Electrocatalytic Properties Improvement on Carbon-Nanotubes Coated Reaction Surface for μDMFC

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ABSTRACT
In this paper, the electrocatalytic performance of CNTs grown on silicon substrate is compared with the conventional reaction surfaces including bare silicon wafer, carbon cloth and carbon paper, and all are with a thin Pt film (10nm) coating. In the measurement of CV for electrocatalytic properties, it has demonstrated that Pt/CNTs electrode possesses high-effect electrocatalytic reactivity and powerful CO₂ microbubbles removal ability although a more rapid poisoning on Pt/CNTs from high-effect electrocatalytic reaction, owning to the large reaction area and smaller footing spots for bubble retention. A new electrochemical characterization method has also been carried out to relate microbubble retention on surface with electrochemical signals, and demonstrates a good agreement with the bubble removal phenomenon on electrode surface.

Keywords: electrocatalytic activity, CNTs, Micro DMFC, micro power generator, Fuel cell

1 - INTRODUCTION
Direct methanol fuel cell (DMFC) is a promising power source for portable applications due to its low operation temperature and reasonable fabrication cost. The performance of DMFC has been remarkably improved in the past years, but the poisoning of the catalyst [1, 2], fuel crossover [3], CO₂ bubbles collection [4, 5], and improvement on reaction surface/area, etc., are still the issues of interest. The last two issues are related to the bubble generation/departure ability and catalytic reaction efficiency in a DFMC system. Furthermore, the structure of the supporting substrates for the performance of catalytic reaction may play important roles [6, 7] in the bubble generation/departure issue and the catalytic mechanism. This paper proposes to employ nanostructured surface by CNTs to both increase reaction area and reduce surface tension/surface friction to enhance the reaction rate and bubble removal speed [8] in a DMFC system.

2 - EXPERIMENTAL

2.1 - Electrodes fabrication process
The fabrication processes of electrodes with different substrates are shown in Fig.1. The substrates used in this study were silicon wafer (500µm in thickness), carbon paper (Electrochem Inc.), carbon cloth (Electrochem Inc.) and CNTs. Except CNTs, all the substrates were coated with titanium (100nm in thickness) and platinum film (10nm in thickness) by E-beam physical vapor deposition. Titanium film was served as adhesion layer and conductor, and Pt film was treated as catalyst layer. The carbon nanotubes were grown directly on silicon wafer by the thermal chemical vapor deposition technique in a tube furnace. The catalyst for the growth of CNTs was nickel which was deposited by E-beam physical vapor deposition. Because of the poor adhesive ability between Nickel and Silicon wafer, the titanium film, deposited by E-beam evaporation, of 100nm in thickness was treated as the adhesion layer and conductor. In order to anneal catalyst film (Ni) to turn into nanoparticles and to decompose the Ethylene gas (C₂H₄) which acted as the source of carbon, the environmental temperature was maintained at 800℃ during the growth process of CNTs for 5 minutes. The grown CNTs and Pt/CNTs were examined by scanning electron microscopy (SEM) as shown in Fig. 2. From Fig. 2, the CNTs were curved and random distributed with a diameter about 100~150 nm, and average height 2μm (Fig. 2b). Figure 2c shows that the conformation of CNTs didn’t change or damage after the Pt film coating.

Pt/Si:

Pt/Carbon paper or Carbon cloth:

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Pt/CNTs:

Si wafer → Ti deposition → Ni deposition → CNTs growth → Pt film deposition → Reaction area definition

Figure 1 – The fabrication process of electrodes with different substrates.

Figure 2 – The SEM images of CNTs (a) top view (40000x), (b) lateral view (10000x), (c) Pt/CNTs (top view, 40000x).

2.2 - Pretreatment of electrodes
To enhance hydrophilic degree and electrochemical activity of the electrode surface, the electrodes were immersed in 30% hydrogen peroxide aqueous solutions for 3-4 minutes. For four type surfaces including Pt/Si, Pt/CNTs, Pt/carbon paper, and Pt/carbon cloth, the contact angle less than 20° was achieved. (Fig. 3)

Figure 3 – The photograph of the contact angle on different electrode surfaces.

2.3 - Electrochemical measurement
The system shown in Fig.4 was a standard three-electrode cell which was employed for electrochemical measurement.

The sample with a definite area of 0.2 cm². A platinum wire, and a Ag/AgCl electrode was employed to act as the working electrode, counter electrode, and reference electrode, respectively. The cyclic voltammetry (CV, potential sweep range: -0.2V~1V) and potentiostatic method (0.8 V in present work) for 1M CH₃OH + 0.5M H₂SO₄ aqueous solutions was used to measure electrocatalytic properties. All experiments were carried out at 27°C with atmospheric pressure except the long-term stability test (30°C). All chemicals were reagent grade and DI water was used throughout all experiments.

Figure 4 – The schematic diagram of electrochemical measurement system

3 - RESULTS AND DISCUSSION

3.1 - Electrocatalytic performance of H2O2 pretreated Pt catalyst
The contact angle and Faradaic current density on Pt catalyst surface are varied after the H₂O₂ pretreatment (Fig. 5). For Pt/Si, the better hydrophilic surface after pretreatment is back to its worse hydrophilic condition with contact angle increasing from 17° to 82°in 4 hours. The Faradaic current density after pretreatment (1.65×10⁻⁴A/cm²) is dropped to the original level of 0.2×10⁻⁴A/cm² in 4 hours, too. Strong oxidation property of H₂O₂ activates the catalytic site and cleans away the impurities on the surface. Additionally, the hydrophilic nature will help the reactants to wet better with the catalytic sites. According to Zidong Wei [9], in the presence of oxide-rich Pt (after pretreatment), it may react with methanol through the following reaction first instead of catalyzing methanol:

\[\text{CH}_3\text{OH} + \text{Pt} \rightarrow \text{H} - \text{C} - \text{H} + \text{H}^\text{+} + \text{e}^-\]

Because of oxide-rich surface, Oxygen atoms will bond to the Pt atoms on the Pt film locally. Then the circled product in the formula may be reacted with Pt-O as follows:

\[2\text{H} - \text{C} - \text{H} + \text{Pt}-\text{O} \rightarrow \text{H} - \text{C} - \text{H} - \text{H}^\text{+} + \text{e}^-\]

\[\text{Pt} \quad \underbrace{\text{Pt}-\text{O} + 2\text{H}^\text{+} \rightarrow \text{Pt}}_{\text{Refreshed Pt}}\]

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In terms of the reactions above, Pt catalyst in circular mark is refreshed by the reaction and then catalyzes methanol normally. Because the refreshed Pt atoms would be oxidized and reduced, the catalytic efficiency of these atoms will raise enormously. The discussions above are the major reasons on catalytic current enhancement of H2O2 pretreated Pt catalyst.

CH3OH + 0.5M H2SO4 aqueous solutions can be properties of Pt catalyst by cyclic voltammetry in 1M CH3OH + 0.5M H2SO4 aqueous solutions with typical cyclic voltammogram (Fig.6). Two oxidation peaks in the cyclic voltammogram are observed and they correspond to the oxidation of methanol and the oxidation peaks in the cyclic voltammogram are observed and they correspond to the oxidation of methanol and the

Electrocatalytic performance of Pt catalyst is obtained by cyclic voltammetry in 1M CH3OH + 0.5M H2SO4 aqueous solutions on different substrates. The sweeping rate of CV: 50mV/s. The ambient temperature: 27℃. Electrode: Pt/Si.

**Figure 6** – The typical cyclic voltammogram in 1M CH3OH + 0.5M H2SO4 aqueous solutions. The sweeping rate of CV: 50mV/s. The ambient temperature: 27℃. Electrode: Pt/Si.

**Figure 7** – The comparison of the peak current density in 1M CH3OH+0.5 M H2SO4 aqueous solutions on different substrates. The sweeping rate of CV is 50mV/s. The ambient temperature: 27℃.

### 3.3. Comparison of methanol concentration, and sweeping rate of CV on electrocatalytic properties between Pt/CNTs and Pt/Si

The effects of methanol concentration on electrocatalytic properties of Pt/CNTs and Pt/Si electrodes are shown in Fig.8(a)(b). From Fig.8(a), the peak current density of both electrodes increases with the increase of methanol concentration, and the slope of Pt/CNTs case is much higher than that of Pt/Si one for different concentrations, representing the activity degradation in Pt/Si case while not occurred in Pt/CNTs one. It implies that the degradation of electrocatalytic activity may attribute to the trap of CO2 microbubbles [8] to hinder the diffusion of the methanol and the intermediate products during the methanol oxidation. This phenomena can be further explained as a irreversible system, and the peak current (Ip) is defined by the following equation [10]:

\[
Ip = \left( \frac{2.99 \times 10^5}{n} \right) \frac{n}{\alpha n_a^{1/2} A D^{1/2} C \nu^{1/2}} \quad (1)
\]

where n is the charge number, \( \alpha \) is the transfer coefficient, \( n_a \) is the electron-transfer number of the rate determining step, and \( \nu \) is the sweeping rate of CV. In our system, all parameters in this equation except surface area (A) and diffusion coefficient (D) will maintain constant with the variation of methanol concentration. The surface area (A) and diffusion coefficient (D) among this equation may reduce as methanol concentration (C) increasing, so no linear relationship of the curves for both electrodes in Fig.8(a) can be observed. However, on Pt/CNTs surface, the effect of microbubble coverage does not pose major problem due to bubble quick removing property on hydrophilic nanostructures, so more linear relationship and higher slop of the peak current-concentration curve can be obtained on Pt/CNTs case.

On the other hand, higher the methanol concentration possesses larger the electrocatalytic current density and more the poison of the active sites, which increases the
oxidation potential of the catalyst and results in a higher peak potential in the curve of cyclic voltammetry. Thus, peak potential not only increases as methanol concentration increases, but also increases on Pt/CNTs surface for keeping more active sites of CO generation, as shown in Fig. 8b.

\[
\text{Concentration (mol/L)} \quad 0 \quad 5 \quad 10 \quad 15 \quad 20 \quad 25
\]
\[
\text{Peak Current Density (mA cm}^{-2}\rangle \quad 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6
\]

(a)

\[
\text{Concentration (mol/L)} \quad 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6
\]
\[
\text{Peak Potential (V vs Ag/AgCl)} \quad 0.59 \quad 0.61 \quad 0.63 \quad 0.65 \quad 0.67 \quad 0.69
\]

(b)

**Figure 8** – Effect of methanol concentration on (a) peak current density and (b) peak potential. The sweeping rate of CV: 50mV/s. The ambient temperature: 27°C.

From equation (1), the peak current density \(I_p\) increases with the square root of scan rate \(\sqrt{\nu}\), which can also be observed in Fig. 9 for both cases except a little curve for Pt/Si one. This suggests that higher the scan rate, more reaction products are accumulated in the vicinity of the Pt/Si electrode surface resulting in a decrement of the rising slope of the peak current density, while this is not occurred in the Pt/CNTs counterpart because of the rapid removal of gas bubbles thus illustrates an almost straight line.

\[
\text{Square Root of Scan Rate [(mV/s)^1/2]} \quad 0 \quad 2 \quad 4 \quad 6 \quad 8 \quad 10 \quad 12 \quad 14 \quad 16
\]
\[
\text{Peak Current Density (mA cm}^{-2}\rangle \quad 0 \quad 2 \quad 4 \quad 6 \quad 8 \quad 10 \quad 12 \quad 14 \quad 16
\]

**Figure 9** – Effect of square root of forward CV scan rate on peak current density obtained in 1M CH₃OH + 0.5M H₂SO₄ aqueous solutions. The ambient temperature: 27°C.

4 - CONCLUSIONS

The electrocatalytic performance of CNTs coating with Pt film (10nm) are compared with conventional substrates of bare silicon wafer, carbon cloth and carbon paper with the same Pt coating. The CNTs is the best carrier for Pt catalyst among these four kinds of substrates, and the peak current density on it is much greater than other three kinds of carriers because of the large surface area and excellent CO₂ microbubble removal induced by CNTs nanostructures. The intermediates diffusion and product collection during methanol oxidation on the electrode surface play an important role in the reaction process. In the experiments of methanol concentration and sweeping rate of CV on the four different electrodes, it indirectly demonstrates that Pt/CNTs electrode possesses highly-effective electrochemical-reactivity and powerful ability of microbubbles removal, but it also shows more serious poison on Pt/CNTs because of high-effect catalytic reaction. This paper also carried out a new electrochemical method to indirectly indicate the effect of microbubble coverage on different surfaces from electrochemical signal. Most of the characterization results suggest that CNTs are good candidates for supporting catalyst to enhance electrochemical activity for the application to micro-DMFC.

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