Hydrothermal Synthesis of Pt-Ru/MWCNTs and its Electrocatalytic Properties for Oxidation of Methanol

Sun Jingyu[1], Huang Jianshu[1], Cao Yanxia[3], Zhang Xiaogang[1,2]*

[1]Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, China
[2]College of Material Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China
[3]School of Material Science and Engineering, Zhengzhou University, Zhengzhou 450001, China
E-mail: azhangxg@nuaa.edu.cn (X.-G. Zhang).

Pt-Ru nanoparticles supported on multiwalled carbon nanotube (MWCNTs) were synthesized by hydrothermal method. The catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). Pt-Ru nanoparticles uniformly dispersed on MWCNTs with the mean diameter of about 3.5 nm. The electro- catalytic oxidation of methanol was studied by cyclic voltammetry, chronoamperometry and impedance spectroscopy in 0.5 M H_2SO_4 solution containing 1.0 M CH_3OH. The results showed that the Pt-Ru/MWCNTs catalysts as prepared had higher electrocatalytic activities for methanol oxidation than that of Pt-Ru/MWCNTs synthesized by microwave heating method.

1. INTRODUCTION

Direct methanol fuel cells (DMFCs), which provide a new way to store and convey energy, have attracted much attention as green power sources for automobiles and portable electronics applications [1-3]. Fuel cells based on the oxidation of methanol require electrocatalysts to achieve the current density needed for commercial fuel cell applications. Among the metal catalysts, platinum shows the highest catalytic activity for electro-oxidation of methanol. However, pure platinum as the catalyst will be rapidly poisoned by the adsorption of CO produced during the oxidation of methanol. In order to enhance the oxidation efficiency and reduce costs, Pt-based alloy catalysts with various transition metals such as Pt–Ru[4-7], Pt–Ni[8,9], Pt–Sn[10,11], et al. have been prepared and studied as the possible catalysts for the electrooxidation of methanol. Among the electrocatalysts used in DMFC, Pt-

Ru alloy catalysts exhibit enhanced tolerance of CO and improved electrocatalytic activities. A number of strategies for synthesis of Pt or Pt-Ru bimetallic catalysts were attempted [12-15]. Two mechanisms have been proposed to account for the promotional effect of Pt–Ru alloy catalysts. One is the so-called bifunctional mechanism, in which the role of ruthenium is to dissociate water to form adsorbed OH species, which then reacts with adsorbed CO to generate CO_2. Another explanation is the electronic ligand-effect mechanism, i.e. the electronic properties of platinum are modified by Pt-Ru orbital overlaps so that the binding strength of CO adsorbed on Pt is weakened, leading to the enhancement of electrocatalytic activities for methanol electro-oxidation [16, 17].

In this paper, a simple hydrothermal synthesis method is presented for preparing Pt-Ru nano-particles supported on multil-walled carbon nanotubes (MWCNTs). In the process, Pt-Ru nano-particles were prepared by a simultaneous reduction of H_2PtCl_6 and $RuCl_3$ using ethylene glycol (EG) as reducing reagent in the autoclave container in 423 K. Pt-Ru nanoparticles with an average diameter of 3.5 nm were dispersed on the surface of MWCNTs and were found to be excellent performances in the electrocatalytic oxidation of methanol. It demonstrates that the hydrothermal synthesis method to prepare Pt-Ru/MWCNTs catalyst is simple and efficacious.

2. EXPERIMENTS

2.1. Preparation of the Pt-Ru/MWCNTs electrocatalyst

To improve their hydrophilicity, raw MWCNTs(procured from Shenzhen Nanotech Port Co., Ltd. in China.) was treated by concentrated nitric acid (65–68 wt.%) following Lordi et al.′ s method [18].

Pt-Ru/MWCNTs (20 wt % Pt and 10 wt % Ru) were prepared by reducing H_2PtCl_6 and $RuCl_3$ (purchased from Shanghai Chemical Company) with ethylene glycol (purchased from Shanghai Chemical Company) under hydrothermal condition. The atomic composition of the catalysts was chosen to Pt:Ru=1:1, the most active composition for the methanol electro-oxidation reaction [16]. Briefly, the preparation procedure consisted of the following steps: In a 50 mL beaker, 2.0 mL 0.05 M H_2PtCl_6 and 2.0 mL 0.05 M $RuCl_3$ aqueous solution was mixed with 30 mL of EG. 0.4 M KOH was added dropwise until pH value was adjusted to 8 under magnetic stirring. About 70 mg of pretreated MWCNTs were added into the solution, and the solution was sonicated for 1 h. After magnetic stirred 3 h again, the solution was transferred into an autoclave container and sealed, then hydrothermal treatment at 423 K for 5 h. The resulting suspension was filtered, and washed with distilled water and acetone respectively, then dried at 353 K overnight in a vacuum oven. The final product was denoted as sample A. To compare the electrocatalytic performance of sample-A, Pt-Ru/MWCNTs (20 wt.% Pt and 10 wt.%Ru) were prepared by microwave heating method [15] and the product was denoted as sample B.

1.2. Morphological and structural characterization of Pt-Ru/MWCNTs

The crystalline structure of sample A and sample B were characterized by powder X-ray diffractometry (XRD) on a MAC M18Xce Diffractometer with Cu Kα radiation source (λ=0.15418 nm). The morphology and granularity of sample A were observed on a Holland Techai G200

transmission electron microscopy (TEM). Energy dispersive spectroscopy (EDS) spectrum analysis for the sample-A was carried out with a Germany Leo 1430 VP scanning electron microscopy and England OXFORD 2000 energy-dispersive X-ray analyzer.

1.3. Electrochemical measurements

Cyclic voltammetry, chronoamperometry and impedance measurements were carried out on AUTOLAB PGSTAT30 electrochemical workstation with use of a three-electrode test cell at room temperature. The impedance spectra were recorded between 100 kHz and 10 mHz. Platinum disk electrode (5 mm in diameter), was used as substrates for the sample A and B. The working electrode was obtained in the following steps: (i) 5 mg of sample-A or sample-B was dissolved in 2 mL 0.05 % Nafion solution (Aldrich) and then sonicated for 0.5 h; (ii) 40 μL of the slurry was injected and spread on the Pt disk electrode; (iii) the electrode was then dried at 80 °C in a vacuum oven, the catalyst loading was about 0.5 mg /cm^2 based on this geometric area. A saturated calomel electrode (SCE) and a Pt foil(1×1cm) were used as the reference and counter electrodes respectively. All electrolytes were deaerated by bubbling purity N_2 for 20 min and protected with a nitrogen atmosphere during the entire experimental procedure.

3. RESULTS AND DISCUSSION

3.1. Surface morphology and structural characterization of Pt-Ru/MWCNTs

The powder X-ray diffraction (XRD) patterns for sample A and sample B are shown in Fig. 1. The sharp peak at about 26° is attributed to the graphite (002) plate of the MWCNTs support in Fig.1. The other four peaks are characteristic of face centered cubic (f. c. c.) crystalline Pt (JCPDS-ICDD, Card no.04-802), corresponding to the planes (111), (200), (220) and (311) at 2θ values of ca. 40, 46, 68 and 82° respectively. The diffraction pattern of sample-A and B display mostly the reflection characteristics of the Pt f. c. c structure, and the diffraction peaks are shifted slightly to higher 2θ values relative to the same reflections on bulk Pt, which suggests that a Pt-Ru alloy has been formed [7,19].
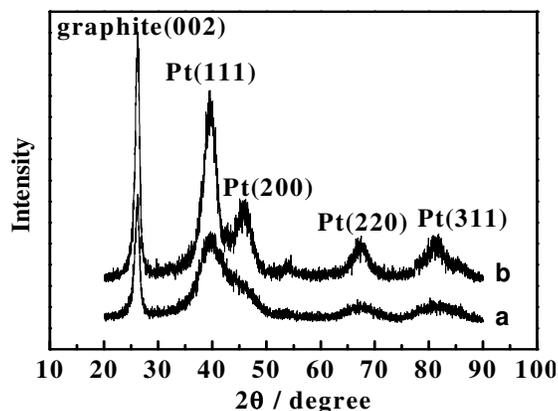
Figure 1. XRD patterns of sample A (a) and sample B (b) catalysts

For the two samples, no peak reflections of the h.c.p. crystal structure of Ru and tetragonal RuO_2 are seen. The pattern of sample A shows that a small amount of amorphous hydrous Ru oxide and /or Pt oxide are probably present. The broader diffraction peaks for the two catalysts also lead to smaller average alloy particle size as calculated by the Scherrer Equation[20]:

$$L = 0.9\, \lambda K\alpha /(B_{2\theta}\cos\theta) \qquad\qquad (2)$$

where L is the average particle size, $\lambda K\alpha$ is the X-ray wavelength (0.15418 nm for Cu $K\alpha$ radiation), $B_{2\theta}$ is the half height peak width, and θ is the Bragg angle corresponding to the diffraction peak . The calculation results evaluated from the (220) reflection peak shows the average size of Pt-Ru nanoparticle is 3.5 nm for sample-A. In our approach, bimetallic nanoparticles were directly deposited on the MWCNTs surface by hydrothermal treatment of EG solutions containing Pt and Ru salts.
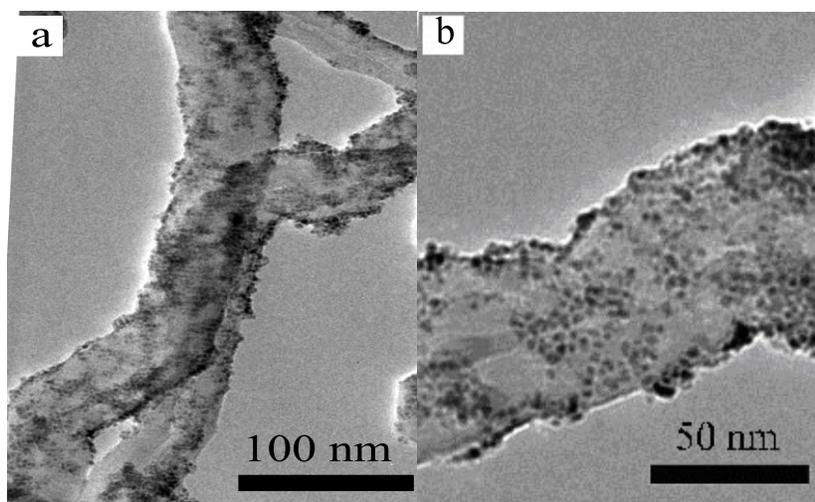
Figure 2. TEM images of sample A catalyst

Fig.2 shows the typical TEM images of sample A, and it shows a remarkably uniform and high dispersion of metal particles on the MWCNTs surface. The particle size distributions of the Pt-Ru alloy in the supported MWCNTs were about 2~6 nm from TEM images, and average particle size was about 4 nm, which were in good agreement with the XRD measurements. And it is just about the ideal size of Pt–Ru electrocatalyst for methanol electrooxidation [21].Hydrothermal condition can provide a uniform environment for the nucleation and growth of metal particles compared with microwave radiating condition.

EDS spectrum analysis was used for the determination of overall Pt:Ru atomic ratio. The result of the EDS analysis for sample A is shown in Fig. 3. From EDS analysis, 68 wt.% carbon , 19.5 wt.% Pt and 9.5 wt.% Ru(2 wt.% O probably derived from oxide or –COOH and -OH) were determined. Fig.3 gives Pt/Ru atomic ratio is nearly 1:1 and that is consistent to the ratio of reaction before. It improved H_2PtCl_6 and $RuCl_3$ can be completely reduced under hydrothermal condition. Chemical functional groups such as –COOH and –OH derived from acid oxidation processes act as anchoring sites for

metal precursors. Thus the particle size of Pt-Ru may be correlated with the oxidation of MWCNTs, as efficient deposition of Pt-Ru nanoparticles results from an interaction between the metal salt precursor and the graphene edges of MWCNTs [22].
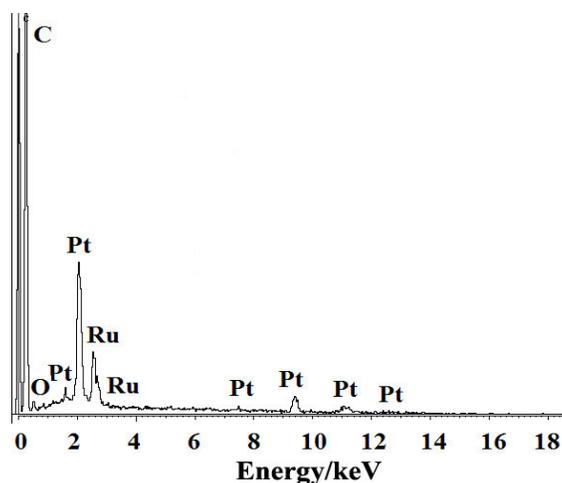
Figure 3. EDX spectrum of sample A catalyst

3.2. Electrochemical performances of Pt-Ru/MWCNTs catalyst

Fig.4 shows the cyclic voltammograms curves of the sample A modified electrode and sample B modified electrode in 0.5 M H_2SO_4 +1.0 M CH_3OH aqueous solution, at a potential sweep rate of 20 mV s^{-1}.
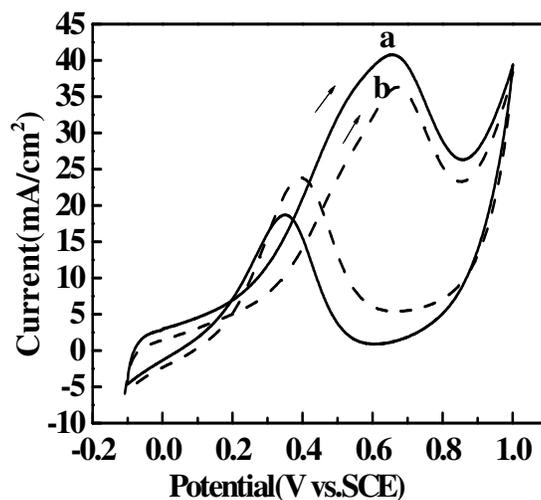
Figure 4. Cyclic voltammograms(CV) curves for methanol electro-oxidation on sample-A electrode (a) and sample-B electrodes(b) in 0.5 M H_2SO_4 +1.0 M CH_3OH solution at the scan rate of 20 mV/s

For the methanol electro-oxidation on sample A electrode (solid line in Fig.4), two oxidation peaks, which are related to the oxidation of methanol and the corresponding intermediates produced during

the methanol oxidation, can be observed clearly at 0.65 V and 0.35 V, respectively. While two oxidation peaks in sample B (Fig.4 b dotted line) are appeared at 0.67V and 0.38V respectively. The shape of the curves and the peak potentials are in accord with other work [7, 16]. However it can be seen that the anodic current on sample A (solid line) is substantially greater than that of on sample B (dotted line). The reasons may be as follows:

(i) Pt-Ru/MWCNTs synthesized by hydrothermal method contains ideal small size and high dispersion of Pt-Ru nanoparticles on MWCNTs surfaces; (ii) the Pt and Ru salt precursors were completely reduced under hydrothermal condition than under microwave heating condition. It can be seen that the anodic currents are significantly decreased when potential above 0.65V at the sample A electrode in the forward scan, indicating the surface active sites have been blocked noticeably by adsorbed CO species. The anodic current peak increases again above 0.85V, which arise from the oxidation of the adsorbed CO and methanol as a consequence of the release of surface active sites by CO removal at high potential. In the reverse scan, one oxidation peak can be seen at +0.35 V, which can be attributed to the removal of the residual carbon species formed in the forward scan. The reaction mechanism for methanol oxidation on Pt-Ru nanoparticle surfaces is proposed as below:

$$Ru\text{-}Pt + CH_3OH \rightarrow Ru\text{-}(Pt\text{-}CHO) + 3H^+ + 3e^- \qquad\qquad (2)$$

$$Ru\text{-}(Pt\text{-}CHO) + H_2O \rightarrow (Ru\text{-}OH)\text{-}(Pt\text{-}CHO) + H^+ + e^- \qquad (3)$$

$$((Ru\text{-}OH)\text{-}(Pt\text{-}CHO)) \rightarrow (Ru\text{-}OH)\text{-}(Pt\text{-}CO) + H^+ + e^- \qquad (4)$$

$$(Ru\text{-}OH)\text{-}(Pt\text{-}CO) \rightarrow Ru\text{-}Pt + CO_2 + H^+ + e^- \qquad\qquad (5)$$
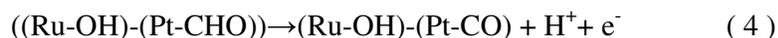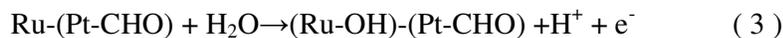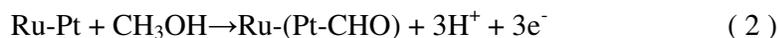
Usually, onset potential and peak current density are the two important parameters to compare the activities of electrocatalysts for the electro-oxidation of methanol. Sample A and sample B electrodes all exhibited onset potentials of about 0V for the electro-oxidation of methanol. The peak current density of sample A in the forward scan is higher than that of sample B. These results also agree well with the excellent CO tolerance of the Pt-Ru /MWCNTs catalysts. The ratio of the forward oxidation current peak (I_f) to the reverse current peak (I_b), that is I_f/I_b, is an index of the catalyst tolerance to the poisoning species. A higher ratio indicates more effective removal of the poisoning species on the catalyst surface. The I_f/I_b ratio of sample-A is higher than that of sample B, which shows better tolerance to CO intermedia of the sample A.

Long-term stability is important for practical applications in DMFC. Pt-Ru alloy nanoparticles on MWCNTs were biased at 0.4 V versus SCE, and the changes in their polarization currents with time were recorded in Fig. 5. The performance of sample B electrode was found to be poor compared with the sample A electrode (Fig.5). In contrast, the sample A catalysts (solid line) has higher currents at all corresponding time than sample B (dotted line), indicating enhanced electrocatalytic activities and better tolerance to poisoning species in methanol oxidation than that of sample B catalyst in acidic solution. The higher current at beginning is attributed to double layers capacitance. The activities of the sample A and sample B catalysts also decreased more moderately with time. The comparative tests also showed that the sample A catalyst is slightly more active than the sample B catalyst.
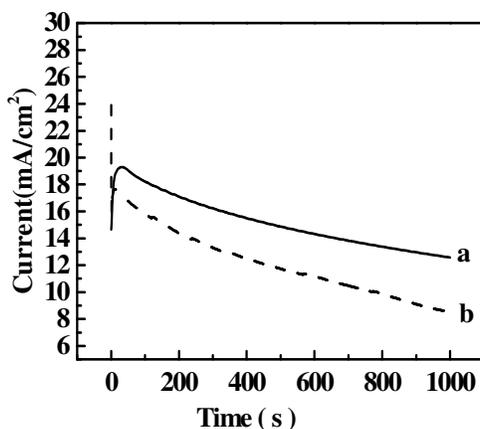
Figure 5. Chronoamperometric curves of methanol electro-oxidation in 1.0 M methanol + 0.5 M H_2SO_4 solution on sample A (a) and sample B (b) electrodes
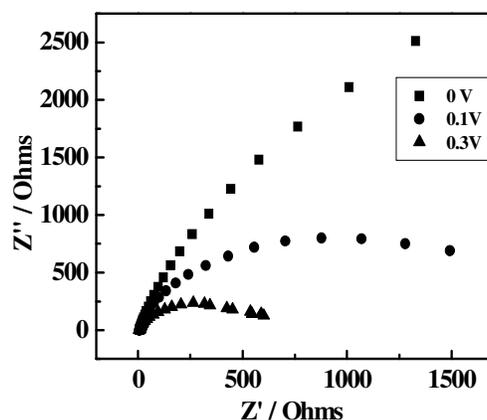
Figure 6. Impedance spectra of methanol electro-oxidation on sample-A electrode at different potentials

Further studies of the electro-oxidation of CH_3OH at the sample A electrode were carried out with electrochemical impedance measurements. Nyquist plots of sample A catalyst in the aqueous solution of 0.5 M H_2SO_4 and 1.0 M CH_3OH at various potential are shown in Fig. 6. At low potential (0 V), the impedance spectrum shows a large arc, with the diameter significantly greater than those at more positive potentials (0.1V and 0.3 V), which can be attributed to the slow reaction rate of methanol electro-oxidation. It deduced a slow reaction rate of methanol oxidation caused by intermediate CO_{ads} poisoning effect, which blocks the continuing adsorption and dehydrogenation of methanol on the electrode surface. With the increase of potential, the diameter of semi-circle decreases sharply, indicating reaction kinetics of the overall electro-oxidation of methanol enhanced. It can be interpreted as at low potential CO adsorbed on Pt active sites restrains the absorption and dehydrogenation of methanol while at high potential the weakly-bound CO will be oxidized, leading to the recovery of the surface reaction sites where electro-oxidation of methanol can take place.

4. CONCLUSIONS

In summary, Pt-Ru alloy nanoparticles on MWCNTs were successfully synthesized by chemical reduction under hydrothermal conditions. The preparation method is simple and efficient and it can be used as a general method of preparation for other supported metal and alloy systems. The Pt-Ru nanoparticles, which were uniformly dispersed on MWCNTs, were about 3.5 nm in diameter. The electro-oxidation of methanol at Pt-Ru alloy nanoparticle surfaces was studied by cyclic voltammetry, chrono amperitry and impedance measurements. The results show Pt-Ru/MWCNTs synthesized by hydrothermal method were an excellent electrocatalyst for the oxidation of methanol in acidic electrolyte.

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