High Performance Nanocatalysts Supported on Micro/Nano Carbon Structures Using Ethanol Immersion Pretreatment for Micro DMFCs

Liang-You Lin¹, Yi-Shiuan Wu¹, Chaun Chang¹ and Fan-Gang Tseng¹,²,³
¹Department of Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan
²Institute of NanoEngineering and MicroSystems, National Tsing Hua University, Hsinchu, Taiwan
³Division of Mechanics, Research Center for Applied Sciences, Academia Sinica, Taipei, Taiwan

E-mail: r20008@hotmail.com

Abstract. In this paper, highly dense platinum (Pt) nanocatalysts were successfully deposited on the hydrophilically-treated nano/micro carbon supports with an ethanol (EtOH) immersion pretreatment and an acidic treatment for the performance improvement of methanol oxidation reaction (MOR). In order to thoroughly immerse the three-dimensional, interwoven structures of the carbon cloth fibers with a 6 M sulfuric acid surface modification, which increasing more oxygen-containing functional groups on the surfaces of the carbon supports, the EtOH immersion pretreatment of the carbon supports was utilized prior to the sulfuric acid treatment. Subsequently, Pt catalysts were reduced on the modified carbon supports by a homemade open-loop reduction system (OLRS) [1]. For comparisons, carbon cloth (CC) and carbon nanotube on CC (CNT/CC) supports were employed with and without EtOH immersion pretreatments before Pt catalyst reduction. In the cyclic voltammetry (CV) curves, the electrosorption charges of hydrogen ion (QH) and the peak current density (IP) of the fabricated Pt/CC and Pt/CNT/CC electrodes with the EtOH immersion pretreatments can efficiently be enhanced due to more active Pt sites for electrocatalytic reactions.

1. Introduction
With the rising price of the fossil, the alternative energy sources have become a significant issue for scientific and technological developments. Direct methanol fuel cells (DMFCs) utilize methanol as the anode fuel, mainly because it offers a high energy density, low pollution, fast refueling, and a low operating temperature [1-3]. Compared to proton exchange membrane fuel cell (PEMFC) using hydrogen gas as the anode fuel, DMFC has some advantages such as the safety of fuel storage, operation at room temperature, and so on. Therefore, DMFCs have potential applications for portable electronics. To obtain smaller particles and uniform dispersion of noble metal catalysts for the achievement of better utilization and activity of electrocatalysts, carbon materials become candidates for catalyst supports such as carbon black, carbon fiber, and carbon nanotube (CNT). In recent years, CNT providing a novel nano-structure with large specific surface area and good chemical resistance has been widely used in many applications. Most of CNTs are directly grown on the carbon cloth [2, 3, 7], on the silicon (Si) [1, 4, 10], or on the graphite substrates [5] as the catalyst supports. However, the
CNT and CC must adopt the hydrophilic treatment due to its instinct hydrophobic property prior to depositing the catalysts. The commonly used oxidants are sulfuric acid, nitric acid, or mixed solutions of H₂SO₄ and HNO₃, and hydrogen peroxide, etc. However, it is still difficult to thoroughly immerse the three-dimensional, interwoven structures of carbon cloth fibers in the acidic solution, resulting in an obvious gradient distribution of the Pt nanoparticles between the inner and outer surfaces of the carbon fibers [2,3]. This result led to low catalyst utilization of Pt and limited electrocatalytic activity for MOR. In order to eliminate the gradient distribution, the EtOH immersion pretreatment of the carbon supports was utilized prior to the above-mentioned hydrophilic surface modification. This can efficiently remove surface impurities of CNT, reducing environmental changes of reaction, and making more catalyst adhere to the surface of CNT due to the oxygen-rich functional groups [6].

To enhance Pt catalyst efficiency, small size (1-5 nm) and uniformly distributed Pt nanoparticles are highly desired. Conventionally, there are two common methods applied for Pt nanoparticle preparation, including chemical reduction [3,7] and electro-deposition [8]. Chemical reduction provides the advantages of easier preparation, direct reaction, and uniform size distribution of the nanocatalysts. However, it usually takes much longer time (24 h) for catalyst preparation due to slow nucleation and growth process at low temperature (60 °C). As a result, recent developed reflux technology [9] can react at higher reaction temperature (160 °C), substantially shorten the time required for catalyst preparation (~3-4 h). The corresponding fabrication process of Pt electrocatalysts is shown in Fig. 1.

2. Experimental

2.1. Growth of Carbon Nanotube

We used a 330 μm-thick carbon cloth (CC) as the substrate followed by respectively coating with Ni/Ti (film thickness: 15/75 nm) for carbon nanotube (CNT) growth by thermal chemical vapor deposition (TCVD) [7, 10]: First, we purged argon (Ar) and heated the quartz tube from room temperature to 800 °C, then maintained the growth temperature at 800 °C while leading to Ar and ammonia (NH₃). The first two steps are called thermal treatment. Ni was deposited as the catalyst for the growth of CNT with ethylene (C₂H₄). The growth time of CNT was 30 min, and this technique is known as the catalytically-growth CVD.

2.2. Ethanol Immersion Pretreatment & Hydrophilic Treatment of Carbon Supports

We used a 6 M sulfuric acid (H₂SO₄) solution as the oxidant for hydrophilic treatment of the CNT/CC supports. In order to remove air bubbles from the surface of the carbon supports to effectively immerse the whole surfaces of the supports in a H₂SO₄ solution for better Pt catalyst adhesion, vacuum means was added in the hydrophilic treatment process [1, 10]. However, it is still difficult to
thoroughly immerse the three-dimensional, interwoven structures of carbon cloth fibers with CNTs in the acidic solution, resulting in an obvious gradient distribution of the Pt nanoparticles between the inner and outer surfaces of the carbon fibers [2, 3]. This result led to low utilization of carbon supports and Pt catalyst so as to limit electrocatalytic activity for MOR. In the present work, the EtOH immersion pretreatment for the CC and CNT/CC carbon supports was utilized prior to the above-mentioned hydrophilic modification of the carbon supports. The wetting properties of the CC surfaces with, without the hydrophilic treatments and with the EtOH immersion pretreatment and hydrophilic treatment were measured by contact angle goniometry (Model Firsttenangstroms, FTA32).

2.3. Open-Loop Reduction System for Platinum Catalyst

According to a homemade open-loop reduction system (OLRS) in our previous study [1], as shown in Fig. 2, we used 0.04392 g H2PtCl6•6H2O and 0.1 mM ethylene glycol as a Pt catalyst precursor and a reducing agent, respectively. Compared with a traditional reflux system that maintains the ratio of water to ethylene glycol (EG) at ~160°C for ~4 h, the gradual concentration increase of EG in the precursor solution can be accomplished by distilling off water in the OLRS while increasing the temperature to 130°C. This process with simultaneous increases in precursor concentration and in reaction temperature rendered high-quality Pt nanoparticles to precipitate with a high-density dispersion on the pretreated CNTs. The OLRS is not only able to only shorten the reduction time (<1.5 h) but is also able to enhance the electrocatalytic activity of the electrodes by creating a preferential orientation of Pt (1 1 1) facets for the methanol oxidation reaction (MOR).

2.4. Electrochemical Measurements

Cyclic voltammetry (CV) was carried out to identify the electrochemical properties of the electrocatalysts. The working principle is to impose a variable voltage at the working electrode (WE) and analyze the current signal received with time to determine the oxidation-reduction (redox) status in the electrochemical reaction. In this case, we imposed time-varying triangular wave of potential in the WE, and then observed the relationship between potential (E, VSCE) and current density (I, mA/cm²) to realize the potential for the redox reaction, electrochemical mass activity (MA, A/gPt) and reaction rate [1, 4]. In the CV curves, we can also obtain the active electrochemical surface area (ESA) of Pt catalysts from the hydrogen ion electro sorption reactions (charge transfer density of H+, QH, mC/cm²) in a H2SO4 aqueous solution. The three-electrode cell was setup for all of the electrochemical tests. Saturated calomel electrode (SCE, 0.241 V vs. standard hydrogen electrode, SHE) and Pt-coated Ti mesh are used as the reference electrode (RE) and the counter electrode (CE), respectively. All of the electrochemical measurements were purged with nitrogen (N2) gas to remove oxygen for extra oxidation reaction.

3. Results and discussion

The contact angle (CA) of the CC electrodes was measured with a droplet of deionized (DI) water. The FTA images and their corresponding CAs are shown in Table 1. Compared to cases 1 and 2 (CAs: 136.74°, 48.72°), the CA of the CC electrode w/ the EtOH immersion pretreatment is smaller (18.05°), suggesting that the wetting surface of carbon fibers is probably prone to absorb many hydroxyl (-OH) and carbonyl (=C=O) oxygen-containing groups for more Pt catalyst nucleation.

| Electrodes       | (1)CC w/o H2SO4 hydrophilic treatment | (2)CC w/ H2SO4 hydrophilic treatment | (3)CC w/ EtOH immersion pretreatment & H2SO4 hydrophilic treatment |
|------------------|--------------------------------------|--------------------------------------|---------------------------------------------------------------|
| FTA image        | ![FTA image](image1.png)                | ![FTA image](image2.png)                | ![FTA image](image3.png)                                         |
| Contact angle    | 136.74°                               | 48.72°                                 | 18.05°                                                          |

Both the QH and the peak current density (Ip) of the fabricated Pt/CC and Pt/CNT/CC electrodes with the EtOH immersion pretreatments obtained in the CV curves, as shown in Fig. 3 and Fig. 4.
respectively, can be significantly improved compared to those without the EtOH immersion pretreatments. Table 2 lists the electrocatalytic properties of the fabricated electrodes at different hydrophilic treatments, depicting that the values of $Q_H$ and $I_P$ for the best performed electrodes of Pt/CNT/CC with the EtOH immersion pretreatment are about 4 and 5 times higher than those of Pt/CC without the EtOH immersion pretreatment, respectively. This is attributed to both nano and micro structured supports together with the enhanced EtOH immersion technique, which provide more active Pt sites for electrocatalytic reactions based on the $Q_H$. This can also be proved from the increasing Pt loading (mass density of Pt, $M_{Pt}$) by 7.6 times. However, the values of ESA and MA for the Pt/CC and Pt/CNT/CC electrodes with the EtOH immersion are less than those without the EtOH immersion. This may result from different agglomeration degrees of the Pt clusters based on higher Pt loading.

Table 2 lists the electrocatalytic properties of the fabricated electrodes at different hydrophilic treatments, depicting that the values of $Q_H$ and $I_P$ for the best performed electrodes of Pt/CNT/CC with the EtOH immersion pretreatment are about 4 and 5 times higher than those of Pt/CC without the EtOH immersion pretreatment, respectively. This is attributed to both nano and micro structured supports together with the enhanced EtOH immersion technique, which provide more active Pt sites for electrocatalytic reactions based on the $Q_H$. This can also be proved from the increasing Pt loading (mass density of Pt, $M_{Pt}$) by 7.6 times. However, the values of ESA and MA for the Pt/CC and Pt/CNT/CC electrodes with the EtOH immersion are less than those without the EtOH immersion. This may result from different agglomeration degrees of the Pt clusters based on higher Pt loading.

Table 2. Electrocatalytic properties of the electrodes pretreated at different conditions.

| Electrodes   | *Treatments | $Q_H$ mC/cm$^2$ | $E_P$ V$_{SCE}$ | $I_P$ mA/cm$^2$ | $M_{Pt}$ mg/cm$^2$ | $ESA$ m$^2$/g$_{Pt}$ | $MA$ A/g$_{Pt}$ |
|--------------|-------------|-----------------|-----------------|-----------------|-------------------|-------------------|----------------|
| Pt/CC        | H           | 6.61            | 0.64            | 50              | 0.095             | 33.1              | 526.3          |
|              | E+H         | 17.08           | 0.62            | 147             | 0.431             | 18.9              | 341.1          |
| Pt/CNT/CC    | H           | 19.67           | 0.62            | 138             | 0.373             | 25.1              | 370.0          |
|              | E+H         | 24.93           | 0.64            | 247             | 0.723             | 16.4              | 341.6          |

*E: ethanol solution (C$_2$H$_6$O), H: sulfuric acid solution (H$_2$SO$_4$).

As shown in Table 3, low-magnification scanning electron microscopic (SEM) images illustrate that denser Pt nanoparticles were apparently deposited on both the inner and outer surfaces of the hydrophilically-treated CC and CNT/CC supports with the EtOH immersion pretreatments. More uniform dispersion of the Pt nanoparticles on a larger surface area results from both micro and nano structured CNT/CC supports. In addition, the corresponding high-magnification images show that the aggregation size and degree of the Pt clusters on the CNT/CC supports was less serious than those on the CC supports. To further solve this problem, a proper sonication technique would be utilized to agitate the Pt reduction process and increase its nano-scale dispersion on the CNT/CC supports.
**Table 3.** Low- and high-magnification (1K & 100K) SEM images of the Pt catalysts on the different carbon supports w/ and w/o the EtOH immersion pretreatments.

| Electrodes       | Pt/CC (1K) | Pt/CNT/CC (1K) | Pt/CC (100K) | Pt/CNT/CC (100K) |
|------------------|------------|----------------|--------------|------------------|
| w/o EtOH         |            |                |              |                  |
| w/ EtOH          |            |                |              |                  |

4. Conclusion

The EtOH immersion pretreatment on nano/micro carbon supports prior to the hydrophilic treatment in an acidic solution was thoroughly to immerse the three-dimensional, interwoven micro structures of CC fibers with CNTs for the improved Pt deposition. The pretreatment helps more Pt catalysts adhere to the nucleation sites of the immersed CC and CNT/CC supports, which were created with the oxygen-rich functional groups by the hydrophilic treatment. For the electrocatalytic properties of the fabricated electrodes, the values of the $Q_H$ and the $I_P$ for the Pt/CNT/CC with the EtOH immersion pretreatment are higher than those of the Pt/CC without the EtOH immersion pretreatment ($Q_H$: 24.93 vs. 6.61 mC/cm², $I_P$: 247 vs. 50 mA/cm²). This is mainly attributed to higher mass loading of the Pt catalysts ($M_P$: 0.723 vs. 0.095 mg/cm²). Results from the SEM measurements show that smaller and highly denser distribution of the Pt nanoparticles were clearly observed on the hydrophilically-treated CNT/CC supports with the EtOH immersion pretreatment compared to the CC supports without the EtOH immersion pretreatment.

Acknowledgment

This research was financially supported by the National Science Council (NSC), Taiwan under grant NSC 101-3113-E-007-002. The authors also thank the Instrument Center at National Tsing Hua University for FE-SEM and ICP-MS examinations.

References

[1] Y. S. Wu et al., “Highly efficient platinum nanocatalysts synthesized by an open-loop reduction system with a controlled temperature loop,” *Electrochimica Acta* 64 (2012) 162–170.
[2] C. H. Wang et al., “High performance of low electrocatalysts loading on CNT directly grown on carbon cloth for DMFC,” *Journal of Power Sources*, vol. 171, pp. 55-62, 2007.
[3] M. C. Tsai et al., “A catalytic gas diffusion layer for improving the efficiency of a direct methanol fuel cell,” *Electrochemistry Communications*, vol. 9, pp. 2299-2303, 2007.
[4] S. K. Wang et al., “Electrocatalytic properties improvement on carbon-nanotubes coated reaction surface for micro-DMFC,” *Journal of Power Sources*, vol. 167, pp. 413-419, 2007.
[5] Z. B. He et al., “Deposition and electrocatalytic properties of platinum nanoparticles on carbon nanotubes for methanol electrooxidation,” *Materials Chemistry and Physics*, vol. 85, pp. 396-401, 2004.
[6] N. Jha et al., “Pt–Ru/multi-walled carbon nanotubes as electrocatalysts for direct methanol fuel cell,” *International Journal of Hydrogen Energy*, vol. 33, pp. 427-433, 2008.
[7] M. C. Tsai et al., “An improved electrodeposition technique for preparing platinum and platinum–ruthenium nanoparticles on carbon nanotubes directly grown on carbon cloth for methanol oxidation,” *Electrochemistry Communications*, vol. 8, pp. 1445–1452, 2006.
[8] M. Watanabe et al., “Preparation of highly dispersed Pt-Ru alloy clusters and the activity for the electrooxidation of methanol,” *Journal of Electroanalytical Chemistry*, vol. 229, pp. 395-406, 1987.
[9] C. Bock et al., “Size-selected synthesis of PtRu nano-catalysts: reaction and size control mechanism,” *Journal of the American Chemical Society*, vol. 126, pp. 8028-8037, 2004.
[10] Y. S. Wu et al., “Characteristics of controlled Nafion® coating inside nano structured anode for three-phase zone arrangement in micro DMFC,” *Proceedings of the 2010 5th IEEE International Conference on Nano/Micro Engineered and Molecular Systems*, Xiamen, China, pp. 698-701, January 20-23, 2010.
[11] X. Wang et al., “Surfactant stabilized Pt and Pt alloy electrocatalyst for polymer electrolyte fuel cells,” *Electrochimica Acta*, vol. 47, pp. 2981-2987, 2002.
[12] Z. L. Liu et al., “Physical and electrochemical characterizations of microwave-assisted polyol preparation of carbon-supported PtRu nanoparticles,” *Langmuir*, vol. 20, pp. 181-187, 2004.