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The stability of Pt/C catalyst in H_3PO_4/PBI PEMFC during high temperature life test

Yunfeng Zhai [a,b], Huamin Zhang [a,*], Danmin Xing [a], Zhi-Gang Shao [a]

[a] Lab of PEMFC Key Materials and Technologies, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

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Abstract

The stability of Pt/C electrocatalyst was investigated by a series of intermittent life tests (100, 300 and 520 h) of single proton exchange membrane fuel cell (PEMFC) with phosphoric acid doped PBI (H_3PO_4/PBI) membranes at high temperature. The electrochemical surface area (ESA) loss of cathode electrocatalyst was investigated by electrochemical techniques (cyclic voltammetry, CV). During the first about 300 h, the ESA decreased fast from 17.2 to 7.8 $m^2\,g_{Pt}^{-1}$ (about 55%), and had only a small decrease (about 5%) in the following 210 h. The tested cathode catalysts were analyzed by transmission electron microscopy (TEM) and X-ray diffraction (XRD) to determine the degree of electrocatalyst sintering. The results showed that the Pt particle size in the cathode increased from 4.0 to 8.3 nm before and after 300 h but it had no obvious growth in the further life tests. The tested MEA was also analyzed by energy dispersive X-ray (EDX) to investigate the platinum deposition in H_3PO_4/PBI membrane. Platinum did not be found in the tested H_3PO_4/PBI membrane. Above results indicated that the agglomeration of Pt particle should be responsible for the ESA loss of Pt/C electrocatalyst. The further analyses on TEM data suggested that agglomeration of platinum particles occurred via coalescence mechanism on carbon at the nanometer scale.

Keywords: High temperature PEMFC; PBI/H_3PO_4; Platinum electrocatalyst; Electrochemical surface area; Coalescence mechanism

1. Introduction

The proton exchange membrane fuel cells (PEMFCs) have been considered as one of the most promising clean energy technologies and suitable primary power source for transportation and stationary applications [1]. Considering some technical and economic challenges, more and more attention has been paid on high temperature (>100 °C) operation of PEMFC due to its greater tolerance to impurities in the fuel stream, easier water-thermal management and faster electrode kinetics [2]. Phosphoric acid doped polybenzimidazole (H_3PO_4/PBI) membrane system is one that has been investigated intensively and used more successfully [3] for PBI possess excellent thermo-chemical stability and mechanical properties, lower gas permeability [4] and good proton conductivity after doped with H_3PO_4 at elevated temperature (200 °C) [5,6].

In general, the stability is the most consideration for the real application and commercialization of fuel cells, and the stability and durability of electrocatalyst is an important factor limiting the life of PEMFCs. The stability and durability of Pt/C electrocatalyst in mid-low temperature PEMFCs with Nafion membrane have been widely investigated. Cheng et al. [7] investigated the change of Pt/C catalyst by a series of single cell life tests. They found that the Pt particle size increased with cell operating time, and which resulted in the decrease of the cathode electrocatalyst activity. Borup et al. [8–12] studied the stability and durability of Pt/C catalyst using artificial potential cycling. Similarly, they found the Pt particle size increased with cycling time. They also detected that Pt dissolution and deposition in the polymer electrolyte membrane was another reason for ESA loss of cathode catalyst, in especially, when a higher cycling potential was used. However, the detailed study on the stability of Pt/C electrocatalyst in PBI/H_3PO_4 high temperature PEMFC has not been reported.

In our previous works [13], we studied the performance degradation of PBI/H_3PO_4 high temperature PEMFC during

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* Corresponding author. Tel.: +86 411 8437 9072; fax: +86 411 8466 5057.
E-mail address: zhanghm@dicp.ac.cn (H. Zhang).

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constant current life test. The results showed that the performance started to reduce after an about 90 h activation. The ESA loss of the platinum catalysts in the cathode occurred and the particles sizes of Pt agglomerated seriously during the life test.

In this study, intermittent life tests were conducted with a series of PBI/H_3PO_4 high temperature PEMFC single cells. Constant current performance curves were recorded and electrochemical method (CV) was applied to study the ESA loss of cathode catalysts during the life tests. The transmission electron microscopy (TEM) and X-ray diffractometer (XRD) were used to detect the increase in particle size of the cathode platinum after 100, 300 and 520 h intermittent operation. The tested MEA was also analyzed by energy dispersive X-ray (EDX) to investigate the platinum deposition in H_3PO_4/PBI membrane.

2. Experimental

2.1. Electrode preparation and single cell test

Catalyst ink was prepared by adding catalyst powder (commercial 47.6% Pt/C from TKK, Japan) into PBI and PVDF solutions in *N*-methyl-2-pyrrolidone (NMP). After dispersed under ultrasonic for 30 min and stirred for 12 h, the catalyst ink was spread on the wet-proofed GDL (SGL GDL 31 BC, 300 μm of thickness) evenly by a tape-casting technique. The electrode was prepared by drying at 80 °C for 2 h and 120 °C for 0.5 h in an inert ventilated oven. The average thickness of catalyst layer was 30 μm, and the mean platinum loading in the electrode was 0.75 mg cm^{-2}. In this work, the same electrode was used in both the anode and cathode.

After electrode was prepared, the electrodes and H_3PO_4 doped PBI membrane (PBI membrane, 36 μm of thickness, prepared by my co-worker according to US005525436A, was immersed in 85% H_3PO_4 for 20 min to obtain proton conductivity) were assembled in a homemade single cell with graphite bipolar plates and gold-plated copper end plates. A trinal serpentine flow field was machined into each graphite plate. The geometrical areas of electrodes were about 7.0 cm^2; the assembling torque was 3 N m. The single cell was installed in our homemade fuel cell test platform. The fuel cells were operated at 150 °C with hydrogen and oxygen without humidification at 0.1 MPa pressure and a flow rate of 100 ml min^{-1}.

In this study, to obtain the Pt/C endured different test periods, a series of reproducible and identical single cells were tested under the same operating condition for 100, 300 and 520 h, respectively. All the single cells were operated intermittently (running from 8:00 to 20:00) at constant current electro-load using our homemade test platform [14]. During the single cell running at constant current (700 mA cm^{-2}), every 2 h the voltage was recorded. The polarization curves were recorded every 24 h on our homemade platform, the voltages were recorded when them reached steady state at different current.

2.2. Electrochemical and physical characterization

2.2.1. Cyclic voltammetry—investigating Pt active surface area loss

The ESA of cathode was tested by the following method once in every 24 h. The cathode side was purged by nitrogen and hydrogen flowed though anode side at 150 °C and 0.1 MPa pressure. The electrochemical working station comprised EG&G model 1025 FRA and model 273A. In a three-electrode configuration: working electrode (WE) was the cathode and the anode acted as reference electrode (RE) and counter electrode (CE) simultaneously. The cathode was cycled between 0 and 0.8 V (referenced to the anode, i.e. the RHE potential scale) at the sweep rate of 20 mV s^{-1}. The cycling was done five cycles.

2.2.2. XRD analysis

After each test, the MEA was carefully removed from the cell, an appropriate strip was first cut from the MEA, and electrode sample was prepared carefully by peeling off the MEA. X-ray diffraction pattern of the sample was collected using a Philips X'Pert PRO X-ray diffractometer (XRD) with copper rotating anode (Cu Kα radiation, $\lambda = 1.54056$ Å, at 40 kV/40 mA). A continuous scan rate of 5° min^{-1} from 20° to 90° of 2θ was used for all samples. In order to reduce the effect of the polymer in the electrocatalyst layer, the untested Pt/C electrode was also analyzed to compare with the tested electrodes.

2.2.3. TEM analysis

The powder samples of Pt/C electrocatalyst were scraped from the surface of the cathode sample by a razor blade. The samples were first immersed in ethanol and subsequently ultrasonicated for 5 min under high frequency to disperse the particles. The suspensions were then deposited on holey amorphous carbon film on a Cu grid for TEM observation. The powder samples were observed in a JEOL JEM-1200EX operated at 120 keV.

2.2.4. EDX analysis

After 520 h lifetime test, a small piece of MEA was cut from the MEA, the elemental distribution of Pt in the cross-sections of MEA and the H_3PO_4/PBI membrane were analyzed by energy dispersive X-ray (EDX, Oxford-Inca). The scan area of electronic probe was about 20 μm × 30 μm.

3. Results and discussion

3.1. Single cell life test

The performance at constant current (700 mA cm^{-2}) and the open current voltage (OCV) of the H_2/O_2 fuel cell with H_3PO_4/PBI membrane during the 520 h life test are shown in Fig. 1. It can be seen that, the performance gradually increased in the first about 100 h; in the following about 400 h it decayed from 0.620 to 0.575 V with a rate of about 0.11 mV h^{-1}; and in the last about 20 h the voltage decreased a lot. It should be noted

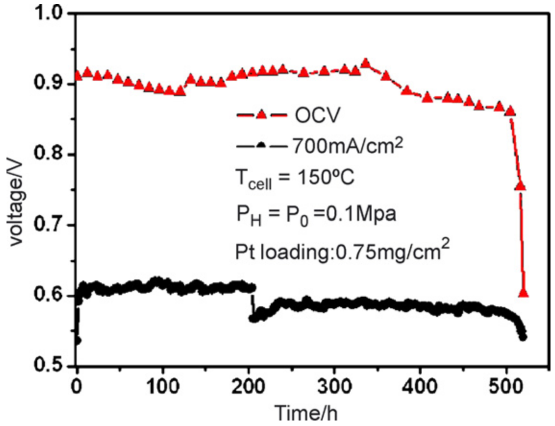


Fig. 1. The performance and OCV of the single cell during the 520 h intermittent test.

that a little performance decrease at 204 h was due to the inleakage of air to the inlet O_2, and the performance recovered after the inleakage stopped (at 240 h), but these fluctuations did not affect the overall degradation tendency. From the OCV curve, we can see that there was little variation during the first about 340 h; and then the OCV decreased from 0.910 to 0.852 V in the following about 170 h; especially in the last about 10 h, the OCV decreased rapidly due to the mechanical properties degradation of H_3PO_4/PBI membrane [13]. During the 520 h life test, polarization curves were recorded every 24 h, the polarization and power density curves are shown in Fig. 2. It is obvious that the cell reaches its best performance at about 96 h, the maximum power density reaches near 0.90 W cm^{-2}, and the power density decreases to 0.70 W cm^{-2} at about 504 h. The results coincide with the constant current performance degradation test.

Generally, the cell voltage losses can be kinetic, ohmic, and mass-transport related. According to Williams et al. [15], the actual cell voltage can be briefly written as:

$$V_{\mathrm{cell}} = V_{\mathrm{OCV}} - \eta_{\mathrm{act}} - \eta_{\mathrm{ohm}} - \eta_{\mathrm{trans}} \tag{1}$$

Here V_{cell} is the experimental cell voltage from an experimental polarization curve; η_{act} the electrode activation overpotential; η_{ohm} the ohmic overpotential; η_{trans} the mass-transport overpotential; V_{OCV} is the equilibrium cell voltage at open circuit. From Figs. 1 and 2, we can see that the influence of η_{trans} on V_{cell} is no obviously in the whole 520 h test, the V_{OCV} and η_{ohm} have no distinct vibration during the first 300 h test, but in the following test, the V_{OCV} decreases a little and the η_{ohm} increases. Those changes are results of the increase in permeability of membrane and the increase in pure ohmic resistance of the single cell due to the degradation of PBI membrane [13]. These results suggest that the main reason for cell voltage decay is the degradation of PBI membrane during the last about 200 h test, but in the first about 300 h, which is not the main reason for the decay.

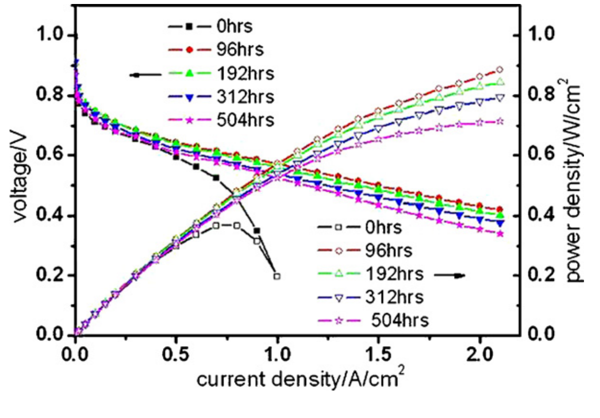


Fig. 2. The polarization and power density curves at different test time.

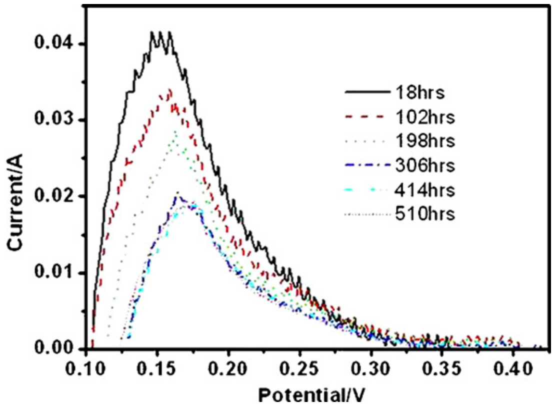


Fig. 3. The hydrogen desorption oxidation curves derived from the cathode CV curves during the 520 h intermittent test.

3.2. Cyclic voltammetry

It is known that, the ESA loss of the catalysts is the main cause of the decay in performance of phosphoric acid fuel cell (PAFC) or mid-low temperature PEMFC, which occurs early in the life of a cell, and the ESA loss of platinum at cathodes is much larger than that at anodes [10]. With this in mind, the ESA loss of platinum in cathode for the H_3PO_4/PBI high temperature PEMFC during the 520 h life test was characterized by CV analysis. The hydrogen oxidation desorption curves derived from the CV analysis are shown in Fig. 3. It is obviously that the activity of cathode reduced rapidly during the first about 300 h life test and decreased a little during the following about 210 h test. To determine the ESA in the cathode, the charge due to

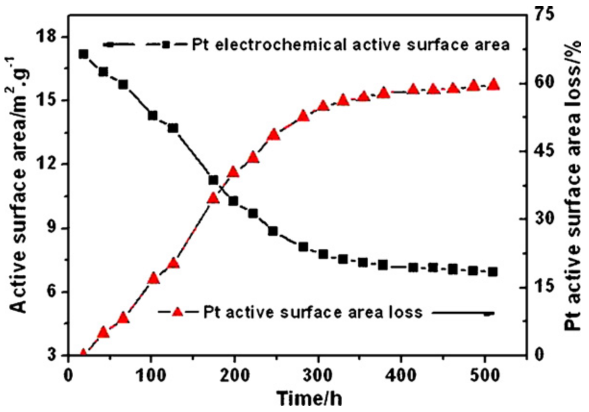
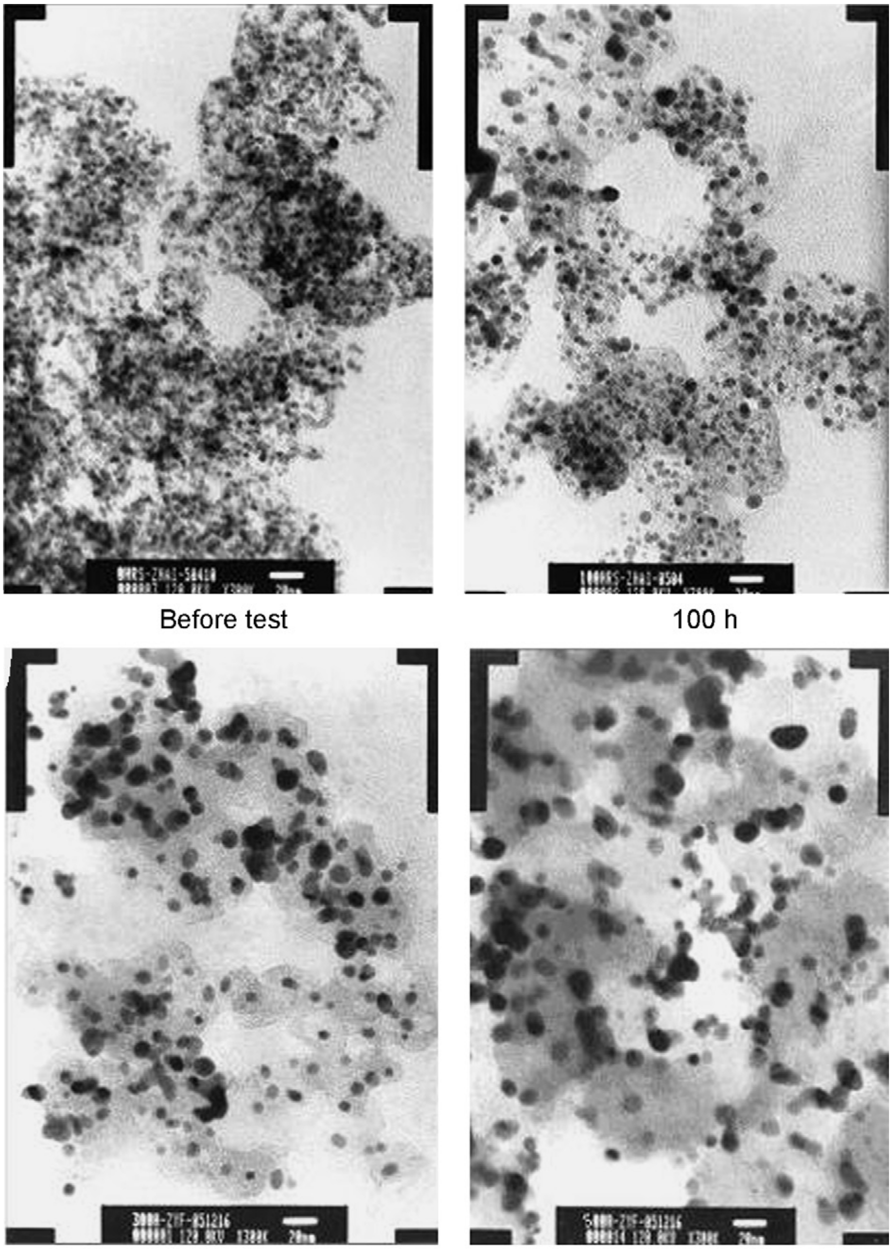


Fig. 4. The Pt electrochemical surface area calculated using Eq. (2) during the 520 h intermittent test.



Before test

100 h

300 h

520 h

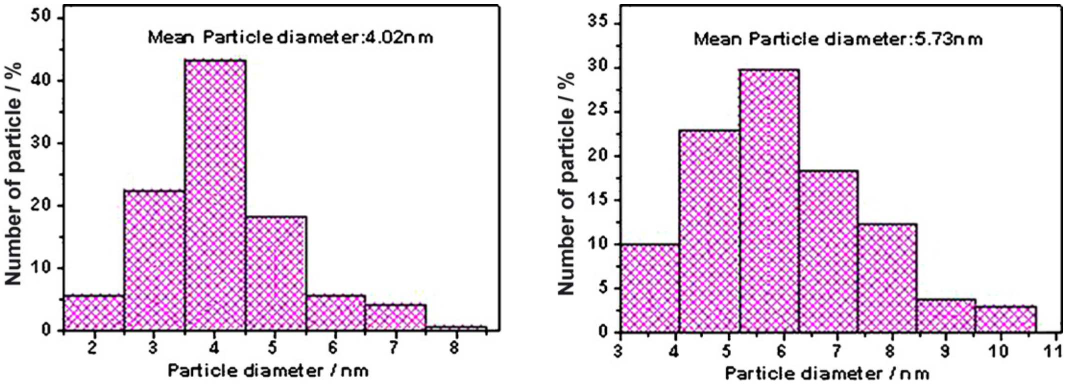
Fig. 5. The TEM photographs of Pt/C in cathodes before and after 100, 300 and 520 h intermittent test.

adsorbed hydrogen on Pt catalyst was obtained by integration of the corresponding peak in the voltammogram with a double layer charging current as a base line. The ESA of Pt/C electrocatalyst in cathode was calculated with the following equation [16]:

$$S_e = \frac{100A_d}{cmv} \tag{2}$$

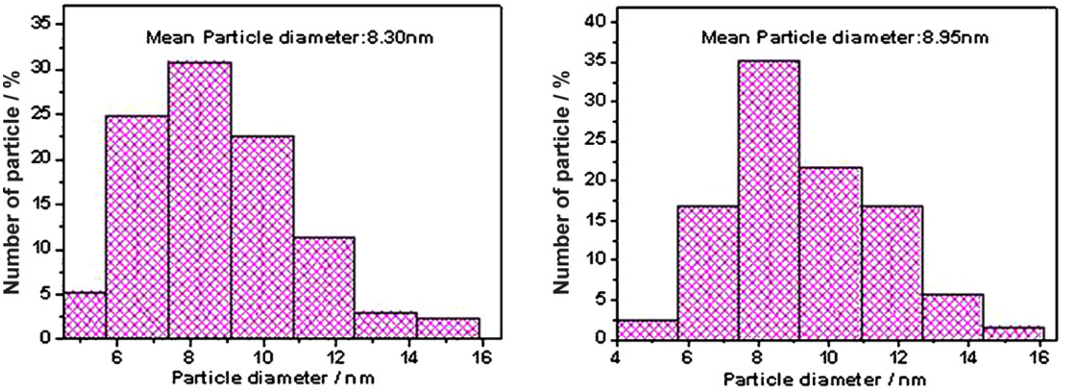
Here S_e is the ESA, $m^2\,g^{-1}$; A_d the integral area of hydrogen oxidation desorption peak in CV curve, A V; c the electrical charge associated with monolayer adsorption of hydrogen on Pt surface, $c = 0.21$ mC cm^{-2}; m the Pt weight in the cathode, mg; v is the sweep rate of CV, mV s^{-1}.

As shown in Fig. 4, during the first about 300 h, the ESA of Pt/C electrocatalyst in cathode decreased fast from 17.2 to 7.8 $m^2\,g_{Pt}^{-1}$ with a rate of 0.03 $m^2\,h^{-1}\,g_{Pt}^{-1}$, losing about 55%, in the following 210 h, the ESA decreased a little, only about 5%. The decrease in ESA brings on an augmentation in the electrode activation overpotential,η_{act}. Comparing with Eq. (1) and Fig. 2, it is evident that the ESA lose of Pt/C in cathode should be response for the cell voltage decay during the first 300 h test. In addition, it should be remarked that the ESA of Pt/C electrocatalyst in this test was much lower than that in mid-low temperature PEMFC with Nafion membrane, which was about 40–60 $m^2\,g_{Pt}^{-1}$ in generally. According to literature [17], the Pt/C electrocatalyst suffered from the strong adsorption effect of anions onto the active sites of catalysts in H_3PO_4 solution. Therefore, the strong



Before test

100 h



300 h

520 h

Fig. 6. The histogram of Pt/C particles sizes distribution from the TEM photographs.

adsorption effect of anions should be responsible for the lower ESA of Pt/C electrocatalyst in the H_3PO_4/PBI high temperature PEMFC.

3.3. TEM and XRD analysis

In generally, the ESA loss can be ascribed to several factors, such as Pt particle size growth (Pt sintering) and Pt dissolving into the solution. In order to detect the reason for the ESA loss of the electrocatalyst, the morphology of catalyst on the cathodes were investigated by TEM and XRD analysis before and after life tests. Fig. 5 presents the TEM images of electrocatalyst on cathodes before and after the life tests. Their particle size distributions for the electrocatalyst were obtained by manually measuring all the particles from the bright-field micrographs, as shown in Fig. 6. The mean particle diameter $\bar{d}_n$ was calculated with the following formula [10]:

$$\bar{d}_n = \frac{\sum_{i=1}^{n} d_i}{n} \qquad (3)$$

Here $\bar{d}_n$ is the averaged diameter of platinum particles in nm.

Comparing all the TEM images in Fig. 5, it is obvious that the size of Pt particles increases after the life tests. Some coalescence of particles is apparent after only 100 h; however, numerous small particles are still evident. After 300 h, the majority of small crystallites appear to be absent. From Fig. 6, it can be seen that the mean particle size increased from 4.0 to 9.0 nm during 520 h life test, the distribution of Pt particle sizes became gradually broader with the prolonging of test time and the number of Pt particles with small diameters (4.0 nm) was largely decreased, and larger Pt particles (larger than 10.0 nm) appeared.

To obtain a comprehensive analysis, the Pt catalysts on the electrode endured different life test durations were also characterized by XRD, and the results are shown in Fig. 7. The characteristic diffraction peaks of the face centered cubic structure are clearly detected in all the electrode samples. The diffraction peaks at 2θ values of 39.8°, 46.3°, 67.5° and 81.4° are associated with the Pt (1 1 1), (2 0 0), (2 2 0) and (3 1 1) lat-

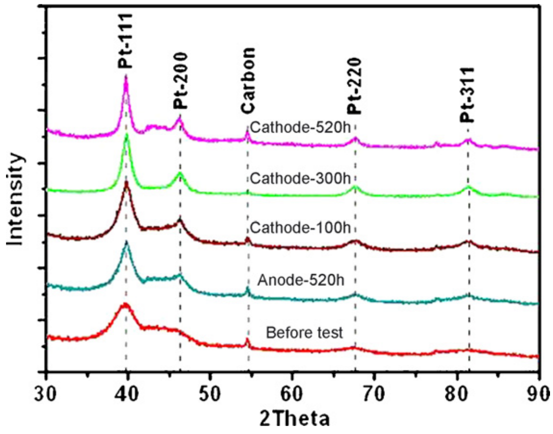


Fig. 7. The XRD patterns of Pt/C in cathodes before and after 100, 300 and 520 h intermittent test.

tice planes, respectively. All the characteristic peaks of Pt in cathode become sharper following the longer test time, which indicates that the Pt particle grew gradually during the lifetime test. It should be noted that the diffraction peaks of Pt in the 520 h-tested anode were much broader than that in the 520 h-tested cathode and had no significant change compared with before test, this suggests that the Pt particle growth in the cathode was more serious than that in the anode. The similar result was also detected by Cheng et al. [7] in mid-low temperature PEMFC. The average particle sizes of Pt in all cathodes were calculated with Scherrer's formula on the basis of all the diffraction peaks. The growth of Pt particle sizes with duration time is shown in Fig. 8. For all the samples, the averaged diameter determined from X-ray powder diffraction is slightly different from the averaged one from TEM measurement. It is believed that this difference results from the fact that platinum particles smaller than 1 nm is poorly represented in the TEM measurements [16], therefore, the averaged diameter from TEM would be slightly larger than that of X-ray diffraction. Except this difference, an accordant result was obtained by the two techniques: the Pt particles size increased rapidly during the first 300 h, and then grew a little in the following 220 h. That is to say, a considerable agglomeration has occurred in cathode electrocatalyst during the first 300 h life test.

In theory, specific surface area of Pt/C electrocatalyst can be computed from the averaged diameter of platinum crystals from TEM and X-ray diffraction data according to the following relationship [18]:

$$S_{\mathrm{v}} = \frac{6000}{\rho d} \tag{4}$$

Here S_{v} is the specific surface area in $\mathrm{m}^2\,\mathrm{g}^{-1}$, d the averaged diameter of Pt particle, and ρ is the density of Pt, 21.45 $\mathrm{g\,cm}^{-3}$. The specific surface areas of Pt particles calculated from the averaged diameters by TEM using Eq. (4) are shown in Fig. 9. Compared with Fig. 4, it is interesting to note that the change in specific surface areas of Pt particles is in good agreement with that in ESA throughout the 520 h life test, and for all the samples, roughly 24% of the specific surface area of Pt particles is electrochemically active. As to the lower efficient electrochemically active area, we believe that the large difference could result from the fact that the strong adsorption effect of $H_2PO_4^-$ anions onto the active sites of Pt catalysts and the agglomeration of platinum particles on the carbon support, in addition to the platinum particle shape factor and platinum particle contact area with carbon support and the polymers in the catalyst layer. In a word, the increase in the averaged diameter of platinum particles corresponds well with the reduction in the active area of Pt/C electrocatalyst in the tested MEA cathode.

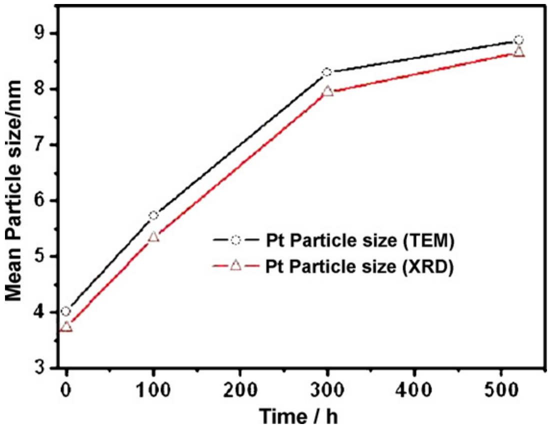


Fig. 8. The change of Pt particles size in cathodes with test time.

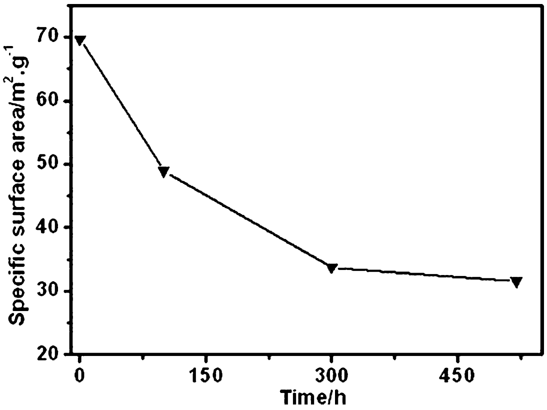


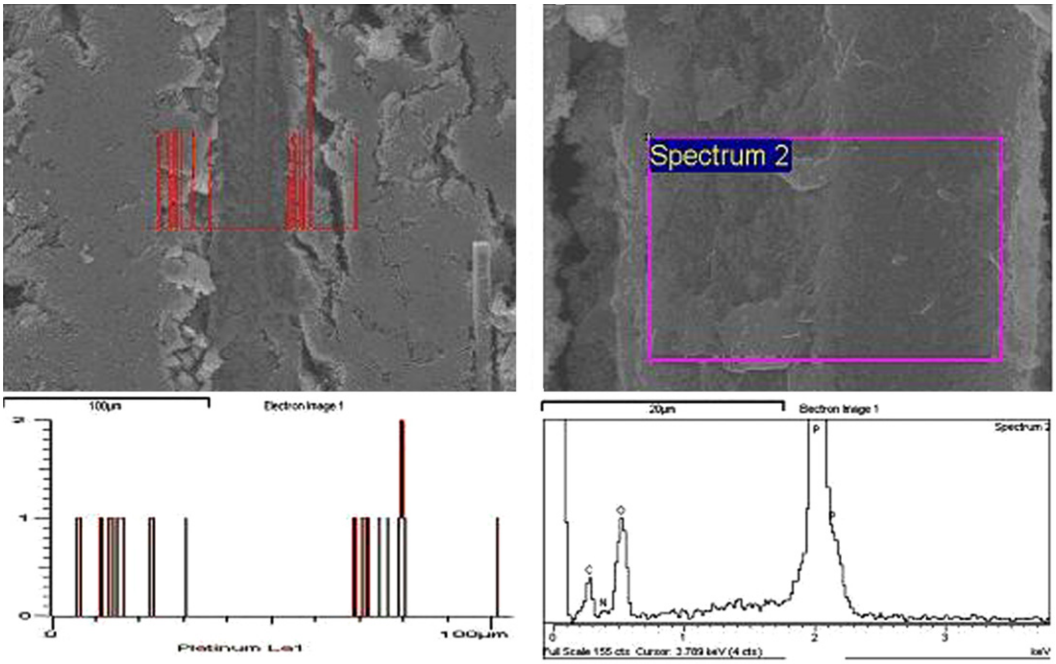
Fig. 9. The specific surface area loss of Pt particles in cathodes calculated using Eq. (4) with time.

3.4. EDX analysis

With regard to the dissolution of platinum, Borup et al. [8–12] have investigated aborative by cyclic voltammetry acceleration test in mid-low temperature PEMFC with Nafion membrane. They found that platinum deposited in the polymer electrolyte membrane near a cathode catalyst layer and the ESA loss and Pt particle size growth in cathode depended on the cycle number and the upper potential limit. In addition, Honji et al. [19] also detected that the dissolution of Pt was considerable in H_3PO_4 at high temperature only when the potential over 0.8 V. In this paper, the 520 h-tested MEA was also analyzed by EDX to detect the Pt in the H_3PO_4/PBI membrane. The EDX spectrums in line and area of the 520 h-tested MEA cross-section are shown in Fig. 10, respectively. As shown in Fig. 10, platinum element is not found in line of crossover the tested H_3PO_4/PBI membrane or in the whole area (20 μm × 30 μm) of the tested H_3PO_4/PBI membrane cross-section. This result implies that the dissolution of Pt is neglectable in this single cell life test. The reason may be that the applied potential on the cell is never higher than 0.8 V during the whole test time. Together with the results from TEM and XRD data, it is proved that the catalyst agglomeration caused the decrease of ESA in H_3PO_4/PBI high temperature PEMFC during the life test.

3.5. Agglomeration mechanism of Pt particles

In general, small metal particles grow on a support via two possible mechanisms: the coalescence growth and the Ostwald ripening process [20]. In the first case, the growth is caused



(a) (b)

Fig. 10. The EDX analysis on platinum in cross-section of 520 h-tested MEA: (a) in line and (b) in area (20 μm × 30 μm).

by cluster–cluster collisions and it is a random process accompanied by liquid-like coalescence of the particles. Whereas in the second case, the growth takes place by atom migration from small crystals to large ones, the driving force of this process being the minimization of the clusters Gibbs free energy. Ascarelli et al. [21] presented a simple method to distinguish between these different growth mechanisms and discussed their applications to Pt/C nanoparticle electrocatalyst with different size distributions. For the coalescence process, particles size distributes in a typical log-normal distribution: the distribution is negligible below a certain finite size and has a maximum on the small-particle side and a tail towards the large-particle side; and for the Ostwald ripening process, the distribution is negligible above a certain finite size, and characterized by a tail towards the small-particle side and has a maximum on the large-particle side.

In this study, the Pt particles size distributions from Fig. 6 are plotted in Fig. 11. It can be seen that, before the test, the Pt particles size distributes in a typical normal distribution, after the different life test time, all the Pt particles size distributions show nearly typical log-normal distribution: the particles distribution is negligible below a certain finite size, has a maximum on the small-particle side and a tail towards the large-particle side. According the method by Ascarelli et al. [21], the Pt/C electrocatalyst in the cathodes agglomerated via coalescence mechanism for particle–particle growth during the H_3PO_4/PBI high temperature PEMFC life test.

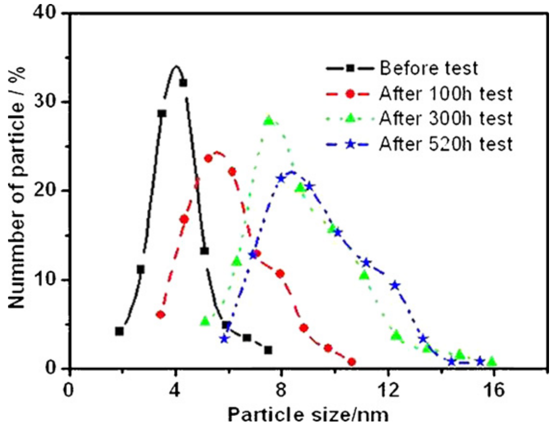


Fig. 11. The distribution curves of Pt particles sizes from the TEM photographs.

4. Conclusions

In conclusion, during the H_3PO_4/PBI high temperature PEMFC single cell life tests, a considerable performance degradation accrued due to the significant ESA loss of Pt/C cathode electrocatalyst, which resulted from the seriously agglomeration of Pt particles on carbon support in the first about 300 h. In the farther life tests, the growth of Pt particles in cathode was not obvious and the ESA of Pt/C electrocatalyst in cathode had only a little loss. On the other hand, the absence of platinum in the tested H_3PO_4/PBI membrane suggested that the dissolution of platinum had not probably happened in the H_3PO_4/PBI high temperature PEMFC single cell life tests. Which and the particles size of the tested Pt electrocatalyst distributes in log-normal distribution suggested that the agglomeration of platinum particles occurred via coalescence mechanism for particle–particle growth at the nanometer scale.

Acknowledgements

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