High Efficient Nanocatalyst Synthesis Using Semi-Reflux Chemical Reduction System with Temperature Regulation in Micro DMFC

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Abstract: In this paper, we successfully fabricated high catalytic activity Pt supported on carbon nanotubes (CNTs) with temperature regulation in the semi-reflux chemical reduction system (SRCRS) demonstrated in our previous study [1]. Compared to traditional reflux system reducing at high temperature of 160℃ [9], the SRCRS can effectively save more than 60% reduction time at lower temperature of 130℃. Besides, the electrochemical results also showed that the mass activity and electrochemical surface area (ESA) of Pt catalysts can dramatically be enhanced by 58% and 63%, respectively.

Keywords: micro DMFC, catalytic activity, CNTs, semi-reflux chemical reduction system (SRCRS)

INTRODUCTION

Fossil fuel has always been an important fuel source for human's long-standing dependence. However, with oil price rising, the problem of oil crisis exists all the time, and environmental pollution is also caused by fossil fuel, so the future search for alternative energy sources has become a significant issue for scientific and technological developments. Direct methanol fuel cell (DMFC) uses methanol as fuel, mainly because it has high energy conversion efficiency, low pollution, and it can operate at low temperature. 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 [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 (1~5nm) 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 (24h) for catalyst preparation due to slow nucleation and growth process at low temperature (60℃). As a result, recent developed reflux technology [9] can react at higher reaction temperature (160℃), substantially shorten the time required for catalyst preparation (~3h); however, it needs high sealing system for pressure control, increasing the difficulty. Therefore, the catalyst preparation of Pt in this study was conducted in the home-made SRCRS, which has simple reaction process and shorts reduction time, coupling with various temperature regulations to effectively fabricate high activity, high-density dispersed Pt catalysts in DMFC. The experimental results show that the best catalyst activity and ESA can be obtained at the reduction temperature of 130℃ for 75min compared to our previous report [1], and the corresponding fabrication process of Pt electrocatalysts is shown in Fig. 1.
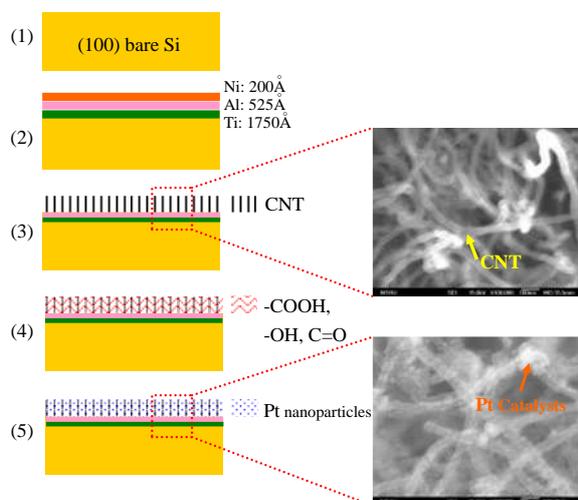

Figure 1. The preparation process and SEM images of (Pt/)CNT/Si-based plate electrodes [1, 3]. (1) Bare Si substrate, (2) Sputter Ni/Al/Ti metal films, (3) CNT growth, (4) Hydrophilic treatment of CNT, and (5) Deposit nano-scale Pt catalyst.

EXPERIMENTAL

● Growth of Carbon Nanotube

We used a 525μm-thick bare Si followed by coating with Ni/Al/Ti (film thickness: 20nm/52.5nm/175nm), respectively, and then grew CNT by thermal chemical vapor deposition (TCVD). First, we purged Ar and heated the quartz tube from room temperature to 800℃, then hold the temperature at 800℃ 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 CNT with C_2H_4. The growth time of CNT was 30 min, and this technique is known as the catalytically-growth CVD.

● Hydrophilic Treatment of Carbon Nanotube

We used 6M sulfuric acid (H_2SO_4) as the oxidant for hydrophilic treatment of CNT. 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, and Fourier transform infrared spectroscopy (FTIR) analysis was carried out for the semi-quantitative relationship of functional groups on the pretreated surfaces of CNTs, comparing the effects with/without vacuum for the hydrophilic treatment.

● Semi-Reflux Chemical Reduction System

The hydrophilic treatment was carried out in 6M H_2SO_4 solution at 80℃ for 1h before catalyst reduction. Wang et al. [10] mentioned that the growth of catalyst particles can be controlled by the reaction temperature. Furthermore, the reflux technique can enhance the reaction temperature and shorten the reduction time. According to our previous study, we used 0.04392g $H_2PtCl_6•6H_2O$ and 0.1mM ethylene glycol as Pt catalyst precursors. The solutions contain too much water as a result of maintaining at 100℃ (boiling point), so the reaction temperature can not rise to 160℃ as mentioned in the literature. However, the reaction pressure and water content of Pt precursor solutions did not mention in the literature, either. In order to simplify the experimental setup, we designed a home-made reflux system to react at high temperatures under atmospheric pressure, and collect the evaporation of the precursor solutions by a condenser tube, so that the concentration of precursor solutions can increase gradually, and temperature regulations can also be easily accomplished for further optimization. The setup is different from traditional reflux device which is a closed system, so it's called semi-reflux chemical reduction system (SRCRS), as shown in Fig. 2(a).
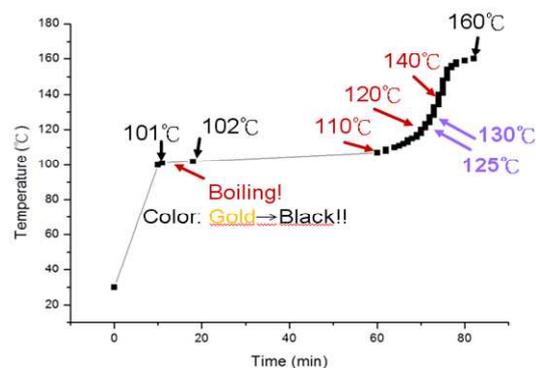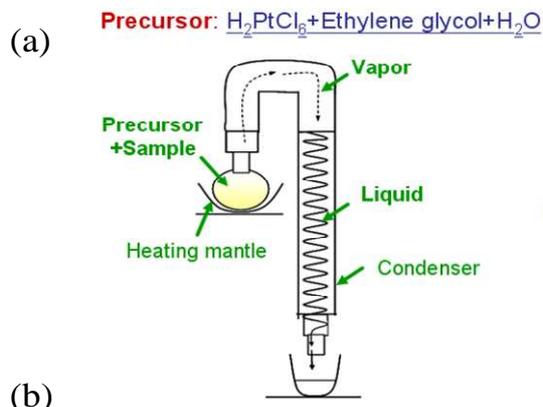

Figure 2. (a) Setup of the SRCRS [1]. The arrows in the system represent the direction of vapor (dash) and water (solid), (b) the relationship between temperature and time of Pt reduction reaction in the SRCRS.
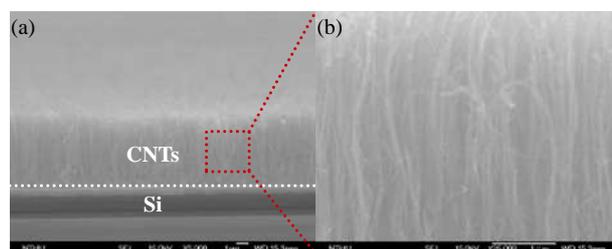

Figure 3. Morphology of CNT array on a Si substrate.

● 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. In the CVs, we can also obtain the active surface area of Pt catalysts from the hydrogen adsorption reactions. The three-electrode cell was setup for the electrochemical tests. Saturated calomel electrode (SCE, 0.241V vs. SHE) and Ti-coated Pt mesh are used as reference electrode (RE) and counter electrode (CE), respectively. All the electrochemical meassurments were purged with N_2 gas to remove oxygen.

RESULTS AND DISCUSSION

- **Morphology and Hydrophilic Treatment of Carbon Nanotube**

We use CNT as the carbon support directly grown on a Si-based substrate coated with Ni/Al/Ti multi-layers for catalyst of CNT growth/electron conductance/adhesion between Si and CNT, respectively. The length and diameter of CNTs are 5~6μm and 40nm, respectively. The advantage of using CNT array is the ability of transport electron along with the direction of CNT. CNT can not only reduce resistance for the cell assembly, but also contribute to the removal of CO_2 in the anode. The morphology of CNTs is shown in Fig. 3.

In Fig. 4, we utilized Fourier transform infrared spectroscopy (FTIR) to measure the types of functional groups on the pretreated CNTs and compare the semi-quantitative relationships after the hydrophilic process with/without vacuum treatment. We can find the peak signals of the functional groups with vacuum treatment are greater than those without vacuum condition, indicating that air bubbles detached effectively from the CNTs surface and enhance their hydrophilic degree for better Pt adhesion in the following preparation of Pt catalyst.
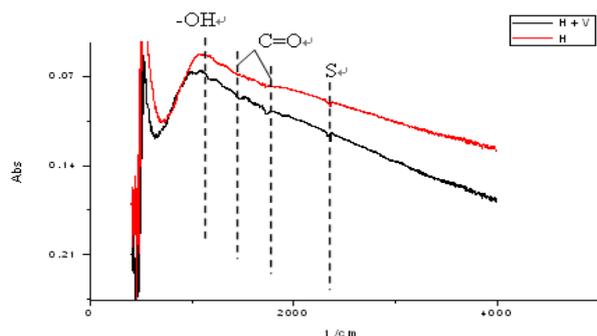

Figure 4. FTIR diagrams of the hydrophilic treated CNTs with/without vacuum conditions. H: 6M H_2SO_4 without vacuum. H+V: 6M H_2SO_4 with vacuum [1].

- **Temperature Control in SRCRS**

As the solution volume and temperature in the SRCRS change with the solution evaporation/condensation process, the mechanism for enhancing the boiling point will be different from the traditional reflux system, so it is imperative to optimize the reaction temperature of Pt reduction in the SRCRS. First, we start with drawing the reduction temperature curve of Pt catalyst with time in the SRCRS, as shown in the above Fig. 2(b), carrying out the experiments with different temperatures started from 30℃ to 110℃, 120℃, 125℃, 130℃, 140℃ and 160℃, then take out the specimens from the reaction tank. During the heating process, we can observe the color of precursor solution varying slowly from gold to black when the temperature approaches about 101℃, and the solution also begin to boil at the same time. We suggest that this is the early stage of Pt catalyst reduction reaction in the SRCRS.

- **Electrochemical Evaluation**

The electrochemical performance for Pt/CNT/Si-based electrocatalysts with various temperature regulations in the SRCRS was conducted in the CVs, as shown in Fig. 5 and Fig. 6. The peak current density (I_P) for the best performed electrocatalysts at 125℃ is about 100mA/cm^2 (E_P: 0.68V vs. SCE). In terms of Pt utilization, the mass activity for the best Pt catalyst at 130℃ is 426A/g with Pt mass of 0.19mg.
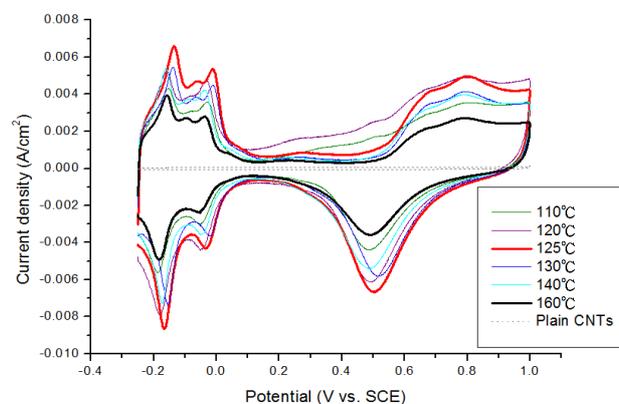

Figure 5. Cyclic voltammograms of Pt nanocatalysts deposited on CNT/Si with various reduction temperatures. All tests were carried out in 0.5M H_2SO_4 with scan rate of 50mV/s, at 25 ℃.
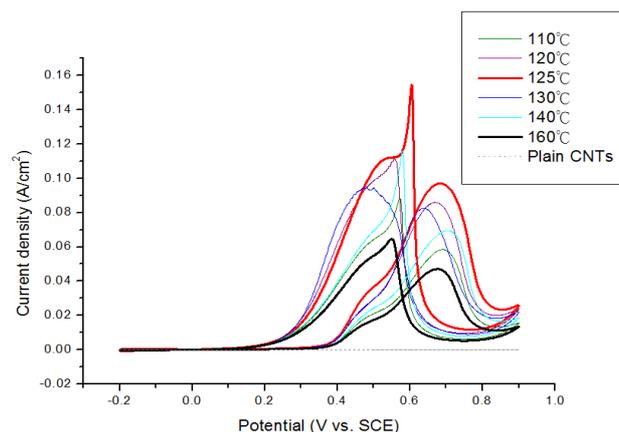

Figure 6. Cyclic voltammograms of methanol oxidation reaction for Pt electrocatalysts with different reduction temperatures. All tests were carried out in 1M CH_3OH and 0.5M H_2SO_4 with scan rate of 20mV/s, at 25 ℃.

The hydrogen adsorption charge (Q_h) of Pt electrocatalysts involved in the charge transfer reaction can be integrated form Fig. 5, and the mass of Pt catalyst can be measured by ICP-MS as well. The active surface area of Pt catalyst so-called electrochemical surface area (ESA) can be obtained using the following formula [12]:

$$ESA \ (m^2/g_{Pt}) = Q_h/0.21 \times 10^{-3} C(g_{Pt})$$

It can directly reflect the activity of Pt catalysts, and it is closely related to their size and dispersion density. The value of 0.21×10^{-3}C is the reaction charge per centimeter square of pure Platinum plane in the sulfuric acid solution. The relationships between ESA and mass activity with various reduction temperatures of Pt catalysts are shown in Fig.7. The ESA value for the

best performed electrocatalyst is consistent with the result of Pt mass activity at the best reduction temperature of 130℃.
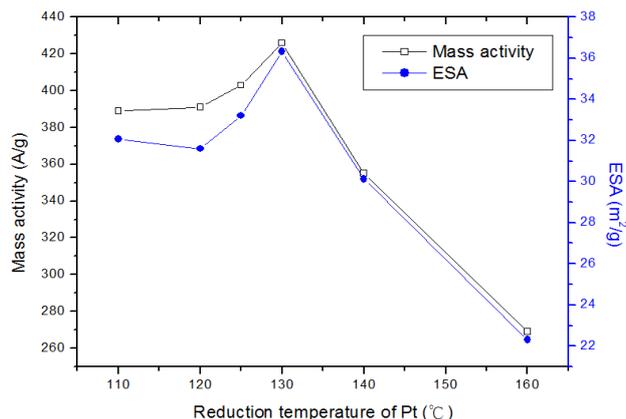

Figure 7. The relationships between catalytic mass activity and ESA of Pt electrocatalyss with various reduction temperatures.

The electrochemical results with different reduction temperatures are listed in Table 1. It can exhibit that the case of Pt reduction at 130℃, not only saves more than 60% reaction time compared to traditional reflux system (3h→75min), but also respectively increases the electrochemical activity and ESA of Pt catalyst by 58% and 63% in comparison with the case at 160℃. In addition, the corresponding SEM micrographs shown in Fig.8, clearly displaying better Pt dispersion in the cases at 125℃ and 130℃ while other cases at 120℃, 140℃ and 160℃ showing thatserious agglomeration of Pt clusters on CNTs, especially in the case at 160℃ (Pt reduction temperature of traditional reflux system).

Table 1. Electrochemical properties of Pt catalyst electrodes with different reduction temperatures.

Temperature (℃) / Properties	110	120	125	**130**	140	160
E_P (V)	0.69	0.67	0.68	0.64	0.70	0.68
I_P (mA/cm^2)	58	86	97	83	70	47
Q_{th} (mC)	10.1	14.6	16.8	14.8	12.4	8.2
Catalyst mass (mg)	0.15	0.22	0.24	0.19	0.20	0.18
Mass activity (A/g)	389	391	403	**426**	355	269
ESA (m^2/g)	32.06	31.60	33.20	**36.33**	30.13	22.31
Reduction time (hr'min")	1'07"	1'14"	1'16"	1'14"	1'21"	1'22"

CONCLUSION

In this paper. we effectively shorten the reaction time (90→75min) at lower temperature (160→130℃) by controlling reduction temperature compared with the results of Pt catalyst preparation in earlier study [1]. In terms of Pt catalyst utilization, the best performed elctrocatalysts we prepared at 130℃ has smaller particle size (5→3nm, Fig. 1), higher ESA (22→36m^2/g), and better catalytic mass activity (269→426A/g). In addition, the mass activity of Pt

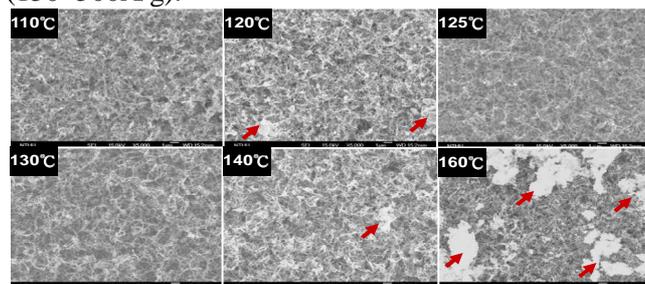catalyst is comparable with other literatures (150~500A/g).

Figure 8. Pt catalyst distribution (SEM magnification: 5,000X) at different reduction temperatures. The red arrow indicates the serious agglomeration of Pt.

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