



Highly effective and CO-tolerant PtRu electrocatalysts supported on poly(ethyleneimine) functionalized carbon nanotubes for direct methanol fuel cells



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ABSTRACT

A highly efficient and CO tolerant PtRu electrocatalysts supported on amino-rich, cationic poly(ethyleneimine) polyelectrolyte functionalized multi-walled carbon nanotubes (PtRu/PEI-MWCNTs) has been developed. The catalysts were characterized by thermogravimetric analysis, Raman spectroscopy, cyclic voltammograms, CO stripping, chronoamperometry, transmission electron microscopy (TEM) and X-ray diffraction (XRD). The PtRu particles with average size ~ 2.5 nm are well dispersed on PEI-MWCNTs. The peak current for the methanol oxidation reaction on 40% PtRu/PEI-MWCNTs is $636 \text{ mA mg}_{\text{Pt}}^{-1}$, 5.7 times higher than $112 \text{ mA mg}_{\text{Pt}}^{-1}$ measured on the 40% PtRu supported on acid treated MWCNTs (PtRu/AO-MWCNTs) under identical conditions. PtRu/PEI-MWCNTs catalysts exhibit a superior electrocatalytic activity and stability for the methanol oxidation reaction due to its high tolerance toward CO poisoning as compared with PtRu/AO-MWCNTs for direct methanol fuel cells.

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1. Introduction

Direct methanol fuel cells (DMFCs) are promising candidates as power sources for portable electronic devices due to the advantages of high volumetric energy density ($17,900 \text{ kJ/L}$) and easy storage of methanol fuel [1–3]. However, the development of DMFCs technology is delayed by the low electrocatalytic activity for the methanol oxidation reaction and poisoning by reaction intermediate species, CO on Pt-based electrocatalysts [4–6]. Intensified research has been conducted all over the world to develop active and stable electrocatalysts for methanol oxidation, particularly in the area of binary alloy catalysts such as, PtRu [7–10], Pt–Os [1,11,12], Pt–Sn [13–15], Pt–Pd [16,17], Pt–Co and Pt–Ni [18,19], Pt–W [1,20,21] and Pt–Mo [22,23]. Among these, PtRu catalysts are considered as the best for the methanol oxidation reaction [7–10,24]. However, the high cost of Pt is one of the most significant barriers for the widespread commercialization of fuel cell technology. One strategy is to increase the utilization efficiency of the precious metal catalysts by introducing high surface area supports such as high surface Vulcan XC-72 carbon [25], carbon nanofibers [26] and carbon nanotubes (CNTs) [1,8,14] to improve the dispersion of catalyst nanoparticles (NPs). High surface area carbon black is favored as a catalyst support; however carbon black tends to corrode in fuel cell environment,

which leads to the detachment and aggregation of catalyst NPs and results in performance degradation [27]. CNTs have been extensively studied as catalyst support for fuel cells due to their unique properties such as large specific surface area, excellent mechanical and electrical properties [28–35]. It has been reported that the CNT-supported Pt (Pt/CNT) catalysts exhibit higher catalytic activity and higher electrochemical stability as compared to Pt/C [36,37,38,39]. However, it is necessary to modify or functionalize the surface of CNTs to introduce active sites before catalyst deposition because of the inert nature of CNTs.

In general, CNTs can be functionalized by covalent attachment of chemical groups through bonding to the π -conjugated skeleton of the CNTs or by non-covalent adsorption or wrapping of various functional polyelectrolytes or compounds. The most common covalent functionalization involves the attachment of carbonyl and hydroxyl groups via an acid oxidation treatment with a mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4$ or by plasma etching [40,41]. The distribution of carbonyl and carboxyl groups generated by acid treatment is not particularly homogeneous and would lead to the aggregation of NPs and thus low utilization of Pt-based electrocatalysts [8]. The distribution of catalysts on acid treated CNTs can be improved by introducing more active sites via treatment with ethylenediamine [42] and polyaniline [43]. But CNTs that were initially treated by acid oxidation prior to the treatment of polyelectrolyte introduces structural defects and disrupts the delocalized π electron system in the CNT sidewalls, and consequently alters the electronic and mechanical properties to a degree that would significantly

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affect the performance of the electrocatalysts. Therefore, development of a better and more effective functionalization method that can not only introduce high density and homogeneous surface functional groups but also has little or no structural damage to CNTs remains a major challenge. Recently, non-covalent functionalization of CNTs by various surfactants [41], aromatic compounds [41,42], functional polymers [36,44] and biomolecules [31] has attracted great interest as such functionalization is effective to introduce high density and uniform active sites with little detrimental effect on CNTs. Self-assembly by *in situ* nucleation of metal NPs on non-covalent functionalized CNTs can achieve better particle distribution and particle size control especially at high catalyst loading. Hu et al. developed a strategy to prepare highly dispersed Pt-SnO_x NPs supported on 8-hydroxyquinoline (HQ) functionalized MWCNTs [14]. Tetrahydrofuran [45], 1-aminopyrene [8] and poly(diallyldimethylammonium chloride) (PDDA) [36] were employed as effective functionalization agents for CNTs for the *in situ* deposition and formation of platinum and platinum based NPs via the self-assembly principle.

Poly(ethyleneimine) (PEI), an amino-rich highly hydrophilic cationic polyelectrolyte, has been used in the synthesis of composite proton exchange membranes for DMFCs [46–49]. Incorporation of small amounts (~1 wt%) of PEI reduced ionic cluster size via electrostatic complex formation between anionic sulfonic groups of the sulfonated poly(ether ether ketone) (sPEEK) and the cationic amine groups of the PEI, and resulted in the reduction of methanol permeability by 85% at room temperature [47]. However, proton conductivity was also reduced by PEI incorporation. PEI has also been used to functionalize CNT via both physisorption and electrostatic adsorption as catalyst supports [50,51]. Hu et al. used PEI as a reducing and functionalization agent to deposit Au NPs on MWCNTs using HAuCl₄ precursor and uniform but large aggregated Au NPs were obtained on PEI-MWCNTs [50]. Yi et al. modified the acid treated MWCNTs with PEI and yielded a Pt catalyst with particle size around 5 nm [52]. Recently Knowles assembled multilayer structure of PEI-stabilized Pt NPs and PEDOT:PSS as anode for methanol oxidation reaction and the activity depends strongly on the number of bilayers [53]. To the best of our knowledge, there is limited research on the synthesis of Pt based binary alloy catalysts on the PEI functionalized CNTs for methanol oxidation reaction. Here, we develop a simple way to synthesize highly dispersed PtRu NPs with a particle size around 2.5 nm on the side walls of PEI functionalized CNTs. The results indicate that the PtRu/PEI-CNTs catalysts exhibit very high catalytic activity and excellent tolerance toward CO poisoning for the methanol oxidation reaction in acid solution.

2. Experimental

2.1. Functionalization of MWCNTs

Materials used in this experiment include sulfuric acid (99.5%, Fluka), nitric acid (65%, Fluka), ethanol (Sigma-Aldrich), methanol (Sigma-Aldrich), multi-walled carbon nanotubes (MWCNTs, Shenzhen Nano, China), hexachloroplatinic(IV) acid (Sigma-Aldrich), ruthenium chloride (Sigma-Aldrich), ethylene glycol (EG, Sigma-Aldrich), Nafion solution (5% in isopropanol and water), poly(ethyleneimine) (branched PEI, molecular weight ~1300, Sigma-Aldrich). All the chemicals were used without further purification.

Pristine MWCNTs (200 mg) was sonicated in 400 mL MilliQ water in the presence of 0.5 wt% PEI for 1 h, then the dispersion was stirred overnight before it was filtered using a nylon membrane and washed for several times to remove the excess PEI. When the pH of the solution is controlled at slight acidity (e.g., pH 6.5), the amino groups of PEI immobilized on the MWCNTs surface become positively charged. Functionalization or wrapping

of MWCNTs occurs between the negatively charged MWCNTs and positively charged PEI. The PEI wrapped MWCNTs were denoted as PEI-MWCNTs. For comparison, MWCNTs were also functionalized by a conventional acid oxidation treatment [40]. In this method, 200 mg of MWCNTs were treated in 200 mL of a mixed acid solution (H₂SO₄:HNO₃ in 1:1, v/v), followed by refluxing at 140 °C for 4 h. The obtained solution was then diluted with 2 L of deionized water to reduce the acidity of the solution, followed by filtration. The acid-treated MWCNTs were washed for several times. The acid-treated MWCNTs are denoted as AO-MWCNTs. Both PEI-MWCNTs and AO-MWCNTs were then dried in vacuum oven for 24 h at 70 °C.

2.2. Synthesis of PtRu/MWCNTs catalysts

PEI-MWCNTs (30 mg) were first ultra-sonicated in 50 mL ethylene glycol (EG) solution for 30 min before the addition of approximate amount of H₂PtCl₆ and RuCl₃. The solution was controlled at a pH of slightly less than 7 (e.g., pH 6.5) to maintain a weak acidity, then stirred for 3 h. The beaker was then placed in a microwave oven and heated for 2 min, followed by stirring overnight under pH 3–4. The solution was then filtered using a nylon membrane and washed for several times. PtRu catalysts on AO-MWCNTs were prepared using similar procedures as described above. PtRu deposited on PEI-MWCNTs and AO-MWCNTs with metal loading of 20 and 40 wt% were synthesized. The as-prepared PtRu electrocatalysts on MWCNTs (PtRu/PEI-MWCNTs and PtRu/AO-MWCNTs) were dried in a vacuum oven at 70 °C for 24 h. Fig. 1 illustrates the principle of the synthesis of PtRu electrocatalysts on PEI-functionalized MWCNTs.

2.3. Characterization

The zeta-potential of the MWCNTs and functionalized MWCNTs was measured during the treatment of MWCNTs, using zeta potential analyzer (Brookhaven Instruments Co., USA). In order to measure the surface properties of different CNTs and self-assembled PtRu/PEI-MWCNTs, the samples were suspended in MilliQ water in very low concentrations and pH of the solution was ~6.5. Distribution of PtRu NPs on MWCNT was characterized using a transmission electron microscope (TEM, JEOL JEM-2000EX) with operating at 200 kV. The mean size of the PtRu NPs on AO-MWCNTs and PEI-MWCNTs supports was obtained by measuring 250 randomly chosen particles in the TEM images. Thermogravimetric analysis (TG, Q5000) was conducted to measure the PEI and PtRu catalyst loading on MWCNT. The products were identified with X-ray diffractometer (XRD, Rigaku D/MAX RINT 2500) operated at 40 kV and 30 mA with Cu K α (λ = 1.5406 Å) in the range of 20–90°.

The electrochemical measurements were conducted in a standard electrochemical cell using a Princeton potentiostat. The electrochemical activities of PtRu/PEI-MWCNTs and PtRu/AO-MWCNTs electro-catalysts for the electrooxidation of methanol were measured. Generally, 4 mg of the catalyst was ultrasonically mixed in 4 mL of ethanol-Nafion mixture (with Ethanol: Nafion 9:1) to form a homogeneous ink, followed by dropping 10 μ L of the catalyst ink onto the surface of a glass carbon electrode (GCE). The diameter of GCE was 4 mm. Pt wire and Ag/AgCl (saturated KCl) electrode were used as the counter and reference electrodes, respectively. All potentials in the present study were given versus Ag/AgCl (saturated KCl) reference electrode. The electrochemical active area of PtRu/MWCNTs electrocatalysts were measured in a nitrogen-saturated 0.5 M H₂SO₄ solution at a scan rate of 50 mV s⁻¹ and the electrocatalytic activity for the methanol oxidation reaction was measured in a nitrogen-saturated 0.5 M H₂SO₄ + 1.0 M CH₃OH solution at a scan rate of 50 mV s⁻¹. The Pt metal loading was kept at 2 μ g. The tests were conducted at room temperature.

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