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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 nanosize 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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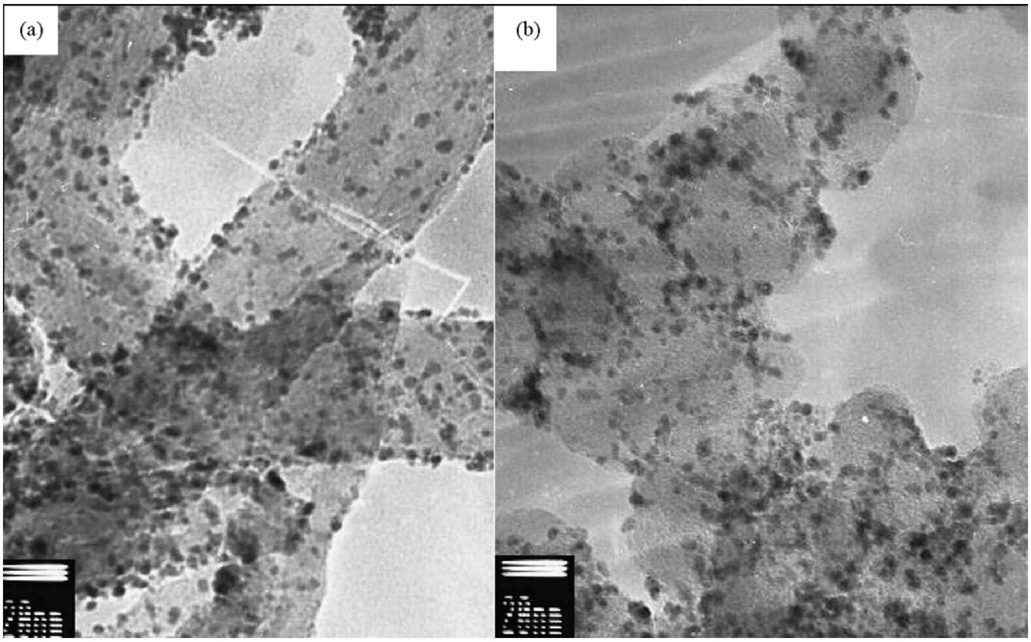

Fig. 1. TEM images of PtRu nanoparticles supported on multiwalled CNTs (a) and Vulcan XC-72 carbon (b).

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

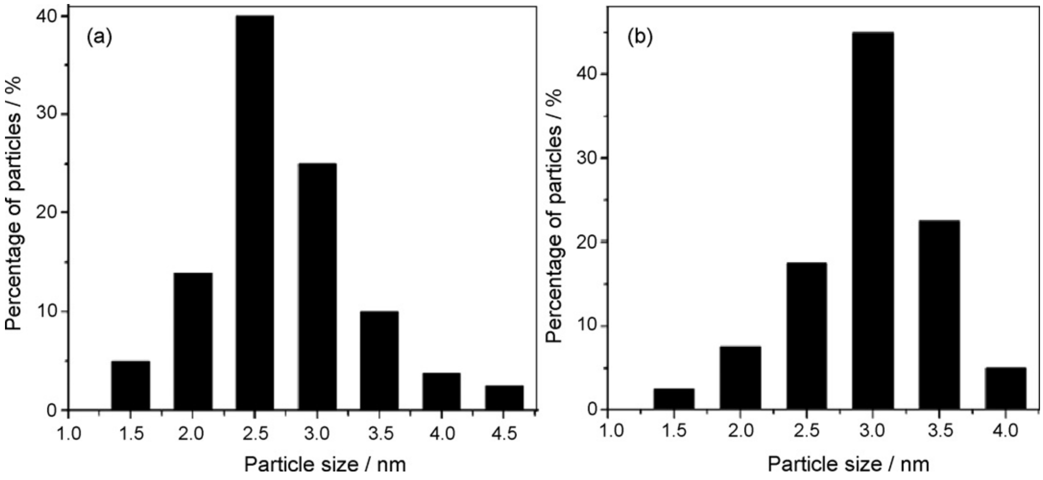

Fig. 2. Particle size distributions for PtRu nanoparticles supported on multiwalled CNTs (a) and Vulcan XC-72 carbon (b).

catalyst. The catalyst loading was 4 mg cm^{-2} for both the anode and the cathode and the effective electrode area of the single cell was 9 cm^2. The fabrication of the membrane electrode assembly (MEA) is the same as that in the literature [35]. The performance of the single cell was measured with a Fuel Cell Test System (Arbin Co.). 2.0 M CH_3OH solution with a flow rate of 20 mL min^{-1} and oxygen with a flow rate of 0.5 L min^{-1} at 0.05 MPa were used. The single cell was operated at 80 °C.

3. Results and discussion

3.1. TEM, EDX and XRD analyses

Part a and b of Fig. 1 show typical TEM images for the Pt-Ru/CNTs and Pt-Ru/C. It is shown that Pt-Ru particles with small average size were uniformly dispersed on carbon supports (carbon nanotubes and carbon black). Histograms of metal particle diameters were obtained by measuring the size of 200 particles in random regions as shown in Fig. 2. The average diameters for metal nanoparticles are 2.7 nm for Pt-Ru/CNTs (MI) and 2.9 nm for Pt-Ru/C (MI). These observations indicate that PtRu catalysts with uniform distribution and small average size can be synthesized by this modified impregnation method. It can be explained as follows: it is known to all that PtRu nanoparticles suspended in solution are easily aggregated. Therefore, before reduction step, $PtCl_6^{2-}$ and Ru^{3+} in the solution were firstly precipitated in the form of $(NH_4)_2PtCl_6$ and $Ru(OH)_3$ and then the precipitates were adsorbed on high-surface-area carbon supports. After the precipitates were reduced, the resulted PtRu nanoparticle were anchored to high-surface-area carbon supports and thus inhibited aggregating.

Fig. 3 shows the EDX results for Pt-Ru/CNTs and Pt-Ru/C samples. The weight contents of Pt-Ru in Pt-Ru/CNTs catalysts and in Pt-Ru/C catalysts are 28.94% and 28.46%, respectively. The Pt/Ru atomic ratio is 1.05 for Pt-Ru/CNTs, and 1.08 for Pt-Ru/C, close to that in the precursor solution.

Typical XRD patterns of the Pt-Ru/CNTs and Pt-Ru/C catalysts are shown in Fig. 4, from which the crystalline lattice fringes of the bimetallic alloy nanoparticles were confirmed. The XRD patterns displayed the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) reflections, confirming that the catalysts exhibit the fcc structures of Pt. The Pt(1 1 1) diffraction peaks for these Pt-Ru catalysts are shifted to higher positions than that for Pt/C, which can be interpreted as evidence of alloying. Diffraction peaks near 38° and 44° in 2θ from Ru are not observed, possibly because Ru has entered the Pt lattice and formed the Pt-Ru alloy or Ru exists as the amorphous form [36]. The diffraction peak at about 24° (carbon black) and 25.5° (CNTs) [37,38] observed is attributed to the hexagonal graphite structure (0 0 2), which can reflect the graphite degree of a carbon material. CNTs have higher diffraction peak (0 0 2) than carbon black, indicating that CNTs have higher graphite degree and better electrical conductivity than carbon black.

3.2. Electrochemical analysis

The Pt-Ru/CNTs and Pt-Ru/C catalysts were characterized at room temperature by cyclic voltammetry (CV) in electrolytes of 0.5 M H_2SO_4 and 1 M CH_3OH at a scan rate of 20 mV/s shown in Fig. 5. For comparison, a commercially available catalyst (20 wt%

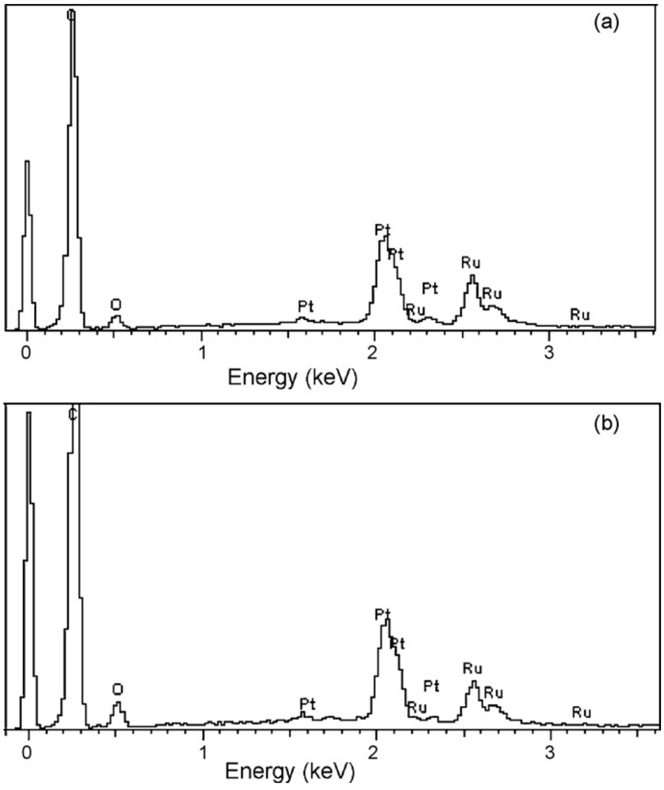

Fig. 3. EDX spectra of PtRu/CNTs (a) and PtRu/C catalysts (b).

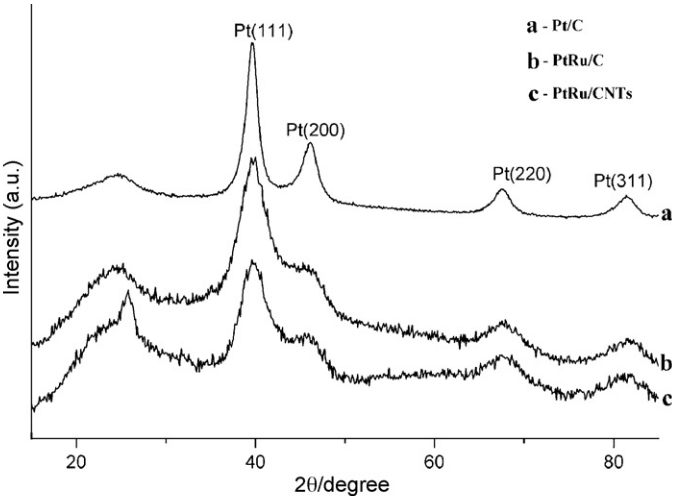

Fig. 4. XRD patterns of the catalysts prepared by modified impregnation method.

Pt + 10 wt % Ru supported on carbon, E-TEK, Inc.) was also studied under the same experimental conditions. It can be observed from Fig. 5 that the onsets of methanol oxidation peaks all begin at about 0.2 V (vs. Ag/AgCl), and the peak potentials of methanol oxidation are similar, at about 0.53 V (vs. Ag/AgCl). However, the peak current densities are different, 34 mA/cm^2 for Pt-Ru/CNTs (MI), 27 mA/cm^2 for Pt-Ru/C (MI), 24 mA/cm^2 for Pt-Ru/C (E-TEK) catalyst. Pt-Ru catalysts prepared in this work exhibit better methanol oxidation activities than commercial Pt-Ru/C (E-TEK) catalyst, which is attributed to uniform distribution and small average size of PtRu nanoparticles. In addition, the Pt-Ru/CNTs (MI) shows superior activity of methanol electro-oxidation to Pt-Ru/C (E-TEK) and Pt-Ru/C (MI), which is associated closely with two aspects: the novel modified impregnation method, and surface structures and electronic properties of CNTs [39,40].

Chronoamperometry (CA) curves for the three Pt-Ru catalysts are shown in Fig. 6. These curves reflect the activity and stability of the three Pt-Ru catalysts to catalyze methanol oxidation. Obviously, the decay in the methanol oxidation current with time was different. The Pt-Ru/CNTs shows the highest initial current density and limiting current density, which indicates the best catalytic activity and stability.

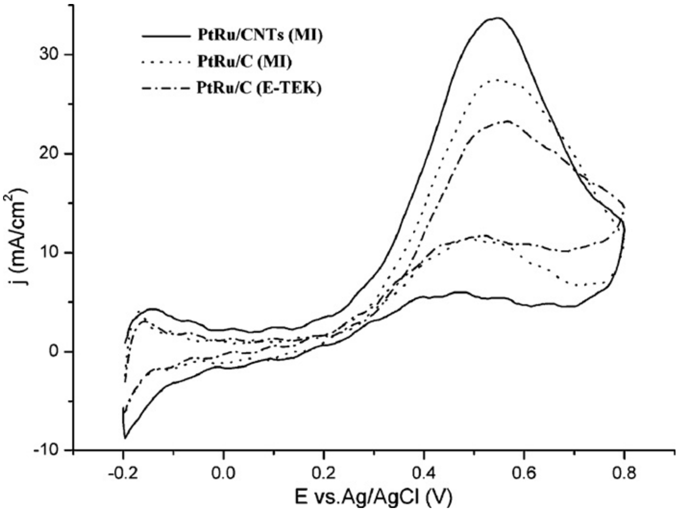

Fig. 5. Cyclic voltammograms recorded at 20 mV/s in 1 M CH_3OH + 0.5 M H_2SO_4 solutions at room temperature.

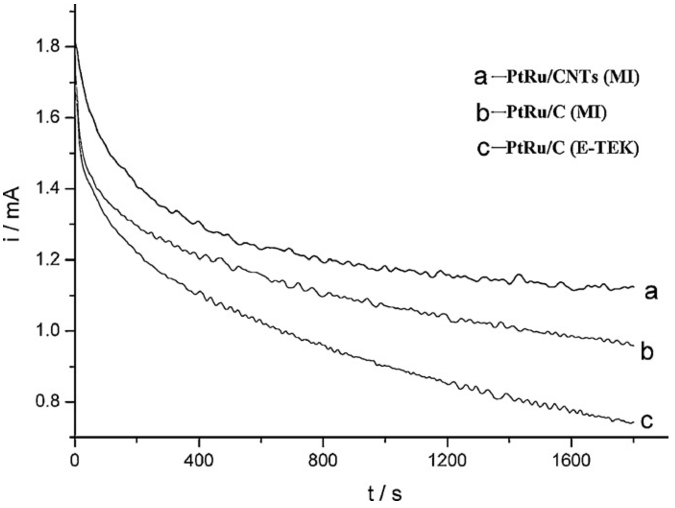

Fig. 6. Current vs. time plots measured by the CA method in1 M CH_3OH + 0.5 M H_2SO_4 solutions at 0.5 V (vs. Ag/AgCl) at room temperature.

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. It can be explained that Pt-Ru/CNTs (MI) prepared by modified impregnation method have uniform distribution and small average size of PtRu particles and CNTs have higher graphite degree and thus better electrical conductivity than carbon black.

3.3. Direct methanol fuel cell performance test

Fig. 7 shows the current density–voltage curves of the single DMFC with different anodic catalysts. Among the three tested Pt-Ru catalysts, the Pt-Ru/CNTs shows the highest performance, e.g., when the current density is 200 mA/cm^2, the voltage of the cell with the anodic Pt-Ru/CNTs is 0.30 V, cf. 0.26 V for Pt-Ru/C and 0.23 V for E-TEK catalyst. It is shown that the single cells with Pt-Ru/CNTs (MI) have higher open circuit voltage (OCV = 0.72 V) and maximal power density ($P_{\max}$ = 61 mW/cm^2) than those of Pt-Ru/C (MI, OCV = 0.68 V, $P_{\max}$ = 52 mW/cm^2) and Pt-Ru/C (E-TEK, OCV = 0.65 V, $P_{\max}$ = 48 mW/cm^2). This result is consistent with that of CVs and the reasons have been discussed in detail in Section 3.2.

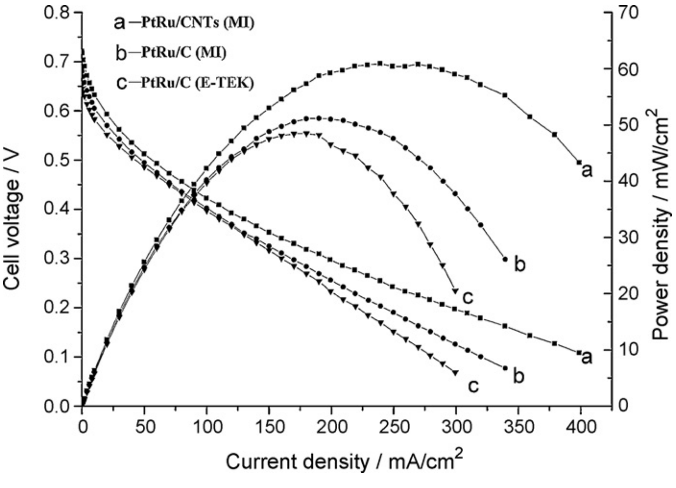

Fig. 7. Single cell performance using different PtRu catalysts at the anode at 80 °C.

4. Conclusion

In this study, a simple and rapid synthesis method for the preparation of PtRu/CNTs (MI) and PtRu/C (MI) was presented. Compared with conventional impregnation method, the modified impregnation method introduces a precipitate step before a reduction step, which prevents PtRu nanoparticles from aggregating. It was shown from TEM and XRD that Pt-Ru particles with small average size were uniformly dispersed on carbon supports (carbon nanotubes and carbon black) and displayed the characteristic diffraction peaks of Pt face-centered cubic structure. 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.

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