

## Electrocatalytic and Lifetime Studies of Commercial Catalysts in a PEMFC

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**Abstract**: A particularly designed H-type cell was used to simulate the operating condition of a hydrogen-air proton exchange membrane fuel cell (PEMFC). The electrocatalytic activity, morphology, structure and lifetime of commercially available catalysts, carbon support platinum (Pt/C) and unsupported platinum-ruthenium (Pt-Ru), were preliminary studied by carrying out electrochemical measurements and by SEM, XRD techniques. The catalysts were simultaneously tested in the H-cell under operation, and also separately tested in a conventional electrochemical cell for comparison. It was found that the characteristic peaks of hydrogen adsorption/desorption on cyclic voltammograms shifted considerably to a more positive direction for Pt/C, while a more negative direction for Pt-Ru. The magnitude of the peak current densities on CV curves, especially observed from Pt/C catalyst, tended to reduce after the lifetime tests. The electrocatalytic activity of Pt-Ru was significantly lower due to carbon monoxide poison, and the effect of CO on catalyst was irreversible.

**Key words**: PEMFC, electrocatalytic activity, lifetime, commercial catalyst

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### 1 Introduction

Proton exchange membrane fuel cells (PEMFC) are promising in both stationary power generation and as vehicular power sources due to their high operational efficiencies, ambient operating

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conditions and exceptional clean environments. However, one challenge for the commercialization of PEMFC is to improve lifetime. Catalyst plays a key role in PEMFC and has attracted significant attention in recent researches<sup>[1~6]</sup>. Platinum or platinum-ruthenium are still considered to be the best catalysts for PEMFC among all those studied. Most works have been focused in improvement of catalyst utilization and synthesis of new and high performance catalysts; however, little information is available for catalyst lifetime.

In this work, an H-cell was especially designed and used to investigate the lifetime and activity of two commercial catalysts, carbon supported platinum (Pt/C) and unsupported platinum-ruthenium (Pt-Ru), in a simulating cell operating condition. The results were also compared with those obtained from a conventional 3-electrode cell measurement. The catalysts were also examined by XRD and SEM for microstructure and morphology information.

## 2 Experimental

### 2.1 Materials

Two commercial catalysts, unsupported Pt-Ru (11) and carbon supported 40 % Pt (Johnson Matthey) and glassy carbon (GC) rods (5 × 100 mm, Alfa Aesar) were used in the preparation of working electrodes. The gases used in this work including nitrogen, hydrogen, air and carbon monoxide were of high-purity (> 99.99 %) and the chemicals were of analytical grade. The deionized water of 18 M $\Omega$  was used to prepare all the aqueous solutions.

### 2.2 Electrochemical Measurements

A conventional 3-electrode cell was fabricated and used in electrochemical measurements. The working electrodes were GC, or catalysts on GC electrodes, respectively. The counter and reference electrodes were a platinized platinum electrode and a standard calomel electrode (SCE) which is separated from the working electrode compartment by a closed electrolyte bridge in order to avoid chloride contamination. The supporting electrolyte was 0.5 mol L<sup>-1</sup> sulfuric acid.

The GC electrode was polished with diamond paste (0.25  $\mu$ m, Beulhur) on a polishing cloth, cleaned ultrasonically in DI water, dried in an oven (120 °C, 1 h), and then weighed. The catalyst inks were made by proportionally mixing the catalysts with isopropanol, 5 % Nafion solution (Electrochem, Inc.) and DI water. The inks were continuously agitated for at least 48h or until they were thoroughly mixed. Camel hair brushes were used to carefully paint the inks onto the polished end surface of the GC electrode. After painting two to three layers, the electrode was dried (120 °C, 1 h) and weighed again.

Electrochemical measurements were performed using an Autolab general-purpose electrochemical system (Ecochemie, Netherlands). The data were acquired with a personal computer. The solutions were purged by continuously passing nitrogen gas at least 30 minutes before each measurement. The nitrogen atmosphere was also maintained during the electrochemical measurement. Unless stated otherwise, all potentials are reported with respect to the RHE.

### 2.3 H-cell Tests

A specially designed H-cell was used in order to simulating continuous operating condition of a hydrogen-air proton exchange membrane fuel cell (PEMFC). The H-cell consists essentially of two respective compartments which are connected by a Nafion<sup>®</sup> 112 membrane in the central part. The cell can be operated by feeding fuels, respectively, from each compartment and the desired electrochemical measurements can also be readily made within the cell.

### 2.4 Characterization of Catalysts

X-ray diffraction (XRD) analysis of commercial catalysts was carried out with a Rigaku D/max-RC diffractometer using a CuK $\alpha$  source. Scanning electron microscopic (SEM) images of the catalysts were obtained using a LEO 1530 microscope. The catalysts were analyzed without coating and at an accelerating voltage of 20 keV.

## 3 Results and Discussion

### 3.1 Morphology and Structure of Catalysts

The surface morphologies of two commercial catalysts on the glassy carbon (GC) are shown in Fig. 1. By comparison, it was found that the Pt/C catalyst particles appeared better-defined granular structure than the Pt-Ru catalyst particles which tended to be aggregated each other. The less soluble nature of Pt-Ru could lead to its poor disperse in the ink, hence reduced its granular property.

Typical XRD spectra obtained from the two catalysts and GC electrode are compared with those of platinum foil and activated carbon, respectively, in Fig. 2. The dashed lines represent five characteristic diffraction peaks of Pt fcc structure which were well matched by those of Pt foil and Pt/C. A significant shift to higher  $2\theta$  values was observed for the diffraction peaks in the Pt-Ru catalyst with respect to the Pt/C catalyst. The lattice parameters were determined to be 0.390 6 nm in Pt/C and 0.389 2 nm in Pt-Ru catalysts, respectively, by fitting the peak profile of (220) reflection. The observed smaller lattice parameter for the

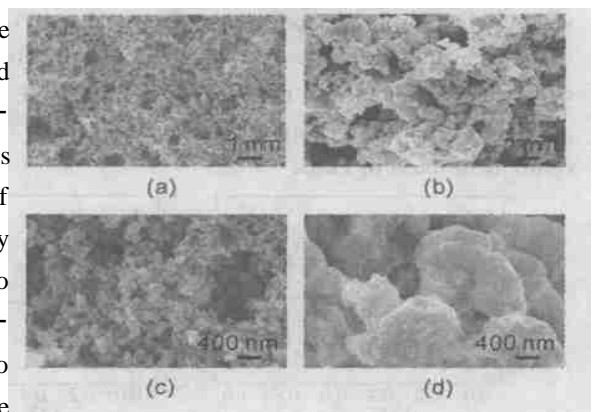


Fig. 1 SEM micrographs of commercial catalysts on glassy carbon electrodes a) , c) Pt/C b) , d) Pt-Ru

Pt-Ru sample accounts for the presence of solid solution of Pt and Ru with Ru atom having smaller radius ( $r_{\text{Pt}} = 0.138 \text{ nm}$ ;  $r_{\text{Ru}} = 0.1322 \text{ nm}$ )<sup>[8]</sup>. Mean particle sizes for the metal crystallites of 3.2 nm and 2.6 nm in the Pt/C and Pt-Ru catalysts, respectively, were also evaluated by using Sherrer equation. Three diffraction peaks observed from the GC were virtually identical to those

of the activated carbon as evident in Fig. 2 (b).

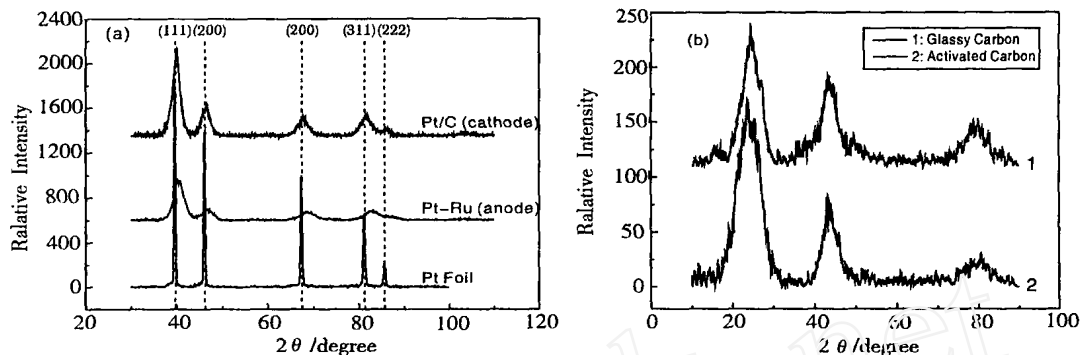


Fig. 2 Comparisons of XRD patterns of commercial catalysts with Pt foil (a), glassy carbon with activated carbon (b) scan rate:  $0.06 \text{ degree} \cdot \text{s}^{-1}$

### 3.2 Electrocatalytic Behavior of Catalysts

Typical cyclic voltammograms of the two commercial catalysts obtained in a conventional 3-electrode cell and in  $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$  solution at three different scan rates are compared in Fig. 3. Two characteristic peaks corresponding to hydrogen adsorption/desorption were seen from Pt/C, while the hydrogen adsorption/desorption peaks of Pt-Ru were less define and became more sensitive to the change of scan rates. In addition, the reduction peak of metal oxide for Pt-Ru (0.4 V) occurred more cathodically than that for Pt/C (0.8 V). The variations in scan rates changed the peaks of hydrogen adsorption/desorption and peak of metal oxide reduction in Pt-Ru more significantly than those in Pt/C.

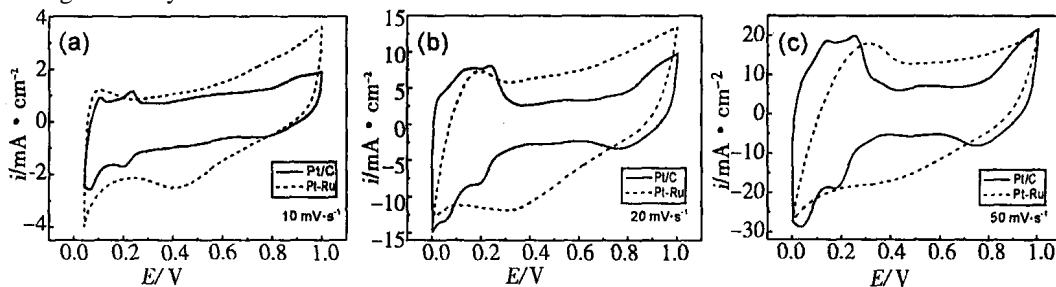


Fig. 3 Typical cyclic vdtammograms of commercial catalysts in  $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$  solutions scan rate/  $\text{mV} \cdot \text{s}^{-1}$ : a) 10, b) 20, c) 50

The CV curves in the same potential regions as in Fig. 3 but obtained from the H-cell are presented in Fig. 4. The key feature of the H-cell is that two half-cells are tightly connected by a Nafion membrane so that two sides of the H-cell can act as an anode and a cathode to simulate a single-cell operation, i. e. the cathode side with Pt/C and aerated with air, the anode side with

Pt-Ru and aerated with H<sub>2</sub>. No matter whether the cell was half-cell (one side respective operation) or full-cell (two-side simultaneous operation) operation, the characteristic peaks observed previously with the conventional 3-electrode measurements remained unchanged and were quite reproducible as compared with those in Fig. 3 at different scan rates.

Fig. 5 shows the effect of scan rates on the electrochemical responses of the two catalysts under full-cell operation. The magnitude of current densities for Pt/C increased considerably with the increase of scan rates, however, the  $i \sim E$  behavior of Pt-Ru appeared more

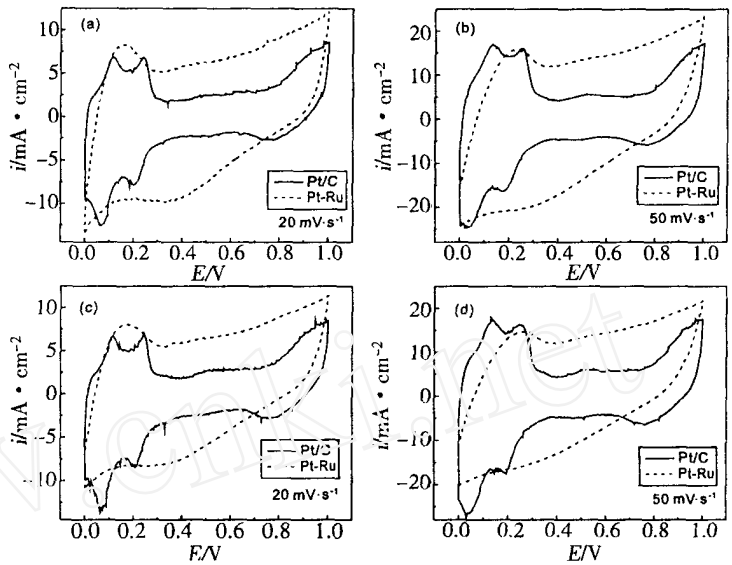


Fig. 4 Typical cyclic voltammograms of commercial catalysts obtained from Hcell in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solutions at 20 mV · s<sup>-1</sup> and 50 mV · s<sup>-1</sup>, respectively  
a) , b) half-cell operation , c) ,d) full cell operation

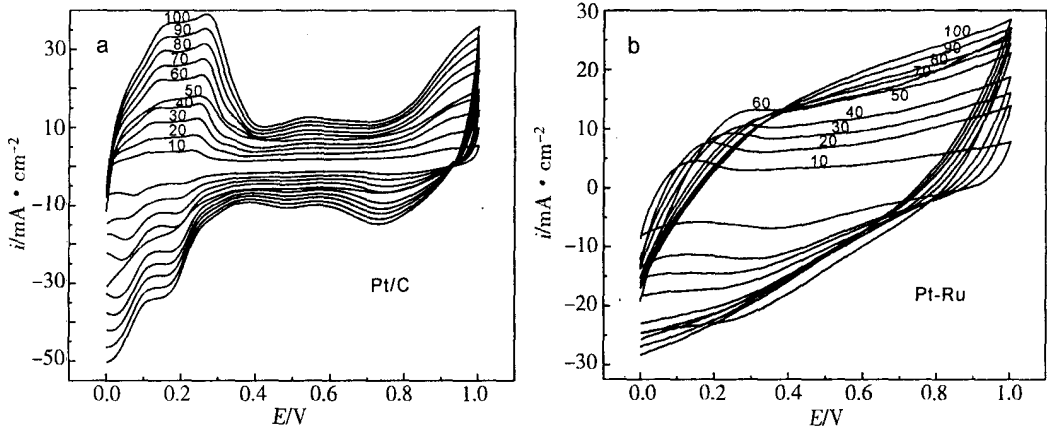


Fig. 5 Cyclic voltammograms of commercial catalysts obtained during Hcell operation in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solutions Numbers refer to different scan rates in mV · s<sup>-1</sup> a) Pt/ C, b) Pt-Ru

complex. The current densities initially went up and the distinct hydrogen peaks shifted to a more anodic direction when the scan rates became larger. Starting from 70 mV · s<sup>-1</sup>, the hydrogen

peaks became less defined and the voltammograms looked very similar to those of GC, suggesting that the amount of Pt-Ru on GC could have been reduced after certain period of testing time.

The discharge curves obtained at  $165 \mu\text{A} \cdot \text{cm}^{-2}$ , measured right after H-cell operation and after 12h cell operation, are given in Fig. 6. It is obvious that the initial discharge voltage obtained right after the cell operation (Curve 1) dropped rapidly before 5 000 s. As time went on, the voltage of Curve 1 was still unstable. However, after the cell was operated for 12h, the discharge voltage values (Curve 2) were higher and the decaying rate was smaller as compared with the curve 1. This phenomenon might be associated with the initial activation process, i. e. the cell was activated during the first period of operation.

### 3.3 Lifetime of Commercial Catalysts

Figure 7 shows the influence of operating time on voltammograms obtained during the H-cell operation. It is evident that the hydrogen adsorption/desorption peaks slightly shifted with the increase of testing time. The peaks of Pt-Ru slightly moved to a more cathodic direction (Fig. 7b) while those of Pt/C shifted to a more positive direction (Fig. 7a). In addition, the magnitude in current densities of Pt/C decreased significantly with the increases of testing time. Thereby, the electrocatalytic behavior of the catalysts was strongly affected by the lifetime test of H-cell.

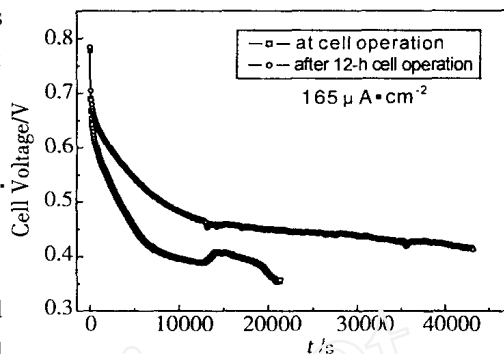


Fig. 6 Discharging curves obtained at  $165 \mu\text{A} \cdot \text{cm}^{-2}$  under H-cell operation and after 12 h cell operation

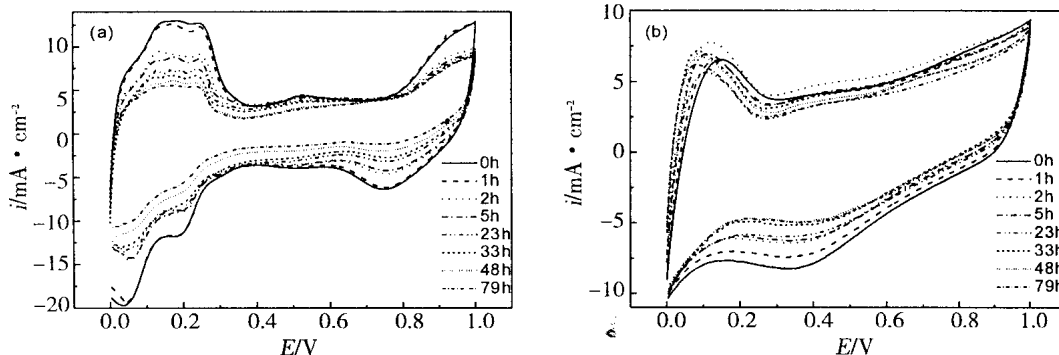


Fig. 7 Cyclic voltammograms of commercial catalysts in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solutions obtained during different periods of H-cell operation Pt/C (a), Pt-Ru (b)

### 3.4 Effect of CO on Catalysts

In an effort to study carbon monoxide effect on catalysts, cyclic voltammograms were obtained with Pt-Ru in the absence and presence of CO gas, the results are provided in Fig. 8. As evident in Fig. 8a, after introducing CO into the solution for 15 and 30 min, the distinctive hydrogen adsorption/desorption peaks were suppressed and the oxidation peak of CO was observed near 0.54 V. The voltammograms obtained after holding the electrode at constant potential 0.09 V for 15 min showed that the hydrogen adsorption/desorption peaks resumed in some extent, however, the oxidation peak of CO did not fully disappeared even after 5 cycles (Fig. 8b), indicating the irreversible influence of CO in catalyst.

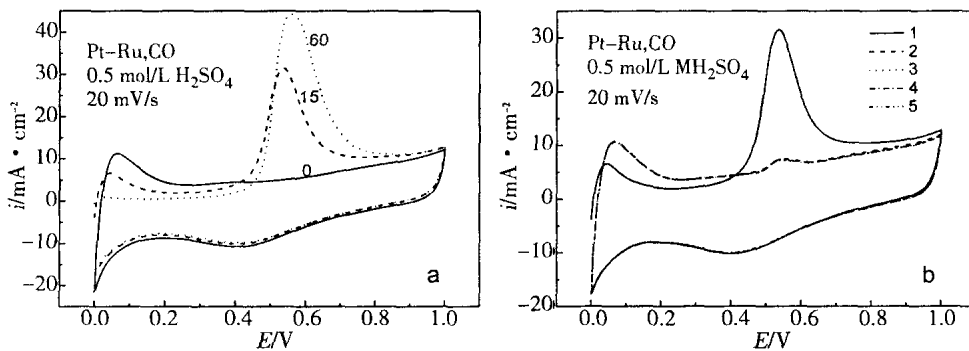


Fig. 8 Cyclic voltammograms of Pt-Ru in  $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$  solutions in the presence of CO  
 a) without CO, ---holding 0.09 V constant for 15 min, .....holding 0.09 V constant for 60 min, b) volatammograms obtained after holding 0.09 V constant for 15 min, Numbers refer to cycles

## 4 Summary and Conclusion

A special H-type cell was fabricated to investigate electrocatalytic and lifetime behaviors of two commercial catalysts. Through this preliminary study it was demonstrated that the information obtained from the H-cell could provide a better understanding for the performance of commercial catalysts since they could be tested under simulating a cell operating condition. Two commercial catalysts, Pt/C and Pt-Ru, exhibited different morphologies and structures. The hydrogen adsorption/desorption peaks of Pt/C and Pt-Ru on cyclic voltammograms shifted more anodically and cathodically, respectively, after lifetime tests. The effect of CO on electrocatalytic behavior of Pt-Ru was irreversible.

## References:

- [1] Ren X, Piotr Z, Sharon T, et al. Recent advances in direct methanol fuel cells at Los Alamos National Laboratory[J]. J. Power Sources, 2000, 86: 111~116.

- [2] Gamburgzev S, Appleby A J. Recent progress in performance improvement of the proton exchange membrane fuel cell (PEMFC) [J]. J. Power Sources, 2002, 107:5~12.
- [3] Antolini E. Formation of carbon-supported PtM alloys for low temperature fuel cells: a review [J]. Mater. Chem. Phys., 2003, 78:563~573.
- [4] Lizcano-Valbuena W H, Paganin V A, Gonzalez E R. Methanol electrooxidation on gas diffusion electrodes prepared with Pt-Ru/C catalysts [J]. Electrochimica Acta, 2002, 47:3 715~3 722.
- [5] Dinh H N, Ren X, Garzon F H, et al. Electrocatalysis in direct methanol fuel cells: in situ probing of PtRu anode catalyst surfaces [J]. J. Electroanal. Chem., 2000, 491:222~233.
- [6] Lee S, Park K, Choi J, et al. Nanoparticles Synthesis and electrocatalytic activity of Pt alloys for direct methanol fuel cells [J]. J. Electrochem. Soc., 2002, 149:A1 304.

## PEMFC 商用催化剂电催化活性和寿命研究

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**摘要:** 采用自设计的特制 H 形电解槽模拟单个氢-空气质子交换膜燃料电池运作, 并以电化学方法、SEM 及 XRD 等技术研究两种商用催化剂, 即碳载铂 (Pt/C) 和纯铂钉 (Pt-Ru) 的电催化活性、表面形貌及其结构和寿命。同时对比了两种催化剂分别放在 H 形电解槽和常规电解槽中运行情况的测试结果。实验表明, 经过 H 形电解槽运行后的催化剂, 其循环伏安曲线表征氢吸脱的特征峰分别发生了正偏移 (Pt/C 电极) 和负偏移 (Pt-Ru 电极), 且对应的峰电流呈现减小的趋势 (特别是 Pt/C 电极)。一氧化碳的毒化造成纯铂钉的电催化活性显著下降, 其影响是不可逆的。

**关键词:** 质子交换膜燃料电池; 电催化活性; 寿命, 商用催化剂