Short communication

Durability and stability test of proton exchange membrane fuel cells prepared from polybenzimidazole/poly(tetrafluoro ethylene) composite membrane

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ABSTRACT

It has been reported that a thin polybenzimidazole (PBI)/poly(tetrafluoro ethylene) (PTFE) composite membrane (thickness 25–30 μm) can be prepared by impregnating a thin porous PTFE (thickness 15–20 μm) in a PBI/N,N′-dimethyl actamide (DMAc) solution. In this paper, a 400 h life test of a fuel cell prepared from PBI/PTFE composite membrane was carried out at 160 °C with a current density $i = 200\,\mathrm{mA\,cm^{-2}}$. During long time test, the i–V curve and AC-impedance measurements were conducted every 12 h. The experiment data showed a 240 h period of activation. After 240 h the cell voltage started to decay. AC-impedance measurements showed internal resistance (R_s) and charge transfer resistance (R_c) decreased in the initial 240 h life test and then R_s remained almost constant and R_c increased after 240 h. The decay of fuel cell performance can be attributed to the migration of phosphoric acid out from membrane leading to the delamination between membrane and electrodes.

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1. Introduction

It is generally accepted that polyelectrolyte membrane fuel cell (PEMFC) presents an attractive alternative to traditional power sources, due to their high efficiency and non-pollution. In the past decade, researchers [1–7] had made effort to develop hydrocarbon membranes for PEMFCs working at high temperatures (120 °C < temperature < 200 °C). One of the most prominent membranes is PBI (polybenzimidazole) doped with phosphoric acid [2], in which phosphoric acid acts as protons conducting carrier and no water is needed for protons conduction in the membranes. Thus PEMFCs using PBI doping phosphoric acid membranes as proton-conducting separators are available to work at high temperatures and low humility environment [2,6,7]. Besides high conductivity at temperatures above 120 °C, PBI membranes also show good thermal stability, high mechanical strength, excellent chemical stability, etc. [8–11]. The high-temperature operation fuel cells offer many advantages such as fast electrode kinetics, high tolerance to fuel impurities such as CO, and simple thermal and water management for cell operations and designs [12].

The preparation of porous poly(tetrafluoro ethylene) (PTFE) ultra-thin film reinforced ionomer membranes was first reported by Bahar et al. [13]. They successfully prepared Nafion/PTFE composite membranes by impregnating porous PTFE thin film in a dilute Nafion solution and applied the composite membrane to PEMFC.

Following Bahar et al. work, we reported PBI/PTFE composite membrane preparation and its application to high temperature PEMFC [14,15]. The main advantage of composite membranes is its low thickness (22–30 μm). The reinforcement of ionomer membranes with high mechanic strength porous PTFE thin film (thickness 16–20 μm) allows us to reduce the membrane thickness without losing mechanic strength. The low thickness of the proton exchange membrane (PEM) causes a reduction in the resistance of PEM and an improvement of fuel cells performance.

In present work, we reported a 400 h life test for a PBI/PTFE composite membrane based fuel cell operated at 160 °C with a constant load current density $i = 200\,\mathrm{mA\,cm^{-2}}$. During long time operation, the i–V curve, AC impedance, and pH value of water drained from outlet of cathode were measured periodically. The cell voltage data showed a 240 h period of activation, after 240 h the cell voltage started to decay. The variations of cell voltage, membrane resistance R_s, charge transfer resistance R_c of catalysis reaction, and pH value of drained water from outlet of cathode versus life test time were investigated and the behavior of the cell voltage decay after 240 h was discussed.

2. Experimental

2.1. Synthesis of PBI

PBI was synthesized from 3,3′-diamino benzidine (Aldrich Chemical Co.) and isophthalic acid (Aldrich Chemical Co.) using polyphosphoric acid (Aldrich Chemical Co.) as a solvent. The detailed polymerization procedures were same as those reported

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by Ueda et al. [16]. The inherent viscosity (I.V.) was measured by dissolving 0.5 wt% of PBI in 98 wt% sulfuric acid solution using an Ubbelohde viscometer (with a water flow time of 98 s) and an I.V. at 30 °C of 2.45 dl g^{-1} was obtained. This I.V. value corresponded to $M_v = 2.3 \times 10^5$ g mol^{-1} calculated using an equation derived by Choe and co-workers [17].

2.2. Preparation of PBI/PTFE composite membrane

PBI/PTFE composite membrane was prepared by fabricating a PBI/DMAc/LiCl solution on a porous PTFE (thickness 16 ± 2 µm, pore seizes 0.5 ± 0.1 µm, and porosity 85 ± 5%, Yu-Ming-Tai Chem. Co., Taiwan) thin film. The concentration of PBI of the PBI/DMAc/LiCl solution was 4.5 wt% and the weight ratio of [LiCl]/[PBI] was 1/1. The detailed preparation procedures were described in Refs. [14,15]. The thickness of the final composite membrane was around 30 ± 2 µm. The composite membrane was doped with a 85 wt% phosphoric acid aqueous solution. The final composition of the composite membrane was PTFE/PBI/Nafion/H$_3$PO$_4$ = 9.3/53.4/1.7/35.6 (w/w). The membrane acid-doping content was determined by weighing the membranes before and after doping phosphoric acid.

2.3. Membrane electrode assembly (MEA) preparation

The composite membrane was used to prepare MEA. The catalyst was Pt-C (carbon supported platinum, E-TEK, 40 wt% Pt). Both the Pt loadings of anode and cathode were 0.5 mg cm^{-2}. Pt-C/PBI/LiCl/DMAc (3.5/1/0.5/49, w/w) catalyst solution was prepared by ultrasonic disturbing for 5 h. In catalyst ink solution, *LiCl* was a stabilizer of PBI/DMAC solution. The catalyst ink was brushed onto a carbon cloth (E-TEK, HT 2500-W) and dried at 110 °C in a conventional oven to calculate catalyst loading. The carbon cloths coated with catalyst layers were immersed in deionized water for 24 h to remove *LiCl*. They were then doped with phosphoric acid by dipping in a 10 wt% phosphoric acid aqueous solution for 24 h and dried in oven at 110 °C. The membrane was sandwiched in between two carbon cloths coated with a catalyst layer and pressed at 135 °C with a pressure of 50 kg cm^{-2} for 5 min to obtain a MEA. The active area of MEA was 50 cm^2.

2.4. Unit cell life performance test

The performance of unit cell was tested at a constant loading current ($i = 200$ mA cm^{-2}) with an ambient pressure at 160 °C using a FC5100 fuel cell testing system (CHINO Inc., Japan). The anode H_2 and cathode O_2 input flow rates were 300 ml min^{-1} at the beginning 372 h of life test and 500 ml min^{-1} after 372 h. Both H_2 and O_2 flows were unhumidified. The voltage at the loading current ($i = 200$ mA cm^{-2}) was recorded every 12 h. The open circuit voltage (OCV), i–V polarization curve, and AC-impedance spectroscopy measurements were carried out every 12 h. The i–V curves were obtained by measuring the current density i with step decrement of voltage by an interval of 0.05 V. The time was held 30 s for each i–V curve measurement. The AC-impedance measurements were carried out at $i = 200$ mA cm^{-2} and the testing frequency scope was from 10^5 Hz to 0.1 Hz. The output water gas at the outlet of cathode was condensed with a condenser and collected every 3 h at the beginning 24 h of life test. After 24 h, the condensed liquid water at outlet of cathode was collected every 6 h. The pH value of water collected at outlet of cathode at various testing time was measured using a pH meter (Horiba pH meter model F-22) at 25 °C.

2.5. Morphology characterization of MEA

The catalyst layer morphology before and after life test was examined using a scanning electron microscope (SEM, JEOL, JSM-6701F) and an energy dispersion spectroscopy (SEM, JEOL, JSM-6701F).

3. Results and discussion

The result of 400 h life test of H$_3$PO$_4$/PBI–PTFE unit cell operated at 160 °C with $i = 200$ mA cm^{-2} is shown in Fig. 1. During the beginning 240 h test, the cell voltage increased from 0.44 V to 0.61 V. A degradation of voltage from 0.61 V to 0.57 V was observed from 240 h to 372 h. Several researchers had reported long time life tests of PBI based high temperature PEMFC [11,17–20]. Under a fixed loading current for a long time fuel cell test, two regions were observed in the output voltage versus testing time curve. The first initial testing period was the "activation region", in which cell voltage increased with operating time. Following the "activation region" was the "decay region", in which the cell voltage decreased with operating time. Liu et al. [18], Hu et al. [11], and Zhai et al. [19] reported the time period of activation region was around 90–130 h for PBI based PEMFC. The period of activation region of PBI/PTFE based PEMFC of present work is obvious longer than that of PBI based PEMFC reported in literature. Liu et al. [18] attributed the improvement of fuel cell performance at "activation region" to the better contact of membrane with catalyst layers by the pressure of the end plates and expansion of the interface for the electrochemical reaction at high temperature. However, the reason of longer activation time of PBI/PTFE based PEMFC than PBI based PEMFC is still not clear to us.

Fig. 2 shows the i–V polarization curves at various life testing times. The open circuit voltage (OCV) data obtained from each i–V measurement during life test are also plotted against testing time and shown in Fig. 1. The OCV data are lower than those of PBI based MEA reported in literature [1,17–20], due to the lower thickness of PBI/PTFE membrane. The results of i–V measurements and OCV data were consistent with the voltage measurements of life test at $i = 200$ mA cm^{-2}. Both results show the cell reaches its best performance at 240 h. Careful investigating the i–V curves, we found there were concentration polarization at high currents ($i > 400$ mA cm^{-2}) after 276 h life test. After 372 h, the flow rates of H$_2$ and O$_2$ were both increased to 500 ml min^{-1}. We found the cell performance was improved at high H$_2$ and O$_2$ flow rates. However, the phenomenon of concentration polarization at high current density was still observed in the i–V curves when the H$_2$ and O$_2$ gases flows were
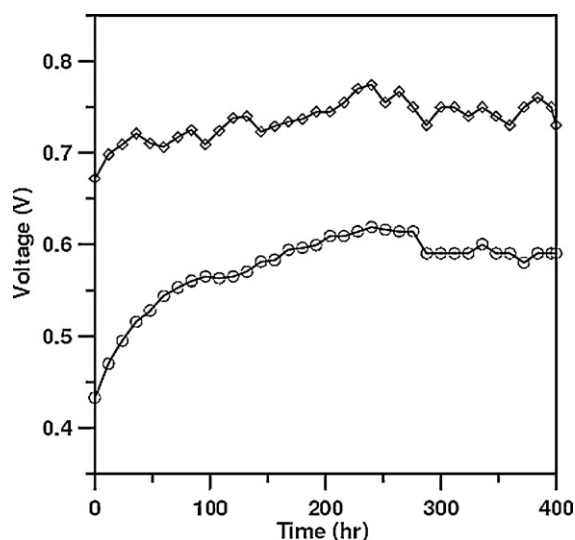

Fig. 1. Plots of cell voltage at constant load current density $i = 200$ mA cm^{-2} and OCV versus life testing time at 160 °C. The H$_2$ and O$_2$ flow rates were 300 ml min^{-1} at the beginning 372 h and 500 ml min^{-1} after 372 h. (○) Cell voltage; (◇) OCV.
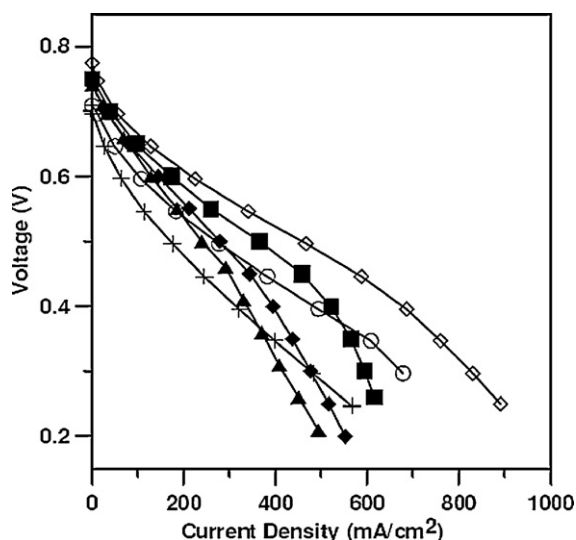
Fig. 2. *i*–V polarization curves of PBI/PTFE based PEMFC at various times of life test. Life testing times: (+) 24 h; (○) 96 h; (◇) 240 h; (■) 276 h; (▲) 372 h; (◆) 396 h. The H$_2$ and O$_2$ flow rates were 300 ml min^{-1} at the beginning 372 h and 500 ml min^{-1} after 372 h.
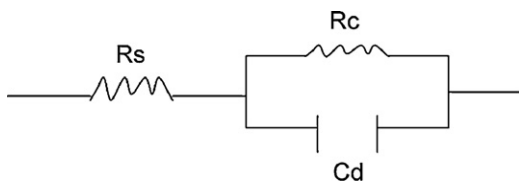

Fig. 3. Equivalent circuit of the AC-impedance diagram of a unit cell. R_s represents high frequency resistance that reflects the internal resistance of the unit cell, R_c represents charge transfer resistance of cathodic chemical reaction, C_d is the constant phase element corresponds to the porous surface of the electrode.

both increased to 500 ml min^{-1}. This result suggests some of the gas flow pathways in the catalyst layers were blocked and the H$_2$ and O$_2$ molecules were not able to reach all the catalyst particles. The blockage of H$_2$ and O$_2$ gases flows indicates changing of catalyst layers morphology after long time test at high temperature.

The AC-impedance measurements were performed to study the performance of membrane and catalyst layer. The AC-impedance
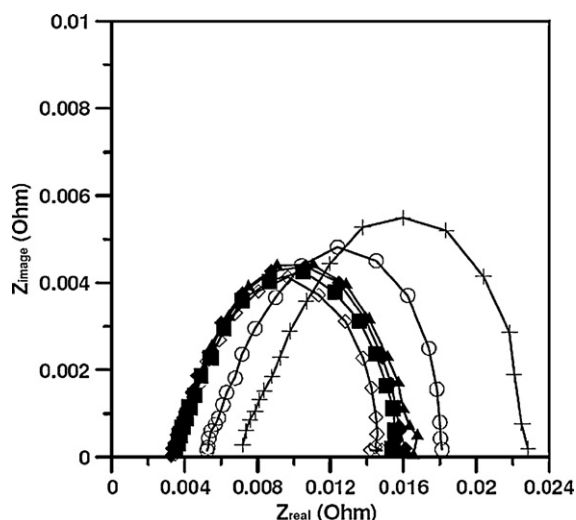

Fig. 4. AC-impedance diagrams of PBI/PTFE based PEMFC at various times of life test. Life testing times: (+) 24 h; (○) 96 h; (◇) 240 h; (■) 276 h; (▲) 372 h; (◆) 396 h.
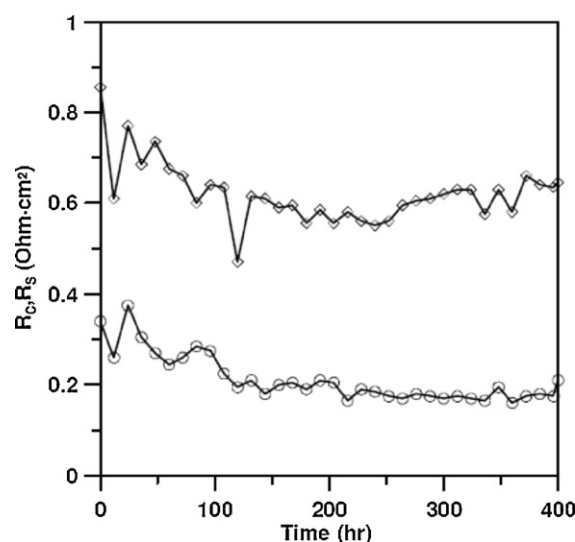

Fig. 5. The variation of R_s and R_c versus life testing time. (○) R_s; (◇) R_c.

diagrams were simulated using an equivalent circuit shown in Fig. 3. In Fig. 3, R_s represents high frequency resistance that reflects the internal resistance of the unit cell, R_c represents charge transfer resistance that reflects the resistance of chemical reaction on catalysts, and C_d represents the constant phase element that simulates the porous surface of the electrode. The main change of R_s comes from the degradation of membrane during the life test. For other components contribute to R_s such as resistance of end-plates, flow field plates, and contact resistance between end-plates and flow field plates remain almost constant during the life test. Since the anodic reaction resistance is negligible, R_c is mainly contributed from the charge transfer resistance of cathodic reaction. Thus the change of R_s and R_c during life test can be used to evaluate the degradations of membrane and catalyst activity, respectively.

Fig. 4 shows the AC-impedance diagrams obtained at life testing times of 24 h, 96 h, 240 h, 276 h, 372 h, and 396 h. The simulated R_s and R_c values are plotted against testing time and shown in Fig. 5. Fig. 5 shows R_s decreases from beginning to 240 h. After 240 h, R_s does not change significantly with life testing time. Fig. 5 shows R_c decreases with testing time and reaches the lowest value at 240 h.
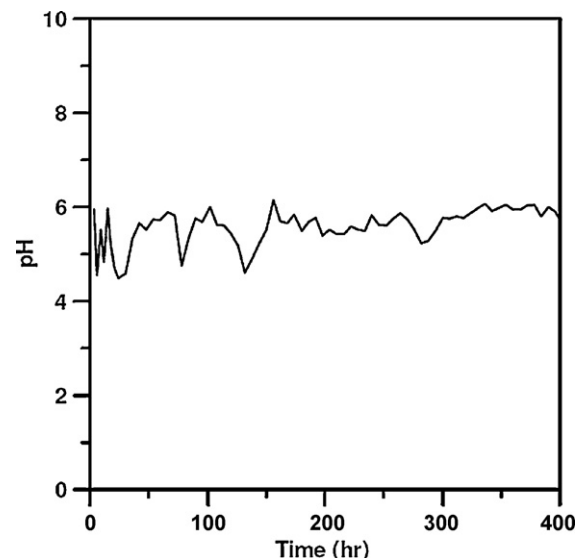

Fig. 6. The variation of pH value of water collected at outlet of cathode versus life testing time.
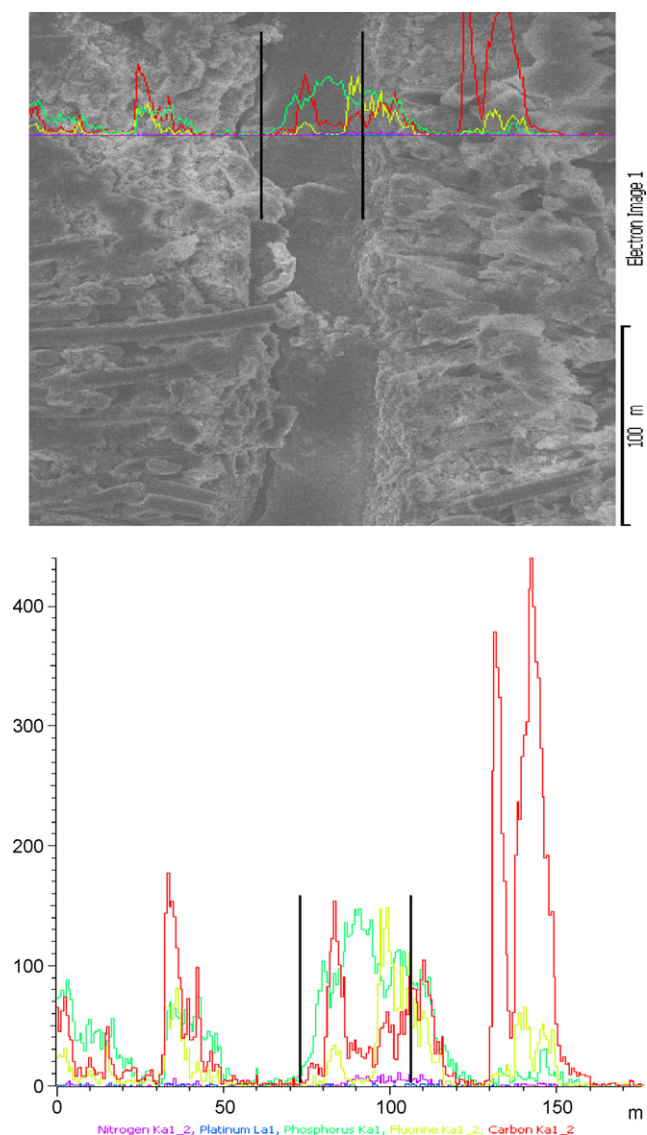
trochemical reaction product water from the outlet of cathode and measured the pH value of each water collected at various life testing time. Fig. 6 shows the variation of the pH value of cathode output water against life testing time. We found that at the beginning 30 h, the pH values were around 4.3–6.0 and lower than the pH values of 5.5–6.0 after 150 h. This result suggests the migration of phosphoric acid from MEA occurs at the beginning 30 h of life test. In literature [21] it had been reported that two groups of phosphoric acid molecules present in PBI membranes. One group is the phosphoric acid molecules protonates the nitrogen atoms of the imidazole groups of PBI and the other group is the excess phosphoric acid molecules inside the PBI membranes. Proton migration along the mixed $H_2PO_4^-\ldots H_3PO_4$ and $NH^+\ldots H_2PO_4^-$ anionic chains by successive proton transfer and anion reorientation process. We believe that in the initial period of life test, the leaking out of phospho-
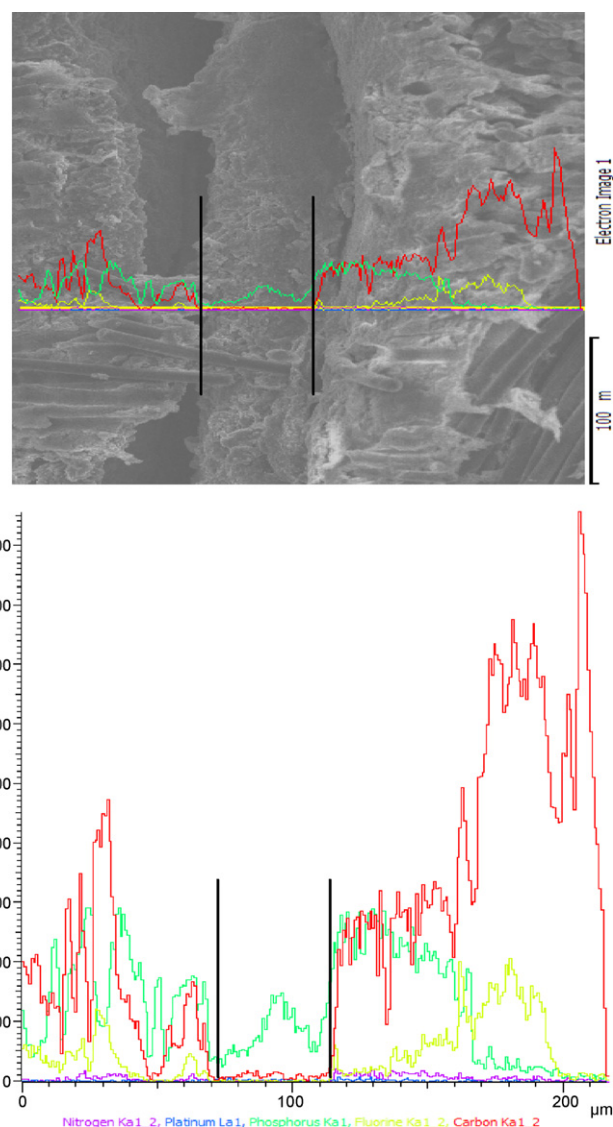

Fig. 7. SEM micrograph (×100) and EDS analysis of the cross section of PBI/PTFE MEA before life test. (up) SEM with EDS analyses elemental intensity distribution curves; (bottom) EDS analysis elemental intensity distribution curves. Elements: (━━ ━━ ━━) N, curve in violet color; (━━ ━━ ━━) Pt, curve in blue color; (━━ ━━ ━━) P, curve in green color; (━━ ━━ ━━) F, curve in yellow color; (━━ ━━ ━━) C, curve in red color; (|) vertical line in black color indicates the boundary between membrane and catalyst layer on the line of EDX analysis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

After 240 h, R_c increases with life testing time. These results are consistent with the cell voltage versus life testing time result shown in Fig. 1, which shows a maximum voltage of cell output at 240 h. These results indicate that in the initial 240 h, the MEA is in activation region and the resistances of membrane and charge transfer in cathode decrease with testing time. After 240 h, Fig. 1 shows the output voltage starts to decay. Since after 240 h of life test, R_s did not change significantly and R_c increased with testing time (Fig. 5), we may conclude the decay of output voltage after 240 h of life test mainly came from the degradation of catalyst.

As mentioned in Sections 2.2 and 2.3. Before the membrane was sandwiched between two electrodes containing carbon cloth and catalyst layer and pressed to make a MEA, the PBI/PTFE composite membrane was doped with a 85 wt% phosphoric acid aqueous solution and the electrodes were doped with a 10 wt% phosphoric acid aqueous solution. In order to observe the phenomenon of the phosphoric acid migration out from MEA, we collected the elec-

Fig. 8. SEM micrograph (×250, 15 kV) and EDS analysis of the cross section of PBI/PTFE based MEA after life test. (up) SEM with EDS analyses of elemental intensity distribution curves, the anode and cathode are on the upper and lower side of the membrane, respectively; (bottom) EDS analysis elemental intensity distribution curves. Elements: (━━ ━━ ━━) N, curve in violet color; (━━ ━━ ━━) Pt, curve in blue color; (━━ ━━ ━━) P, curve in green color; (━━ ━━ ━━) F, curve in yellow color; (━━ ━━ ━━) C, curve in red color; (|) vertical line in black color indicates the boundary between membrane and catalyst layer on the line of EDX analysis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

ric acid was due to the migration of the excess phosphoric acid molecules. After most of the excess phosphoric acid molecules migrated out from MEA, the pH value of output water from cathode was stable and higher than that obtained in the initial period of life test.

Figs. 7 and 8 show the SEM micrograph and EDS analysis of PBI/PTFE based MEA before and after life test, respectively. In Fig. 7, the SEM micrograph (upper graph) showed the MEA was well laminated before life test. No cracks were found between membrane and electrodes. The EDS elemental analyses distribution curves along the horizontal line from the anode (left hand side of the membrane) through membrane to the cathode (right hand side of the membrane) are shown in the micrograph. In order for easy view, the N (violet color curve), Pt (blue color curve), P (green color curve), F (yellow color curve), and C (red color curve) elements distribution curves of EDS analyses are enlarged and shown in the bottom figure of Fig. 7. The EDS analyses show P element has a highest intensity among all of the elements in membrane (it is within two vertical lines in the graph) and a higher intensity in membrane than in anode and cathode, indicating high content of phosphoric acid in the membrane. In Fig. 8, the SEM micrograph shows delamination of MEA after life test. The EDS elements analyses show the intensity of P (green color curve) element is lower in membrane than in anode and cathode. Comparing the EDS elemental analysis of Fig. 8 with that of Fig. 7, we found the P element content in the membrane after life test was lower than that before life test. This result suggests that phosphoric acid migrates out from membrane during life test at 160 °C. The migration of phosphoric acid causes delaminations between membrane and anode and between membrane and cathode. The delamination might one of the reasons for the increment of charge transfer resistance R_c at the later stage of life test.

4. Conclusions

In this paper, a 400 h life test of a fuel cell prepared from PBI/PTFE composite membrane was carried out at 160 °C with a current density $i = 200\,mA\,cm^{-2}$. The experiment data showed a 240 h period of activation, after 240 h the cell voltage started to decay. AC-impedance measurements showed R_s and R_c decreased in the initial 240 h of life test and then R_s remained almost constant and R_c increased after 240 h. The pH values of water output from cathode suggested that most of the migration of phosphoric acid from MEA happened at the beginning 30 h of life test. The SEM study showed delamination between membrane and electrodes after life test. The EDS elements analyses of MEA before and after life test also showed migration of phosphoric acid out from membrane during life test. The decay of fuel cell performance after 240 h of life test can be attributed to the migration of phosphoric acid out from membrane, which may cause delamination of membrane with electrodes.

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