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# Highly active PtRu catalysts supported on carbon nanotubes prepared by modified impregnation method for methanol electro-oxidation

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## ABSTRACT

A simple and rapid synthesis method (denoted as modified impregnation method, MI) for PtRu/CNTs (MI) and PtRu/C (MI) was presented. PtRu/CNTs (MI) and PtRu/C (MI) catalysts were characterized by transmission electron microscopy (TEM) and X-ray diffractometry. It was shown that Pt-Ru particles with small average size (2.7 nm) were uniformly dispersed on carbon supports (carbon nanotubes and carbon black) and displayed the characteristic diffraction peaks of Pt face-centered cubic structure. Cyclic voltammetry and chronoamperometry showed that the Pt-Ru/CNTs (MI) catalyst exhibited better methanol oxidation activities than Pt-Ru/C (MI) catalyst and commercial Pt-Ru/C (E-TEK) catalyst. The single cells with Pt-Ru/CNTs (MI) catalyst exhibited a power density of 61 mW/cm$^2$, about 27% higher than those single cells with commercial Pt-Ru/C (E-TEK) catalyst.

## 1. Introduction

Direct methanol fuel cells (DMFCs) are commonly considered as candidates for future energy-generating devices, but there are two key problems inhibiting the commercialization of DMFCs: the poor kinetics of methanol oxidation reactions in the anode, and methanol crossover from anode to cathode causing poisoning of the cathode [1–3]. On the issue of improving the kinetics of the methanol oxidation reaction, Pt- and PtRu-based nanoparticles are of major interest as anode catalysts for DMFCs. Up to now, PtRu catalysts have still been the most active binary catalysts. The oxidation of $CH_3OH$ to $CO_2$ at “low” potentials takes place via a bifunctional mechanism posited by Watanabe and Motoo [4,5]. It is assumed that Ru provides an oxygenated surface species by dissociating water at the Ru sites at lower potentials against pure sites, leading to the accelerated $CO_2$ formation and a decrease in the CO poisoning, thus improving the CO tolerance. Several groups have investigated the origin of the Ru enhancement by using various types of model bimetallic Pt/Ru electrodes, including Pt/Ru alloy [6–10] and Ru-decorated Pt electrodes [11–15]. The Urbana-Champaign group led by Wieckowski reported the combined electrochemistry NMR (EC NMR)/electrochemistry approach, which provides new insights into the promotion of CO tolerance in Pt/Ru catalysts [16,17].

Preparation methods have an important influence on the particle size and size distribution of PtRu catalysts; therefore, numerous studies have been directed toward the synthesis [18–27]. To achieve fine dispersion and high utilization, PtRu catalysts are usually supported on some high-surface-area materials such as carbon black and CNTs. Among the synthetic methods reported in the literature for PtRu catalysts, the most popular are colloidal method [18–23] and impregnation method [24–29]. The colloidal method often uses surfactants or polymer as the stabilizers which not only protect the nanocatalysts but also create a space for nano-size particles to grow [23]. But how to remove the stabilizer after reduction becomes a major problem; in particular, repeated filtering and washing procedures are time-consuming and easy to cause the loss of noble metals [30,31]. Impregnation method includes an impregnation step, followed by a reduction step. During the impregnation step, the precursors of Pt and Ru are mixed with high-surface-area catalyst supports in aqueous solution to form a homogeneous mixture. In comparison to colloidal method, impregnation method is relatively simple, but Pt-Ru catalysts prepared by this method do not show good control of particle size and distribution [31,32].

In this work, we presented a simple and rapid route (denoted as modified impregnation method) to prepare PtRu/CNTs (MI) and PtRu/C (MI). The PtRu catalysts prepared in this work were characterized by transmission electron microscopy and X-ray diffraction. The methanol electro-oxidation activities of the PtRu catalysts were also discussed and compared with commercial PtRu catalysts.

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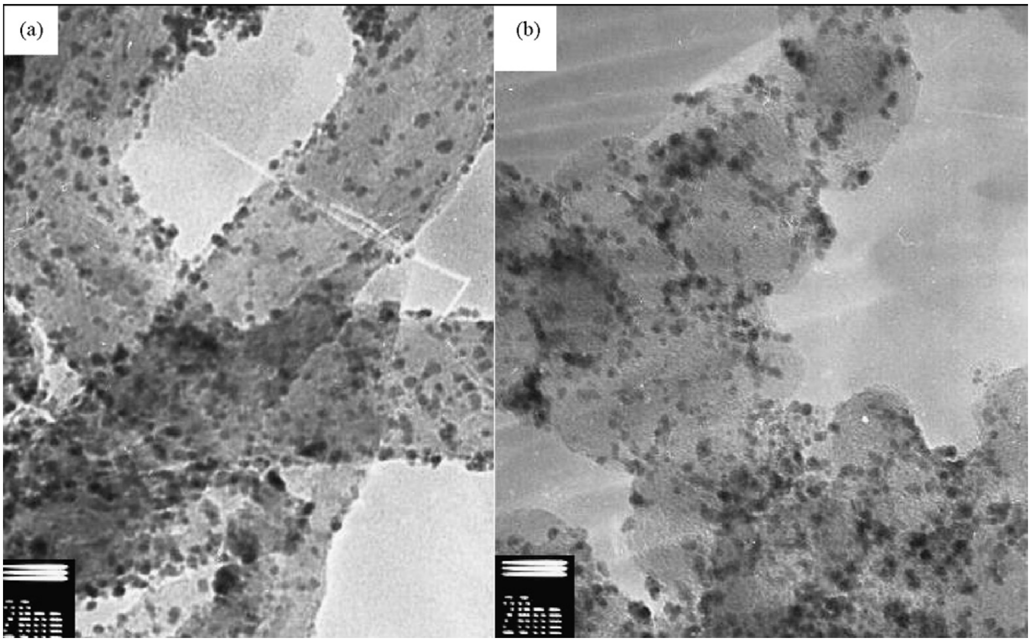

**Fig. 1.** TEM images of PtRu nanoparticles supported on multiwalled CNTs (a) and Vulcan XC-72 carbon (b).

## 2. Experimental

### 2.1. Materials

The metal sources were an aqueous solution of $H_2PtCl_6$ and $RuCl_3$ freshly prepared in order to avoid the formation of complex $[RuO(H_2O)_4]^{2+}$, which is difficult to be reduced [33]. Multiwalled CNTs with ≥95% in purity, 40–300 $m^2/g$ in specific surface area, 10–20 nm in diameter and 5–15 μm in length, were purchased from Shenzhen Nanotech Port Co., Ltd., China. The as-purchased CNTs were surface oxidized by $H_2SO_4$-$HNO_3$ mixture (8.0 M for each acid) for 4 h in an ultrasonic bath [34]. Vulcan XC-72 carbon black was purchased from Cabot Corporation. Deionized water (18.23 MΩ) was produced by a Milli-Q ultrapure system from Millipore Ltd., USA.

### 2.2. Preparation of PtRu nanoparticles on the MWCNTs and on the Vulcan XC-72 Carbon

Pt-Ru/CNTs (20 wt% Pt + 10 wt% Ru) and Pt-Ru/C (20 wt% Pt + 10 wt% Ru) were prepared by a modified impregnation method and the preparation procedure is briefly described below using CNTs as example. The surface-oxidized CNTs were suspended in deionized water and treated in an ultrasonic bath. Then $H_2PtCl_6$ and $RuCl_3$ solution were added dropwise under mechanically stirred conditions for 2 h. Then 5% (v/v) $NH_3{\cdot}H_2O$ solution was added to adjust PH of the mixture solution to above 12, therefore $PtCl_6{}^{2-}$ and $Ru^{3+}$ were precipitated due to the formation of $(NH_4)_2PtCl_6$ and $Ru(OH)_3$ and the precipitate was adsorbed on CNTs. With dropwise addition of $NaBH_4$ solution, $(NH_4)_2PtCl_6$ and $Ru(OH)_3$ were reduced to Pt and Ru nanoparticles. Subsequently, the suspension was filtered and washed with hot deionized water until no $Cl^-$ was detected. Finally, the resulting catalysts were air-dried at 100 °C in a drying oven for 24 h and then kept in desiccator. The PtRu catalysts supported on CNTs and carbon black were noted Pt-Ru/CNTs (MI) and Pt-Ru/C (MI), respectively.

### 2.3. Physicochemical characterization of catalysts

Transmission electron microscopy (TEM) analysis was carried out with a JEOL2010 microscope operating at 200 kV with nominal resolution. Samples were first ultrasonicated in alcohol for 1 h and then deposited on 3 mm Cu grids. The composition and content of Pt and Ru in the Pt-Ru/CNTs and Pt-Ru/C catalysts were evaluated with energy-dispersive X-ray (EDX) analysis in a scanning electron microscope (JEOL JAX-840). X-ray diffraction spectra were measured with a Philips PW1700 diffractometer using Cu Kα (λ = 1.5405 Å) radiation source operating at 40 kV and 30 mA.

### 2.4. Electrochemical measurements

Electrochemical measurements were carried out with an EG & G mode 273 potentiostat/galvanostat and a conventional three-electrode test cell. Glassy carbon (GC) was polished with 0.05 μm alumina suspension before each experiment and served as an underlying substrate of the working electrode. The catalyst ink was prepared by ultrasonically dispersing the mixture of 5 mg catalysts, 1 mL ethanol, and 50 μL 5 wt.% Nafion solution. 10 μL catalyst ink was pipetted and spread on the glassy carbon disk. Then the electrode was dried at 80 °C for 1 h. A Pt foil and an Ag/AgCl were used as the counter and reference electrodes, respectively. All potentials in this report were quoted against Ag/AgCl. All electrolyte solutions were deaerated by high-purity nitrogen for 15 min prior to any measurement. The electrolyte solution was 1 M $CH_3OH$ in 0.5 M $H_2SO_4$. The cyclic voltammetries of methanol were measured between −0.2 and 0.8 V vs. Ag/AgCl at 20 mV/s. For chronoamperometry, the electrode potential was fixed at 0.5 V vs. Ag/AgCl.

### 2.5. Performance tests for single cells

The performance of a single DMFC with the anodic Pt-Ru/CNT (MI) catalyst was measured and compared with that with the anodic Pt-Ru/C (MI) and the Pt-Ru/C (E-TEK) catalyst (20 wt% Pt + 10 wt% Ru). Pt/C catalyst (20 wt.% Pt) was used as the cathodic