Synthesis of a New Type of CMK-3-Pt with the In-situ Growth Method and Its Characterization

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Abstract. With the growing consumption of fossil energy, fuel cells are now playing an increasingly important role in production and life. However, the battery electrode materials synthesized by traditional methods often have defects such as Pt particle agglomeration and shedding in use which can result in unsatisfactory performance of electrode materials and reduced electrical energy transfer efficiency and electrocatalytic efficiency, thereby leading to lower fuel cell efficiency. In this research, a new method is proposed for synthesizing the most important component of fuel cells—electrode materials, that is, the precursors of C and Pt are simultaneously added to the CMK-3-Pt produced with in-situ grow and one-step synthesis in the SBA-15 template. The elements and micro-areas were characterized by XRD, SEM, TEM and other test methods, and the CHI700E electrochemical workstation was used to test the electrocatalytic activity and electrocatalytic stability. The experimental results show that the Pt particles of electrode materials synthesized by the new method have the characteristics of smaller particle size (4~6 nm), better dispersion, and less falling off. Besides, these materials have a larger pore volume (0.66 cm³/g), a higher active surface area (803 m²/g, ECSA: 452 cm²/mg), and more excellent electrocatalytic performance (the ratio of peak forward and reverse current: CH₃OH catalyst is 1.95, and CH₃CH₂OH catalyst is 1.38) and better electrocatalytic stability (82.6%). To sum up, electrode materials synthesized once by the in-situ growth method can achieve better performance of the mesoporous electrode materials than those with the traditional synthesis method.

1. Introduction
Continuous economic and social development have led to increasing consumption of fossil energy, thus resulting in a series of environmental problems including the most worrying atmospheric pollution. Therefore, in order to change the status quo, it is essential to find clean energy to replace fossil fuels. A fuel cell, which is also called an electrochemical generator, is a chemical device that converts the chemical energy possessed by fuel into electrical energy directly. The fuel cells convert part of the Gibbs free energy in the chemical energy of the fuel directly into electrical energy through an electrochemical reaction, which is not limited by the Carnot cycle effect and shows higher efficiency. In addition, fuel cells use fuel and oxygen as raw materials and produce only water and carbon dioxide, which are almost pollution-free and now playing an increasingly important role in production and life [1].
The working principle of fuel cells is shown in Figure 1, which illustrates that a fuel cell is mainly composed by the electrode, electrolyte, electrolyte membrane and external circuit. Fuel cells combine many advantages of internal combustion engines and batteries, which are far more efficient than internal combustion engines because they directly convert chemical energy into electrical energy. Besides, fuel cells can be an all-solid-state mechanical structure, which can have high reliability and long service life without moving parts, are very quiet, and produce no bad products such as NOx and Sox[2]. More importantly, unlike small-sized ordinary batteries in which the relationship between power and capacity is usually interrelated, fuel cells allow power (determined by the size of a fuel cell) and capacity (determined by the size of fuel storage) to be freely scaled and expanded, from one watt (mobile phones) to megawatt (power plants). Compared with ordinary batteries that requires time-consuming charging, fuel cells have the potential to provide higher energy density and can realize fast charging by supplementing fuel.

| Battery type | PEMFC | PAFC | AFC | MCFC | SOFC |
|--------------|-------|------|-----|------|------|
| Operating temperature /℃ | 60-80 | 100-200 | 50-200 | About 650 | 600-1000 |
| Charge carrier | H⁺ | H⁺ | OH⁻ | CO₃²⁻ | O²⁻ |
| Catalyst type | Platinum | Platinum | Platinum | Nickel | Perovskite (Ceramics) |
| Battery pack | Carbon-based | Carbon-based | Carbon-based | Stainless steel base | Ceramic base |
| Fuel compatibility | H₂ | H₂ | H₂ | H₂, CH₄ | H₂, CH₄, CO |
| Fuel efficiency /% | 40-50 | 40-45 | 65 | 50-55 | 50-60 |
| Service life /h | 30000-100000 | 30000-40000 | 30000-10000 | 30000-40000 | 30000-40000 |

According to different electrolytes, fuel cells can be divided into five main types (as shown in Table 1) [1][2][3][4] including polymer electrolyte membrane fuel cells (PEMFC), phosphoric acid fuel cells (PAFC), alkaline fuel cells (AFC), molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC). Among them, PEMFC and SOFC have the best application prospects. PEMFC is very suitable
for portable energy devices due to its high energy density/power density and low operating temperature, while the circle technology combining SOFC and turbine (SOFC/turbine) is most suitable for high power applications [1][2][3][4].

The magnitude of fuel cell currents is directly proportional to the contact area of the reactants, electrodes, and electrolyte. Therefore, when the area of a fuel cell is doubled, its currents will be roughly doubled. Since fuel cells generate electrical energy by converting its initial energy (fuel) into electron or ion currents. During this process, the energy of the fuel is transferred to the electrons to form electric currents, which must occur at the reaction surface and interface with a limited speed. Therefore, the amount of electricity generated is directly proportional to the effective area of the reaction surface or interface used for energy conversion.

Mesoporous carbon plays a crucial role in catalysis, adsorption and separation, electrochemistry, solar cells, lithium batteries (electrode materials), and hydrogen storage due to its larger surface area, large pore structure, and its own electronically conductive framework [5]. Ryoo pioneered the synthesis of mesoporous carbon materials using mesoporous silica as a template. Jun et al. [6] first proposed the synthesis of CMK-3 copies using SBA-15 mesoporous silica as the hard template and sucrose as the carbon source. Cubic mesoporous silica MCM-48 and mesoporous silica (SBA-15) were used as templates respectively to synthetize cubic mesoporous carbon (CMK-1) and two-dimensional hexagonal mesoporous carbon (CMK-3), as well as hexagonal hollow carbon tubes CMK-5. The mesoporous silica SBA-15 is a hexagonal plane with a high degree of order, which can generate mesoporous materials after being burned at 500°C (solvent extraction can also be used to remove the template). The pore size of the obtained sample can be from 4.6 to 30 nm, and the thickness of the silicon oxide pore wall is 3.1 to 6.0 nm. The thermal stability of SBA-15 is higher than 900 °C, which still has high thermal stability (high temperature resistance) and stability to water (cold water or hot water) after the template is removed. Mixed with a small amount of H2SO4, sucrose is usually used as a precursor, added into mesoporous silica template, and decomposed and carbonized at high temperature under the protection of nitrogen to prepare mesoporous carbon with reverse phase structure (the template can be removed by HF [7][8]). Since the micropores in the SBA-15 structure interpenetrate, the synthesized CMK-3 still has a hexagonal structure. Subsequently, chloroplatinic acid was added to CMK-3 to react under certain conditions to obtain CMK-3-Pt, which was used in electrode materials. However, during the application of the CMK-3-Pt prepared with the above method, there often appear defects such as agglomeration and shedding of Pt particles, which can result in in a loss of the performance of electrode materials and a decrease in power transmission efficiency and electrocatalytic efficiency. Niebrzydowska, P. et al. proposed using the acid-catalyzed polycondensation product of furfurane and polyfurfuryl alcohol (PFA) as the carbon precursor to synthesize mesoporous carbon materials [6]. Juliana M. Juárez et al. carbonized the silica/triblock copolymer/sucrose composite system in a sulfuric acid environment to directly synthesize ordered mesoporous carbon (OMC) [9].

Different from the synthesis methods mentioned above, the preparation of the precursor used in this research is simpler and more universal. The one-step synthesis of CMK-3-Pt CMK-3 by the in-situ growth method demonstrates a better performance than the secondary synthesis, and Figure 2 illustrate the synthesis ideas. In the subsequent experiments, the one-step synthetized CMK-3-Pt was characterized by XRD, SEM, and TEM, and the location of the elements and Pt particles contained in the CMK-3 were analyzed. Then after various electrocatalytic properties were characterized and compared with the CMK-3-Pt, it is found that the electrocatalytic activity of CMK-3 has been significantly improved.
2. Experiment

2.1. Material preparation
Materials include sucrose (analytical reagent, purchased from Beijing Chemical Plant), sulfuric acid (analytical reagent, purchased from Beijing Chemical Plant), EO20PO70EO20(P123) (analytical reagent, purchased from German Sigma Aldrich), tetraethyl orthosilicate (TEOS) (analytical reagent, purchased from German Sigma Aldrich), hydrochloric acid (analytical reagent, purchased from Beijing Chemical Plant), and H2PtCl6·6H2O (guaranteed reagent, purchased from German Sigma Aldrich).

In this research, the CMK-3-Pt sample was synthesized by a one-step method, that is, the precursors of C and Pt were added to the SBA-15 template together. The specific experimental procedures are as follows. First, 1.7g sucrose was slowly dissolved in 5ml deionized water by magnetic stirring. Then, 1g H2PtCl6·6H2O was added, and the stirring was continued for 30 min. After that, 1.7g SBA-15 was slowly added and the sample was stirred at room temperature for 30 min and vacuumed twice (once every 10 min), which made the sample obviously thicker. Subsequently, the sample was placed in a muffle furnace and heated to 100 ℃ (5 ℃/min) and preserved for six hours. After this, the sample was heated to 160 ℃ (2 ℃/min) and preserved again for six hours. After the sample was cooled to room temperature, the brown solid obtained by the calcination was ground in a mortar. Then the ground solid powder was placed under the protection of high purity N2 (99.99%) atmosphere, heated to 900 ℃ (2.5 ℃/min) in a tube furnace, and preserved at 900 ℃ for five hours to be carbonized and obtain in situ reduction of Pt element. Finally, the obtained black solid was immersed in HF solution for four hours to remove the silica template, washed with deionized water multiple times, and kept dried at 60°C to obtain CMK-3-Pt.

2.2. Material characterization
XRD characterization of the samples was carried out on a Phillips X’pert Pro MPD diffractometer (Cu-Ka radiation), 5°<2θ<80°, with the step size being 0.033°. The N2 adsorption and desorption properties of the samples were tested with a Quantachrome NOVA 2000e adsorption analyzer (at liquid nitrogen temperature). After the solid sample was dissolved in the aqua regia, the Pt content was analyzed by ICP atomic emission spectrometry (Jarrel ASH, ICAP-9000). The samples were characterized by TEM with JEOL-2011 transmission electron microscope (200 kV) and SEM with JEOL-JSM-6700F electron microscope (5 kV).

2.3. Electrocatalytic performance test
CHI700E electrochemical workstation was used to test the electrocatalytic activity and electrocatalytic stability. CHI700E electrochemical workstation adopts the “one-chamber and three-electrode” system, which is mainly composed of working electrode, counter electrode and reference electrode. The working electrode is a glassy carbon GC electrode covered with a catalyst material film; the counter electrode is a platinum wire electrode; and the reference electrode is a saturated calomel electrode. Using 0.5M H2SO4 solution as electrolyte to test H2 adsorption and desorption and get the CV curve and using 0.5M H2SO4 and 1M methanol (or ethanol) solution as electrolyte to test the performance of the catalyst.
electro-catalyzing and oxidizing methanol. Cyclic voltammetry was used to test the electrocatalytic activity and stability of the catalyst. All the tests above are conducted at room temperature.

3. Results and Discussion

3.1. Analysis of XRD results

![Figure 3. XRD diffraction pattern of in-situ growth and secondary synthesis](image)

The angle range of XRD measurement is $5^\circ < 2\theta < 80^\circ$, and the step size is 0.033°. After comparing the XRD diffraction pattern with the pdf standard card, it is found that the sample contains the required element Pt (Figure 3). By measuring the width of the main peaks of the two synthesis methods (in situ: 8°; secondary: 4°), it can be found that the main peak of the in-situ growth method is wider and thus its half peak is wider, indicating that the Pt particle size synthesized by the in-situ growth method is smaller and good for the dispersion of Pt particles.

3.2. BET-N$_2$ multilayer adsorption

![Figure 4. N$_2$ adsorption equilibrium isotherms of in-situ growth and secondary synthesis](image)

Various parameters used to describe porous solid materials can be obtained through nitrogen adsorption-desorption technology, such as surface area, pore volume, pore size distribution, adsorption-desorption
isotherm (shape), adsorption characteristics, pore geometry, and other macro parameters. With the test materials used in this research, discussions can be made based on the multilayer adsorption theory (the BET theory) proposed by S. Brunauer, P. Emmett, and E. Teller in 1938. There are two hypotheses. First, adsorption can be single-layer or multi-layer; second, the adsorption heat of each layer except the first layer is equal to the liquefaction heat of the adsorbate. When the adsorption is infinite multi-layer, the BET two-constant formula is [10]

$$V = \frac{V_m c P}{(P_0 - P)[1 + (c - 1) \frac{P}{P_0}]}$$

(1)

Where $V$ is the equilibrium pressure, $P$ indicates the adsorption capacity, $V_m$ is the saturated adsorption capacity of the single layer, $P_0$ is the saturated vapor pressure of the adsorbate at the adsorption temperature, and $c$ is the constant related to the adsorption heat of the first layer and the liquefaction heat of the adsorbate.

The obtained adsorption equilibrium isotherms are shown in Figure 4, which conforms to the iv-type adsorption equilibrium isotherms and the characteristics of mesoporous materials. It can be seen that the N2 adsorption is multilayer adsorption and the hysteresis ring is the H1 type. Further measurements show that the surface areas of the two synthetic methods are 803 m$^2$/g (in-situ growth) and 687 m$^2$/g (secondary growth); the pore volumes are 0.66 cm$^3$/g (in-situ growth) and 0.48 cm$^3$/g (secondary growth); both of pore sizes are 3.7 nm (Figure 5). From the experimental results, it can be seen that the one-step synthesized CMK-3-Pt by the in-situ growth method has a larger pore volume (0.66 cm$^3$/g) and a higher active surface area (803 m$^2$/g), thereby demonstrating more excellent performance.

Figure 5. Aperture characterization of in-situ growth and secondary synthesis
3.3. SEM, TEM characterization

By conducting SEM and TEM characterization (Figure 6) of the two methods, the distribution difference of Pt on CMK-3 synthesized by the two synthesis methods can be compared and analyzed. It can be seen from the SEM image that the particles grown in situ are more dispersed and show no agglomeration, while the particles of the secondary growth obviously have agglomeration. The size of Pt particles obtained by the in-situ growth method is smaller than that of the secondary growth method. The TEM results are the same with the SEM conclusions.

3.4. Comparison of electrochemically active surface area

By conducting SEM and TEM characterization (Figure 6) of the two methods, the distribution difference of Pt on CMK-3 synthesized by the two synthesis methods can be compared and analyzed. It can be seen from the SEM image that the particles grown in situ are more dispersed and show no agglomeration, while the particles of the secondary growth obviously have agglomeration. The size of Pt particles obtained by the in-situ growth method is smaller than that of the secondary growth method. The TEM results are the same with the SEM conclusions.

Figure 7. Electrochemically active surface areas for in-situ growth and secondary synthesis
In order to compare the electrocatalytic performance obtained by the two methods, it is necessary to hold the Pt loading of the two the same as much as possible. ICP results show that the Pt loading of in-situ growth and secondary growth is 18.1 wt% and 17.8 wt% respectively.

Certain parameters were set and 0.5M H\textsubscript{2}SO\textsubscript{4} was selected to carry out the characterization test of the electrochemical active surface area (ECSA). The measurement results are shown in Figure 7, in which the black curve is the H\textsubscript{2} absorption and desorption of the in-situ growth method and the red one is the H\textsubscript{2} absorption and desorption of the secondary growth method. The black curve is used as an example for analysis. In this figure, -0.25—0.00V represents the absorption and desorption of H\textsubscript{2}; a complex peak to the right is formed at 0.05 V due to the adsorption of -OH on the electrode and the redox of the platinum electrode (oxidation of peak forward current, reduction of peak reverse current); the smooth part of the curve (the 0.00-0.05V region) represents the electric double layer area of the platinum electrode, which should be deducted when calculating the ECSA of hydrogen. In short, the adsorption capacity Q\textsubscript{h} of H\textsubscript{2} by the in-situ growth method is the integral area below the dotted line in Figure 7, whose formula \[11\] is as follow:

\[
Q_h = \frac{1}{v} \int idE
\]  

\[ \text{(2)} \]

Where v is the scanning speed. Since the adsorption capacity of hydrogen per unit area of Pt is 210 \textmu C/cm\textsuperscript{2}, the ECSA of the electrode can be calculated by the following formula \[11\]:

\[
ECSA = \frac{Q_h}{210 \mu\text{C/cm}^2 \cdot m}
\]  

\[ \text{(3)} \]

Where m is the mass of Pt actually participating in the catalysis.

The calculations of ESCA are 452 cm\textsuperscript{2}/mg (in-situ growth) and 360 cm\textsuperscript{2}/mg (secondary growth). It can be seen that the in-situ growth method is better for H\textsubscript{2} adsorption and desorption, and that the in-situ growth method has a larger electrochemically active surface area.

3.5. CV curve comparison: methanol catalysis

Figure 8. CV curves of in-situ growth and secondary synthesis under methanol catalysis

While the oxidation peak during forward scanning in the CV curve is related to methanol oxidation, the oxidation peak formed during reverse scanning is formed due to the reoxidation of residual carbon species (mainly CO) formed during forward scanning. Greater current density during the forward scanning indicates higher efficiency of methanol oxidation and better electrocatalytic performance. However, the greater current density during the reverse scanning means that the oxidation of methanol
during the forward scanning is not complete and that the CO-type substances generated during reverse scanning poison the catalyst and affect the catalytic activity. In Figure 8, the current density during forward scanning (0.97 mA/cm²) of the in-situ growth method (black curve) is significantly greater than that (0.64 mA/cm²) of secondary growth method (red curve), and the ratios of peak forward/reverse current are 1.95 (in-situ growth) and 1.83 (secondary growth) respectively. Generally speaking, the greater the ratio, the better the performance. Therefore, the electrode materials prepared by the in-situ growth method have better performance for catalyzing methanol.

3.6. CV curve: ethanol catalysis

![CV curve of the in-situ growth method under ethanol catalysis](image)

Figure 9. CV curve of the in-situ growth method under ethanol catalysis

After the test under the methanol environment was completed, the electrochemical performance test of the electrode prepared by the in-situ growth method under the catalyst of ethanol was conducted as a supplementary experiment, results of which are shown in Figure 9. It can be seen that CMK-3 grown in situ still has a higher peak forward current density (0.75 mA/cm²) under ethanol catalysis. However, since ethanol is more toxic, the peak reverse current is higher and the ratio between the two is 1.38.

3.7. Electrocatalytic stability

![Comparison of electrocatalytic stability between in-situ growth and secondary synthesis](image)

Figure 10. Comparison of electrocatalytic stability between in-situ growth and secondary synthesis
In order to compare the stability of the two synthesis methods in the electrocatalytic process, a certain number of cycles was set in the experiment to obtain a comparison chart of electrocatalytic stability as shown in Figure 10. To begin with, it can be seen from the volatility of the curve that the in-situ growth method is more stable with a smaller fluctuation, while the curve of the secondary growth has obvious ups and downs. Second, electrochemical stability can be characterized by calculating the ratio of the current density after a certain number of cycles to the initial current density. The data of two synthetic methods are 82.6% (in-situ growth) and 68.8% (secondary growth). Therefore, the electrode obtained by the in-situ growth method has better electrocatalytic stability than that obtained by the secondary growth.

4. Conclusion
This paper proposes a new method of synthesizing CMK-3-Pt. The electrode materials are prepared by this in-situ synthesis method show more excellent performance than those prepared by the traditional secondary synthesis method. The elements and micro-regions were characterized by XRD, SEM, TEM, etc., verifying that the Pt particles of the electrode materials prepared by this in-situ synthesis method had the advantages of smaller size, better dispersion, and less falling off.

CHI700E electrochemical workstation was used to test the electrocatalytic activity and electrocatalytic stability. The test results show that the electrode materials obtained by the new synthesis method possess more satisfying pore volume and active surface area, thus having wider application range and higher usage efficiency. In addition, the electrode materials obtained by the new synthesis method also demonstrate better electrocatalytic performance and electrocatalytic stability. Therefore, the fuel cells equipped with such electrode materials have higher work efficiency, better safety factor, and longer service life. In summary, the electrode materials synthesized by the in-situ growth method can considerably improve the performance of mesoporous electrode materials, which provide a new idea for the future synthesis of electrode materials.

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