

IMPROVEMENT OF CATALYTIC ACTIVITY OF NANOCATALYSTS USING MODIFIED OPEN-LOOP REDUCTION SYSTEM WITH A CONTROLLED PRESSURE LOOP FOR MICRO DMFCS

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Abstract: In this paper, the electrocatalytic activity of platinum (Pt) nanoparticles supported on carbon nanotubes (CNTs) as the electrodes for micro direct methanol fuel cells (μ DMFCs) was improved by a modified open-loop reduction system (MOLRS) with a pressure control. The mass density of Pt catalysts (M_{Pt}) was inversely proportional to the reduction pressure in the MOLRS. However, the electrochemical surface area (ESA) of the prepared Pt/CNTs electrodes increased with an increase in the reduction pressure and the ESA at larger pressure was improved by 17% compared to that in the OLRs at atmospheric pressure. The best performing electrodes prepared at larger pressure could obtain a higher peak current density (or mass activity, MA) of $457 \text{ A g}_{Pt}^{-1}$ at a peak potential (E_p) of $0.62 V_{SCE}$ compared to that prepared at atmospheric pressure (MA: $393 \text{ A g}_{Pt}^{-1}$, E_p : $0.64 V_{SCE}$). In conclusion, small-size and uniformly dispersed Pt catalysts on the CNTs was obtained by the MOLRS at larger pressure, which are applicable to be utilized as electrode catalysts for micro DMFCs.

Keywords: electrocatalytic activity, platinum, micro direct methanol fuel cells, modified open-loop reduction system

INTRODUCTION

All human beings have realized that how important the fossil fuel is. But with the rising price of the fossil, to search for alternative energy sources has 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, so 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 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 H_2SO_4 and HNO_3 , and hydrogen peroxide, etc. They can remove surface impurities of CNT, reducing environmental changes of reduction, and making the 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 ($60^\circ C$). As a result, recent developed reflux technology [9] can react at higher reaction temperature ($160^\circ C$), substantially shorten the time required for catalyst preparation ($\sim 3-4$ h); however, the pressure controlling was not discussed clearly in the earlier documents. In order to investigate the effect of the reduction pressure on the electrocatalytic properties of Pt catalysts based on our previously-developed open-loop reduction system (OLRS) at atmospheric pressure [1], we modified the OLRs (MOLRS) by equipping with a pressure device. The corresponding preparation process of Pt catalysts is shown in Fig. 1.

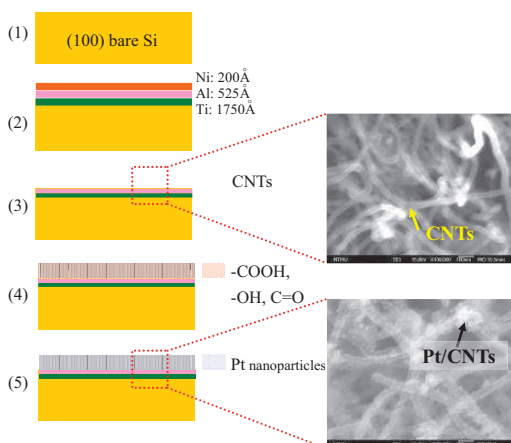


Figure 1. The preparation process and the corresponding SEM images of (Pt)/CNTs electrodes: (1) Bare Si substrate, (2) Sputter Ni/Al/Ti metal films, (3) CNTs growth, (4) Hydrophilic treatment of CNTs, and (5) Deposit nano-scale Pt catalysts [1, 3].

EXPERIMENTAL

Growth of Carbon Nanotubes

We used a 525 μm -thick bare Si followed by coating with Ni/Al/Ti (film thickness: 20 nm/52.5 nm/175 nm), respectively, and then grew CNT by thermal chemical vapor deposition (TCVD) [7, 10]. First, we purged Ar and heated the quartz tube from room temperature to 800 $^{\circ}\text{C}$, then hold the temperature at 800 $^{\circ}\text{C}$ while leading to Ar and NH_3 . The first two steps are called thermal treatment. Ni was deposited as the catalyst for the growth of CNTs with C_2H_4 . The growth time of CNTs was 30 min, and this technique is known as the catalytically-growth CVD.

Hydrophilic Treatment of Carbon Nanotube

We used 6 M sulfuric acid (H_2SO_4) as the oxidant for hydrophilic treatment of the CNTs. In order to remove air bubbles from the surface of CNTs to effectively immerse the roots of CNTs in H_2SO_4 solution for better Pt catalyst adhesion, vacuum means was added in the hydrophilic treatment [1, 10, 13].

Modified Open-Loop Reduction System

The hydrophilic treatment was carried out in 6 M H_2SO_4 solution at 80 $^{\circ}\text{C}$ for 1 h before catalyst reduction. Wang et al. [10] mentioned that the growth of Pt catalyst particles can be controlled by the reaction temperature. Furthermore, the reflux technique can enhance the reaction temperature and shorten the reduction time [9]. According to our previous study [1, 13], we used 0.04392 g $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 0.1 mM ethylene glycol as Pt catalyst precursors in the OLRS. The solutions contain too much water as a result of maintaining at 100 $^{\circ}\text{C}$

(boiling point), so the reaction temperature can not rise to 160 $^{\circ}\text{C}$ easily as mentioned in the literature. It is indicated that the OLRS can shorten the reduction time by 50% at atmospheric pressure, and the pressure is much different from the reflux system. In order to find out the effect of the reduction pressure on the electrocatalytic properties of the Pt catalysts, we modify the OLRS setup by adding the pressure knob, as shown in Fig. 2. This system can react at high temperature under controlled pressure by adjusting the pressure knob and collect the evaporation of water in the precursor solution, so that the concentration of ethylene glycol in the precursor solution would be increased gradually with elevated temperatures.

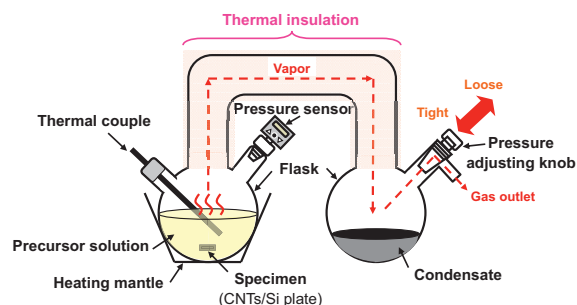


Figure 2. Setup of the MOLRS. The arrows in the system represent the direction of water vapor.

Electrochemical Measurements

Cyclic voltammetry (CV) was carried out to identify the electrochemical activity 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 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 and current density to realize the potential for oxidation-reduction reaction, electrochemical activity and reaction rate [1, 4]. In the CVs, we can also obtain the active surface area of Pt catalysts from the hydrogen adsorption reactions in H_2SO_4 . The three-electrode cell was setup for the electrochemical tests. Saturated calomel electrode (SCE, 0.241 V vs. SHE) and Pt-coated Ti mesh are used as reference electrode (RE) and counter electrode (CE), respectively. All the electrochemical measurements were purged with nitrogen (N_2) gas to remove oxygen.

RESULTS AND DISCUSSION

Morphology and Hydrophilic Treatment of Carbon Nanotubes

We used the CNTs as the carbon support directly grown on a Si-based substrate, which was coated with Ni/Al/Ti multi-layers for catalyst of CNTs growth, electron conductance and adhesion between Si and

CNTs, respectively [1, 10, 13]. The length and diameter of CNTs are 5-6 μm and 40-50 nm, respectively. The advantage of using CNT array is the ability of transport electron along with the direction of CNTs. CNTs can not only reduce resistance for the cell assembly, but also contribute to the removal of CO_2 in the anode. The morphology of the CNTs growth on a Si plate is shown in Fig. 3.

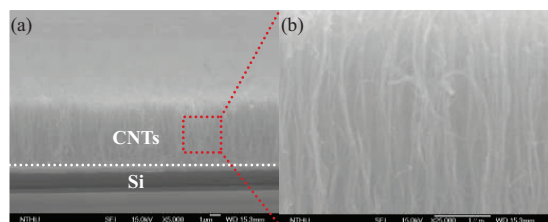


Figure 3. Morphology of the CNT array on a Si substrate.

Pressure Control in MOLRS

According to our previous study, the solution volume and temperature in the OLRS changed with the solution evaporation or condensation process, and the optimum reaction temperature of Pt reduction in the OLRS was obtained by increasing the ethylene glycol in the precursor solution at elevated temperature [1]. In the present study, we utilized the previous Pt reduction temperature, heating the precursor solution from 30 $^{\circ}\text{C}$ to 130 $^{\circ}\text{C}$. The modified Pt reduction experiments with different pressure regulations were carried out in the MOLRS and the pressure conditions were large (P_L), small (P_S), and normal atmospheric pressure (P_N) in the OLRS. We then illustrated the reduction pressure curves of Pt catalysts with time in the MOLRS, as shown in Fig. 4.

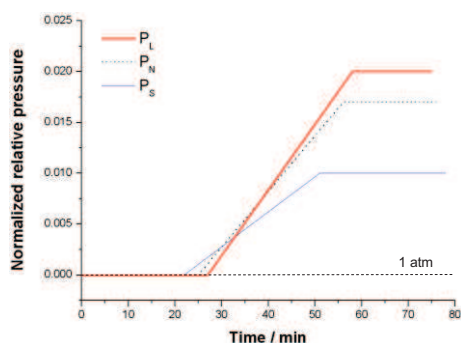


Figure 4. the relationship between pressure and time of the Pt reduction reactions in the modified OLRS.

Figs. 5 and 6 show the corresponding SEM images with different pressure conditions. The red arrows show that serious agglomeration of Pt clusters on CNTs, clearly displaying better Pt dispersion in the case of larger reduction pressure. Fig. 6 also shows

the high-magnification SEM images at the three different pressure conditions. The mean particle size of the Pt catalysts on the CNTs at the three different pressures of P_L , P_N and P_S are 2.2, 3.2 and 4.6 nm, respectively.

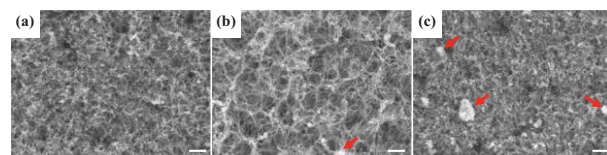


Figure 5. Pt catalyst dispersions on CNTs prepared at different pressure conditions: (a) the larger pressure (P_L), (b) unmodified normal pressure (P_N), and (c) the smaller pressure (P_S). The red arrow indicates the serious agglomeration of the Pt clusters. (SEM magnification: 5,000X)

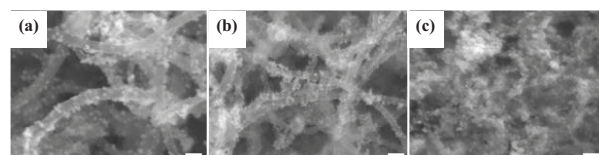


Figure 6. Pt nanocatalyst dispersion on the CNTs at different pressure conditions: (a) P_L , (b) P_N , and (c) P_S . (SEM magnification: 100,000X)

Electrochemical Evaluation

The electrochemical performance for Pt/CNT/Si-based electrocatalysts with various pressure regulations in the OLRS was conducted in the CVs, as shown in Figs. 7 and 8. The mass activity for the best Pt catalyst is at the larger pressure, which is 447 $\text{A g}_{\text{Pt}}^{-1}$ with a Pt mass density of 0.18 mg cm^{-2} .

The hydrogen adsorption charge (Q_H) of Pt electrocatalysts involved in the charge transfer reaction can be integrated from Fig. 7, and the mass density of Pt catalysts can be measured by ICP-MS as well. The so-called active surface area of Pt catalysts, electrochemical surface area (ESA), can be obtained using the following formula [12]:

$$\text{ESA (m}^2/\text{g}_{\text{Pt}}) = Q_H / 0.21 \times 10^{-3} \times \text{g}_{\text{Pt}}$$

It can directly reflect the activity of Pt catalysts, and it is closely related to their size and dispersion density. The value of $0.21 \times 10^{-3} \text{ C}$ is the reaction charge per centimeter square of pure platinum plane in the sulfuric acid solution. The relationships between the ESA and the MA at various Pt reduction pressures are shown in Table 1, showing that the best performed electrocatalysts with a higher ESA of 41.25 $\text{m}^2 \text{g}_{\text{Pt}}^{-1}$ is the Pt electrodes reduced at larger pressure.

The electrochemical properties of the Pt/CNTs electrodes prepared at different reduction temperatures in the MOLRS are listed in Table 1, exhibiting that the

electrochemical MA and ESA of the Pt catalysts in the case of the Pt reduction at larger pressure respectively increased by 17% and 13% in comparison with the case at atmospheric pressure.

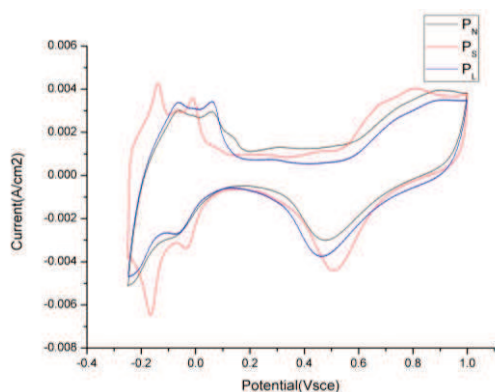


Figure 7. Cyclic voltammograms of the Pt nanocatalysts deposited on CNTs electrodes at various reduction pressures. All tests were carried out in 0.5 M H₂SO₄ with a scan rate of 50 mV s⁻¹, at 25 °C.

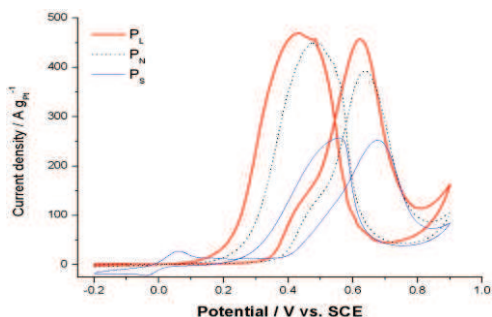


Figure 8. Cyclic voltammograms of the Pt electrode catalysts for methanol oxidation reaction at different reduction pressures. All tests were carried out in 1 M CH₃OH and 0.5 M H₂SO₄ with a scan rate of 20 mV s⁻¹, at 25 °C.

Table 1. Electrochemical properties of the Pt/CNTs electrode catalysts prepared in the MOLRS at different reduction pressures.

Pressure condition	E _p (V _{SCE})	Q _H (mC cm ⁻²)	M _{Pt} (mg cm ⁻²)	ESA (m ² g _{Pt} ⁻¹)	MA (A g _{Pt} ⁻¹)
P _L	0.62	15.93	0.18	41.25	447
P _N	0.64	14.80	0.20	35.24	394
P _S	0.68	13.17	0.23	21.76	277

CONCLUSION

In this paper, the electrochemical properties of the Pt/CNTs electrode catalysts with the small size and uniform dispersion of Pt catalysts were improved by controlling the reduction pressure in the MOLRS compared with the results in our earlier study [1]. In terms of Pt catalyst utilization, the best performed electrocatalysts prepared at larger pressure has smaller

Pt particle size (3→2 nm), higher ESA (35→41 m² g⁻¹), and superior catalytic mass activity (394→447 A g⁻¹). Small-size and uniformly dispersed Pt catalysts on the CNTs (Pt/CNTs) was obtained by the MOLRS at larger pressure, which are applicable to be utilized as electrode catalysts for micro DMFCs.

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