Stabilization and dispersion of PtRu and Pt nanoparticles on multiwalled carbon nanotubes using phosphomolybdic acid, and the use of the resulting materials in a direct methanol fuel cell

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ABSTRACT
PtRu and Pt nanoparticles were deposited on the surface of multiwalled carbon nanotubes (MWCNTs) with the assistance of phosphomolybdic acid (PMo) by a one-pot hydrothermal reduction strategy. Transmission electron microscopy shows a high-density PtRu (or Pt) nanoparticles uniformly dispersed on the surface of the MWCNTs with an average diameter of 1.8 nm for PtRu nanoparticles and 2.4 nm for Pt nanoparticles. Moreover, the as-prepared PMo/PtRu/MWCNT and PMo/Pt/MWCNT electrocatalysts are highly electroactive for the electrochemical oxidation of methanol. Cyclic voltammograms show a high electrochemical surface area (ESA) and a large current density for methanol oxidation at the modified electrode by PMo/PtRu/MWCNT and PMo/Pt/MWCNT electrocatalysts. Electrochemical impedance spectroscopy reveals a high CO tolerance for PMo/PtRu/MWCNT and PMo/Pt/MWCNT electrocatalysts in the electrochemical catalysis of methanol oxidation. For comparison, PtRu/MWCNT and Pt/MWCNT electrocatalysts were prepared in control experiments without PMo. The results demonstrate that PtRu and Pt nanoparticles deposited on MWCNTs in the presence of PMo were superior to those on MWCNTs without PMo in several respects including: (1) a smaller size and a higher dispersion; (2) a higher ESA; (3) a larger current density for methanol oxidation; (4) a higher tolerance for CO poisoning.

1. Introduction
Over the last several decades, a continuing demand arises for portable, high energy-density, yet less environment-pollution power sources, which directs the researches on a low-cost, high-efficiency anode electrocatalyst for use in direct methanol fuel cells (DMFCs). Pt and its alloy are widely used as anode electrocatalysts in DMFCs. However, at present, these catalysts are not efficient enough to make DMFCs economical, because Pt is expensive. Moreover, it will lose its activity toward the oxidation of methanol because it is prone to be poisoned by CO in the process of catalysis [1].

Intense researches have been devoted to Pt-based multi-component catalysts to enhance their poison tolerance with the ultimate goal of creating a cost-effective catalyst in practical DMFCs. Previous reports have shown that the activity of Pt on methanol oxidation can be improved by introducing some metal [2,3] or metal oxide [4,5] on the basis of
bifunctional mechanism or electronic effect. In the bifunctional mechanism, cocatalyst serves as a promoter which can favor the oxidation of CO or CHO by the oxygen-containing species formed on the neighboring poisoned Pt sites, for example, Ru-OH [6,7]. In electronic effect, cocatalyst acts as a modifier that can change the electronic structure of Pt, which can decrease the bond strength of intermediate Pt–CO like materials [8].

Heteropolyacid (HPA) is a subset of polyoxometalate capable of fast reversible multi-electrons transfer under mild condition. On the other hand, it has strong Bronsted acidity and high proton conductivity [9]. These properties make HPA available in fuel cells involved in the applications such as hydrogen oxidation, oxygen reduction and membrane fabrication [10–12]. Keggin PMo12O40 (PMo), one type of HPA, can be used as a promoter in the electrochemical conversion of CO and H2O to CO2 over gold catalysts in aqueous solution [13]. Similarly, Keggin HPA can favor CO conversion in the methanol oxidation process at Pt-based anode catalyst [14–20]. Han et al. [14] have reported PMo can act as a redox mediator for the electrochemical oxidation of CO originated from methanol oxidation at the electrode modified with multiwalled carbon nanotubes (MWCNTs)-supported PtSn nanoparticles in the presence of PMo. Maiyalagan [15] also have found the oxidation power of PMo can be enhanced at Pt catalysts in the presence of PMo12O40, which is owing to its assistance in the oxidative removal of poisoning species such as CO on the surface active site of Pt catalysts.

The specialty of Pt catalysts is a dominant factor that has influence on the efficiency of methanol oxidation. On the other hand, supports that used for Pt catalysts also play an important role in the enhancement of DMFCs performance. MWCNT is promising for the Pt catalysts support due to its great specific areas, high electrical conductivity, excellent chemical stability, and so on [21]. However, it is well-known that MWCNTs cannot be dispersed in the solution due to lack of surface modification [22]. On the other hand, MWCNTs without modification cannot supply sufficient surface sites to anchor the precursors of Pt nanoparticles, which will result in poor dispersion, and furthermore, aggregation of Pt nanoparticles on the surface of MWCNTs, especially under high loading [23,24]. Surface functionalization of MWCNTs is a prerequisite to the synthesis of Pt/MWCNT hybrids including non-covalent modification [24], layer-by-layer deposition [25,26], chemical oxidation [27–29], covalent binding [30,31], and in-site grafting by polymerization [23,32]. HPA can be readily adsorbed onto the surface of MWCNTs, which makes it very useful in the synthesis of Pt/MWCNT catalysts for DMFCs. Pan et al. [16] modified MWCNTs with PMo, and subsequently electrochemically deposited PtRu and Pt onto the surface of MWCNTs. These PtRu and Pt catalysts show a great enhancement in specific activity and exchange current density for the methanol oxidation. See et al. [17] deposited Pt onto the surface of MWCNTs, and subsequently impregnated PMo into the Pt catalysts by chemisorption. The impregnated PMo can improve stability and catalytic mass activity for the electrooxidation of methanol. On the other hand, HPA possesses affinity to noble metal [33,34], such as Au, Ag, Pd and Pt, which enable its use as a stabilizer for these noble metal colloids in synthesis.

Herein, a one-pot hydrothermal reduction strategy was put forward for the synthesis of PMo/PtRu/MWCNT and PMo/Pt/MWCNT electrocatalysts (Fig. 1). Before the procedures of synthesis, PMo was adsorbed on the surface of MWCNTs by sonication. It acted as a modifier to supply MWCNTs with sufficient surface sites for Pt or PtRu nanoparticles to anchor. Noted, by this way, MWCNTs were functionalized with PMo. Moreover, their structural and chemical integrity remain avoid of destruction by oxidation or covalent reaction. In the procedures of synthesis, PMo served as a stabilizer to prevent PtRu or Pt nanoparticles from overgrowth and aggregation on the surface of MWCNTs. Thus, it can be expected that PMo/PtRu/MWCNT and PMo/Pt/MWCNT catalysts hold the significant advantages over Pt/MWCNT and PtRu/MWCNT systems on the electrochemical performance of methanol oxidation.

2. Experimental

2.1. Chemicals and materials

All chemicals and standard solution were purchased from ACROS, HNO3 and HCl, were trace metal grade. Water was purified by a Milli-Q system.

MWCNTs were obtained from Chengdu organic Chemics Co. Ltd. (purity > 95% out diameter 10–20 nm, length–30 μm) and purified as follows [1]: The raw MWCNTs were dispersed by ultrasonication in water for several minutes. A H2O2 (18%) solution was added into this solution to decompose amorphous carbon by boiling for several hours. Then, a concentrated HCl (63%) solution was introduced to dissolve the metal particles inside the raw MWCNTs by refluxing for 8 h. After the solution was filtered through a 0.45 μm PTFE filter membrane, the filtered mass was collected and dried at 100 °C in vacuo.
Fourier transform infrared spectroscopy (FTIR) was performed on PMo/PtRu/MWCNT (or PMo/Pt/Ru/MWCNT) hybrids were synthesized by sonication according to [16]: 5 mg of MWCNTs and 10 mg PMo were dispersed in 10 mL of de-ionized water by sonication for 24 h under 45 Hz frequency at room temperature. Then, 20 mL of ethanol, 75 µmol H2PtCl6 and 25 µmol RuCl3 (100 µmol H2PtCl6 for PMo/Pt/MWCNT hybrids) were added into the mixture solution in batches. This mixture solution was sonicated for 0.5 h, and then transferred into a 100 mL flask charged with a magnetic bar. This flask was placed in a thermostated oil bath. The reaction solution was deoxygenated by nitrogen for 15 min, and then refluxed for 10 h at 140 °C. The obtained samples were collected by centrifugation and thoroughly rinsed with de-ionized water to remove non-adsorbed PMo until the washing solution became colorless. Then PMo/MWCNT hybrids were dried at 80 °C in vacuo for characterization.

2.3. Preparation of PMo/Pt/MWCNT and PMo/PtRu/MWCNT hybrids

PMo/Pt/MWCNT and PMo/PtRu/MWCNT (or PMo/Pt/Ru/MWCNT) hybrids were prepared by sonication according to [16]: 5 mg of MWCNTs and 10 mg PMo were dispersed in 10 mL of de-ionized water by sonication for 24 h with a set frequency of 45 Hz at room temperature. The obtained sample was collected by centrifugation and thoroughly rinsed with de-ionized water to remove non-adsorbed PMo until the washing solution became colorless. Then PMo/MWCNT hybrids were dried at 80 °C in vacuo for characterization.

2.4. Characterization

Fourier transform infrared spectroscopy (FTIR) was performed on Nicolet Nexus 670 spectrometer using KBr pellets after baseline-correction.

X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB-MKII spectrometer with an unmonochromated Al KR X-ray source (1486.6 eV) for excitation. High-resolution spectra were obtained at a perpendicular takeoff angle, using the pass energy of 20 and 0.05 eV steps.

Transmission electron microscopy (TEM) observation was performed on a JEOL 2010 microscope equipped with an electron energy dispersive X-ray spectroscopy (EDS), operating at 200 kV using a high-brightness LaB6 electron gun. The composition of different catalysts was determined by its EDS at 100 kV.

Inductively coupled plasma-atom emission spectroscopy (ICP-MS) was performed on Agilent 7500ce quadrupole ICP-MS. Different catalysts, PMo/PtRu/MWCNT, PMo/Pt/MWCNT, PtRu/MWCNT and Pt/MWCNT hybrids, were sampled by treatment with aqua regia. MWCNTs cannot be dissolved, which can be discarded by centrifugation. The elements, Pt, Ru and Mo were dissolved, and left in solution for ICP-MS analysis.

2.5. Electrochemical investigation

We used a 15 mL glass electrochemical cell containing three electrodes: a glassy carbon disk working electrode (3 mm in diameter) embedded in Teflon, a platinum wire counter electrode (1 mm in diameter, 5 cm in length), and a saturated KCl Ag/AgCl electrode as the reference electrode. Before use, the glassy carbon electrodes were polished with 0.5 µm alumina slurry, washed with the de-ion water, then immersed for 20 min in a sonicator bath, and finally washed with the de-ion water.

To modify the glassy carbon electrode with different catalysts, 4.0 mg of these materials (PMo/PtRu/MWCNT, PMo/Pt/MWCNT, PtRu/MWCNT and Pt/MWCNT hybrids) were dispersed in 400 µL de-ion water to form a homogenous catalyst ink by sonication, and then a 5 µL of this catalyst ink was mixed with a 2.5 µL of 0.5% Nafion®117 ethanol solution. The mixture was spread and air-dried on a glassy carbon electrode at room temperature.

A three-electrode setup was configured with CHI 660C interfaced to a personal computer at room temperature for the electrochemical characterization of the as-prepared modified glassy carbon electrodes. The electrolytic solution was bubbled with nitrogen for 15 min before the electrochemical experiment.

Electrochemical impedance spectroscopy (EIS) measurements were performed in CHI750C with a 5 mV of amplitude of modulation potential in the frequency ranged from 0.01 Hz to 100 kHz.

3. Results and discussion

3.1. Characterization of PMo/MWCNT hybrids

PMo/MWCNT hybrids were characterized by TEM, FTIR and XPS. Their morphology was shown in Fig. S1 (supporting information), PMo is covered on the surface of MWCNTs to form a membranous structure with a thickness of 10–20 nm, whereas purified MWCNTs are clean and free of particles deposited. The presence of PMo on the surface of MWCNTs was confirmed by FTIR and XPS (Fig. S2). As shown in Fig. S2A, four peaks at 1065, 968, 869 and 790 cm−1 can be observed at the spectrum of PMo, which are assigned to an inner P–Oa–Mo, Mo–Od–Mo, Mo–Ob–Mo and an external Mod–Oc band [16], respectively. For the purified MWCNTs, no obvious peaks were presented in their spectrum ranged from 700 to 1100 cm−1, except for a broad peak at 1000 cm−1 corresponding to a vibration of C–O group [16]. The spectrum of PMo/MWCNT hybrids exhibit four peaks, which is close to that of PMo. The result is indicated that the PMo was chemically adsorbed on the surface of MWCNTs. As shown in Fig. S2B, after PMo was deposited on to the matrix of MWCNTs, it will give rise to a XPS signal attributed to Mo 3d spectrum at interval between 230 and 238 eV [23], which is consistent with the result of FTIR spectrum.
3.2. Characterization of PMo/PtRu/MWCNT and PMo/Pt/MWCNT hybrids

The morphology of PMo/PtRu/MWCNT and PMo/Pt/MWCNT hybrids was imaged by TEM (Fig. 2). Their full TEM images with different magnifications are provided in supporting information (Figs. S3–S6). TEM images show a high-density PtRu (Fig. 2A and B) and Pt (Fig. 2C and D) nanoparticles were uniformly deposited onto the surface of MWCNTs in the presence of PMo. Their size distributions (Fig. 2E and F) were evaluated statistically by measuring the diameter of PtRu and Pt nanoparticles on the surface of MWCNTs in the selected area. The diameter of PtRu nanoparticles averages 1.6 nm, for Pt nanoparticles, it is 2.4 nm. The size distribution of PtRu nanoparticles is 1–2.6 nm, for Pt nanoparticles, it is 1–3 nm.

For comparison, PtRu/MWCNT and Pt/MWCNT hybrids were prepared in accordance with the procedures for the synthesis of PMo/PtRu/MWCNT and PMo/Pt/MWCNT hybrids except for the absence of PMo. Fig. 3 shows that PtRu (Fig. 3A and B) and Pt nanoparticles (Fig. 3C and D) are distributed unevenly on the surface of MWCNTs, and some smaller nanoparticles are aggregated to form a bigger one. The diameter of PtRu nanoparticles averages 3.5 nm, for Pt nanoparticles, it is 8 nm. The size distribution of PtRu nanoparticles is 1–6 nm, for Pt nanoparticles, it is 1–12 nm.

The composition of four hybrids was determined by EDS attached to TEM (Fig. S7). The relative stoichiometry of Pt, Ru, and Mo for PMo/PtRu/MWCNT hybrid is 4:1:1. In the case of PMo/Pt/MWCNT hybrid, the relative stoichiometry of Pt and Mo is 4:1. The results are consistent with the data of ICP-MS (Table S1). Obviously, PMo make a difference for the preparation of MWCNTs-based PtRu (or Pt) hybrids. For the purified MWCNTs, there are few defects on the surface of MWCNTs originated from purification. These defects supply...
sites for the deposition of Pt or PtRu nanoparticles. However, they are not uniform and not adequate, especially to load high-density PtRu or Pt nanoparticles, which will result in a poor dispersion of PtRu (or Pt) nanoparticles on the surface of MWCNTs. When MWCNTs were functionalized with PMo, a PMo layer will be formed. This PMo layer produces a uniform distribution of OH and Mo–O groups. The oxygenic group can act as a coordination site bond with Pt in the form of PtO\textsuperscript{x} at the outermost perimeter of PtRu or Pt nanoparticles [28,29]. Therefore, a much more uniform distribution of Pt or PtRu nanoparticles can be observed on the surface of PMo/MWCNT hybrids. On the other hand, PMo possess 3–4 negative charge, which makes PMo available in use as a stabilizer to protect against aggregation and overgrowth of PtRu (or Pt) nanoparticles in the synthesis of PMo/PtRu/MWCNT and PMo/Pt/MWCNT hybrids. In the absence of PMo, PtRu (or Pt) nanoparticles will be unstable, small PtRu (or Pt) nanoparticles will aggregate to form a big one. Therefore, PtRu and Pt nanoparticles with a much smaller size can be deposited on the surface of MWCNTs in the presence of PMo.

### 3.3. Electrochemical catalysis of methanol oxidation

A comparative investigation on the electrochemical behavior of the different catalysts modified electrode was conducted by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometric method (Fig. 4). Before the electrochemical investigation, the as-prepared catalysts modified electrode was activated by CV in N\textsubscript{2}-saturated 1 M H\textsubscript{2}SO\textsubscript{4} solution (Fig. S8, supporting information). For PMo/PtRu/MWCNT (or PMo/Pt/MWCNT) catalysts, the non-adsorbed PMo present in catalysts will detach from the matrix of PMo/PtRu/MWCNT and PMo/Pt/MWCNT, and thus a refined CV curve of Pt catalysts will remain stable after suc-
cessive cyclic potential sweeping (40 cycles) in the range from −0.2 to 1.0 V. (Fig. S9, supporting information). In addition, a new distinct couple of redox peaks (I) take place at 0.23 V, meanwhile two unconspicuous couples of concomitant peaks are also presented at 0 (II) and −0.15 V (III), which are assigned to multiple electrons transfer of Keggin PMo\[16\]. The oxidation peak (I) current at 0.23 V is linear to the scan rate of CV curves obtained from the modified electrode by PMo/PtRu/MWCNT catalysts, indicating a surface-confined redox process for PMo adsorbed on the surface of PtRu nanoparticles and MWCNTs in N\textsubscript{2}-saturated 1 M H\textsubscript{2}SO\textsubscript{4} solution [16] (Fig. S9, supporting information).

Fig. 4A shows CV curves of the modified electrodes by different catalysts in N\textsubscript{2}-saturated 1 M H\textsubscript{2}SO\textsubscript{4} solution. In the case of CV curve from PtRu/MWCNT (or Pt/MWCNT) catalysts, both the reductive adsorption region of protons in the reverse cathodic scan and the oxidative desorption region of hydrogen atom in the forward anodic scan between −0.2 and 0.1 V show signatures of polycrystalline PtRu (or Pt) catalysts [35]. This potential region is defined as the hydrogen area, which can be used to calculate the electrochemical surface area (ESA) of PtRu (or Pt) nanoparticles [23]. After the double layer charge is corrected from CV curve, ESA is determined as 76.23 m\textsuperscript{2} g\textsuperscript{-1} of Pt for PtRu/MWCNT catalysts. (Table S2, supporting information). As discussed above, CV curves from PMo/PtRu/MWCNT and PMo/Pt/MWCNT catalysts also show a dominant property of polycrystalline PtRu (or Pt) catalysts. Moreover, their CV curves contain the characteristic redox current peaks from PMo itself around −0.15, 0, and 0.23 V. Thus, it is difficult to accurately measure ESAs of PMo/PtRu/MWCNT and PMo/Pt/MWCNT catalysts from the hydrogen region of CV curves because of the superimposed redox peaks from PMo [35]. Without regard to the contribution from PMo, ESAs of PMo/PtRu/MWCNT and PtRu/MWCNT catalysts are estimated to be 103.84 and 91.34 m\textsuperscript{2} g\textsuperscript{-1} Pt, respectively, being higher than those of PtRu/MWCNT and Pt/MWCNT catalysts. The higher ESAs of PMo/PtRu/MWCNT (or PtRu/MWCNT) catalysts are mostly dependent on smaller size and higher dispersion of PtRu (or Pt) nanoparticles. It also means more active PtRu (or Pt) surface sites accessible to the electrochemical oxidation of methanol. Thus, a higher catalytic activity can be expected for the electrochemical catalysis of methanol oxidation at the electrode modified with PMo/PtRu/MWCNT (or PMo/Pt/MWCNT) catalysts.

The electrocatalytic oxidation of methanol was studied at the as-prepared modified electrodes by CV in N\textsubscript{2}-saturated 1 M H\textsubscript{2}SO\textsubscript{4} solution containing 1 M methanol. Fig. 4B shows...
a significant enhancement of the peak current concomitant with an obvious negative shift of peak and onset potentials of methanol oxidation present at CV curve of PMo/PtRu/MWCNT (or PMo/Pt/MWCNT) catalysts as compared to PtRu/MWCNT (or Pt/MWCNT) catalysts. The forward peak is due to oxidation of methanol, and the backward peak is regarded as the oxidation of adsorbed CO which results from incomplete oxidation of methanol in the forward scan [32]. The forward peak current of PMo/PtRu/MWCNT catalysts is 263.4 mA/mg, which is 4.17 time higher than that of PtRu/MWCNT catalysts (63.1 mA/mg). Similar results were obtained on Pt catalyst, the forward peak current of PMo/Pt/MWCNT catalysts is 164.7 mA/mg, which is a 4.15 times higher than that of Pt/MWCNT catalyst. It should be noted that PMo/PtRu/MWCNT and PMo/Pt/MWCNT catalysts have superior efficiency on methanol oxidation over PtRu/MWCNT and Pt/MWCNT nanohybrids prepared with ionic liquid polymer (PIL). Under the same experimental condition, the forward peak current of methanol oxidation is 242.3 mA/mg for PtRu/MWCNT-PIL catalyst, and 155.7 mA/mg for Pt/MWCNT-PIL catalyst, respectively, [23] being lower than those of PMo/PtRu/MWCNT and PMo/Pt/MWCNT catalysts. On the other hand, by comparison with PtRu/MWCNT (or Pt/MWCNT) catalysts, PMo/PtRu/MWCNT (or PMo/Pt/MWCNT) catalysts show a negative shift of over 0.60 V for onset potential. The forward peak potential and backward peak potential of methanol oxidation at PMo/PtRu/MWCNT and PMo/Pt/MWCNT catalysts are also lower than those of PtRu/MWCNT and Pt/MWCNT catalysts by over 0.50 V (Table S3, supporting information).

The constant potential amperometry technique can be employed as a useful method for the evaluation of the electrocatalytic performance toward methanol oxidation at the electrodes modified with the different catalysts. The typical steady-state currents were recorded from chronoamperometry in N2-saturated 1 M H2SO4 solution containing 1 M methanol. As shown in Fig. 4C, the oxidative currents of methanol decrease for all catalysts at the beginning, which resulted from the deactivation of the Pt sites by adsorbed CO species generated from methanol oxidation process. When the processes of accumulation and removal of CO species research a balance, the currents of methanol oxidation at all catalysts will arrive at a stable stage [32]. Overall, PMo/PtRu/MWCNT (or PMo/Pt/MWCNT) catalysts show a higher current response than PtRu/MWCNT (or Pt/MWCNT) catalysts under over 1.25 h continuous electrocatalysis at an applied potential of 0.6 V.

EIS technique has been used to demonstrate the interfacial processes of methanol oxidation at these catalyst modified electrodes. The impedance curves of methanol electrooxidation are dependent on the applied potentials that used for the Pt catalysts. In the case of PMo/PtRu/MWCNT catalyst, its Nyquist curves show an impedance behavior from a resistive type to a pseudoinductive one and then to inductive one in the potential ranged from 0.3 to 0.7 V (Fig. S10, supporting information). On the other hand, the impedance behaviors of methanol electrooxidation are related to the catalysts that used in EIS. Fig. 4D shows Nyquist plots of four catalysts in N2-saturated 1 M H2SO4 solution containing 1 M methanol at an applied potential of 0.4 V. All Nyquist plots appear as a multitude of semicircle composed of a large arc in the first quadrant and a small loop in the fourth quadrant which can be characterized as an inductive behavior. The intersection of the semicircle with the real part of the impedance (Z) at high frequencies (105–107 Hz) is associated with the resistances of catalysts, electrolyte and electrical circuit (Fig. S11, supporting information). PMo/PtRu/MWCNT and PMo/Pt/MWCNT catalysts exhibit a lower resistance than those of PtRu/MWCNT and Pt/MWCNT. Considering that the resistances of the electrical circuit and the electrolyte were the same in all cases, the difference of the resistance in this frequency range may stem from the distinctness in the mass of Nafion used in the preparation of these catalysts modified electrodes. Meanwhile, the semicircle intersection with the real part of the impedance (Z) at lower frequencies (0.18–104 Hz) gives the charge transfer resistance of the catalysts toward the oxidation of methanol. It can be used to compare the activities of different catalysts. The diameter of arc for PMo/PtRu/MWCNT (or PMo/Pt/MWCNT) catalysts is smaller than that of PtRu/MWCNT (or Pt/MWCNT) at this investigated frequency region, suggesting a smaller charge transfer resistance, namely, a higher activity of PMo/PtRu/MWCNT (or PMo/Pt/MWCNT) catalysts on methanol oxidation, which should be attributed to a faster oxidative removal of adsorbed CO that occurs at the surface of PtRu or Pt nanoparticles. When the frequency varied from 0.18 to 0.01 Hz, Nyquist curves extended to the fourth quadrant with a characteristic of inductive behavior. The negative impedance of small loop is attributed to the formation of chemisorbed hydroxyl species, which facilitate the oxidation of adsorbed CO originated from methanol oxidation [36].

In summary, PMo/PtRu/MWCNT (or PMo/Pt/MWCNT) catalysts have a higher CO tolerance for methanol oxidation than PtRu/MWCNT (or Pt/MWCNT) catalysts. A feasible explanation may be associated with the two facts. At first, for PMo/PtRu/MWCNT (or PMo/Pt/MWCNT) catalysts, they have a smaller size and a higher dispersion of PtRu (or Pt) nanoparticles on the surface of MWCNT, which allows more active sites for CO oxidation. Secondly, the presence of PMo itself can assist the electrochemical oxidation of methanol by oxidative removal CO to prevent PtRu (or Pt) catalysts from poisoning [35]. Meanwhile, the efficiency of the electrochemical catalysis on methanol oxidation can be significantly after the introduction of Ru component into Pt catalysts regardless of PMo/Pt/MWCNT and Pt/MWCNT. It should be attributed to the formation of Ru–OH on the neighboring poisoned Pt sites, which will be in favor of the removal of intermediate products such as CO and CHO from the surface of Pt plane.

4. Conclusions

A one-pot procedure has been developed for the synthesis of PMo/PtRu/MWCNT and PMo/Pt/MWCNT catalysts. As a result from the assistance of PMo, PtRu and Pt nanoparticles supported on PMo/MWCNT hybrids have a smaller particle size, a better dispersion and a higher ESA than those on MWCNT’s alone. Therefore, PMo/PtRu/MWCNT (or PMo/Pt/MWCNT) electrocatalysts exhibit a better performance on the direct electro-oxidation of methanol with a higher current density and a faster charge transfer as compared to PtRu/MWCNT.
(or Pt/MWCNT) hybrids, which will make them available as a promising catalyst in DMFCs.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 20903082).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2012.03.004.

REFERENCES


