微波功率和微波作用时间对脉冲微波辅助化学还原合成的 Pt/C 催化剂性能的影响

王喜照^{1,2}, 郑俊生^{1,2,a}, 符蓉^{1,3}, 马建新^{1,2,b}

¹ 同济大学新能源汽车工程中心, 上海 201804

² 同济大学汽车学院, 上海 201804

³ 华东理工大学资源与环境工程学院, 上海 200237

摘要: 采用脉冲微波辅助化学还原法制备了质子交换膜燃料电池 (PEMFC) 用 Pt/C 催化剂. 通过 X 射线衍射 (XRD) 和高分辨透射电镜 (HRTEM) 等分析技术对催化剂的微观结构和形貌进行了表征. 利用循环伏安 (CV) 法计算了催化剂的电化学比表面积. 在此基础上制备了膜电极 (MEA) 并组装成单电池, 考察了制备的 Pt/C 催化剂作为单电池阴极催化剂材料的电催化性能. 微波功率和微波作用时间对 Pt 颗粒直径和分散有重要影响. XRD 和 HRTEM 结果表明, 在微波功率为 2 kW, 微波作用 12 s, 豫驰 180 s, 且重复 6 次的条件下, 制得的催化剂中铂纳米粒子颗粒直径小, 分散均一, 其平均粒径为 1.9 nm. CV 结果表明, 该条件下制得的催化剂电化学比表面积达到 72.3 m²/g, 且该催化剂对应的单电池最高功率密度为 0.572 W/cm².

关键词: 脉冲微波; 微波功率; 微波作用时间; 铂; 碳; 负载型催化剂; 燃料电池

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^a 通讯联系人. Tel: (021) 69583891; Fax: (021) 69583850; E-mail: jszheng@tongji.edu.cn

^b 通讯联系人. Tel: (021) 69589480; Fax: (021) 69589121; E-mail: jxma@tongji.edu.cn

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Effect of Microwave Power and Irradiation Time on the Performance of Pt/C Catalysts Synthesized by Pulse-Microwave Assisted Chemical Reduction

WANG Xizhao^{1,2}, ZHENG Junsheng^{1,2,a}, FU Rong^{1,3}, MA Jianxin^{1,2,b}

¹ Clean Energy Automotive Engineering Center, Tongji University, Shanghai 201804, China

² School of Automotive Studies, Tongji University, Shanghai 201804, China

³ School of Resource and Environment Engineering, East China University of Science and Technology, Shanghai 200237, China

Abstract: Pt/C catalysts for polymer electrolyte membrane fuel cells were synthesized by pulse-microwave assisted chemical reduction. X-ray diffraction (XRD) and high resolution transmission electron microscope (HRTEM) were used to investigate the microstructure and morphology of the as-prepared catalysts. The electrochemical surface area (ESA) was studied by cyclic voltammetry (CV). Membrane electrode assemblies were fabricated and the as-prepared catalysts were evaluated. The particle size and distribution of Pt nanoparticles on the carbon support greatly depended on the microwave power and irradiation time. XRD and HRTEM showed that the Pt/C catalysts possessed the smallest mean Pt particle size (1.9 nm) and the most uniform distribution among all the synthesized catalysts when the microwave was on for 12 s and off for 180 s, and this was repeated 6 times at a microwave power of 2 kW. A CV revealed that the ESA of the catalyst was 72.3 m²/g and the corresponding maximum power density was 0.572 W/cm².

Key words: pulse-microwave; microwave power; irradiation time; platinum; carbon; supported catalyst; fuel cell

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^aCorresponding author. Tel: +86-21-69583891; Fax: +86-21-69583850; E-mail: jszheng@tongji.edu.cn

^bCorresponding author. Tel: +86-21-69589480; Fax: +86-21-69589121; E-mail: jxma@tongji.edu.cn

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Clean energy and alternative vehicles are required to reduce crude oil consumption and to curb air pollution because of the impact of climate change and other energy security issues. It has been reported that hydrogen-powered fuel cell electric vehicles can reduce oil consumption and greenhouse gas emissions in a steady downward trajectory [1]. Hydrogen energy represents an important alternative energy feedstock because it can be produced easily from renewable energy resources and one of the best ways to use hydrogen is in fuel cell technology. Among the various types of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) are considered to be the most suitable for automotive applications. The reason for this is that PEMFCs have high energy conversion efficiency and zero emissions and can also operate under low temperature conditions [2–4]. Catalysts play an important role in the hydrogen oxidation reaction and the oxygen reduction reaction (ORR) of PEMFCs. However, conventional approaches of preparing PEMFC catalysts such as impregnation and colloids [5–8] either cause the agglomeration of metal particles or the approach is too complex. Therefore, it is important to find a rapid and efficient approach to prepare high performance catalysts.

As a rapid, simple, and efficient method, microwave synthesis has a remarkable influence on the preparation of nanomaterials [9–12]. The temperature rise in a reaction system is fast under a microwave field because of the high dielectric constant. Additionally, the temperature of a reaction system is homogeneous under a microwave field because of the penetrability of microwaves. These two points are of importance for the synthesis of Pt/C catalysts based on the microwave assisted chemical reduction process [13]. The carbon support is also a microwave-sensitive material. When the temperature of the reaction system is high enough, a large amount of homogeneous reaction points are generated on the interface between the carbon particles and the precursor leading to the formation of a homogeneous crystal nucleus [14]. Furthermore, the crystal nucleus may not grow because of the short irradiation time and the steric effect of the carbon particles. Therefore, the synthesized metal particles are small and well distributed on the carbon support. Chen et al. [15] prepared Pt/XC-72 with a particle size range of 3.5–4.0 nm by a microwave-assisted polyol process with an irradiation time of 50 s. The preparation of a carbon

nanotubes supported Pt catalyst (Pt/CNTs) by continuous microwave irradiation has also been reported recently [16]. However, in the above-mentioned process the reactant may be at high temperature for a long time. This is not conducive to control and separate the nucleation and growth steps, which influences the structure and the morphology of the metal nanoparticles [17,18]. Some work has been carried out to resolve these issues [19–22]. Lebegue et al. [22] revealed that Pt/C catalysts that were prepared by pulse-microwave had a higher active surface area and better kinetic parameters in the ORR compared with the Pt/C catalyst prepared by classical polyol synthesis based on heating at reflux. The catalysts synthesized using a pulse-microwave had a mean particle size of 2.5 nm and a non-negligible level of particle agglomeration. Furthermore, they designed experiments to optimize the experimental parameters such as the duration of microwave pulses, the maximum temperature and the total duration of the synthesis to control the different steps of platinum nanoparticle formation on the carbon support. In the pulse-microwave process, the relaxation time affects cooling in the rapid temperature variation period. In this process, the relationship between the microwave power and the irradiation time both contribute to the temperature change, which can result in a change in the nucleation number and its growth rate. This can result in a change in the microstructure and morphology of the as-prepared catalysts.

In this work, the synthesis of Pt/C catalysts, based on the pulse-microwave process under various microwave conditions is presented. The effects of microwave power and irradiation time on the microstructure and morphology of the as-prepared catalysts and their corresponding catalytic activities toward the ORR were investigated. To evaluate the catalysts, membrane electrode assemblies (MEAs) with an apparent area of 50 cm² were fabricated and evaluated in a single cell testing platform.

1 Experimental

1.1 Catalyst preparation

Pt/C catalysts were prepared by the pulse-microwave assisted chemical reduction method. Briefly, 30 ml ethylene glycol, 0.25 g carbon black (Vulcan XC-72), and a 4.2 ml

H₂PtCl₆ ethylene glycol solution (with a H₂PtCl₆ concentration of 0.077 mol/L) were mixed in a 100 ml quartz beaker. NaOH ethylene glycol solution (2 ml, with a NaOH concentration of 0.5 mol/L) was added and the mixture was uniformly dispersed by ultrasound. The mixture was then placed in a microwave reactor. The pulse-microwave program was active over different time periods under a certain microwave power. The product was then washed with de-ionized water and dried in a vacuum oven at 70 °C. Finally, the required catalyst with a nominal Pt loading of 20 wt% on carbon was obtained. In this work, the catalysts were prepared over a microwave irradiation time of 8, 10, 12, 14 s under a microwave power of 2 kW and these are designated Pt/C-8s, Pt/C-10s, Pt/C-12s, and Pt/C-14s, respectively. A catalyst prepared over a microwave irradiation time of 12 s under a microwave power of 1 kW was also prepared and is designated Pt/C-1kW.

1.2 Physical characterization

The mass fraction of Pt in the Pt/C catalyst was determined by inductively coupled plasma (ICP, 7500A, Agilent). The catalyst morphologies were characterized by high resolution transmission electron microscope (HRTEM, JEOL TEM 2010), which was operated at 200 kV. The crystalline phase X-ray diffraction (XRD) patterns were collected on a D/max 2550 powder diffractometer using Cu K_α radiation. The working voltage was 40 kV and the current was 40 mA. The intensity data were collected over a 2θ range of 10° to 100° at a scan rate of 0.02°/min.

1.3 Electrode preparation and modification

The electrochemical surface area (ESA) was measured by cyclic voltammetry (CV) and the experiment was carried out using a CHI 730C electrochemical workstation (CHI Instrument, Inc., USA) in 0.5 mol/L HClO₄. The working electrode was glassy carbon (GC, 5 mm in diameter) coated with the as-prepared catalysts. A saturated calomel reference electrode (SCE) was used for all the electrochemical measurements and a Pt clump was used as the counter electrode. The CV scan rate was 20 mV/s and the potential range was 1.0–0.2 V (vs SCE). The modification of the electrode was carried out as follows: the as-prepared catalyst was dispersed ultrasonically in a 5 wt% Nafion solution (DuPont) to obtain a homogenous black suspension with a concentration of 2 mg/ml. Then 10 μl of the mixture was pipetted onto the surface of the GC electrode to form a catalyst thin film. After drying, the working electrode with a Pt content of 0.02 mg/cm² on the surface of the GC was ready. Before coating, the GC was polished to a mirror finish using a 0.05 μm alumina paste. Before the measurement,

the electrolyte was bubbled with nitrogen for 30 min and the current-potential curve was recorded in the presence of nitrogen. The CV scan rate was 20 mV/s and the potential range was 1.0–0.2 V.

1.4 MEA fabrication and single cell test

MEA was fabricated using the catalyst coated in membrane method. An appropriate amount of catalyst powder was mixed with a solution of nafion (5 wt%) and isopropyl alcohol and then the mixture was dispersed ultrasonically to form a homogeneous ink (the weight ratio of catalyst to Nafion was 3:1). After that, the catalyst ink was sprayed onto a 50 cm² of Nafion membrane (NR212). The other side of membrane was sprayed in the same way. The nafion membrane containing the catalyst on both sides was then sandwiched between two gas diffusion layers (Toray TGP-H-090). Five pieces of MEA were fabricated using the prepared Pt/C-8s, Pt/C-10s, Pt/C-12s, Pt/C-14s, and Pt/C-1kW as cathode catalysts and the commercial Pt/C catalyst (Johnson Matthey, HiSPEC 4000) as an anode catalyst. Both sides contained a Pt loading of 0.2 mg/cm² for each MEA.

The measurements were carried out using a single cell testing platform. Pure hydrogen and compressed air were fed to the single cell and the pressure was 80 kPa for both inlets. The stoichiometry coefficient of hydrogen and air was 1.3 and 2.5, and the flow rate was adjusted to the current automatically by a mass flow controller. Before entering the cell, the hydrogen and air mixture was humidified in a bubbling humidifier. The cell was operated at 80 °C, and this was controlled by a thermostatic water bath. After a break-in period, a polarization curve was recorded.

2 Results and discussion

2.1 Physical properties of the catalysts

ICP indicated that the mass fraction of Pt in the five Pt/C catalysts prepared by pulse-microwave assisted chemical reduction is close to the theoretical value of 20 wt%. The XRD patterns of the catalysts prepared using different irradiation time and microwave power are shown in Fig. 1. The 2θ peak at about 26.4° can be attributed to the graphite structure of the carbon support. The major peaks were located at 2θ of 39.7°, 46.2°, 67.4°, and 81.2° and are assigned to the Pt(111), (200), (220), and (311) characteristic diffraction peaks, respectively. These characteristic diffraction peaks agree well with those reported previously [23,24]. Generally, a broader Pt peak at (220) indicates a smaller Pt particle size. The fitted Pt(220) plane was isolated from the diffraction peaks of the carbon support and it is always used

Fig. 1. XRD patterns of Pt/C-8s, Pt/C-10s, Pt/C-12s, Pt/C-14s, and Pt/C-1kW.

to calculate the metal particle size according to the Scherrer formula [25]. The calculation results are listed in Table 1.

HRTEM micrographs of the as-prepared catalysts are shown in Fig. 2. It is widely accepted that the metal particle size has a large influence on catalyst performance [26–31]. As shown in Fig. 2, the metal particles prepared using different irradiation time and microwave power are uniform in size and are nearly monodispersed on the surface of the carbon support. The Pt particle size was obtained by measuring the nanoparticles on the HRTEM images. Nearly 300 nanoparticles from random regions were measured to ensure a statistically significant representation of the nanoparticle sizes. Corresponding histograms of the size distribution are shown in Fig. 3, which reveals that the particle size distribution for each catalyst is rather narrow and exhibits the features of a Gaussian distribution. This also illustrates that pulse-microwave assisted chemical reduction is a good method to prepare supported catalysts. The average diameter for each catalyst was calculated and is listed in Table 1. The average diameters for Pt/C-8s, Pt/C-10s, Pt/C-12s, and

Table 1 Comparison of the particle size, ESA, and the corresponding maximum power density for various catalysts

Catalyst	Particle size from XRD (nm)	Particle size from HRTEM (nm)	ESA from CV (m^2/g)	Maximum power density (W/cm^2)
Pt/C-8s	2.6	2.6	54.3	0.520
Pt/C-10s	2.4	2.5	56.2	0.541
Pt/C-12s	2.0	1.9	72.3	0.572
Pt/C-14s	2.3	2.3	63.1	0.543
Pt/C-1kW	2.8	2.9	41.5	0.467

Fig. 2. HRTEM images of Pt/C-8s (a), Pt/C-10s (b), Pt/C-12s (c), and Pt/C-14s (d) prepared using different irradiation time.

Fig. 3. Histograms of the Pt particle size distribution for Pt/C-8s (a), Pt/C-10s (b), Pt/C-12s (c), and Pt/C-14s (d) prepared over different irradiation time.

Pt/C-14s are 2.6, 2.5, 1.9, and 2.3 nm, respectively, which is similar to the XRD results. The average Pt particle size decreases with an increase of the irradiation time from 8 s to 12 s, and it reaches a minimum at an irradiation time of 12 s. The Pt particle size was larger when the irradiation time was extended to 14 s. This indicates that the irradiation time has an important effect on the metal particle size.

During pulse-microwave irradiation, the temperature fluctuates during the start-stop irradiation. The temperature rises rapidly during irradiation and drops gradually after irradiation. Over the relaxation time, the temperature reduction may retard nanoparticle growth. Furthermore, multiple pulse-microwave irradiation cycles may ensure a complete reaction. For the preparation of Pt/C-8s, Pt/C-10s, Pt/C-12s, and Pt/C-14s the highest temperatures were found to be 118, 125, 141, and 141 °C, respectively. During one irradiation cycle, a longer irradiation time resulted in a higher temperature. A high temperature may contribute to the formation of a crystal nucleus. A higher crystal nucleus formation rate results in a faster depletion of the surrounding reactants and, therefore, the crystal nucleus can not grow because of a lack of growth substance. In this way the metal particle size may be controlled. This indicates that the Pt particle size decreases with an increase in the irradiation time from 8 s to

12 s. For the final irradiation cycles during the preparation of Pt/C-14s, a visible vapor was observed. The reaction solution spilled out of the quartz beaker and the resultant product became dense. This might have resulted from the temperature of the reaction solution reaching the solution's boiling point and it may have boiled for some time. We also found that the solution, to some extent, plays a role in controlling the temperature, which may prevent this temperature runaway. During the boiling time the metal nanoparticles may have more chance to grow so that the average size of the Pt/C-14s metal nanoparticles is larger than that of the Pt/C-12s.

A HRTEM micrograph of Pt/C-1kW and its corresponding size distribution histogram are shown in Fig. 4. The average diameter of the Pt particles in Pt/C-1kW was found to be 2.9 nm, which is larger than that for the catalyst prepared under a microwave power of 2 kW. The rate of the temperature rise is faster when using 2 kW of microwave power. This may shorten the time required for the reactant to reach the proper reaction temperature and it accelerates the rate of crystal nucleus generation. This shows that microwave power is a crucial factor in the preparation of the catalyst when using pulse-microwave assisted chemical reduction. A higher microwave power leads to a higher rate

Fig. 4. HRTEM image and the corresponding particle size distribution of Pt/C-1kW.

of temperature increase. A high rate of temperature increase may contribute to nucleation and reduce the time required for growth in the rapid temperature-rise period. Therefore, the average diameter the Pt nanoparticles in the catalysts prepared using 2 kW is smaller than that for the catalyst prepared using 1 kW. However, if the microwave power is too high the reactant solution may boil vigorously and spill out of the quartz beaker. Therefore, a suitable microwave power is required for the reaction process.

2.2 Performance of the Pt/C catalysts

Figure 5 shows CV curves for Pt/C-8s, Pt/C-10s, Pt/C-12s, Pt/C-14s, and Pt/C-1kW. ESA is a critical parameter that represents the intrinsic electrocatalytic activity of Pt catalysts, and it can be estimated by considering the integrated charge in the hydrogen absorption region of CV curves and the Pt poly-crystallite hydrogen adsorption/desorption constant of 0.21 mC/cm² [32–34]. As shown in Fig. 4, well-defined hydrogen adsorption/desorption characteristics were observed for all the catalysts that were prepared using different irradiation time and microwave powers. A strong desorption peak in the potential range from –0.2 to –0.1 V and a weak desorption peak between –0.1 and –0.0 V were observed during the positive-direction potential scan, and these are assigned to strongly and weakly bonded hydrogen adatoms, respectively. Corresponding adsorption peaks were observed during the reverse potential scan. The ESA can be calculated using the followed equation:

$$\text{ESA} = \frac{(1/\nu) \int i(E) dE}{Q_0 \times m_{\text{catalyst}}}$$

where ν is the linear potential scan rate (V/s), i is the current (A), E is the electrode potential (V), m_{catalyst} is the mass of

Fig. 5. CV curves of Pt/C-8s, Pt/C-10s, Pt/C-12s, Pt/C-14s, and Pt/C-1kW.

catalyst deposited on the electrode (4 μg), and Q_0 is the charge required for the adsorption of a monolayer of atomic hydrogen onto a polyoriented platinum surface (0.21 mC/cm²).

Based on the experimental results and the above equation, the calculated ESAs are summarized in Table 1. The ESA increases with a decrease in the Pt particle size. The ESA of Pt/C-12s is 72.3 m²/g, which is larger than that of Pt/C-8s (54.3 m²/g), Pt/C-10s (56.2 m²/g), Pt/C-14s (63.1 m²/g), and Pt/C-1kW (41.5 m²/g). This mainly results from the smaller particle size and better dispersion of Pt nanoparticles in Pt/C-12s.

Figure 6 shows the polarization curves for single cells using various MEAs. From Fig. 6 the open-circuit potentials for all the catalyst samples are high at 0.96 V regardless of the irradiation time and the microwave power. All the current densities decrease with an increase in the potential over the whole current density region. The discharge performance of the cell improves along with an increase in the irradiation time and the best performance was obtained at an irradiation time of 12 s. However, the cell performance decreased when the irradiation time was increased to 14 s. The lowest loss in polarization voltage was observed for Pt/C-12s, indicating that it has the highest electrocatalytic activity. The maximum power density of 0.572 W/cm² was determined for Pt/C-12s, which is higher than that for Pt/C-8s (0.520 W/cm²), Pt/C-10s (0.541 W/cm²), and Pt/C-14s (0.543 W/cm²). Additionally, the catalyst prepared at a microwave power of 2 kW (Pt/C-12s) gives better performance in comparison with that of the catalyst prepared at a microwave power of 1 kW (Pt/C-1kW). This agrees with the ESA result. The highest catalytic activity was found for Pt/C-12s and this may be attributed to its highest ESA, which is closely related to the smallest and most uniformly distributed Pt particles on the carbon support.

Fig. 6. Polarization plots of Pt/C-8s, Pt/C-10s, Pt/C-12s, Pt/C-14s, and Pt/C-1kW.

3 Conclusions

Pt/C catalysts were synthesized by a pulse-microwave assisted chemical reduction method over different microwave irradiation time and microwave powers. The microwave irradiation time and microwave power are shown to be crucial factors that influence the Pt particle size and the distribution of Pt nanoparticles on a carbon support. The irradiation time and microwave power may control the temperature of the reaction system, which may affect the microstructure and morphology of the as-prepared catalysts. Catalysts with high catalytic activity were prepared at an irradiation time of 12 s and at a microwave power of 2 kW. This also showed that the pulse-microwave assisted chemical reduction method is an effective way to prepare Pt/C catalysts for PEMFCs.

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