Well-controlled Platinum Nanoparticles Uniformly Dispersed on Nitrogen-doped Carbon Nanotubes for Methanol Oxidation

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Abstract: The direct methanol fuel cell (DMFC) is a kind of power source which generates the electrical power by the redox reaction feeding methanol fuel and oxygen directly to the anode and cathode, respectively. This is due to the fact that carbon nanotubes (CNTs) with high surface area and good electronic conductivity are more suitable for electrocatalysts. On the other hand, the catalyst plays an important role in DMFC system. Pt is catalytically active in room temperature electro-oxidation reactions of interest to fuel cell applications. It is well known that the catalytic activity of the metal is strongly dependent on particle size and size distribution. Conventional preparation techniques are based on wet impregnation and chemical reduction of metal precursors.

To improve the DMFC performance, CNTs with high conductivity and well-dispersed Pt nanoparticles (NPs) with high activity are necessary. From scanning electron microscopy (SEM) images in Fig.1 (a), the CNTs are directly grown on carbon cloth. From transmission electron microscopy (TEM) images in Fig.1 (b), the as-grown CNTs are bamboo-like structures with diameter of 20-30 nm and they also show highly dispersed metal particles accompanied by the uniform dispersion. By tuning the pH value, the grain size of Pt NPs can be manipulated using impregnation method. The average diameter of Pt NPs is 2 nm at pH 11, which infers the relatively narrow particle size distribution. Meanwhile, we compare the electrochemical activity of Pt NPs on CNTs under different pH values. As a result, the Pt surface activity area is higher with the synthesis solution pH increasing due to the phenomenon that the shrinkage of metallic particle size as the pH value raises.

1. Introduction
The electrocatalytic activity is known to depend strongly on the shape, size and distribution of the particles. The carbon-supported platinum electrocatalyst (Pt/C) with a narrow particle size distribution and good dispersion has been extensively studied for their use in proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC). The Pt/C can be prepared by numerous techniques including wet-chemical processes, such as impregnation, ion exchange and colloidal method, as well as physical deposition processes, such as sputter deposition. Impregnation is an extensive method of preparation, in which the carbon supports and the Pt precursor salts are reduced in a hydrogen atmosphere at high temperature [1-3]. However, the heat treatment often increases the particle size and reduces the catalytic activity. Ion-exchange is suitable only for carbon supports with a number of ion-exchange sites [4-5]. The colloidal procedure produces nanoscale electrocatalysts in the homogeneous phase using ligands, surfactants or polymers as the stabilizer [6-9]. Once the electrocatalysts deposited on the carbon supports, the stabilizer molecules need to be removed, because they detrimentally undermine the access of the fuel to the electrocatalysts. Sputter deposition, a procedure that is routinely adopted to manufacture thin films, has been employed to deposit the Pt electrocatalysts on gas diffusion layers or membranes [10-12]. Carbon nanotubes (CNTs), as a new form of carbon, have been utilized as new supports for metal catalysts because of their nanosizes, high conductivity (102 – 103 S cm⁻¹), high chemical stability and large surface-to-volume ratio. Recently, platinum and platinum-based alloy (such as Pt-Ru), loaded on multi-walled CNTs and single-walled CNTs, have become promising electrocatalysts in anodes and cathodes [13-17]. In these works, electrocatalysts have typically been prepared on CNTs using a wet-chemical approach (electro catalyst/CNT). For fabricating the electrocatalyst layer, the electrocatalyst/CNT mixed with Nafion® solution was employed on a gas diffusion layer (such as carbon paper and carbon cloth) using conventional screen-printing process. An active electrocatalyst must simultaneously support the triple access of fuel, electrons and protons. However, the addition of Nafion® solution tends to isolate a significant fraction of electrocatalysts, which are isolated from the triple access in the electrocatalyst layer. In this work, nitrogen-doped CNTs were grown directly on the carbon cloth as an electrode.
(CNT-CC electrode), and the electrocatalysts were subsequently deposited on the CNT-CC electrode (Pt/CNT-CC). To improve the DMFC performance, CNTs with high conductivity and well-dispersed Pt nanoparticles (NPs) with high activity are necessary. Physicochemical and electrochemical characterizations of the CNT supports and the corresponding Pt/CNT-CC are provided. By tuning the pH value, the grain size of Pt NPs can be manipulated using impregnation method. The average diameter of Pt NPs is 2 nm at pH 11, which infers the relatively narrow particle size distribution.

2. Experimental:
Firstly iron layer is deposited on carbon clothes using ion beam sputtering system. The iron were the catalytic active site for growing CNT. Then the microwave plasma enhanced chemical vapor deposition (MPECVD) is used to grow directly grown CNTs on carbon cloth. After 10 minutes hydrogen plasma treatment, the step will clean the carbon surface and synthesis the iron particle as the active site. The CNT growth condition is 2 kW microwave power, a chamber pressure of 40 Torr, a substrate temperature of 900 °C for 10 minutes and reaction gas are CH4/H2/N2.

The Pt NPs deposit on CNT using the ethylene glycol method. Ethylene glycol is both the reducing agent and dispersion agent, and sodium hydroxide (NaOH) is added to change the reaction take place condition. Fig. 1 shows alcohol groups of ethylene glycol are easily oxide to aldehyde group, which are unstable in solution and are further oxidized to acid group. H2PtCl6 · 6H2O is used as Pt source and dissolved on different NaOH concentration ethylene glycol solution. The CNT-CC and XC-72 are immerse in the solution and stirring for 30mins and the solution were heated to 160 °C for 2 hours. The Pt NPs on CNTs or XC-72 was washed by DI water and ethanol. The Pt/CNT-CC was dried in a vacuum oven at 60 °C for 2 h to remove residual solvents. The mass per unit area of the Pt/CNT-CC was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, PerkinElmer ICP-OES Optima 3000). Commercial 20 wt.% Pt loaded on activated carbon (Vulcan XC-72) and mixed with Nafion® solution was spread on carbon cloth by the screen-sprinting method (Pt/XC-72) for comparison. All samples had the same Pt loading (0.5 mg cm−2) here in work. High-resolution scanning electron microscopy (HRSEM, JEOL-6700F) was employed to determine the micro-structured surface morphologies of the CNT-CC electrode and the Pt/CNT-CC. Transmission electron microscopy (TEM) of the Pt NPs and the Pt NPs loaded on the CNTs was performed using a JEOL-2000FX TEM system equipped with a high-speed slow scan CCD camera with a LaB6 filament at 200 kV. Electrochemical measurements were performed using a Solartron electrochemical test system (SI 1280Z) in a conventional three-electrode glass cell. The sample was placed into a specific holder as a working electrode, which was connected to the test system via a gold wire. The counter and reference electrode were Pt foil and Ag/AgCl 3MKCl (0.207 V vs. SHE), respectively.

3. Results and discussion:
Figure 1 presents the growth by MPECVD, a tangled bundle of CNTs are directly grown on the carbon cloth. Therefore, the electrocatalysts deposited on the CNT-CC electrode ensure the electronic access of catalysts. Besides, other works have demonstrated fast electron-transfers in the CNT-based electrodes, which were attributed to either ballistic electron transport or the high density of states in the CNT [18-21]. Morphological characteristics and Pt surface areas of the Pt/CNT-CC electrode (Pt/CNT-CC). The lattice of the N-doped of the carbon nanotube, grown by MPECVD, leads to the substitution of N into the C network. The results demonstrate that pyridine-like N units are embedded in nanotube carbon lattice, which differs from the direct substitution of three-fold coordinate carbons. Therefore, bamboo-type structures are often observed using this process [22]. The N-doped carbon nanotube distorts the wall by exhibiting some disordered atomic layers and dangling bonds, which serve as the capture sites for fixing the Pt NPs on the wall of the nanotube [23]. Besides, from previous paper studies, the zeta potential of the CNT exhibits a positive value over a pH range [24-25]. The zeta potential of the Pt NP exhibits a negative value, and therefore the electrostatic attraction between the Pt NP and the CNT is beneficial for the deposition process of the Pt NP on the CNT. The microstructures of the Pt/CNT-CC prepared using various NaOH concentrations of the ethylene glycol solutions were observed from HRSEM images, as shown in Fig. 2. The Pt NPs are successfully and uniformly dispersed on the CNTs at various NaOH concentrations. Comparison of methanol-oxidation activities on the Pt/CNT-CC and Pt/XC-72. For investigating the methanol-oxidation properties of the Pt/CNT-CC, the Pt/CNT-CC prepared using 15
mM NaOH of the ethylene glycol solution, which has the smallest Pt NP size, is chosen as the following study. The methanol-oxidation activities of the Pt/CNT-CC and the Pt/XC-72 were obtained by conducting CV scans in 1 M methanol and 1 M sulfuric acid solution at a scan rate of 5 mV s\(^{-1}\), as presented in Fig. 3. The methanol-oxidation onset potentials of the Pt/CNT-CC and the Pt/XC-72 were almost equal, at 0.43 V. However, the peak-current density of the Pt/CNT-CC was about double that of the Pt/XC-72, according to a forward scan. In conventional screen-printing, the isolation of the Pt NPs in the electrocatalyst layer causes low utilization, and energy is lost as electrons cross the interfaces of the activated carbon and the carbon cloth. The CNT-CC electrode not only is responsible for the Pt utilization but also allows the fast transfer of electrons through the highly conductive CNT, such that they are directly delivered to the carbon cloth and outlet circuit. Therefore, the Pt/CNT-CC has low internal and interfacial resistances, reducing energy loss.

4. Conclusions
The pH value of the solution strongly affects the size of the Pt NPs due to the existence of the stabilizers. The synthesis of the Pt NPs on a CNT-carbon cloth electrode in an ethylene glycol solution with various NaOH concentrations has been studied. Besides, new evidence shows the higher absolute value of the zeta potential of the as-prepared Pt NP the smaller Pt NP size due to the stronger electrostatic repulsion between NPs. The methanol-oxidation activities of Pt/CNT-CC prepared using 15 mM NaOH and Pt/XC-72 have been studied by CV measurements in 1 M methanol and 1 M sulfuric acid solution. The anodic peak-current of the former is double that of the latter indicating that the CNT-CC electrode increases the Pt utilization and provides rapid electron transfer, which is ideal for fuel cell electrode.

Reference: