

Improvement on electrochemical performance by partial replacement of Ru@Pt core-shell nanocatalyst by temperature modification

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Abstract. In this paper, the homemade open-loop reduction system (OLRS), and redox transmetalation method were utilized to produce the core-shell Ru (ruthenium)/Pt (platinum) catalysts on the carbon cloth (CC) for direct methanol fuel cell (DMFC) application. By adjusting pH value and heating to proper temperature of the ionized reduction environment, Pt^{4+} can be first converted into Pt^{2+} to allow partial Ru replacement with Pt by redox transmetalation and produce Ru@Pt core-shell nanostructures[1]. And we change the reduction temperature to see how it affects the efficiency of the DMFC.

The scanning electron microscopic (SEM) top-view micrographs showing that the apparent Ru@Pt nanoparticles successfully deposited on both the inner and outer surfaces of the hydrophilically-treated CC. At high SEM magnification, the small size and high-density distribution of the Ru@Pt nanoparticles were clearly observed on the hydrophilically-treated CC, and much more Pt@Ru catalyst deposit on the CC surface with the sample of 80°C. The electrosorption charges of hydrogen ion (Q_H) and the peak current density (I_p) of the samples in the cyclic voltammetry (CV) curves. The magnitude of peak current density is positive correlation to the temperature. However, the CO tolerance, indicated that the better CO tolerance contributed to the less Pt replace on Ru cluster, which allow the Ru oxidizing CO to CO_2 efficiently, is negative correlation to the temperature. The sample of 50°C shows the better combination catalyst efficiency between the CO tolerance and the electrochemical performance.

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 [2-4]. 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 reduce the amount of noble metal catalyst and achieve uniform dispersion on the carbon support for the achievement of better utilization and activity of electrocatalysts. And reduce the effect of CO poisoning during the catalytic reaction which is used to produce energy. We choose Ru@Pt core-shell nanoparticle structure, the characteristics of Ru is to oxidize CO become CO_2 , and suppress the effect of CO poisoning. To enhance Ru@Pt catalyst efficiency, small size and uniformly distributed nanoparticles are highly desired. Conventionally, there are two common methods applied for Ru nanoparticle preparation, including chemical reduction [4, 6] and electro-deposition [7]. 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[8]called Open-Loop reflux system(OLRS), can react at higher reaction temperature (160°C), substantially shorten the time required for catalyst preparation (~1.5 hr) and better electrochemical performance with Cyclic Voltammetry testing[5]. For preparing uniform Ru@Pt nanoparticles as catalyst, redox transmetalation reaction for Pt catalyst[11] provided better CO tolerance comparing to the high temperature OLRS. By adjusting the pH value, Pt^{4+} can be first



converted into Pt^{2+} to allow partial Ru replacement with Pt and produce Ru@Pt core-shell nanostructures. To more control the Pt shell thickness, Patil et al [12] suggested the redox transmetalation reaction at lower temperature. However, the temperature effect of Ru@Pt core-shell structure was not discussed clearly in the earlier documents. To find out exact effect of the electrocatalytic properties of Ru@Pt catalysts, the effect of the variable reduction temperature would be discussed in the paper.

2. Experiment

2.1 Ethanol Immersion Pretreatment & Hydrophilic Treatment of Carbon Supports

We used a 6 M sulfuric acid (H_2SO_4) solution as the oxidant for hydrophilic treatment of the 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 H_2SO_4 solution for better Pt catalyst adhesion, vacuum means was added in the hydrophilic treatment process [2, 9]. However, it is still difficult to thoroughly immerse the three-dimensional, interwoven structures of carbon cloth fibers in the acidic solution. In the present work, the EtOH immersion pretreatment for the CC carbon supports was utilized prior to the above-mentioned hydrophilic modification of the carbon supports.

2.2 Open-Loop Reduction System for Ruthenium Catalyst

According to a homemade open-loop reduction system (OLRS) in our previous study [2], as shown in Fig. 1(a), we used 0.0222 g $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and 0.1 mM ethylene glycol as a Ru catalyst precursor and a reducing agent, respectively. Heating to 160°C and then naturally cooled to room temperature. Compared to the traditional reflux system, as shown in Fig. 1 (b), the reduction time of OLRS is only about 1.5 hours. The distribution of Ru is also more uniform with the OLRS contrast to the traditional reflux system.

2.3 Redox transmetalation reaction for Pt Catalyst

We used 0.0432 g $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 0.1 mM ethylene glycol as a Pt catalyst precursor and a reducing agent, respectively. Adjust the pH value of the solution with sodium hydroxide (NaOH). Then heating the solution to 80°C to make Pt^{4+} in the solution convert to Pt^{2+} . Immersed the above-mentioned CC which is deposited Ru into the solution, control working temperature as constant (80°C , 50°C , 30°C) for 3 hours. The redox transmetalation is an efficient way to produce Ru@Pt core-shell nanocatalyst.

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 , V_{SCE}) and current density (I , mA/cm^2) to realize the potential for the redox reaction, electrochemical mass activity (MA, $\text{A}/\text{g}_{\text{Pt}}$) and reaction rate [2, 5]. In the CV curves, we can also obtain the active electrochemical surface area (ESA) of Pt catalysts from the hydrogen ion electrosorption reactions (charge transfer density of H^+ , QH , mC/cm^2) in a H_2SO_4 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 (N_2) gas to remove oxygen for extra oxidation reaction.

3. Results and discussion

Both the Q_{H} and the peak current density (I_{p}) of the different reaction temperature but the same reaction time electrodes with the EtOH immersion pretreatments obtained in the CV curves, as shown in Fig. 2 and Fig. 3. Apparently, the electrode which reaction temperature is 80°C , has better Q_{H} and I_{p}

than the other two electrodes. *Table 1* lists the electrocatalytic properties of the three electrodes with different reaction temperature. The efficiency of the 80°C electrode has better electrochemical performance than the others. For Q_H , the magnitude of 80°C electrode is 3.28 times higher than the 50°C electrode, and 22 times higher than the 30°C electrode; and for I_p , the magnitude of 80°C electrode is 3.39 times higher than the 50°C electrode, and 5.06 times higher than the 30°C electrode. However, the performance of reducing CO poisoning, the 80°C electrode is surprisingly the lowest of the three, and the 30°C electrode is the best. I_f/I_b in *Table 1* shows the ability to reduce CO poisoning, the higher magnitude the better ability to reduce CO poisoning.

The result data of the above EDS graph is shown in *Table 1*. Indicated that there is a big difference of Pt content between the two electrodes, 80°C and 30°C. The atomic percent of 80°C electrode is 18.94%, much more than which of 30°C electrode, 2.17%. Which lead to better CO tolerance of the 30°C electrode.

Table 2 shows the microscopic picture of three electrodes under the different magnifications of SEM. At low magnification, we can see high density, small particle nanocatalyst attached around the CC fiber. As the higher the reduction temperature, the distribution of the nanoparticle become denser. At high magnification, the Pt particles of the 80°C electrode seriously agglomerated. The particle size of the 80°C electrode is also the largest, about 50 nm. In the contrary, the particle size of the 30°C electrode is only about 16 nm. According to the above-mentioned, we inferred that the reduction temperature can affect the reaction rate while the redox transmetalation reaction. Therefore, the 80°C electrode loads much more Pt than others, its electrocatalytic properties is the best. However, if the temperature was too high, it may cause the Pt particles cluster, which leads to the limitation of the mass activity, because of the too fast reaction rate of Redox transmetalation reaction for Pt Catalyst. For further exact analysis for electroactivity per unit mass, the Inductivity Coupled Plasma-Mass Spectrometer (ICP-MS) would be utilized in future work.

4. Conclusion

By redox transmetalation reaction, different redction temperatures effect obviously on the efficiency of electrocatalytic properties. For Q_H and I_p , we can find that 80°C electrode is better than the 30°C one (Q_H : 12.46 vs. 0.585 mC/cm², I_p : 130 vs. 25.7 mA/cm²). However, for CO tolerance, the 30°C electrode is yet better than the 80°C one (I_f/I_b : 1.15 vs. 1.627). Speculated that is because as the reaction temperature of Pt rises, it fastens the replacement reaction rate, make more Pt deposit on Ru and improves its electrocatalytic properties. However, the more Pt covered on Ru particle also means less Ru surface disposed, and reduce the CO tolerance of the electrode. Results from the SEM measurements show that 80°C electrode has occurred the Ru@Pt cluster, and it is less clutch for the 50°C electrode.

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Figures & Tables

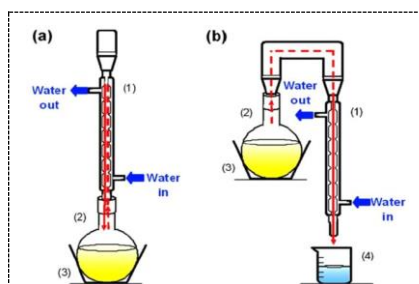


Figure 1. Schematic setup of the (a) traditional reduction system and (b) open-loop reduction system (OLRS).

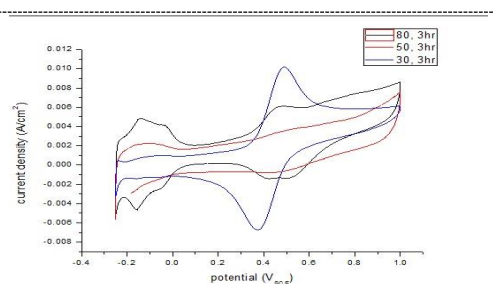


Figure 2. Cyclic voltammograms of the three different electrodes. Electrolyte: 0.5 M H₂SO₄ aqueous solution. Scan rate: 50 mV/s. Temperature: 25°C.

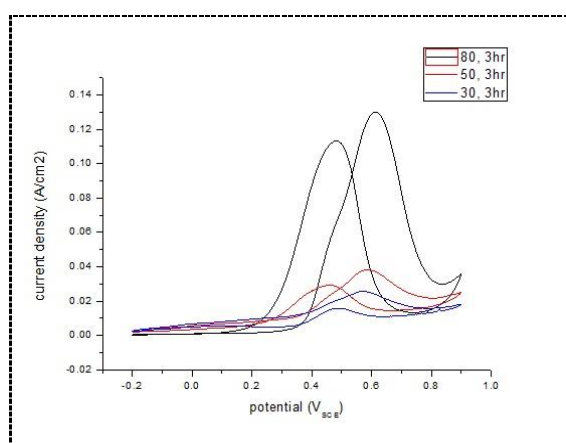
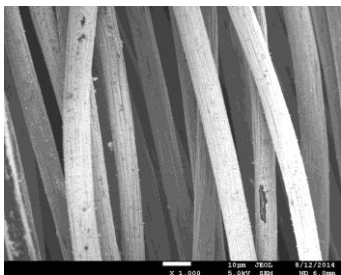
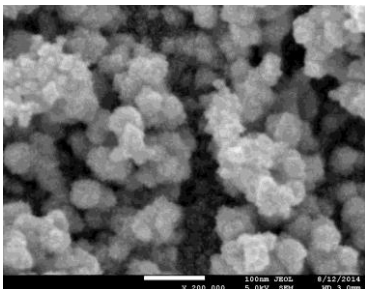
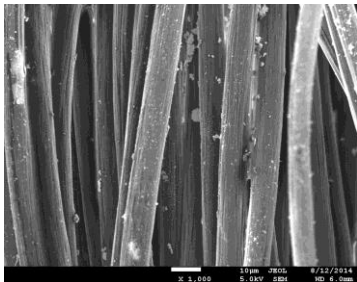
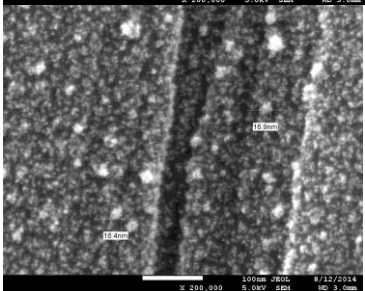
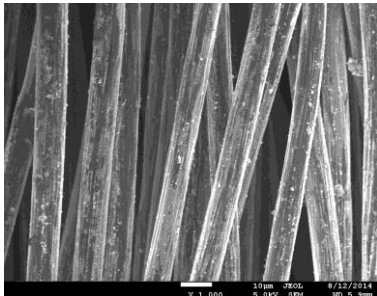
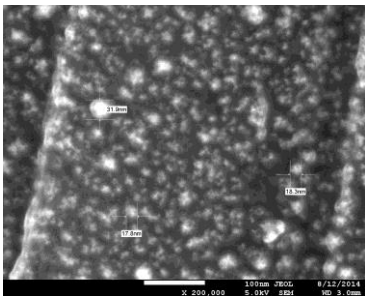


Figure 3. Cyclic voltammograms of the three different electrodes. Electrolytes: 1 M CH₃OH + 0.5 M H₂SO₄ aqueous solutions. Scan rate: 20 mV/s. Temperature: 25°C.

Table 1. The electrocatalyst property of different Pt replacement reaction temperature.

| Electrodes | Q_H (mC/cm ²) | I_P (mA/cm ²) | I_f/I_b | Ru wt% | Pt wt% | Ru atom% | Pt atom% |
|------------|--------------------------------|--------------------------------|-----------|-----------|-----------|-------------|-------------|
| 80°C, 3hr | 12.46 | 130 | 1.15 | 0.68 % | 78.37 % | 0.32 % | 18.94 % |
| 50°C, 3hr | 3.803 | 38.3 | 1.316 | 11.85 % | 50.37 % | 3.36 % | 7.41 % |
| 30°C, 3hr | 0.585 | 25.7 | 1.627 | 43.85 % | 15.97 % | 11.51 % | 2.17 % |

Table 2. Low- and high-magnification (1K & 200K) SEM images of different electrodes.

| Electrodes | Low-magnification (1K) | High-magnification (200K) |
|------------|---|--|
| 80°C, 3hr |  |  |
| 50°C, 3hr |  |  |
| 30°C, 3hr |  |  |