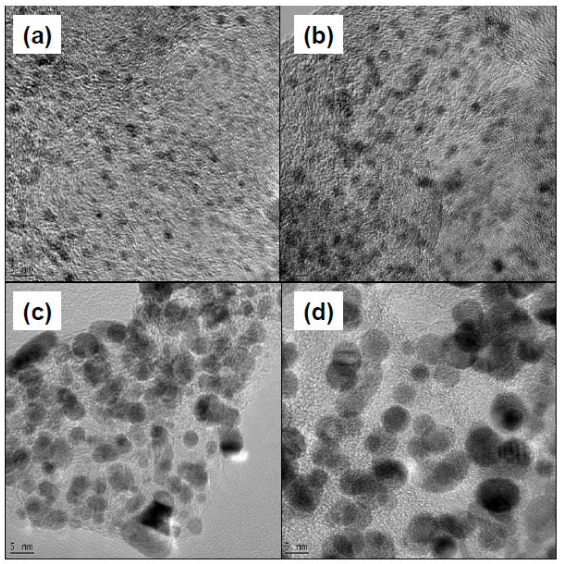

Figure 7: TEM images of anode (a,b) and cathode (c,d) catalysts before (a,c) and after (b,d) long time test.

Figure 7 illustrates the TEM images of the anode and cathode catalysts before and after the long-term test. All the particle size of catalysts increased after long-term performance test as shown in Figure 7. The particle size of the cathode catalyst increased much higher than the

anode catalyst after the long-term test (Figure 7(b) and 7(d)). Also, the morphology of the catalysts was changed to circle-like shape.

SEM images of cross-sectional of the MEA and PF50-SS50 membrane are shown in Figure 8. The PF50-SS50 membrane thickness of the initial MEA was 50 μm, and the anode and cathode catalyst layer was 25 μm and 32 μm. The thickness of PF50-SS50 membrane and anode catalyst layer remained constant after 2000 h of long-term test.

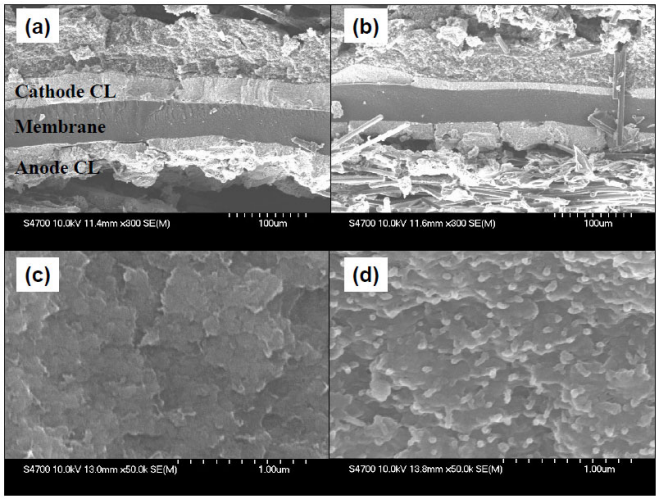

Figure 8: SEM images of cross-section of MEA (a,b) and surface of PF50-SS50 membrane (c,d) before (a,c) and after (b,d) long time test.

However, the thickness of the cathode catalyst layer decreased to roughly 15 μm. Decrease of the thickness of the cathode catalyst layer was attributed to the oxidation of the carbon support by the hydrogen peroxide, which was formed during the oxygen reduction reaction. The samall granins was formed on the surface of the prepared PF50-SS50 membrane owing to thermal decomposition of polystyrene into grafted PFA film after the long-term test for 2000 h.

4 Conclusions

In this work, the long-term performance of prepared MEA with PF50-SS50 membrane was tested with a constant load 150 mA/cm^2 for 2000 h at 60 ^{o}C. The observed power density loss over the 2000 h period is about 26.2% (70mW/cm^2 → 51.6 mW/cm^2). The decay rate of voltage for the cell operation up to 2000 h was determined to be about 61.6 μV/h. The performance loss of the single cell is considered to be due to increase of particle size of catalysts, reduction of the cathode catalyst and thermal decomposition of the PF50-SS50 membrane.

Acknowledgments

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