

Short communication

Studies of performance degradation of a high temperature PEMFC based on H₃PO₄-doped PBI

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Abstract

In this paper, a 600 h life test of a high temperature PEMFC based on phosphoric acid (H₃PO₄)-doped polybenzimidazole (PBI) (H₃PO₄/PBI HT-PEMFC) at a current density of 714 mA cm⁻² (the beginning 510 h continuous test) and 300 mA cm⁻² (the last 90 h intermittent test) was carried out. After the life test, degradation of the MEA occurred. The H₂ crossover rate through the PBI membrane and the open circuit voltage (OCV) of the cell were tested with time. The results showed that, at the beginning of 510 h continuous test, the PBI membrane did not show much physical degradation, but during the last 90 h test there was a remarkable physical degradation which resulted in a higher H₂ crossover. The catalysts, PBI membranes and the membrane electrode assemblies (MEAs) before and after the life test were comprehensively examined by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). TEM results showed that the particle size of the Pt/C catalysts in the anode and cathode increased from 3.72 to 7.40 and 8.39 nm, respectively. SEM images of MEA in cross-section revealed that the PBI membrane became thin after the life test. EDS analysis implied the leaching of H₃PO₄ from the PBI membrane had occurred. Therefore, we conclude that physical degradation of PBI membrane, agglomeration of the electrocatalysts (both anode and cathode) and the leaching of H₃PO₄ from the PBI membrane were responsible for the performance degradation of the H₃PO₄/PBI HT-PEMFC.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) as clean and efficient power sources are receiving increasing attention both for stationary and transportation applications [1–4]. The currently well-developed PEMFC technology is based on perfluorosulfonic acid (PFSA) polymer membranes (e.g., Nafion[®]) [5]. This polymeric membrane is dependent on the presence of water to solvate the protons from the sulfonic acid groups. Consequently, the operational cell temperature is limited to below 100 °C [6]. These kinds of PEMFCs face two main limitations. Firstly, the use of PFSA polymer membranes requires proper humidification to keep the ionic conduction high enough for

PEMFC applications, which complicate the design of the fuel cell system; secondly, CO impurities seriously poison the Pt/C catalysts below 100 °C [7]. The H₃PO₄/PBI HT-PEMFC operates at temperatures around 150–200 °C without humidification which not only resolves the above mentioned problems but also provides other advantages, such as enhanced reaction kinetics at the elevated cell temperature for both electrodes [5,8], elimination of cathode flooding and ease of heat management [9,10].

The life of a PEMFC is a major concern for commercialization. The life tests of mid-low temperature PEMFCs have been widely investigated [11–13]. However, the detailed reasons for the performance degradation of H₃PO₄/PBI HT-PEMFC have not been reported. In this paper, employing commercial Pt/C (46.2%, TKK Corp.) as the cathode and anode catalyst, a H₃PO₄/PBI HT-PEMFC was operated at 150 °C without humidification. A 600 h life test of the H₃PO₄/PBI HT-PEMFC at a current density of 714 mA cm⁻² (the beginning 510 h continu-

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ous test) and 300 mA cm^{-2} (the last 90 h intermittent test) was carried out. After the test, the catalysts, the PBI membrane and the MEA structure were analyzed by TEM, SEM and EDS. On the basis of the preliminary results, the deterioration of the MEA performance was determined.

2. Experimental

2.1. Preparation of the membrane electrode assembly (MEA) and single cell life-time test

The electrode was prepared as follows: mixing TKK 46.2% Pt/C and 5% *N*-methylpyrrolidone (NMP) solution of PBI and polyvinylidene fluoride (PVDF) in NMP to form a homogeneous mixture, spraying the mixture onto the wet-proofed carbon paper (SGL GDL 31 BC, $300 \mu\text{m}$ of thickness) by a tape-casting technique. The electrode fabrication was completed by drying at 80°C for 2 h and 130°C for 0.5 h in air. The loading of platinum, PBI and PVDF in the electrode were about 0.7, 0.1 and 0.05 mg cm^{-2} , respectively. This electrode was used both for the anode and the cathode. The PBI membrane ($35 \mu\text{m}$, provided by our copartner) was first doped with 85% H_3PO_4 at 60°C for 20 min. The MEA was made as follows: firstly, the doped PBI membrane was sandwiched between two electrodes, and then placed between two graphite plates with parallel gas channels. Two aluminum end plates with attached heaters were used to clamp the graphite plates by eight bolts with a torque of 3 N m. The active area at the anode and cathode was 7 cm^2 .

In our experiment, the cell was tested at 150°C without humidification. The single cell was fed with pure hydrogen and oxygen and operated at a current density of 714 mA cm^{-2} for the beginning 510 h (continuous test) and 300 mA cm^{-2} for the last 90 h (intermittent test). The performance curves of the life test were obtained periodically during different stages of cell operation. Points of the performance curves were measured at 5 min intervals to ensure the cell was under steady-state conditions.

2.2. Electrochemical and physical characterization

The electrochemical method of chrono-coulometry [12] was used to measure the H_2 crossover rate through the PBI membrane using a CHI 660 electrochemical station (CH Corporation, USA). The single cell was operated with hydrogen at the anode and nitrogen at the cathode. A 0.2 V was applied between the anode and cathode, so that hydrogen permeating through the membrane was oxidized electrochemically.

After the life test, the MEA was carefully removed from the cell, and cut into small pieces, which were used in the subsequent TEM, SEM and EDS studies.

The electrocatalysts were scraped from the used anode and cathode and then were placed in vials containing ethanol. The mixture was agitated to form a homogeneous slurry by sonication. A drop of this slurry was dispersed on a polyvinyl formal microgrid for analysis in a JEOL JEM-2011 TEM at 100 kV. Particle size distributions for the catalysts were obtained by manually measurement of 200 particles from the bright-field micrographs.

The morphologies of cross-sections of the fresh and used MEA were investigated with a JEOL JSM-6360LV SEM. The phosphorus contents of the fresh and used doped PBI membranes in the MEAs were determined with an SEM-EDS system (Oxford-Inca).

3. Results and discussion

Fig. 1 shows the result of the 600 h life test of the $\text{H}_3\text{PO}_4/\text{PBI}$ HT-PEMFC at 714 mA cm^{-2} (the beginning 510 h continuous test) and 300 mA cm^{-2} (the last 90 h intermittent test) at 150°C without humidification. During the first 130 h operation, the cell voltage increased from 0.437 to 0.582 V. One reason for this improvement is the better contact of the PBI membrane with the catalyst layers at the high temperature and by the pressure of the end plates. Another possibility is expansion of the interface for the electrochemical reaction. Subsequently, the cell voltage decreased continuously. A steady degradation rate of $81.6 \mu\text{V h}^{-1}$ was observed from 130 to 510 h. After the beginning 510 h continuous test, the discharge current density was decreased to 300 mA cm^{-2} , and in the following 90 h test, the cell was operated in an intermittent mode with an average operation time of 12 h per day. Unexpectedly, the cell voltage dropped rapidly from 0.672 to 0.648 V with a degradation rate of $266.7 \mu\text{V h}^{-1}$ in the last 90 h intermittent operation. This might be due to severe degradation of membrane and further agglomeration of the Pt/C catalysts when the cell was operated in the intermittent mode.

Fig. 2 shows the H_2 crossover rate as a function of the operation time together with the cell OCV versus time. It can be seen that the H_2 crossover rate increased slightly and the OCV was maintained higher than 1 V in the first 510 h operation. The slight increase of the H_2 crossover rate indicated that the PBI membrane did not have major physical degradation. When the Pt/C catalyst is adopted as the anode and cathode catalyst and the structures of the MEA do not change much, the OCV is primar-

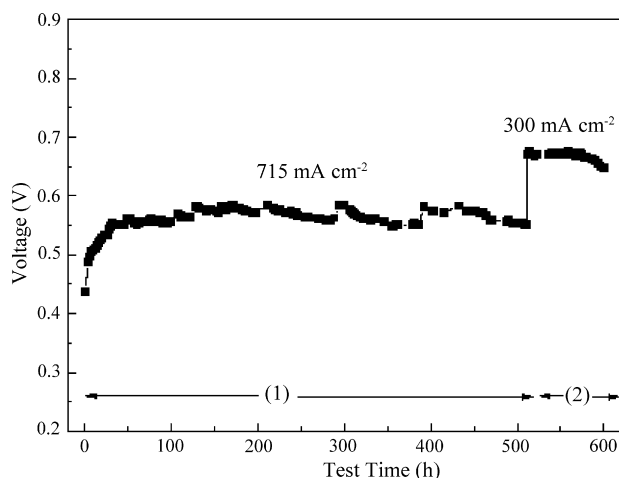


Fig. 1. Stability of the single $\text{H}_3\text{PO}_4/\text{PBI}$ HT-PEMFC: (1) 714 mA cm^{-2} (continuous test); (2) 300 mA cm^{-2} (intermittent test). Cell temperature at 150°C without humidification, anode/cathode feed streams: $\text{H}_2/\text{O}_2 = 0.1/0.1 \text{ MPa}$, 100 mL min^{-1} flow rate of anode and cathode, Pt loading: 0.7 mg cm^{-2} (anode and cathode).

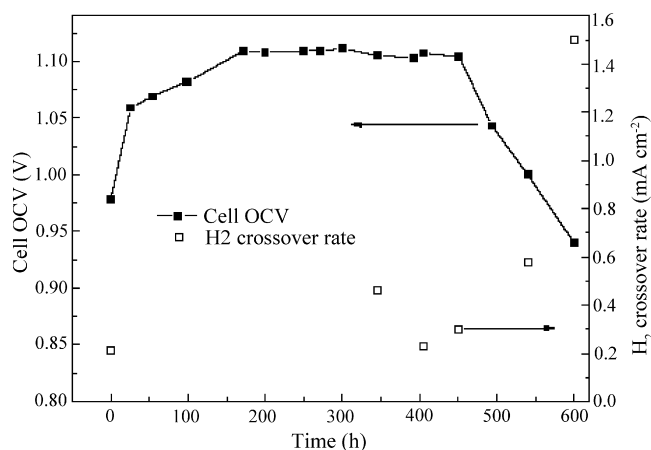


Fig. 2. H₂ crossover rate and Cell OCV with life test time: cell temperature at 150 °C without humidification, gas pressure H₂–N₂ (O₂) at 0.1 MPa, flow rates H₂–N₂ for H₂ crossover rate test and H₂–O₂ for OCV test are all 100/100 ml min⁻¹.

ily determined by the mixed potential due to the H₂ crossover. In the first 510 h of the continuous life test, the environment of the MEA was stable and the physical character of the PBI membrane was nearly the same, so the physical morphology of the catalyst-membrane interface did not have a visible change as seen from the SEM images in Fig. 6 and the mixed potential was very small since H₂ crossover did not increase remarkably. Therefore, the OCV was stable in the first 510 h continuous life test. However, after intermittent operation, the H₂ crossover rate increased from 0.3 to 1.5 mA cm⁻² and the OCV decreased from 1.043 to 0.94 V. In the intermittent life test, the PBI membrane suffered repetitious cold and hot changes. The degradation rate in PBI membrane may be increased by the strict operating conditions, which resulted in the increase of H₂ crossover. This increasing H₂ crossover could be responsible for the decline of the OCV and the degradation of cell performance, as shown in Fig. 1.

Fig. 3 shows the performance of the H₃PO₄/PBI HT-PEMFC at different times. As can be seen, the best cell performance was at 130 h. Then the cell performance decreased slightly from 130

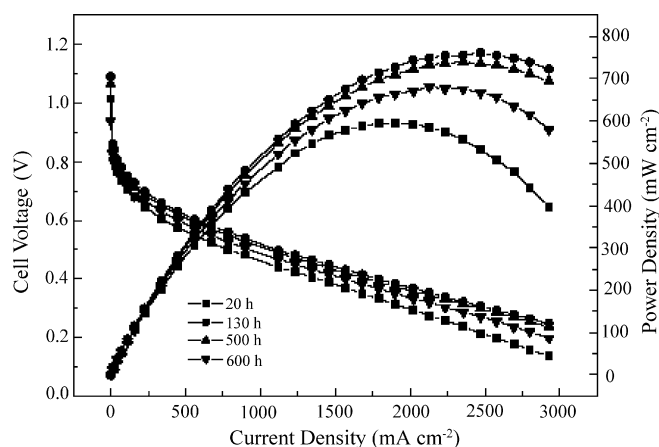


Fig. 3. Performance of the H₃PO₄/PBI HT-PEMFC, at different times. The operation conditions of the cell are the same as those in Fig. 1.

to 500 h with a loss of about 10 mV cell voltage at 500 mA cm⁻². The drop in performance after 130 h was due to two possible reasons. The prime reason was the agglomeration of the cathode and anode catalyst during the life test and the secondary reason was the leaching of a small amount of H₃PO₄ during the life test. Subsequently, an obvious cell performance drop was observed at 600 h. About 11% of the maximum power density was lost after the life test when compared to the initial peak power density of 0.761 W cm⁻². This may be due to the accelerated H₂ crossover rate through the PBI membrane as shown in Fig. 2 and further agglomeration of the Pt/C catalyst that is shown in Fig. 4.

The stability of the electrocatalysts plays an important role on the long-term operation of an acid-type fuel cell. In the phosphoric acid fuel cell (PAFC), the loss of activity in Pt/C due to the agglomeration of the platinum particles is considered to be a major cause of the decay in cell performance [14]. The working environment of H₃PO₄/PBI HT-PEMFC is analogous to that of the PAFC. Similarly, the surface area of the catalysts in the anode and cathode were reduced and considerable growth of the Pt particles occurred over the 600 h life test in the single cell, which had a significant effect on the cell performance. Fig. 4 presents the TEM images of Pt/C catalysts in the anode and cathode before and after the life test and the corresponding histograms are shown in Fig. 5. The histograms of Pt particle size of Pt/C were based on measurements of over 200 Pt particles. The results show that the dispersion of the Pt particle size of the fresh Pt/C was relatively narrow with a dispersion of 2–5 nm and that the mean particle size was 3.72 nm. After the 600 h life test, the dispersion of the Pt particle size was quite broad, both for the anode and the cathode Pt/C catalyst. The agglomeration of the Pt/C particles on the cathode after the test was more severe than on the anode. Obvious coalescence of the Pt particles can be seen in Fig. 4. The Pt particle size dispersion of the used cathode Pt/C was very broad, from 4 to 14 nm, averaging 8.39 nm. Unfortunately, more than 30% of Pt particles were between 10 and 14 nm. The Pt particle size dispersion of the used anode Pt/C also became wider, from 4 to 12 nm, averaging 7.4 nm, but only 7.8% Pt particles were bigger than 10 nm.

Rapid growth of the Pt particles occurred in the presence of the H₃PO₄ and high temperature environment because this environment speeds up the process of Pt dissolution and redeposition which causes growth of platinum particles [15,16]. Another reason for the agglomeration of the Pt/C catalyst is the migration of Pt crystallites on the carbon support. Bett et al. [17] found that in the H₃PO₄ and high temperature environment, Pt transfers from one crystallite to another and can lead to a decrease in the Pt crystallite density and an increase of Pt particles [18]. The faster sintering rate of the cathode catalyst particles may be due to the higher potential of the cathode than in anode, but Blurton et al. [19] observed from results of PAFC that the growth rate of Pt particles is independent of the electrode potential in the range of 0.1–0.8 V versus RHE. During our life test, the cathode potential was in the range of 0.4–0.7 V versus RHE, so the influence of the potential is minor. Another possible reason for the different growth rate of particles between the anode and cathode is the different water vapor density in the two electrodes. Several studies by Geus [20] have revealed accelerating effects

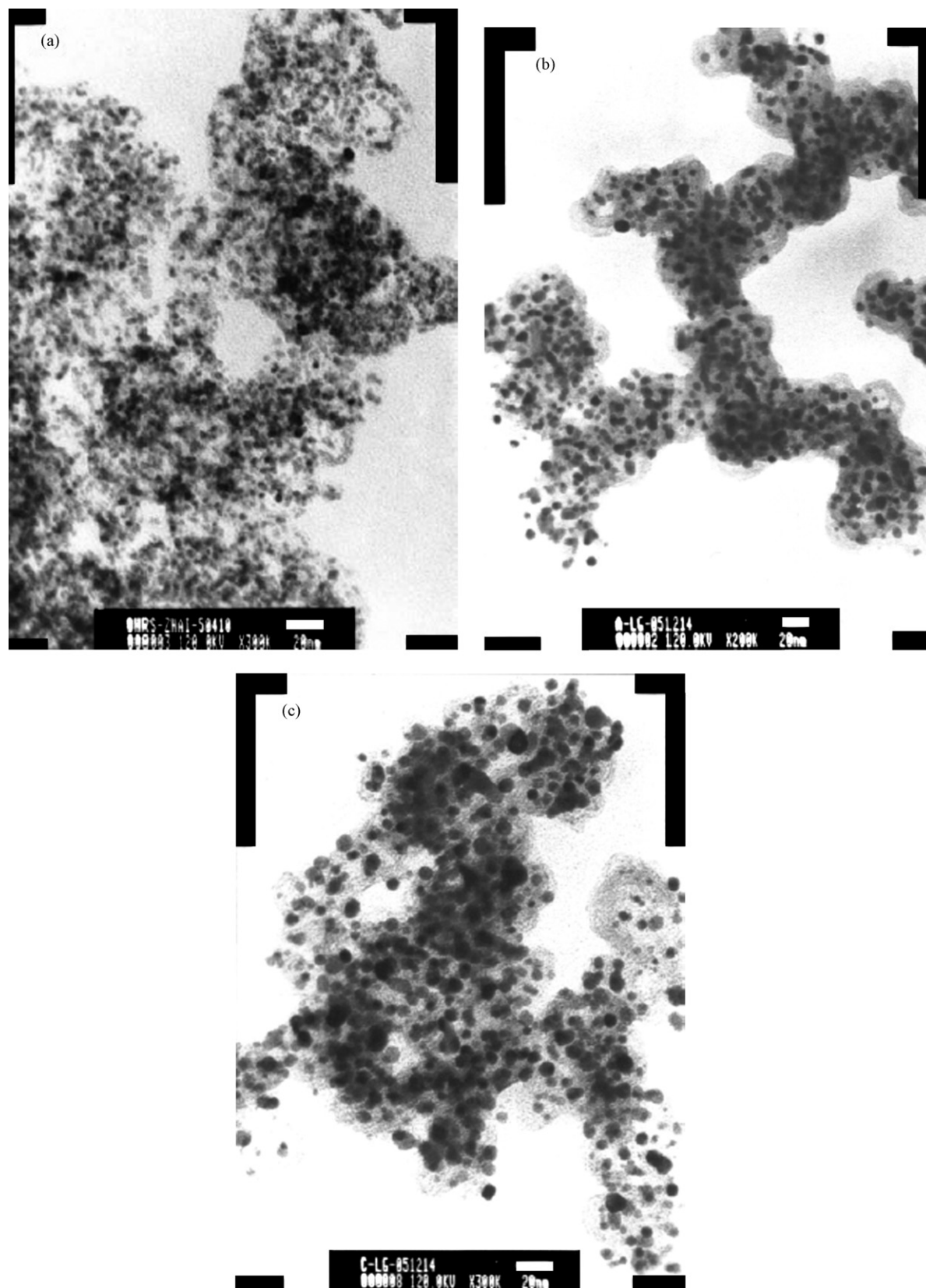


Fig. 4. TEM images of Pt catalysts: (a) fresh TTK 46.2% Pt/C; (b) Pt/C at anode after 600 h life test; (c) Pt/C at cathode after 600 h life test.

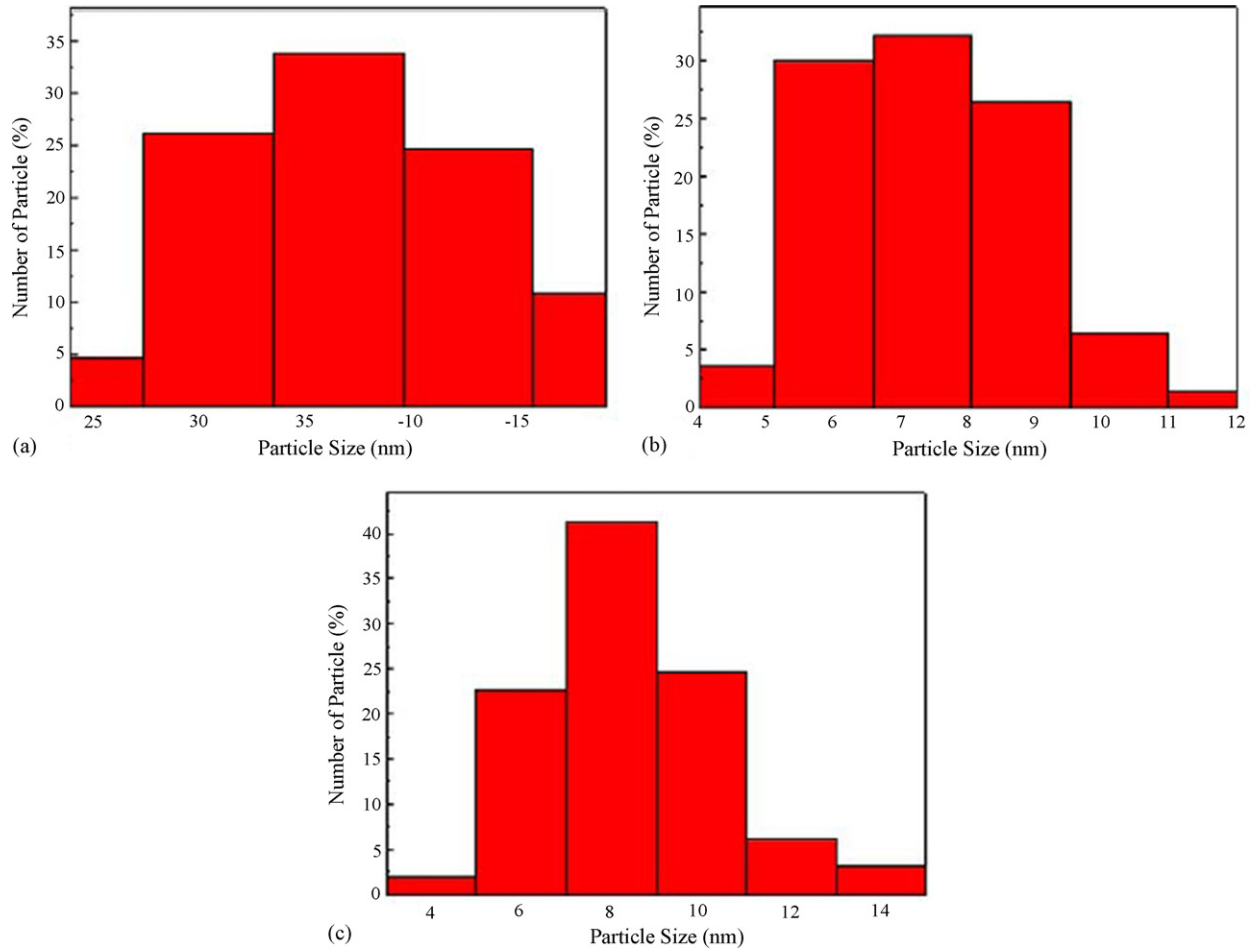


Fig. 5. Histograms of particle size distributions of Pt catalysts: (a) fresh TKK 46.2% Pt/C; (b) Pt/C at anode after 600 h life test; (c) Pt/C at cathode after 600 h life test.

of water vapor on crystallite migration. It was suggested that water molecules were able to penetrate between the metal islands and the substrate to lower the metal/substrate bonding energy and to facilitate migration of the metal crystal. Thus, a highly stable electrocatalyst that has stronger corrosion resistance and sintering resistance has to be developed for the H_3PO_4/PBI HT-

PEMFC. In our group, we prepared a Pt_4ZrO_2/C catalyst [21], which showed a higher stability than the Pt/C catalyst in a preliminary experiment. This catalyst would be a good candidate for the H_3PO_4/PBI HT-PEMFC.

Fig. 6 shows the SEM images of the fresh and used MEA in cross-section. Because the MEA does not have any hot-pressure,

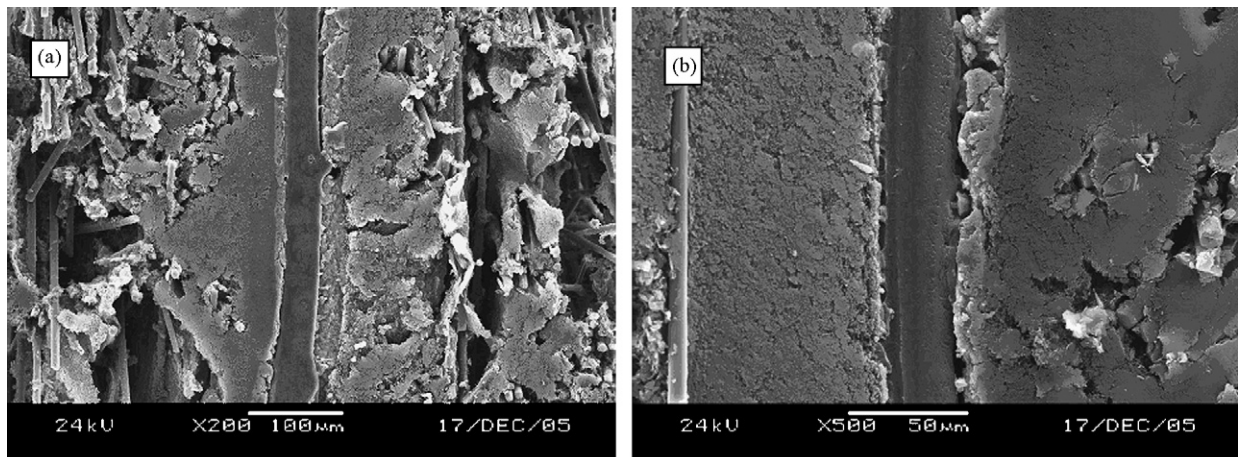


Fig. 6. SEM images of MEA in cross-section: (a) fresh MEA (after operated for 100 h); (b) MEA after the life test.

Table 1
EDS results of the section of doped PBI membrane in MEA before and after the life test (mass%)

Sample	C	N	O	P
Doped PBI (before test)	21.69	6.41	43.57	28.33
Doped PBI (after test)	29.29	9.68	43.08	17.95

there are lots of delaminations between the electrodes and the PBI membrane in the fresh and used MEA. The H₃PO₄/PBI HT-PEMFC is dependent on liquid H₃PO₄ to conduct the protons, so the delamination will not affect the cell performance too much. After the life test, the catalyst layers partly adhered to the PBI membrane and formed a semi-CCM structure. By a simple averaging calculation, the thickness of the doped PBI membrane before the life test was 38.5 μm, which was thicker than the undoped PBI membrane (35 μm) owing to the swelling of the PBI membrane. The thickness of the doped PBI membrane after the life test was 30.3 μm, which was thinner than its original thickness. It is known that the attack of HO• and HO₂• radicals produced by the incomplete reduction of oxygen on the cathode side is the main factor for the oxidative degradation of the PBI membrane [22,23]. Thus, the H₂ crossover rate through the PBI membrane will increase and the cell performance will decrease. A detailed mechanism for PBI membrane degradation is in progress.

Table 1 shows the EDS result of the section of doped PBI membrane in the MEA before and after the life test. It is noteworthy that the phosphorus content decreased greatly after the life test, which implied the leaching of H₃PO₄. In the long-term life test, the content of H₃PO₄ in the PBI membrane might be decreased by the volatilization due to the corrosion of the cell material. Unexpectedly, the leaching of H₃PO₄ decreased the proton conductivity of the H₃PO₄/PBI composite membrane and resulted in the degradation of the long-term cell performance.

4. Conclusions

A 600 h performance degradation of a high temperature PEMFC based on H₃PO₄-doped PBI has been studied. During the life test, the particle size of the electrocatalysts increased with test time, and the sintering rate was faster in the cathode than in the anode. This difference was attributed to the different environments of potential and water vapor density of the cathode and anode, which sped up the agglomeration of Pt/C cathode catalyst particles. SEM characterization indicated that the degradation of the PBI membrane occurred after the life test, which may be due to the attack by HO• and HO₂• radicals produced by the incomplete reduction of oxygen on the cathode side. EDS results showed the leaching of H₃PO₄ from the PBI

membrane, which may decrease the proton conductivity of the H₃PO₄/PBI composite membrane. In brief, it could be deduced that the agglomeration of the Pt/C catalysts in the electrodes, the physical degradation of the PBI membrane and the leaching of H₃PO₄ from the PBI membrane are the major reasons for the performance degradation of the H₃PO₄/PBI HT-PEMFC.

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