Preparation and Application of Porous Graphene in Supercapacitors

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Abstract. The experiment was designed by using the catalytic etching method to prepare porous graphene hrGO, which was applied in the production of supercapacitors. The experimental results showed that in the application of supercapacitors prepared by porous graphene, the specific capacitance of porous graphene was 33 mF/cm² at the scanning rate of 10 mV/s. When the current is 0.2 mA/cm², the electrode modified by porous graphene has a specific capacitance of 37 mF/cm², and the specific capacitance can reach 87% after 3,000 cycles of constant current charge-discharge test. This study shows that porous graphene is of great value in the preparation and application of supercapacitors, and can be used as the negative electrode material of supercapacitors.

Keywords: Porous Graphene, Supercapacitors, HrGO, GO, Structural Characterization, Specific Capacitance

1. Introduction
At present, carbon materials are widely used in electrocatalysis, electrochemical sensing, fuel cell and other fields. Graphene is one of the most important carbon materials, which is widely used in supercapacitors, public transportation, power stations and other fields. The research on porous graphene can promote the research and application of supercapacitors, which matters a lot energy storage [1].

Graphene is a high quality base carbon material that can be loaded with metal oxides as positive electrodes in asymmetric capacitors and pseudocapacitors. At present, active carbon, carbon nanotubes and biochar are widely used negative electrode materials. Porous graphene is now widely used in research [2]. Its surface structure is relatively loose and porous, and a large effective specific surface area can be made in the application process, which has significant effect on improving the ion transport rate. In the study, an experiment was designed to analyze the preparation process of reduced porous graphite oxide hrGO, and a graphite oxide (GO) was catalyzed by adding silver acetate at high temperature, which can be used for research on the negative electrode materials of supercapacitor [3].

2. Experiment
2.1 Instruments and Reagents
The experimental instruments selected in this study include KQ-10 ultrasonic cleaning instruments produced by CH Instruments, Inc., N W series ultra-pure water system developed by Heal Force Bio-Meditech Holdings Limited and JEOL-JSM-7100F transmission electron microscope produced by Japan. For the pure water instrument, clamp wire electrode, modified electrode and glassy carbon electrode were selected as the reference electrode for this study [4].

2.2 The Main Reagent
The reagents selected for this study include 95% quality fraction perfluorosulfonic acid produced by Aladdin, potassium ferrous oxide; absolute ethyl alcohol, potassium oxide of iron; sodium sulfate and silver acetate. Besides, analytical reagent produced by Sinopharm Chemical Reagent Co., Ltd. was selected and the single-layer GO produced by Nanjing Xianfeng Nanotechnology Co., Ltd. was used [5].

3. Material and Electrode Preparation
3.1 Material Preparation
7.68mg silver acetate powder and 50mg G0 are added into 30mL deionized water, which are transferred to porcelain boat after 2 hours of ultrasonic mixing. It can be dried off at 60 °C and then transferred into tube furnace with the rate of 5 °C /min and the temperature can rise from room temperature to 350°C for duration of 3 hours. After the material is cooled to room temperature, the temperature would rise from room temperature to 350°C at a rate of 5°C/min for 3h. After cooling, the material was taken out, 30ml 3.6mol/L nitric acid solution was added into the solution, the temperature was set at 80°C, and 2h of reflux was conducted. After that, it was pumped to the filtrate pH>6 and the water in the material was filtered out, thus hrGO solid particles were obtained [6].

3.2 The Electrode Preparation
The ratio of nafion, ethanol and water in the preparation of the mixed solution was 1:80:80, and 6mg hrGO solid particles were added into the mixed solution to obtain 3mg/mL hrGO suspension in the ultrasonic manufacturing. Ultra pure water and anhydrous ethanol were used for ultrasonic cleaning in the solution for 5min. After drying, 5uL turbid liquid was selected and dropped onto the surface of GCE electrode. After dried in the drying box of the infrared lamp, the glassy carbon electrode hrGO/GCE made by porous graphene could be obtained. RGO /GCE modified electrode and 3mg/mL rG0 suspension were obtained by the same preparation method [7].

4. Results and Discussion
4.1 HrGO Morphology and Structure Characterization
The TEM characterization of hrGO with etching holes and without holes was studied. Porous reduction graphene oxide, etching graphene oxide are presented in the form of lamelliform. The surface of graphene without etching hole is dense and uniform. While, there are many circular holes on the surface of reduction and porous oxide graphene with diameters reaching 20 nm in diameter and uniform size. It shows that the study has been successfully made to produce porous reduction graphene oxide [8].

The main components of porous reduction graphene oxide are oxygen element (0), carbon (C) by EDX qualitative analysis on elements of materials of reduction-oxidation graphene and graphene oxide etched. The two kinds of materials are prepared by the raw material GO and there are incompletely reduced components in the material. At about 8keV, the characteristic peak of copper network reached Cu peak. At this time, the peak value of non-material itself was reached. As shown in figure 1.
Figure 1. EDX map of rGO and hrGO

There was no characteristic peak of Ag in silver acetate in the porous GO map, indicating that the silver nanoparticles on the surface of the porous GO had been completely removed during pickling. At 10mV/s scanning rate, the specific capacitance of porous graphene was up to 33mF/cm², and the current density of 0.2mA/cm² was tested. The specific capacitance of the modified electrode of porous graphene reached 37mF/cm², and 3000 cycles of constant current charging and discharging were tested. The specific capacitance of the supercapacitor prepared by porous graphene was 87% [9].

4.2 Research on Electrochemical Properties of hrGO

The performance of electrical double-layer capacitor represented by three different electrodes in Na2SO4 solution GCE(I), rGO/GCE(II) and hrGO/GCE(III) was analyzed. The potential range of -1-0V and the scanning rate of 10mV/s were set. As shown in figure 2.

Figure 2. Potential vs. SCE/V

Under 10mV/s scanning state, rGO/GCE(II) and hrGO/GCE(III) presented symmetric rectangular-like shapes, indicating that the double layer had good characteristics at a low scanning rate. Compared with GCE(I), the specific capacitors of rGO/GCE(II) and hrGO/GCE(III) were significantly increased at a scanning rate of 10mV/s, reaching 21mF/cm², and 33mF/cm² for hrGO/GCE(III). Compared with the unetched modified electrode rGO/GCE(II), the effective specific surface area of porous graphene is significantly larger and the ions can contact more materials per unit time. It can be seen that after modifying the hrGO material, the capacitance of the double layer of the electrode can be significantly enhanced [10].

5. Comparison of Different Materials in Performance

The performance differences between the supercapacitors prepared with porous graphene and those prepared with spongy graphene, N-dopedrgo, EG-RGO, GR/NF, N-GR/CNT, and microporous porous graphene are compared. The results are shown in Table 1.
Table 1. Literature comparison of graphene-based supercapacitors

| Electrode material | Specific capacitance/(F/g) | Electrolyte          |
|--------------------|---------------------------|----------------------|
| Spongy graphene    | 68                        | 1mol/LH$_2$SO$_4$    |
| N-doped rGO        | 103.2                     | 1mol/LH$_2$SO$_4$    |
| EG-rGO             | 131.6                     | 1mol/LNa$_2$SO$_4$   |
| GR/NF              | 164                       | 6mol/LKOH            |
| N-GR/CNT           | 180                       | 6mol/LKOH            |
| Microporous porous | 93                        | 1mol/LH$_2$SO$_4$    |
| graphene           |                           |                      |
| hrGO               | 178                       | 1mol/LNa$_2$SO$_4$   |

As the specific capacitance was conversed with the current density of 0.2 mA/cm$^2$, the specific capacitance of supercapacitor made of porous graphene is about 178 f/g. Compared with that of the materials such as spongy graphene, N-dopedrGO, EG-rGO, GR/NF, N-GR/CNT, microporous and porous graphene, the specific capacitance of porous graphene is larger. At the same time, other electrolyte show the characteristics of strong acid, alkali, and the capacitor can be corroded, and thus causing the potential safety risks. The 1mol/LNa$_2$SO$_4$ solution used in this study is a neutral electrolyte, and the operating environment is relatively safe and good.

6. Conclusion
In this paper, the preparation process of hrG with the application of catalytic etching method is studied, which is of great value in the application of supercapacitors. With the application of porous structure, ions can be rapidly diffused on the electrode surface, increasing specific capacitance and improving the performance. The scanning rate was 10mV/s, and the specific capacitance of porous graphene reached 33mF/cm$^2$.Providing that the current density is 0.2 mA/cm$^2$, the specific capacitor of modified electrode of porous graphene is 37 mf/cm$^2$.The specific capacitor can still reach 87% after the test on the charge and discharge of 3000 laps of continuous current in the operation of super capacitor. Through the study in this paper, it can be seen that the performance of electrical double-layer capacitor is relatively stable, and it can be used as a preferred material in the manufacture of supercapacitor with a broad market.

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