

Surface and Structure Investigations of Membrane Electrode Assembly in DMFC Lifetime Testing*

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Abstract: The lifetime and performance of a direct methanol fuel cell (DMFC) were investigated to understand the correlation between the structure of catalysts/membrane and cell performance versus time. The cell polarization and performance curves were obtained during the DMFC operation with the time. The catalysts and Nafion membrane of the membrane electrode assembly (MEA) from the lifetime test were comprehensively examined by XRD, HRTEM, FTIR and Raman spectroscopy techniques. The results revealed that there was significant performance degradation during the first 200 hours operation; while the degradation was slowing down between 200 and 704 hours operation. The degradation became worse after 1 002 h operation. The increases of the catalyst particle size from both anode and cathode catalysts were observed after the DMFC lifetime test. The changes of microstructure, surface composition, the interfacial structure of the MEA, and the aging of Nafion under the DMFC lifetime tests were also observed.

Key words: DMFC, Lifetime, Aging, Degradation, Particle agglomeration

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1 Introduction

Direct methanol fuel cells (DMFC) convert methanol directly into electricity without using a reformer, and have advantage of a higher power density than the reformer based hydrogen polymer electrolyte membrane fuel cell (PEMFC) system.

Membrane electrode assembly (MEA) is a key component in a polymer electrolyte membrane fuel cell. The MEA mainly is comprised of a proton conducting electrolyte, a cathode and an anode. In the PEMFC, Nafion based membrane is widely used as an electrolyte, while Pt and Pt-based catalysts are commonly used as electrocatalysts. The cell performance is greatly affected by the microstructure

properties of MEA. In a DMFC, methanol oxidation at the anode and oxygen reduction at the cathode limits the cell performance. However, due to six electrons involved in the methanol oxidation, the anode reaction is more important than the cathode. In addition, methanol crossover from anode to cathode also drastically reduces the cell performance. The electrocatalysts in the PEMFC are required to have a high intrinsic activity to enhance the electrochemical oxidation of the fuel at the anode and electrochemical reduction of oxygen at the cathode, good electrical conductivity to enable the electron transfer, and good tolerance to resist poisoning caused by CO, CO₂ and other contaminants. The electrolyte for

PEMFC must be high proton conductive, impervious to fuels and oxidants, electrically resistive and chemically stable. Under long-term operation, the electrolyte should have sufficient mechanical and chemical integrity to avoid developing cracks or pores.

During recent years significant efforts have been made to develop improved catalysts and membranes, to optimize the electrode structure and to improve the fuel cell design, which have led to a rapid improvement in the performance of the PEMFC and DMFC^[1-7]. Most studied and operated catalysts for DMFC are supported or unsupported Pt and PtRu. In addition to Ru, platinum alloying with other metal species, such as Au, Co, Cu, Fe, Mo, Ni, Sn, W, Os, Rh, Pd, and Bi^[8-11] or carbon supported Pt-metal alloys^[12] to form CO-tolerant binary and ternary catalysts, has also shown to enhance the activity for methanol oxidation. The use of unsupported catalyst features a lower methanol crossover rate than carbon supported catalyst due to the carbon soaks more methanol in the catalyst layer.

One of the major concerns in the commercialization of DMFC is the stability of the cell after a long-term operation. Previous systematic lifetime study in a hydrogen-air PEMFC single cell demonstrated that the apparent particle agglomeration and the formation of metal oxide at the anode surface reduced the active surface area and ultimately resulted in slight degradation in cell performance^[13]. Degradation rates of DMFC are presumably higher than that of hydrogen PEMFC due to the poisoning of the intermediates from the methanol oxidation. In order to gain more information for better understanding the correlation between the cell performance and microstructure of MEA, this investigation was focused on the DMFC lifetime study by using electrochemical methods and analytical instruments, such as XRD, HRTEM, FTIR and Raman spectroscopy.

2 Experimental

(1) Single Cell Lifetime Tests

The membrane electrode assembly (MEA) for the DMFC lifetime test was made by hot-pressing pre-

treated Nafion 117 (Dupont) with cathode and anode, both consisting of backing material and catalysts. The cathode and anode catalysts were unsupported Pt and unsupported PtRu (1:1 ratio), respectively. The catalyst loading was 2 mg/cm² on each side. The backing material was made using carbon cloth (Zoltek) and a layer of carbon black mixed with hydrophobic polytetrafluoroethylene (PTFE). The catalyst ink was made from a portion of 5% Nafion solution (DuPont) and a certain amount of catalysts (Johnson Matthey). Using a coating apparatus, the catalyst ink was coated on the carbon black layer of the carbon cloth backing material. The catalyzed backings and a piece of Nafion 117 were sandwiched and hot-pressed at 120 °C. The active area of the cell was 6.45 cm². The MEA was then assembled into a single cell with graphite bipolar plates and gold-plated copper end plates. A double-serpentine flow field was machined into each graphite plate.

During the single cell operation, methanol solution (0.5 mol/L, 1 cm³/min) was pumped into the anode chamber at room temperature and atmospheric pressure through a model BT00-100M peristaltic pump (Lange Company, China), while purified air was fed to the cathode chamber at 300 cm³/min. The cathode pressure was 0.1 MPa. An insulating heating belt and an AF808P computer-programmed temperature controller (Yuguang, China) were used to heat the cell to 60 °C. The cell was discharged via an ohmic resistance, variations of cell voltage and current with operating time were automatically recorded through a data acquisition system (controlled by a PC computer and software) during the cell operation. After each test, the MEA sample was carefully taken out from the cell, labeled, and frozen with liquid nitrogen for a while. The frozen MEA sample was immediately cut by a razor blade into several pieces for further examinations.

(2) Characterization of MEA

The instruments and experimental procedures of XRD and Raman analyses used for the MEA characterization were the same as those described previously^[13]. A Tecnai F30 300 kV field emission high

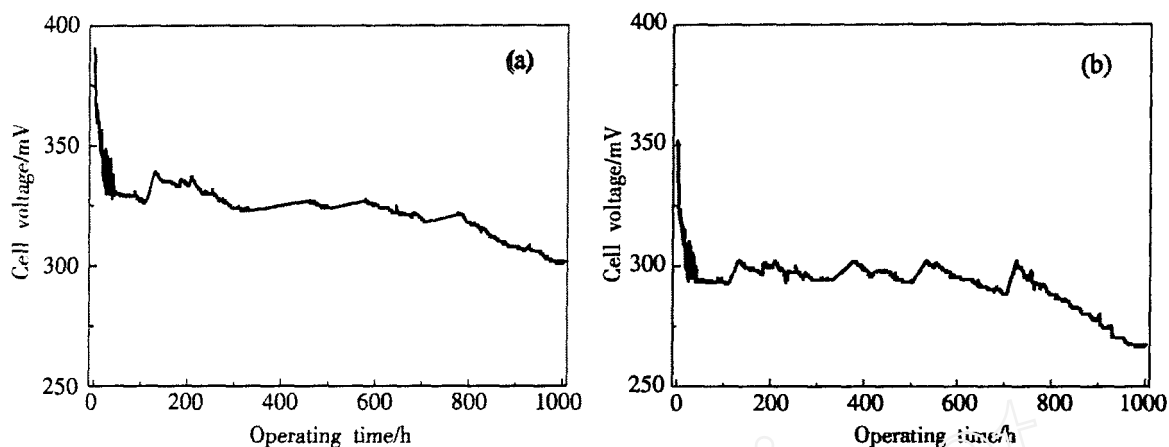


Fig 1 Variations of cell voltage (a) and current (b) with operating time during a DMFC single-cell operation

resolution transmission electron microscope (HR-TEM) (FEI Company) was used for TEM studies of the catalysts. A Fourier Transform Infrared (FTIR) spectrometer (Nicolet Company) was used to obtain IR spectra of the membranes. The scan range was $4\,000 \sim 400 \text{ cm}^{-1}$, and the scan numbers were 32 with the resolution of 4 cm^{-1} .

3 Results and Discussion

(1) Single Cell Performance

The cell voltage and current as a function of operating time measured during the DMFC 1 002 h lifetime testing is shown in Fig 1. It was observed that both the cell voltages and currents dropped remarkably at the first 50 h operation, and then remained relatively stable afterwards. It will take some time to "warm up" the cell, and this precondition leads to the initial decrease in the cell voltage and current. The cell voltages and currents decreased noticeably after 700 h operation.

The polarization and power density curves measured during the DMFC 1002 h lifetime testing are given in Fig 2. As can be seen from the figure, the open circuit voltage (OCV) was approximately 627 mV at the beginning of the operation. This value is much lower than 960 mV, the OCV value observed from the hydrogen-air PEMFC single cell operated previously^[13]. The significant decrease in OCV when using methanol as a fuel might be caused by the crossover of methanol from the anode to cathode and

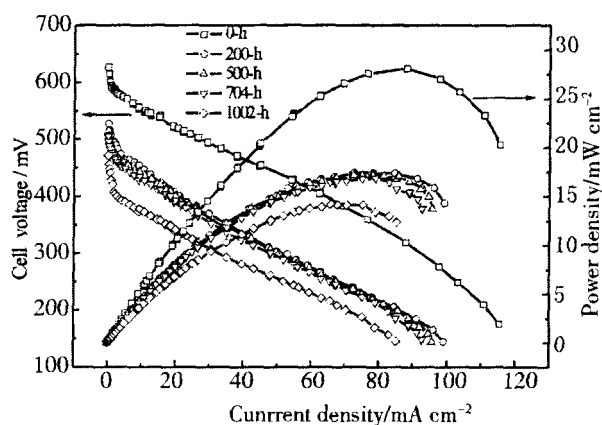


Fig 2 A comparison of polarization and power density curves at the beginning (0 h), after 200 h, 500 h, 704 h and 1 002 h DMFC single-cell operations

this adversely influences the kinetics of cathode^[11]. The OCV dropped to 527 mV and 427 mV, respectively, after 200h and 1002h operations. The maximum power density was only 28 mW/cm^2 at 88 mA/cm^2 when the cell operation started, while the power density decreased to 17 mW/cm^2 at the same current density after 200 h operation. Compared to 435 mW/cm^2 at 88 mA/cm^2 obtained from the hydrogen-air PEMFC single cell operated previously^[13], even after 200 h operation under the same load, the operation of DMFC single cell was rather preliminary because it did not operate at the optimizing conditions. The cell performance slightly degraded during the period of 200 h to 704 h. More significant degradation in cell

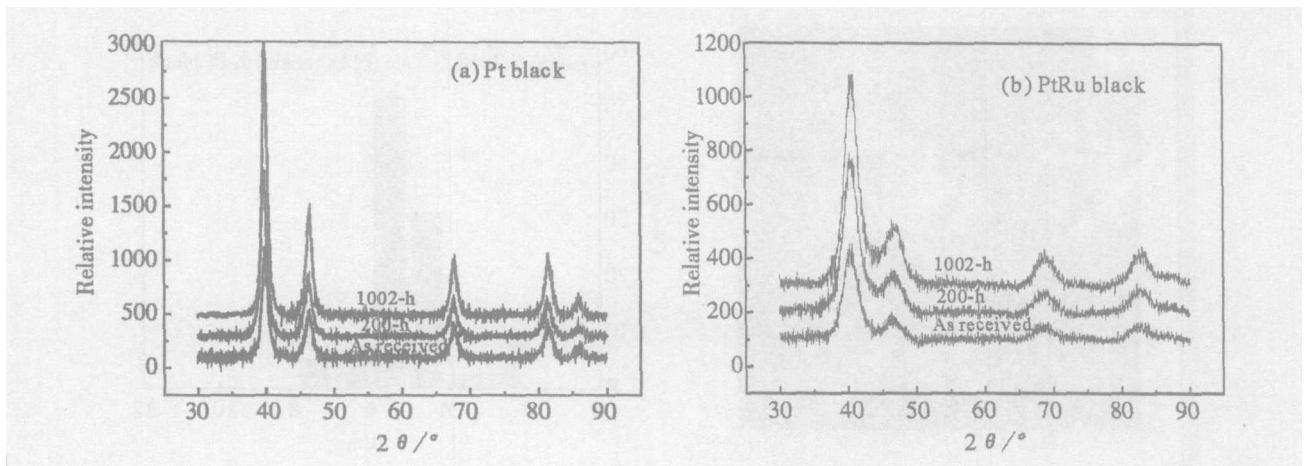


Fig 3 A comparison of XRD spectra obtained from the catalysts before and after DMFC single-cell operations (a) Pt black (b) Pt-Ru black

performance occurred after 704 h operation as evident in Fig 2

(2) Structure of Catalysts

In an effort to find the relationship between the microstructure, chemical composition of the catalysts, membrane properties, and the cell performance, the MEAs from the single cell after 200 h and 1 002 h lifetime tests were examined, respectively, by XRD, SEM, HRTEM, FTIR and Raman spectroscopy techniques. Fig 3 compares the XRD spectra of as received catalysts with those of catalysts from the MEAs after 200 h and 1 002 h lifetime tests. Five characteristic peaks corresponding to platinum (111), (200), (220), (311) and (222) were identified from both the Pt black and PtRu black. The strongest peak of Pt (111) appeared sharper after the lifetime testing, implying an increase in the particle sizes. In addition, all the characteristic peaks of PtRu black shown in Fig 3b appeared broader than those of Pt black shown in Fig 3a, in particular, Pt (111) and Pt (200) of PtRu black became more overlapped, while Pt (222) became less defined as compared to those of Pt black. It was reported that the increase in Ru content when alloying with Pt reduced the intensities of Pt (200) and Pt (222), and that Pt (222) almost disappeared when the Ru content increased to 62%^[14]. The Bragg angles of PtRu black shifted to higher degrees as compared to those of Pt black, indicating the catalyst consisting of face-centered cubic PtRu alloy particles. The mean particle sizes of catalysts were calculated using Debye-Scherrer equation

based on Pt (111) and Pt (220) by taking the average of three sets of XRD data and are summarized in Tab 1. It is evidential from Tab 1 that the mean particle sizes of both cathode and anode catalysts slightly increased with the increase of operating time. This is consistent with the previous lifetime testing results from hydrogen-air PEMFC single-cell^[13]. The increase in particle sizes resulted in the reduction of active surface areas of catalysts, accordingly, adversely affected the reaction kinetics and ultimately degraded the cell performance.

The HRTEM images for as received catalysts, along with their corresponding size distributions, are presented in Fig 4. Similarly, the mean particle sizes of 200 h and 1 002 h tested catalysts were also obtained. In general, larger particle sizes for Pt black and apparent particle agglomeration for PtRu black were observed after the lifetime testing. The particle sizes of Pt black observed from HRTEM analysis agreed reasonably well with those calculated from the XRD data given in Tab 1. However, the particle sizes of PtRu black after the lifetime testing were slightly larger from the HRTEM analysis than from the XRD data due to difficult evaluation resulted from severe particle agglomeration, as evident in Tab 1.

Typical Raman spectra of PtRu black are shown in Fig 5. Three characteristic Raman bands appeared after the lifetime testing, suggesting the presence of

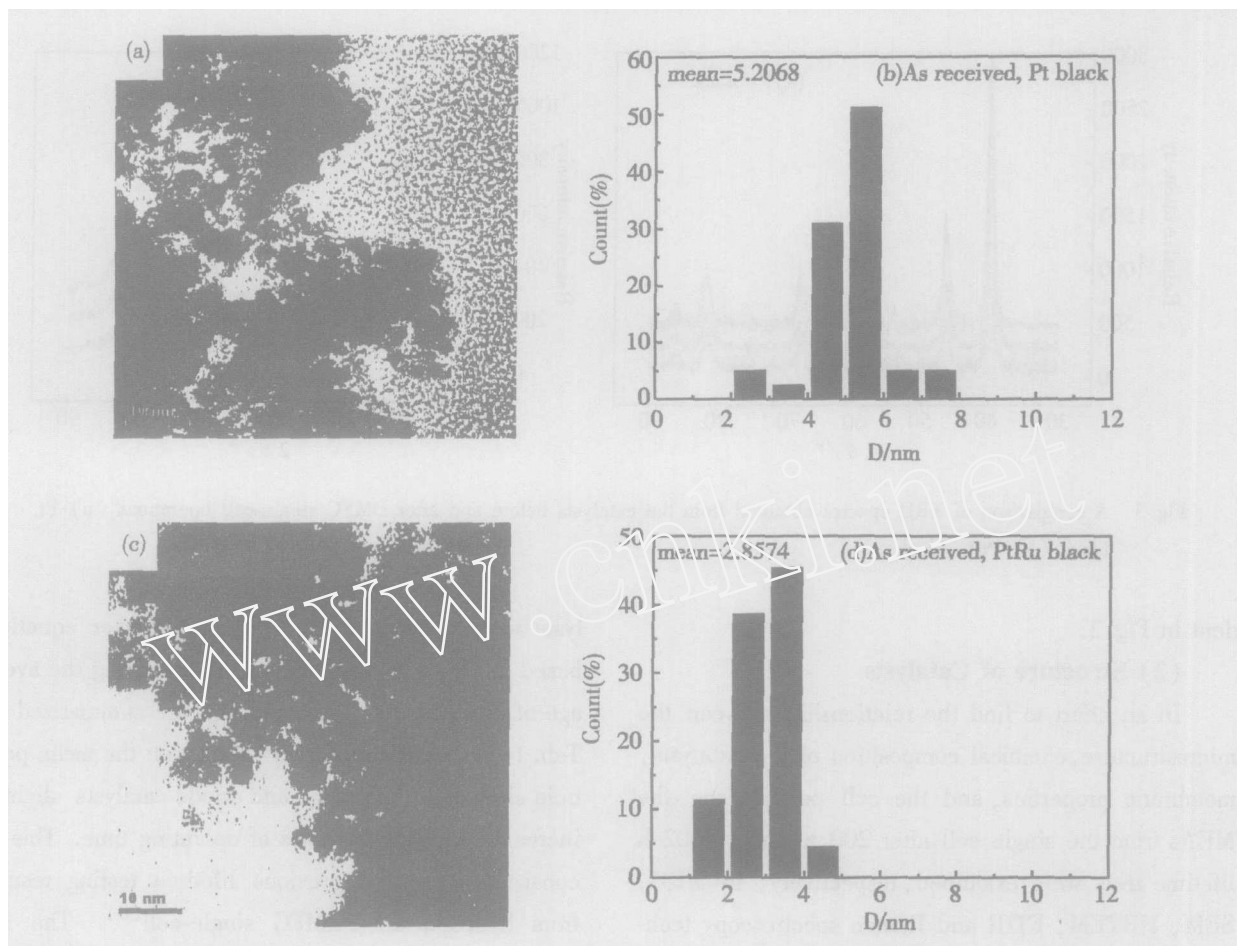


Fig 4 HRTEM images and size distributions of catalysts a, b) as received Pt black, c, d) as received PtRu black

metal oxide species, i.e., ruthenium oxide, which was also identified from the anode catalyst (carbon supported PtRu) during a hydrogen-air PEMFC single-cell lifetime testing reported previously^[13]. The intensity of Raman bands enhanced with the increase of operating time. No metal oxide species was found from the cathode catalyst.

The chemical bonding and structure information of Nafion 117 membranes before and after the lifetime testing were also obtained by performing FTIR and XRD measurements. The infrared spectra of as received, 200 h and 1 002 h tested Nafion 117 membranes are compared with that of polytetrafluoroethylene (PTFE) in Fig 6. For the PTFE two strong IR bands occurred near 1151 cm^{-1} and 1209 cm^{-1} corresponded to the main chain of symmetric stretch and anti-symmetric stretch of (CF_2), respectively^[15]. More adsorption bands were observed from Na-

tion 117 and their origins are summarized in Table 2. The IR band appeared near 1057 cm^{-1} is related to symmetric stretch of (SO_3)^[15]. Therefore, the change in the ratio of band intensities for 1057 cm^{-1} (SO_3) and 1151 cm^{-1} (CF_2), I_{1057}/I_{1151} , indicates the extent of chemical degradation for (SO_3) in Nafion. The value of I_{1057}/I_{1151} was calculated to be 0.35 for as-received Nafion 117, while the ratio decreased to 0.31 and 0.25, or 11.4% and 28.6% reduction, respectively, after 200h and 1 002 h lifetime tests, suggesting possible chemical aging of (SO_3) in Nafion.

Fig 7 compares the XRD spectra of as received and lifetime tested Nafion 117 membranes. The diffraction peak appeared around 12 ~ 20 degrees indicates the hexagonal structure of Nafion, which in fact overlaps with the amorphous and crystalline regions^[5,7]. The second diffraction peak appeared near

Tab 1 Mean particle sizes from XRD and HRTEM

Sample	Pt black /nm		HRTEM	PtRu black /nm		HRTEM
	XRD			XRD		
	(111)	(220)		(111)	(220)	
As received	8.2	6.8	5.2	3.4	2.7	2.9
200 h	9.5	8.2	6.5	3.3	2.9	5.0
1 002 h	10.2	8.6	8.7	3.9	3.2	5.4

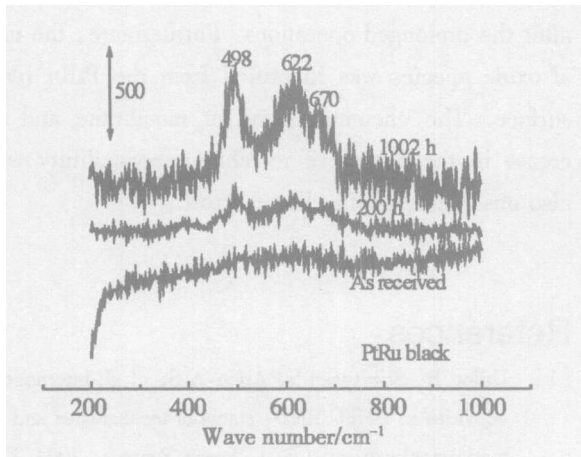


Fig 5 Raman spectra of PtRu black

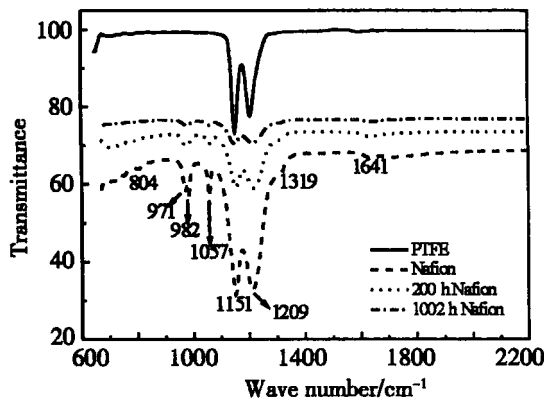


Fig 6 FTIR spectra of PTFE and various Nafion 117 membranes

40 degrees is associated with the polyfluorocarbon chains in the Nafion structure^[7]. The peak near 12 ~ 20 degrees can be deconvoluted into two peaks corresponding to the amorphous (~16 degrees, Peak 1) and crystalline (~17.5 degrees, Peak 2) structures^[7], as illustrated in Fig 8. The ratio under the area of Peak 2 over the total areas of Peak 1 and Peak 2 reflects the change in crystallinity of the membrane. The calculated results after averaging six sets of

measurements are summarized in Tab 3. It can be seen from Tab 3 that the degree of crystallinity (i.e., the value of the ratio) slightly increased from 0.42 of as received to 0.63 and 0.64, respectively, for 200 h and 1 002 h tested Nafion 117 when taking the average values of six sets of experimental data. The change in crystallinity of the membrane could imply that the physical properties of Nafion 117 had been changed after lifetime testing, e.g., the hydrophilic ionic zone (sulfonic zone) in net structure of Nafion, which is considered to be crystalline and proton conductive, might have become shrunken.

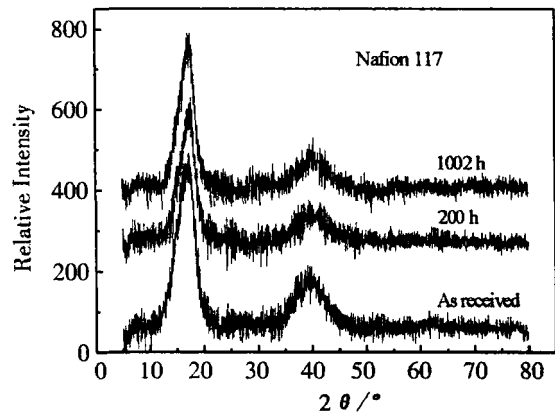


Fig 7 A comparison of XRD spectra for Nafion 117 membrane before and after DMFC single-cell operations

Tab 2 Identification of Infrared absorption bands of Nafion 117

Origin	IR band position	Assignment ^[15]
—C—C	1 319 cm ⁻¹	(C—C) sym. stretch
—CF ₂ —CF ₂ —	1 209 cm ⁻¹	(CF ₂) antisym. stretch
		(SO ₃) antisym. stretch
—CF ₂ —CF ₂	1 151 cm ⁻¹	(CF ₂) sym. stretch
—SO ₃ —	1 057 cm ⁻¹	(SO ₃) sym. stretch
—C—O—C	982 cm ⁻¹	(C—O—C) antisym. stretch
C—O—C	971 cm ⁻¹	(C—O—C) sym. stretch
C—S	804 cm ⁻¹	(C—S) sym. stretch

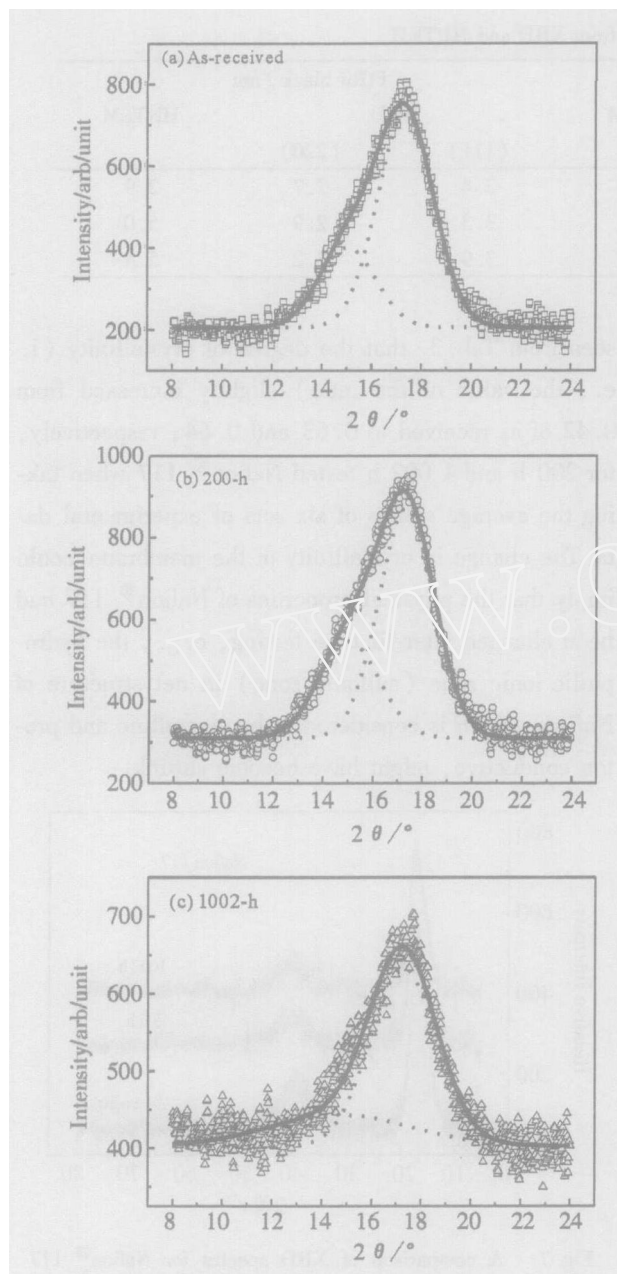


Fig 8 Peak deconvolution analyses for amorphous and crystalline structure of Nafion 117 membrane

Tab 3 The peak deconvolution analysis results from XRD

	Membrane		
Crystallinity	As received	200h	1 002 h
X_c (average)	0.42	0.63	0.64

4 Summary and Conclusion

Preliminary DMFC lifetime tests were carried out, and the catalysts and membrane from original and tested MEAs were characterized by

XRD, HRTEM, FTIR and Raman spectroscopic techniques. It was found that significant degradation in cell performance occurred after 200 h operation and became worse after 1 002 h operation. The mean particle sizes of both anode and cathode catalysts became larger, while the particles of PtRu black agglomerated after the prolonged operations. Furthermore, the metal oxide species was identified from the PtRu black surface. The chemical aging of membrane and increase in the degree of membrane crystallinity were also observed after the lifetime test.

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DMFC寿命测试过程中膜电极的表面和结构研究

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摘要: 设计并组装单电池寿命测试系统, 测试直接甲醇燃料电池 (DMFC) 的运行寿命, 获得不同运行时间下单电池的极化和功率曲线. 测试结束后, 分别对运行过的膜电极 (MEA) 催化剂 (铂黑和铂钉黑) 和 Nafion 117 膜作 XRD, HRTEM, FTIR 及 Raman 等表征. 考察在长期运行条件下电池寿命性能与膜电极中催化剂的颗粒大小、分布、形态、表面物种以及膜的结构之间的关系. 寿命测试结果表明, 单电池在不同运行阶段其性能变化也不同. 运行前 200 h, 电池性能衰减较显著; 运行 200 ~ 704 h 性能较稳定, 运行 1 002 h 后电池性能恶化. 波谱实验发现, 单电池长期运行后, 其膜电极的阴、阳极催化剂颗粒变大. 电池寿命性能的衰退伴随膜电极微结构、表面组成、催化剂/膜界面结构的变化以及 Nafion 117 膜的老化.

关键词: 直接甲醇燃料电池; 寿命; 老化; 衰减; 颗粒团聚