Synthesis of PtRu/C-CNTs electrocatalysts for DMFCs with treated-CNTs and composition regulation

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Abstract
In the present work, PtRu/C-CNTs catalyst samples were studied for potential applications in direct methanol fuel cells (DMFCs). Carbon nanotubes (CNTs) were treated by H2SO4 98% and HNO3 65% at different temperatures and with different stirring periods. As a result, the PtRu/C-CNTs catalyst was successfully synthesized by using H2PtCl6 and RuCl3 precursors with the efficient reduction of NaBH4 agent in ethylene glycol (e.g.). In addition, we controlled the ratios of treated-CNTs on carbon vulcan XC-72 treated-CNTs substrate (C-CNTs) with the different values: 50 wt%, 25 wt%, and 12.5 wt%, respectively. The PtRu/C-CNTs electrocatalyst samples were investigated by experimental methods including x-ray diffraction (XRD), transmission electron microscopy (TEM), and cyclic voltammetry (CV). Importantly, the CV results show the best treated-CNTs and the most suitable ratio of CNTs composition on C-CNTs substrate to be controlled in order to produce various efficient PtRu/C-CNTs catalysts with high catalytic activity for DMFCs.

Keywords: carbon nanotubes, direct methanol fuel cells, PtRu/C-CNTs electrocatalyst
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1. Introduction

Fuel cells (FCs) are recognized as promising energy power sources for the future [1]. Among various FCs, direct methanol fuel cells (DMFCs) are known as a low operation temperature cell, using methanol fuel and the membrane–electrode assembly (MEA) technology [2]. The Pt based catalysts are used in the electrodes of DMFCs, following operation principle [3]:

Anode: CH3OH + H2O → CO2 + 6H+ + 6e−,
Cathode: $\frac{3}{2}$O2 + 6H+ + 6e− → 3H2O,
Overall reaction: CH3OH + $\frac{3}{2}$O2 → CO2 + 2H2O.
However, the Pt catalyst is easily poisoned by carbon monoxide (CO) which was produced from hydrogen oxidation reaction (HOR). This problem is solved by using Pt–Ru based catalysts. The Ru metal composition will reduce CO in Pt–CO bondings as follows [2]:

\[
\text{Ru} + \text{H}_2\text{O} \rightarrow \text{Ru} - \text{OH} + \text{H}^+ + e^-,
\]
\[
\text{Ru} - \text{OH} + \text{Pt} - \text{CO} \rightarrow \text{Pt} + \text{Ru} + \text{CO}_2 + \text{H}^+ + e^-.
\]

Conventionally, highly conductive carbon blacks, such as vulcan XC-72, are used as supports for Pt electrocatalysts. After the discovery of carbon nanotubes (CNTs) [4], Pt/CNTs based catalysts were investigated by many authors [1, 5–11]. Before the use of CNTs, they must be treated in strong acids, such as HNO$_3$ or a mixture of HNO$_3$ and H$_2$SO$_4$, at a temperature and a period value to remove impurities and generate amounts of functional groups, e.g., –OH, –COOH, –C=O on the CNTs surfaces [1]. However, there are significant differences about temperatures and periods treated between authors. For example, Li et al refluxed CNTs in 70% HNO$_3$ at 120 °C for 4 h and then treated them in a 4.0 N H$_2$SO$_4$–HNO$_3$ mixture for 4 h [5]; Zhao et al purified MWNTs by refluxing them with 60% HNO$_3$ at 90 °C for 2 h and then the surface oxidation of the MWNTs was carried out by refluxing MWNTs in 4 M H$_2$SO$_4$+ 4 M HNO$_3$ at 90 °C for 5 h [7], the group of Lee treated CNTs for 36 h at 110 °C in a mixed solution of HNO$_3$ and H$_2$SO$_4$ [11], and so forth [1, 8–10]. Besides, the effect of the ratio of CNTs composition on C-CNTs substrate on quality of PtRu/C-CNTs electrocatalyst has not been studied so far.

In this work we have prepared PtRu/C-CNTs catalyst samples using many types of CNTs that were treated at different temperatures and with different stirring periods. Besides, we have also prepared PtRu/C-CNTs electrocatalyst samples using different ratios of treated-CNTs. Our purpose is to find out the best treated-CNTs sample and the best ratio of treated-CNTs for PtRu/C-CNTs electrocatalysts.

2. Experimental

2.1. CNTs treatment

The CNTs material in our work was manufactured by Ho Chi Minh City University of Technology, Vietnam. Parameter and image of CNTs are shown in figure 1 and table 1.

In our experiments on treated-CNTs (called experiment 1), CNTs samples were dissolved in H$_2$SO$_4$ 98%–HNO$_3$ 65% mixture with the volume ratio 1:1 under ultrasonic treatment for 15 min They were refluxed at temperatures and with stirring periods, as presented in table 2.

In the experiment on the ratio of CNTs composition with C-CNTs substrate (called experiment 2), CNTs sample was dissolved in H$_2$SO$_4$ 98%+HNO$_3$ 65% with the volume ratio 1:1 under ultrasonic treatment for 15 min This mixture was then stirred at room temperature for 5 h. After 5 h, activated CNTs were washed by centrifugal filter method to remove acid impurities. Finally, it was dried at 100 °C under vacuum condition for several hours.

![Figure 1. The image of CNTs, supplied by producer.](image1)

![Figure 2. XRD pattern of PtRu/C-CNTs catalyst sample.](image2)

| Table 1. Data sheet of CNTs, supplied by producer. |
|-----------------------------------------------|
| Properties | Value |
|-----------|-------|
| C-purify  | >95 wt% |
| Outer diameter | <12 nm |
| Inner diameter | ~2 nm |
| Length   | >1 μm  |

| Table 2. CNTs treatment samples. |
|--------------------------------|
| Sample name | Temperature | Time (hours) |
|-------------|-------------|--------------|
| PtRu/C-CNTs 01 | Room | 5 |
| PtRu/C-CNTs 02 | 50 °C | 5 |
| PtRu/C-CNTs 03 | 50 °C | 10 |
| PtRu/C-CNTs 05 | 100 °C | 5 |
| PtRu/C-CNTs 06 | 100 °C | 10 |
| PtRu/C-CNTs 07 | Room | 10 |
2.2. Preparation of PtRu/C-CNTs electrocatalysts

2.2.1. Experiment 1 (on treated-CNTs). Firstly, we have used 4 mg activated CNTs, 36 mg carbon vulcan XC-72 (10% CNTs), 10 ml acid H₂SO₄ 98%, and 40 ml ethylene glycol. Their mixture was treated by ultrasonic method for 15 min. Then the mixture was stirred at 150 °C for 30 min. After that, the precursor of PtRu (H₂PtCl₆.6H₂O and RuCl₃.xH₂O solution) was added. Here, atomic ratio of Pt:Ru was equal to 1:1. The ratio of PtRu composition with 20 wt% on PtRu/C-CNTs was controlled in all samples. Next, 0.4 g NaBH₄ and 20 ml DI water solution was sprinkled into the mixture. The pH was adjusted to about 12 by using NaOH. The mixture was stirred at room temperature for 6 h. It was dried at 100 °C under vacuum condition for several hours. Finally, we gained the PtRu/C-CNTs electrocatalyst sample.

2.2.2. Experiment 2 (on the ratio of CNTs composition with C-CNTs substrate). Firstly, mixtures of activated CNTs and carbon vulcan XC-72 were produced following the ratios below (table 3). Next, these samples were treated by ultrasonic method in 10 ml acid H₂SO₄ 98% and 40 ml ethylene glycol solution for 15 min, then they were stirred at 150 °C for 30 min. After that, the precursor of PtRu, H₂PtCl₆.6H₂O and RuCl₃.xH₂O solution (atomic ratio Pt:Ru = 1:1, the ratio of PtRu composition with 20 wt% on PtRu/C-CNTs was controlled in all samples) was added. Solution of 0.4 g NaBH₄ and 20 ml DI water was sprinkled into the mixture. The pH was adjusted to about 12 by using NaOH. The mixture was stirred at room temperature for 6 h. It was dried at 100 °C under vacuum condition for several hours. Finally, we gained the PtRu/C-CNTs electrocatalyst sample.

### Table 3. Ratios of treated-CNTs in different PtRu/C-CNTs samples

| Sample name       | Carbon vulcan mass (mg) | CNTs mass (mg) | Ratio of CNTs |
|-------------------|-------------------------|----------------|--------------|
| PtRu/C-CNTs 23    | 20                      | 20             | 50%          |
| PtRu/C-CNTs 24    | 30                      | 10             | 25%          |
| PtRu/C-CNTs 25    | 35                      | 5              | 12.5%        |

### Table 4. The result of CV investigation of PtRu/C-CNTs electrocatalyst samples.

| Sample name       | I₀ (A cm⁻²) | Iᵣ (A cm⁻²) | I₀/Iᵣ |
|-------------------|-------------|-------------|-------|
| PtRu/C-CNTs 01    | 0.03 145    | 0.01 048    | 3.0   |
| PtRu/C-CNTs 02    | 0.02 034    | 0.00 553    | 3.7   |
| PtRu/C-CNTs 03    | 0.02 086    | 0.00 150    | 13.9  |
| PtRu/C-CNTs 05    | 0.01 554    | 0.00 155    | 10.0  |
| PtRu/C-CNTs 06    | 0.06 150    | 0.02 557    | 2.4   |
| PtRu/C-CNTs 07    | 0.03 323    | 0.02 804    | 1.9   |

Figure 3. TEM images of PtRu/C-CNTs catalyst samples. (a): PtRu/C-CNTs 03 sample; (b): PtRu/C-CNTs 06 sample; (c): PtRu/C-CNTs 23 sample; and (d): PtRu/C-CNTs 24 sample (see also tables 2 and 3).
The pH was adjusted to about 12 by using NaOH. Mixtures were stirred for 6 h at room temperature. Finally, they were dried at 100 °C under vacuum condition for several hours. We gained PtRu/C-CNTs electrocatalyst samples.

All of PtRu/C-CNTs electrocatalyst samples were investigated by x-ray diffraction (XRD), transmission electron microscopy (TEM) and cyclic voltammetry (CV).

### 2.3. Electrochemical investigation on methanol electro-oxidation

Electrochemical investigation on methanol electro-oxidation of PtRu/C-CNTs samples was carried out by cyclic voltammetry. Each PtRu/C-CNTs sample was prepared by coating 2 mg PtRu/C-CNTs electrocatalyst on 1 cm² Toray carbon paper and it was a working electrode in CV system. CV investigation was performed on PARSTAT 2273 system using 0.5 M H₂SO₄ + 1.0 M CH₃OH solution, with a sweep rate of 50 mV s⁻¹.

### 3. Results and discussion

#### 3.1. XRD and TEM characterizations

XRD spectrum of a typical PtRu/C-CNTs catalyst sample was surveyed in figure 2. It has four diffraction peaks at the angle 2θ of 39.7°, 46.3°, 67.9° and 81.6° corresponding to the surface (111), (200), (220) and (311), respectively. These
peaks are characteristic of the fcc structure of platinum. According to Sherrer’s formula, the average size of PtRu nanoparticles is about 5.2 nm.

Figure 3 presents a typical sample of PtRu/C-CNTs nanoparticles. It clearly shows that PtRu nanoparticles were made up on CNTs and carbon vulcan with a high homogeneousness.

3.2. Cyclic voltammetry investigation

3.2.1. Experiment 1 (on treated-CNTs). CV investigation of PtRu/C-CNTs electrocatalyst samples is presented in figure 4. According to previous results [12], the oxidation of methanol is observed in the forward scan at point A, and an oxidation peak in the reverse scan at point B, which is attributed to the
clearly shows that the electrocatalyst samples. CV investigation of PtRu/C-CNTs mostly in the form of linearly bonded formed in the forward scan. These carbonaceous species are removal of the incompletely oxidized carbonaceous species between samples, presented in table 4.

Table 4 provides the value of peak current density of the methanol oxidation peak in the forward scan \(I_f\) and the reverse scan \(I_r\) of PtRu/C-CNTs electrocatalyst samples. It clearly shows that the \(I_f\) of PtRu/C-CNTs 06 sample (strirred for 10 h at 100 °C) receives the highest value, 61.5 mA cm\(^{-2}\). It also proves that \(I_f\) value of samples under stirring for 10 h is higher than that of samples under stirring for 5 h at the same temperature, this is confirmed by figure 5.

The ratio of the forward peak current density to the reverse peak current density \(I_f/I_r\) can be used to describe the issue of catalyst tolerance to CO accumulation [12, 13]. From table 4, the lowest and highest values of \(I_f/I_r\) ratio are 1.9 and 13.9 for the sample PtRu/C-CNTs 07 and PtRu/C-CNTs 03, respectively. It means that PtRu/C-CNTs 03 sample (strirred for 10 h at 50 °C) has the best CO tolerance.

3.2.2. Experiment 2 (on the ratio of CNTs composition with C-CNTs substrate). CV investigation of PtRu/C-CNTs electrocatalyst samples in this experiment is presented in figure 6 and the result of CV investigation shows a wide difference between samples presented in table 5.

Similarly to experiment 1, table 5 provides the value of peak current density of the methanol oxidation peak in the forward scan \(I_f\) and the reverse scan \(I_r\) of PtRu/C-CNTs electrocatalyst samples. The table clearly shows that the \(I_f\) of PtRu/C-CNTs 24 sample (ratio of CNTs 25 wt%) receives the highest value (77.09 mA cm\(^{-2}\)), while the \(I_f\) of PtRu/C-CNTs 25 sample (ratio of CNTs 12.5 wt%) is the lowest (15.78 mA cm\(^{-2}\)).

From table 5, the lowest and highest value of \(I_f/I_r\) ratio are 2.25 and 27.21 for the sample PtRu/C-CNTs 24 and PtRu/C-CNTs 25, respectively. This means the PtRu/C-CNTs 25 sample (ratio of CNTs 12.5 wt%) has the best CO tolerance.

Despite the PtRu/C-CNTs 25 sample having the highest value of \(I_f/I_r\) ratio, it methanol oxidation ability has the lowest value. Hence, we make the choice between the PtRu/C-CNTs 23 sample and the PtRu/C-CNTs 24 sample. In this case, the PtRu/C-CNTs 24 sample has methanol oxidation ability superior to that of PtRu/C-CNTs 23 sample but their \(I_f/I_r\) ratio is similar, 2.94 and 2.25, respectively (figure 7 and table 5).

4. Conclusion

PtRu/C-CNTs electrocatalyst was successfully synthesized by using of H₃PtCl₆ and RuCl₃ precursors with the reduction of NaBH₄ agent in ethylene glycol with high homogeneity. In the first experiment, PtRu/C-CNTs electrocatalyst samples using CNTs were treated by H₂SO₄ 98% and HNO₃ 65% at different ratios of treated-CNTs in the second experiment. The results showed that the methanol oxidation ability of samples under stirring for 10 h was always higher than samples under stirring for 5 h. In addition, the sample stirred at 100 °C for 10 h has the highest methanol oxidation ability. The CV results also show that the methanol oxidation ability of PtRu/C-CNTs 24 sample (ratio of CNTs 25 wt%) is far superior compared with other samples. Therefore, it may be the best choice sample of PtRu/C-CNTs electrocatalyst for DMFCs.

References

[1] Jeng K, Chien C, Hsu N, Yen S, Chiou S, Lin S and Huang W 2006 J. Power Sources 160 97
[2] Long N V, Thi C M, Yong Y, Nomagi M and Ohtaki M 2013 J. Nanosci. Nanotechnol. 13 4799
[3] Hoogers G 2003 Fuel Cell Technology Handbook (Boca Raton, FL: CRC Press)
[4] Iijima S 1991 Nature 354 56
[5] Li W, Liang C, Qiu J, Zhou W, Han H, Wei Z, Sun G and Xin Q 2002 Carbon 40 791
[6] Wang C, Waje M, Wang X, Tang J M, Haddon R C and Yan Y 2004 Nano Lett. 4 345
[7] Prabhuram J, Zhao T S, Liang Z X and Chen R 2007 Electrochim. Acta 52 2649
[8] Wu G and Xu B Q 2007 J. Power Sources 174 148
[9] Jha N, Reddy A L M, Shaijumon M M, Rajalakshmi N and Ramaprabhu S 2008 Int. J. Hydrogen Energy 33 427
[10] Xu J, Hua K, Sun G, Wang C, Xiangyu L and Wang Y 2006 Electrochem. Commun. 8 982
[11] Lee T K, Jung J H, Kim J B and Hur S H 2012 Int. J. Hydrogen Energy 37 17992
[12] Naidoo Q, Naidoo S, Petrik L, Nechaev A and Ndungu P 2012 Int. J. Hydrogen Energy 37 9459
[13] Liu Z and Hong L 2007 Electrochem. 37 505