Preparation and properties of porous electrode of supercapacitor based on particulate leaching method

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Abstract. Supercapacitor is a new type of energy storage element between traditional capacitor and battery. Particulate leaching method, which was used to increase specific surface area, was the main idea of this article. First of all, GR-PPy material was prepared by chemical in situ polymerization (FeCl3-MO self-degradation template was used to polymerize pyrrole monomer on GR layer). Subsequently, acetylene black and polytetrafluoroethylene emulsion were added and carbon paste electrode was obtained. At the same time, the porous electrode was prepared by particulate leaching method. Cyclic voltammetry, constant current charge and discharge test and AC impedance test were conducted in 1mol· L-1 Na2SO4 electrolyte. The results showed that the specific capacity of the porous electrode was increased by 12% compared with the normal electrode, and the ion diffusion rate was faster than the blank group. In addition, this porous treatment had little effect on the stability of circulation and the electrode resistance. Therefore, it could be concluded that the porous electrode is a promising electrode of supercapacitor.

Keywords. Supercapacitor; chemical in situ polymerization; particulate leaching method; graphene.

1. Introduction
Humans are currently eager to find green and renewable energy sources to replace existing disposable energy sources that cause serious pollution, and super capacitors[1]. The advent of the company brings the gospel to the sustainable development of mankind. As a new energy storage element between traditional capacitors and batteries-super capacitors have ultra-high capacity, high power density, and long cycle life[2]. High charging and discharging efficiency, maintenance-free, economic and environmental protection, etc[3]. Super capacitors are widely used in communication, electric vehicles, military, industrial and other fields[4]. At present, there are many materials used in supercapacitors[1], such as carbon materials, metal oxide or hydroxide materials, conductive polymer materials, composite materials and so on[5].

Among them, the graphene (GR) material in the carbon material has a flexible and open pore structure, which is favorable for forming an electrode material / electrolyte double layer interface[6]. In this way, the surface of the material was used more efficiently because it had better energy-storage
power characteristics. The current research focus was mainly on the preparation of graphene with different morphologies, and the specific surface area of graphene with different morphologies was also different. The electrolyte enters the pores more easily, so graphene fully had displayed its excellent electrochemical performance[7]. Conductive polymers[8] polypyrrole (PPy) had the advantages of low cost, high capacity, short charge and discharge time, low pollution, and high safety. It had also attracted much attention and had developed rapidly[8]. However, graphene was easily folded by van der Waals force [9], PPy had poor cycle stability, and its electrochemical performance will deteriorate after repeated charge and discharge [10] Composite material [8, 11]. It can overcome the shortcomings of pure materials and therefore has good electrochemical properties.

Because the specific surface area of the electrode was an important factor affecting the performance of the electrode, this paper uses chemical in situ polymerization[12]. After the graphene poly and pyrrole monomers were made into GR / PPy composites, the porous materials were processed by particle leaching to make the composites into multiple carbon paste electrodes. The electrode was prepared through an electrochemical workstation and a blue-current system. Electrochemical analysis was performed, and physical characterization analysis were performed by scanning electron microscopy. The effect of porous treatment on the electrochemical performance of carbon paste electrodes was investigated.

2. Experiment Section

2.1. Instruments and drugs

The experimental drug and equipment used in the paper were shown in Table 1 and Table 2.

| Name                          | Content | Factory                                           | Purity |
|-------------------------------|---------|---------------------------------------------------|--------|
| Highly oriented pyrolytic graphite | —       | Beijing Jinglong Special Carbon Graphite Factory | AR     |
| Methyl orange                 | 80%     | Tianjin Hengxing Chemical Reagent Manufacturing Co.,Ltd. | AR     |
| FeCl₃                         | 99%     | Tianjin Kemiou Chemical Reagent Co.,Ltd.          | AR     |
| Pyrrole monomer               | 99.9%   | Sinopharm Chemical Reagent Co.,Ltd.               | CP     |
| Nano Fe₃O₄                    | 98%     | Guangzhou Hongwu Material Technology Co.,Ltd.     | AR     |
| Acetylene black               | SAG     | Shenzhen Beiterui New Energy Co.,Ltd.              | AR     |
| Ptfe                          | 60%     | Daikin Corporation                                |        |

| Name                          | Model   | Factory                                           |
|-------------------------------|---------|---------------------------------------------------|
| Glass instrument             | Various | Sichuan Shuniu Glass Group Co.,Ltd.               |
| Vacuum drying box            | DZF-6032| Shanghai Instrument Co.,Ltd.                      |
| Shanghai Instrument Co.,Ltd. | FCD-178XHT| Qingdao Haier Special Electric Freezer Co.,Ltd.   |
| Precision electronic Balance | BSA124S | Maiyi Scientific Instrument Co.,Ltd.             |
| Ultrasonic cleaner           | KQ-250E | Xiaoxiao Home Store                               |
| Circulating Water Vacuum Pump| SHZ-III | Shanghai Yarong Biochemical Instrument Factory    |
| Carbon paste Electrode mold  | φ4      | Electrode mold                                    |
| Electrochemical Workstation  | 660e    | Shanghai Chenhua Instrument Co.,Ltd.              |
2.2. Preparation of layered graphene

We took a piece of highly oriented pyrolytic graphite and passed the mechanical friction method[13] for the preparation of graphene powder. As the connection between graphite layers became fragile during the high-temperature directional cracking of graphite, the method of customs clearance could obtain graphene powder with lower yield but better properties. Deionized water was added to the beaker, and the ultrasonic vibration was performed in an ultrasonic cleaning machine, so that the graphene layer folded during the scraping process was stretched, thereby obtaining a better graphene (hereinafter referred to as GR) layered structure. The layered structure continued to prepare subsequent materials. The resulting gr layer suspension was sampled and observed for physical characteristics under an optical microscope.

2.3. Preparation of self-degrading templates and GR/PPy

We added 0.1g of methyl orange to 60ml of GR water mixture, ultrasonically dispersed for 1h, then we weighed and added 1g of FeCl$_3$, sonicated again for 30min, to let methyl orange complex with FeCl$_3$, make GR FeCl$_3$-methyl orange (MO) self-degrading template formed on layered structure[4]. As shown in Figure 1, the template can gather pyrrole monomers in this position and automatically degrade. It could be removed by washing without affecting the purity of the material. It was a good self-degrading template. A GR / PPy material intermediate was prepared in the middle 0.4g of pyrrole monomer was added to the body mixture, and it was left to stand at 0 ~ 5°C for 24 hours. The black precipitate was obtained by suction filtration, washed repeatedly with deionized water and absolute ethanol, and dried in a vacuum drying box at 60°C for 24 hours. We ground the solid into powder to obtain GR / PPy material.

2.4. Preparation of electrodes using the particulate leaching method

We added acetylene black to the electrode material at a ratio of 1: 0.3, then we added tetrafluoroethylene emulsion dropwise to a certain viscosity, filled the electrode material in the electrode mold with 4 turns, and entered 2 turns after the completion, extruded the electrode dry in a vacuum drying oven at 60°C for 12h. We took an equal amount of electrode material and added acetylene black at a ratio of 1: 0.3, mixed well, dropped ptfc emulsion into a slurry, and then doped with nano Fe$_3$O$_4$ was filled into the carbon paste electrode mold that was returned 4 times and 2 times, dried in a 60°C drying box for 12 hours, and then treated with dilute hydrochloric acid to dissolve Fe$_3$O$_4$ on the electrode surface to form holes. And we washed and dried with water to prepare porous electrodes. The process was shown in Figure 2.
3. Results and discussion

3.1. Physical characterization of graphene

Figure 3 is an image of graphene under an optical microscope. From the microscope, it could be seen that the size of the material was relatively uniform, the overall phase was a sheet-like structure, the color was dark green, and multiple observations could find the shape of the side. The length-to-thickness ratio of the prepared graphene material was very large. The results were consistent with those in the literature [13]. It was a well-formed graphene structure.

3.2. SEM analysis of self-degraded template and GR/PPy

The prepared self-degrading template, GR / PPy and the two electrodes were sampled on the copper sheet and coated with gold film. The prepared sample was observed under a field emission scanning electron microscope, and the sample image was captured and analyzed, as shown in Figure 4. According to the scanning image of the electron microscope, layered graphene could be observed in the left image of the material, and a dense self-degrading template was gathered on it. This indicated that the intermediate material was successfully prepared. There was a layered graphene in the right image of the material. Structure, and a dense polypyrrole layer was formed on the graphene surface, so analysis showed that GR/PPy material was obtained by chemical in situ polymerization. According to Figure 5, it could be seen that more and more obvious Hole, according to the ruler, the hole diameter was 12μm.
3.3. Electrochemical performance analysis

The electrochemical analysis of electrodes affected the results not only the properties of the electrodes themselves such as conductivity and stability, but also the properties of the electrolyte such as the resistance, capacitance, stable potential window, and manufacturing cost of the electrolyte. 1 mol·L⁻¹ Na₂SO₄ solution as an electrolyte had environmentally friendly, high capacitor safety, low cost and good cycle performance. It would not generate toxic gases and plated metals during electrode scanning advantage.

The prepared electrode was used as a working electrode, a saturated calomel electrode was used as a reference electrode, and a platinum wire electrode was used as a counter electrode to form a three-electrode system, which was assembled in an electrochemical workstation, with 1mol·L⁻¹ Na₂SO₄ was the electrolyte. Chi660e was driven by an electrochemical workstation to perform cyclic voltammetry and AC impedance tests on the electrode to obtain an image and analyze the electrochemical performance of the electrode to compare the performance of the porous electrode.

3.3.1. Cyclic voltammetry test. Cyclic voltammetry was a commonly used method for electrochemical analysis. The capacitance and properties of the electrodes could be analyzed by the shape and size of the cyclic voltammetry curve, and the stability of the electrodes could also be analyzed by using multiple test cycles. Figure 6 shows GR / Cyclic voltammogram of PPy ordinary and porous electrodes in 1 mol·L⁻¹ Na₂SO₄ solution, the potential range is -0.2 --- 0.2 V. As can be seen from the figure, GR / The cyclic voltammetry curves of the two electrodes of PPy in both electrolytes showed symmetry, indicating that the electrodes maintained good electrochemical characteristics in both electrolytes and had a good charge transfer process on the electrode surface. The scanning pattern of the porous electrode in the electrolyte was closer to a rectangle, which indicated that the charge transfer of the porous electrode in the electrolyte was smoother. The area enclosed by the CV curve of the porous electrode was larger, and it could be seen that the capacitance of the porous electrode was more Big[4] And
through 500 cv cycles, it was observed that the capacitance retention rate of the two electrodes was basically the same, there was no obvious attenuation, the capacitance stability was good, and the capacitance retention rate was high.

3.3.2. Constant-current charge-discharge test. The important electrochemical analysis method of constant current charge and discharge test was mainly the test method to measure the capacitance, charge and discharge efficiency and capacity retention rate. This article used multiple discharge cycle tests to determine the electrode capacity, capacity retention rate, and efficiency. The charge and discharge curves of the two electrodes were shown in Figure 7. According to the driving analysis, the specific capacities of the porous electrode and the ordinary electrode were respectively 0.13 mAh/g and 0.12 mAh/g under a current scan of 20 mA. Compared with ordinary electrodes, the specific capacity of porous electrodes was increased by 12%, and the results were consistent with the cyclic voltammetry curve. The output efficiency and capacity retention rate of the two electrodes after multiple cycles are about 99.9%, which was in line with the capacitance properties and was consistent with the cyclic voltammetry test. The results were consistent.

3.3.3. AC impedance test. AC impedance spectroscopy was an electrochemical measurement technique commonly used to study electrode process dynamics, electrode surface phenomena, and solid conductivity. AC impedance measurements could be used to measure the impedance characteristics of two electrodes. Figure 8 showed the two electrodes at 1 mol·L⁻¹ AC impedance spectrum in Na₂SO₄ electrolytes, the tested frequency range was 1-10⁵ Hz. The Nyquist curve was composed of the real part (Z') and imaginary part (Z'') of the impedance in the high frequency region, the solution resistance (Rs) of the electrode could be estimated from the intersection of the impedance curve and the real axis. The semicircle indicates the charge transfer process in the electrode material, that was, the charge transfer resistance (Rct). Warburg impedance caused when ions in the electrolyte diffuse to the electrode surface. As can be seen from Fig. 7, it can be seen that the two semicircles in the high frequency region had the
same diameter and the same focus, so the two electrodes were at 1 mol·L$^{-1}$ Na$_2$SO$_4$ electrolyte had basically the same resistance value of the two equivalent circuits, and the slope of the porous electrode in the low frequency region is greater than that of the ordinary electrode, indicating that the ion diffusion rate of the porous electrode was greater than that of the ordinary electrode. It shows that the conductivity and capacitance performance of the porous electrode were more OK, with cyclic voltammetry test results Character.

Fig. 8 Porous electrode (right) ordinary electrode (left) impedance image

4. Conclusion
In this paper, pyrrole monomer was polymerized on the GR layer by using FeCl$_3$-MO self-degrading template by chemical in situ polymerization method to prepare GR-PPy material. The characteristic structure of GR / PPy was analyzed by scanning electron microscope analysis. Degree of polymerization of pyrrole monomer. Carbon paste electrode was made by adding acetylene black and polytetrafluoroethylene emulsion for adhesion, and the electrode was made porous by particulate leaching method, analyzed by scanning electron microscope and analyzed at 1 mol·L$^{-1}$ Na$_2$SO$_4$ electrolyte was subjected to cyclic voltammetry test, constant current charge and discharge test, and AC impedance test analysis. The electrochemical performances of the two electrodes were analyzed and compared. The test results had showed that the specific capacity was increased by 12% compared with ordinary electrodes, the ion diffusion rate was faster, and this porous treatment had little effect on cycle stability and did not affect electrode resistance. Therefore, porous electrodes can better represent the performance of electrode materials, and can optimize the performance of super capacitors.

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