RESEARCH ARTICLE

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Accelerated life-time test of MEA durability under vehicle operating conditions in PEM fuel cell

Abstract In this paper, a novel accelerated test method was proposed to analyze the durability of MEA, considering the actual operation of the fuel cell vehicle. The proposed method includes 7 working conditions: open circuit voltage (OCV), idling, rated output, overload, idling-rated cycle, idling-overload cycle, and OCV-idling cycle. The experimental results indicate that the proposed method can effectively destroy the MEA in a short time (165 h). Moreover, the degradation mechanism of MEA was analyzed by measuring the polarization curve, CV, SEM and TEM. This paper may provide a new research direction for improving the durability of fuel cell.

Keywords polymer electrolyte membrane fuel cell, accelerated life-time test, load cycling test, durability

1 Introduction

Proton exchange membrane fuel cell (PEMFC), which is a kind of clean energy with high efficiency and environment friendly, has become one of the research hotspot in the field of energy [1–3]. Currently, the related research on PEMFC has been focused on improving its performance [4], prolonging its durability [5], and reducing its cost [6]. The poor durability of PEMFC is one of the major bottlenecks that impede its commercialization in the vehicle filed.

Lots of research show that the performance loss in PEMFC after a long-running process mainly occurs in the membrane electrode assembly (MEA), such as the degradation of catalyst [7] and membrane [8]. Therefore, it is of great importance to find a simple and effective way to prolong the durability of MEA. At present, the durability of MEA is mainly evaluated using the steady-state life test [5,9]. However, this method is time-consuming and expensive, which seriously hinders its large-scale practical application. Therefore, researchers have proposed to evaluate the durability of MEA using the durability accelerated test [10–12]. The accelerated test not only reduces the testing time and saves cost, but also fits well with the steady-state life test result. Therefore, the accelerated test method is proven to be an effective way to predict and analyze MEA's life.

A series of accelerated test methods, such as humidity cycle [13], open circuit voltage [14], load cycle [15], voltage cycle test [16], hot-cold cycle [17], cold start [18], fuel shortage [19], start-stop cycles [20] and pollution poisoning [21] have been developed, providing a theoretical basis and experimental method to analyze the durability failure mechanism of MEA. Usually, the working conditions in vehicle fuel cell includes OCV, idling, rated output, overload, idling-rated cycle, idling-overload cycle, and OCV-idling cycle. However, the conventional accelerated test method only includes one or two conditions, without considering the actual operation of the fuel cell vehicle (all working conditions). Therefore, it is necessary to establish a novel accelerated test method to detect the durability of MEA, taking into consideration the 7 of working conditions in the actual operation of fuel cell vehicle.

In this paper, a novel, effective evaluation method to analyze the durability of MEA was proposed by taking into consideration the 7 working conditions of fuel cell vehicle in the actual operation. The characterizations of MEA before and after accelerated test were conducted to analyze the material degradation and failure mechanisms.

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2 Evaluation of vehicle accelerated test method

2.1 Vehicle accelerated test method

The operating condition of the proposed vehicle

accelerated test is shown in Fig. 1 and listed in Table 1. The start and end stages are using the OCV condition with 10 minutes, which simulates the start and stop phases in the fuel cell vehicle. The idling condition simulates the membrane and catalyst damage in the fuel cell vehicle at idling operation (The low efficiency in idling operation will cause less water to be produced by reaction. At the same time, the fuel cell operating voltage is very high (>0.8 V). These will cause the damage and failure of PEM and catalyst in MEA). The rated condition simulates the working state in the fuel cell vehicle. The overload condition simulates the overload state in the fuel cell vehicle. Moreover, the idling-rated cycle condition, the idling-overload cycle condition, and the OCV-idling cycle condition are designed due to the fact that in the fuel cell running state is not independent.

This proposed vehicle accelerated test condition has the following advantages. It simulates the actual operating environment of the vehicle fuel cell, and the 7 accelerated conditions are real existence in the vehicle fuel cell running. It can effectively destroy the MEA in a short time (165 h). It uses a voltage control mode, making voltage control easier than the conventional control and power control, while both the decay of catalyst and the corrosion of carbon are related to the potential. It uses different humidity in different operating condition. When the fuel cell is working in the OCV and the idling condition, it requires a low humidity operating environment. When the fuel cell is working in the rated condition and the overload condition, it requires a high humidity operating environment. So this frequent humidity cycle will accelerate the degradation of the PEM and catalytic layer. Therefore, the humidity in OCV, in the idling condition, and in the OCV-idling condition is set at 30%, while the humidity in other conditions is set at 70%.

2.2 Evaluation method

In this experiment, the MEA performance is evaluated by using the voltage loss of the polarization curve (600 mA/cm²), the electrochemical surface area (ECSA) of the catalyst, and the hydrogen permeability. Voltage loss is the most direct expression for fuel cell performance loss. The current density is chosen to be 600 mA/cm² because the polarization curve of MEA is in the ohmic polarization region, and the fuel cell does not experience great changes in its performance. The decrease of ECSA is one of the main reasons for the linear attenuation of fuel cell performance, which mainly reflects the loss of Pt in the catalyst. The hydrogen permeability is the main degradation symbol of the fuel cell PEM, whose sudden increase indicates that the perforation in the PEM leads to the direct reaction of hydrogen and oxygen.

3 Experiment and characterization

3.1 Preparation of MEA

In this experiment, the standard MEA used is produced by Wuhan New Energy Co., Ltd. The active area is 25 cm², the PEM is the Nafion211 thin film, and the catalyst is the 60% Pt/C commercial catalyst with the Pt loading of 0.4 mg/cm².

3.2 Single cell testing

This experiment uses a single cell, whose active area is 25 cm², and the flow channel is single snake-type flow channel with the PTFE for sealing. N_2 gas is used to check the impermeability after single cell assembly, and the
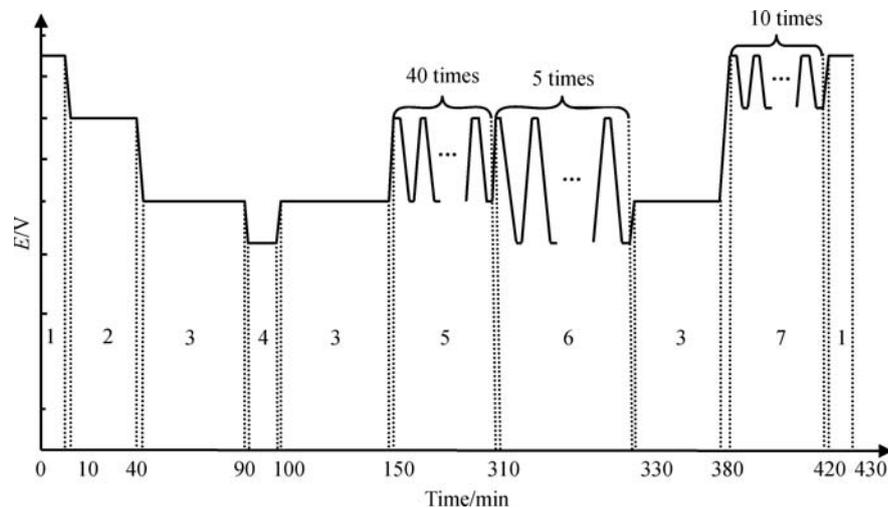

Fig. 1 Testing voltage in different working conditions versus time

leakage in anode and cathode is less than 0.2 mL/min.

3.3   Durability testing

Before the vehicle accelerated test, the fuel cell is activated by 3 time cycle test until the performance comes to a stable state. The fuel cell temperature is 65°C, the gas temperature and dew point are both 65°C, the humidity is 100%, and the excess coefficient of H_2/air is 1.5/2.5. The test condition of fuel cell is kept at 600 mA/cm^2 for 6 hours until the performance of the fuel cell is no longer increased.

The vehicle accelerated test conditions of this experiment are listed in Table 1. The fuel cell temperature is 65°C and the excess coefficient of H_2/air is 1.5/2.5. The humidity in OCV, idling condition, and OCV-idling condition are 30%, and the humidity in rated condition, overload condition, idling-rated condition and idling-overload condition are 70%. The polarization curve, cyclic voltammetry curve and linear scan of the fuel cell are tested after each condition. The SEM, TEM and XPS are measured after the vehicle accelerated test.

3.4   Equipment and characterization

In this experiment, the G50 fuel cell test platform (Canada Greenlight Company) is used to test the fuel cell performance. The resistance meter (Japan Rizhi Company) is used to test the fuel cell resistance.

The Autolab electrochemical workstation (Netherlands, PGSTA30) is used to test the cyclic voltammetry and linear scans. The electrode to be tested is used as the working electrode and purge with N_2 gas. The other electrode is used as the reference electrode and purge with H_2 gas. The cyclic voltammetry curve test is conducted at a scanning speed of 50 mV/s and a scanning range of 0.05–1.25 V. The linear scanning test is conducted at a scanning speed of 2 mV/s and a scanning range of 0–0.7 V.

4   Results and discussion

Figure 2(a) depicts the polarization curves and resistance

of PEMFC after each durability test cycle. The experiment data demonstrate that the fuel cell performance gradually decreases with the increase of cycle numbers. After 23 cycles, the voltage of MEA dropped from 0.692 V to 0.635 V at an attenuation rate of 8.2% and a current density of 600 mA/cm^2. Figure 2(b) illustrates the performance degradation rate under different current densities. The performance degradation rates are 1 mV/cycle, 1.61 mV/cycle, and 1.94 mV/cycle at current densities of 200 mA/cm^2, 600 mA/cm^2 and 1000 mA/cm^2, respectively. The results show that the performance degradation rate of fuel cell increases with the current density increasing. Besides, the performance degradation rate at 1000 mA/cm^2 is about twice as large as that of the low current density (200 mA/cm^2). The main reason is that the ECSA of Pt catalyst has become lower after the vehicle accelerated test (Fig. 3). With the decrease of the ECSA, the catalyst cannot provide a sufficient number of hydrogen reactive sites under high current density, so the performance loss is higher than the low current density region. More interestingly, no matter it is under low current density or high current density, the performance degradation is not a straight line down but follows a drop-increase-drop rule (Fig. 2(b)). The possible reason is the oxidation and reduction of the Pt catalyst. The reaction mechanism is shown as follows:
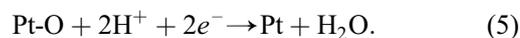
$$Pt + O_2 \rightarrow Pt\text{-}O_2, \tag{1}$$

$$Pt\text{-}O_2 + H^+ + e^- \rightarrow Pt\text{-}HO_2, \tag{2}$$

$$Pt\text{-}HO_2 + Pt \rightarrow Pt\text{-}OH + Pt\text{-}O, \tag{3}$$

$$Pt\text{-}HO + H^+ + e^- \rightarrow Pt + H_2O, \tag{4}$$

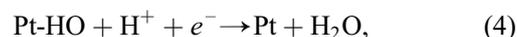$$Pt\text{-}O + 2H^+ + 2e^- \rightarrow Pt + H_2O. \tag{5}$$
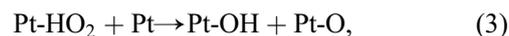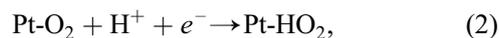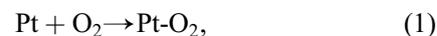
Figure 2(c) displays the relationship between the resistance and the cycle times. It can be observed that the resistance during the test is always below 2.5 mΩ, which proves that each component in MEA is in close contact.

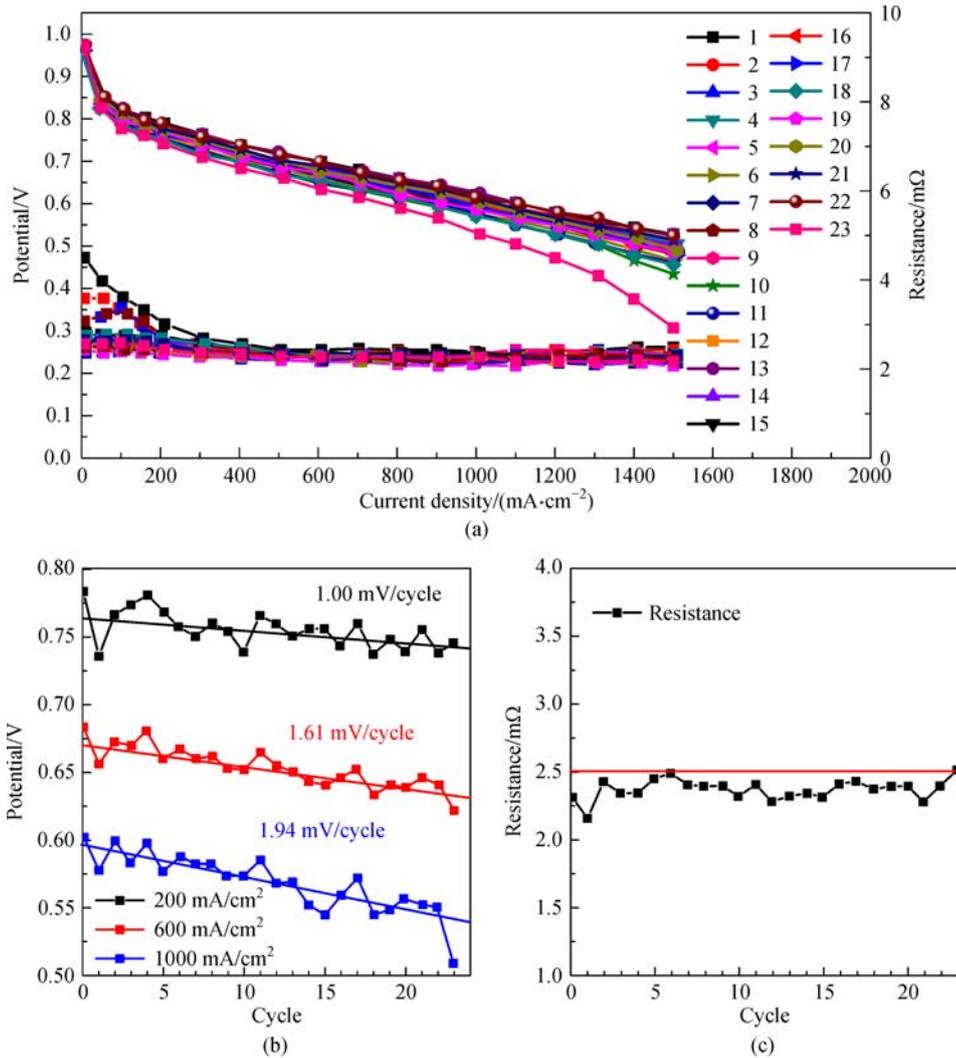The ECSA is an important indicator for the performance

Table 1   Vehicle accelerated test condition

Operation conditions	Voltage/V	Humidity (RH)/%	Time/min
OCV	OCV	30	10
Idling	0.8	30	30
Rated output	0.6	70	50
Overload	0.5	70	10
Idling-rated cycle	0.6–0.8	70	160 (40 times cycle, 2 min idling, 2 min rated)
Idling-overload	0.8–0.5	70	20 (5 times cycle, 2 min idling, 2 min overload)
OCV-idling	OCV–0.8	30	40 (10 times cycle, 2 min OCV, 2 min idling)

Fig. 2 Resistance versus cycle times
(a) Polarization curves and resistance of PEMFC after each durability test cycle; (b) performance degradation rate under current density of 200 mA/cm^2, 600 mA/cm^2 and 1000 mA/cm^2; (c) relationship between resistance and cycle times

of catalyst. Figure 3 shows the CV curves and ECSA decrease rate after different cycles in the cathode (Fig. 3(a)) and anode (Fig. 3(c)) of MEA. As the vehicle accelerated test continues, the scan area of the CV curve of MEA is gradually reduced. The hydrogen adsorption current and the desorption current gradually decrease and the oxygen adsorption potential gradually shift to the high potential. This indicates that the catalyst has degraded during the vehicle accelerated test. Compared with the decrease rate of ECSA between cathode (Fig. 3(b)) and anode (Fig. 3 (d)), it can be seen that the decay rate in cathode is significantly higher than that in anode, which is also shown in Fig. 3(a) and Fig. 3(c). After 23 cycles, the ECSA of the cathode catalyst decreased by 57% from 247 cm^2/cm^2 to 106 cm^2/cm^2. At the same time, the active area of the anode catalyst decreases from 168 cm^2/cm^2 to 114 cm^2/cm^2, a decrease of about 32%. The main reason for this is that the potential of cathode is higher than that of anode during the

test process, and the cathode catalyst is in the oxidation environment, the anode is in the reducing atmosphere, and, therefore, the catalyst of cathode is easier to be oxidized than that of anode. Moreover, the volume of hydrogen molecule is smaller than that of oxygen molecule, which is easier to penetrate through the PEM into the cathode catalyst layer, and the hydrogen and oxygen combustion reactions occur to accelerate the decay of the cathode catalyst.

In this accelerated test experiment, the humidity cycle accelerates the physical and chemical deterioration of the PEM. But after 23 cycles, the PEM does not have perforation and crack (Fig.4) and the hydrogen permeation current remains almost unchanged (Fig. 5). This proves that the durability of the PEM in MEA is not a major degradation factor, and the degradation rate of catalyst is much faster than that of the PEM.

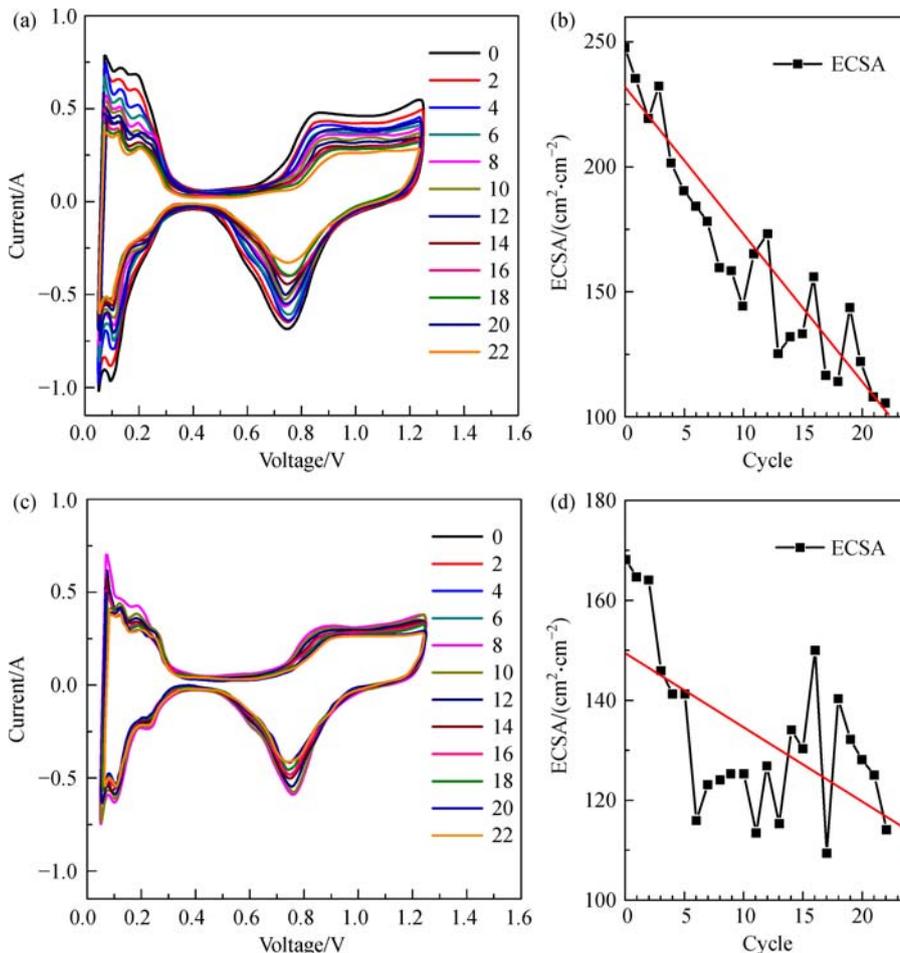Figure 4 is the cross-sectional scanning electron

Fig. 3   CV curves and ECSA decrease rate after different cycle times in the cathode and anode of MEA
(a) CV curves after different cycle times in the cathode of MEA; (b) ECSA decrease rate after different cycle times in the cathode of MEA; (c) CV curves after different cycle times in the anode of MEA; (d) ECSA decrease rate after different cycle times in the anode of MEA

microscopy (SEM) picture of the MEA before and after the vehicle accelerated test. It can be noticed from Fig. 4 that the thickness (all about 24 μm) of the PEM does not change before and after the test. This result also confirms the resistance (Fig. 2(c)) and hydrogen permeation current (Fig. 5) results. After 23 cycles, the cathode and anode catalyst layers are reduced from both 10 μm to 7 μm and 6 μm, respectively. The cathode catalyst layer is more seriously destructed than the anode catalyst layer. The possible reason is that the carbon in cathode is in a higher potential environment which is more susceptible for corrosion. If the part of carbon in cathode and anode is corroded by the accelerated test, the Pt nanoparticle will fall off, and the ECSA value will decrease. The thickness change in the cathode catalytic layer after the vehicle accelerated test shows that the corrosion of the catalytic layer begins at the interface between the membrane and catalyst layer. The possible reason for this is that the protons transfer from the anode through the PEM to the cathode, and the catalytic reaction begins at the interface.

Figure 4(c) and (d) are the distribution of the elements in

MEA before and after the vehicle accelerated test. Before the vehicle accelerated test, the cathode catalyst layer is between 0 μm and 10 μm, the anode catalyst layer is between 34 μm and 44 μm, and the middle part is PEM. The result shows that the distribution of Pt elements in the cathode and anode catalyst layer is uniform and the Pt elements are not present in the PEM. After 23 cycles, the content of Pt in the cathode catalyst layer is significantly decreased. In addition, the content of Pt in the anode catalyst layer is also decreased, but not as significant as that in the cathode catalyst layer. Moreover, the Pt element appears in the part of the PEM near the cathode catalyst layer, which indicates that the Pt particles migrate in MEA. First, the Pt particles are oxidized to Pt^{2+}, and Pt^{2+} is migrated through the Nafion resin to the PEM. When the migrated Pt^{2+} encountered the H_2 permeates from the anode, it is reduced to Pt particles and deposites in the PEM.

The morphology of the catalyst in MEA is examined by using the transmission electron microscope (TEM) (Fig. 6). In the pristine catalyst, the Pt nanoparticles are
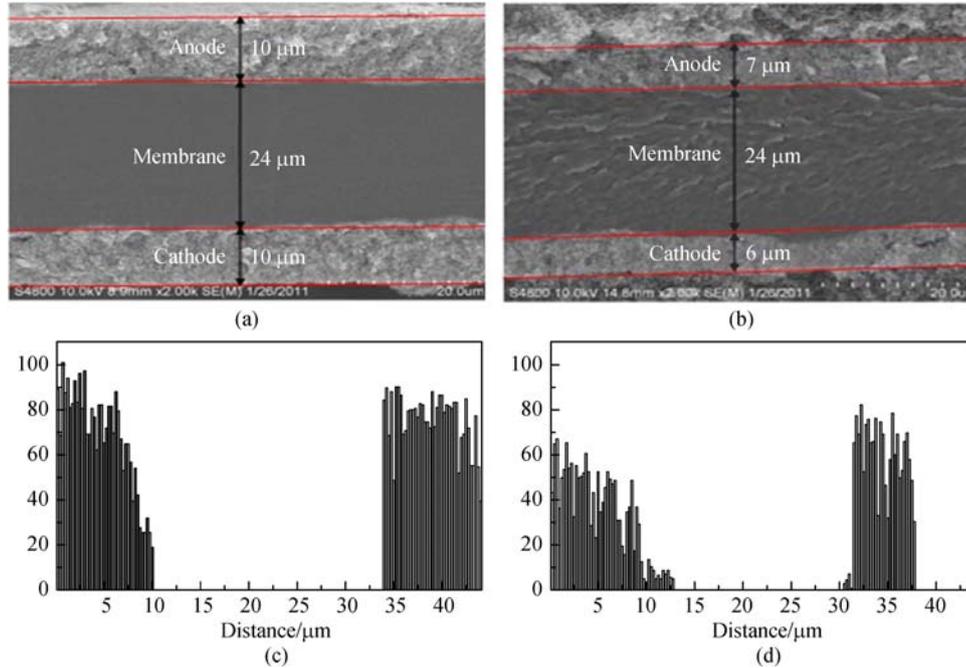
Fig. 4 Cross-sectional SEM picture of the MEA before (a) and after (b) vehicle accelerated test and distribution of the elements in MEA before (c) and after (d) vehicle accelerated test
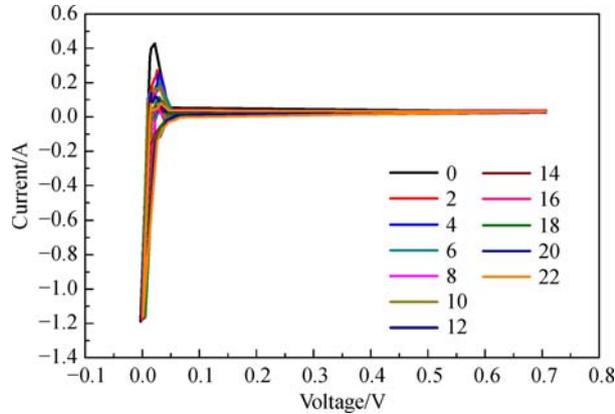

Fig. 5 Linear simulation curve of PEMFC after each durability test cycle

dispersed uniformly, and the particle size is also consistent with an average size of 2–3 nm. After 23 cycles, the Pt nanoparticles in the cathode and anode catalyst layers grow significantly (The particle size in cathode and anode are about 5 nm and 4 nm, respectively.), and the Pt nanoparticles in cathode grow faster than anode. The possible reason is that the potential of cathode is higher than that of anode. Before the vehicle accelerated test, the Pt nanoparticles are spherical. But after 23 cycles, the Pt nanoparticles appear to be irregular due to the aggregation of several Pt particles. At the same time, it could be seen that the Pt nanoparticles on the cathode catalyst carbon are significantly reduced after the vehicle accelerated test (See EDX data in Table 2).

5 Conclusions

In this paper, the durability of MEA has been measured by the vehicle accelerated test. This vehicle accelerated test condition simulates the actual operating environment of the vehicle fuel cell, and the results conform to the degradation in the real operation. Besides, this accelerated test method can effectively destroy MEA in a short time (165 h). Based on the experiment data, the following conclusions can be reached.

The durability of MEA in high current density is weaker than that in low current density under the testing condition. After 23 cycles, the performance of the MEA decreases from 0.692 V to 0.635 V at an attenuation rate of 8.2% and a current density of 600 mA/cm². The performance degradation rates are 1.00 mV/cycle (200 mA/cm²), 1.61 mV/cycle (600 mA/cm²) and 1.94 mV/cycle (1000 mA/cm²), respectively, which increase with the increase of current density.

The decrease of the ECSA of catalyst is the main reason for the performance degradation of the MEA. After 23 cycles, the ECSA in the cathode and anode decreases from 247 cm²/cm² and 168 cm²/cm² to 106 cm²/cm² (57%) and 114 cm²/cm² (32%), respectively. But the hydrogen permeation of the PEM does not change. This result indicates the catalyst aged is more detrimental than membrane perforated after long-running vehicle accelerated test process.

The main reasons for the catalyst decline are carbon carrier corrosion and Pt particle growth/loss in MEA. After 23 cycles, the thicknesses of the anode and cathode
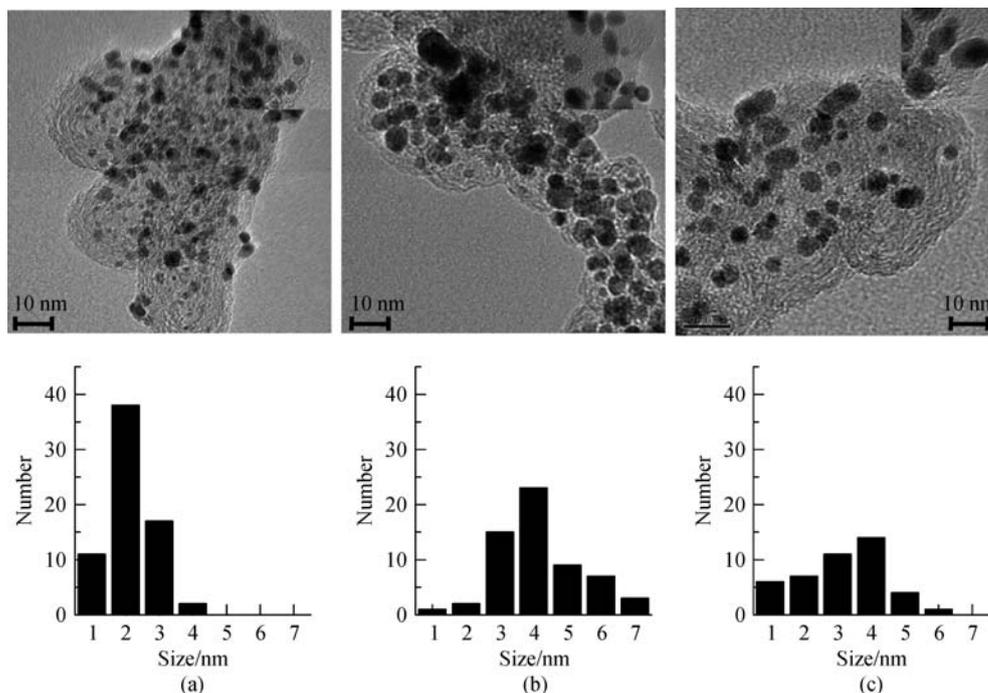
Fig. 6   TEM picture (up) and histograms of Pt nanoparticles size distribution (down)
(a) Pristine catalyst; (b) after vehicle accelerated test catalyst in cathode; (c) after vehicle accelerated test catalyst in anode

Table 2   Elemental composition of the MEA before and after vehicle accelerated test from EXS testing

| Elements | Elemental composition/% | | |
| | Before vehicle accelerated test | After vehicle accelerated test | |
		Anode	Cathode
C	46.61	41.09	42.50
O	6.28	6.18	6.23
F	44.71	50.44	49.16
S	1.10	1.23	1.17
Pt	1.30	1.06	0.95

catalytic layer decreases from both 10 μm to 7 μm (anode) and 6 μm (cathode), respectively. At the same time, the average particle size of the anode and cathode catalyst particles increases from both 2–3 nm to 4 nm (anode) and 5 nm (cathode), respectively.

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