Mn doped graphene aerogels for high capacity and long-life supercapacitor

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Abstract. The pure graphene aerogel material is a double-layer capacitor material which provides capacitance by the surface area. Its conductivity and specific capacitance require further improvement. In this work, manganese doped graphene aerogels were synthesized by hydrothermal method using manganese chloride as a source of manganese. The effect of manganese content on the structure and properties of the material was studied. It is found that the specific surface area and pore volume of aerogels decrease with the increase of Mn content. The Mn doped graphene aerogel prepared at the current density of 0.1 A/g shows a capacitance of 180 F/g and exhibits pseudo capacitance performance in the three-electrode test. After assembling the button capacitor, the capacity retention rate is 93% after 1000 cycles at a current density of 0.5 A/g.

1. INTRODUCTION

Nitrogen doped carbon-based porous materials, such as nitrogen doped graphene aerogels have the characteristics of large surface area and rich pore structure [1-4]. This allows nitrogen doped graphene aerogels as a good carbon skeleton for carrying capacitive properties of the materials with pseudocapacitor materials [5-7]. As a common pseudocapacitor material, manganese oxide has attracted extensive attention because of its low price and rich content. In recent years, a lot of progress has been made in the research on the action mechanism and synthesis methods of manganese oxides with various valence states and crystal structures in the field of energy storage [8]. Manganese oxide, as a pseudocapacitor material, has made significant performance improvement in supercapacitors. However, manganese oxide is difficult to obtain good performance when used as electrode material alone because of its poor conductivity and the volume change caused by redox reaction in the cycle process.

Nitrogen doped graphene loaded manganese can make the two materials integrate their advantages and make up for their disadvantages, to improve the properties of the materials. Therefore, in this work, manganese doped graphene aerogels were prepared by hydrothermal method. The influence of different ratios of Manganese Sources on the structure and capacitance properties of aerogels is mainly studied.
2. Experimental methods

2.1 Preparation of Mn doped graphene aerogels
Firstly, graphene oxide dispersion is prepared. Weigh a certain amount of graphene oxide and add it into a beaker containing an appropriate amount of deionized water to prepare graphene oxide dispersion with a concentration of 4 mg/ml. After that, the solution was sonicated using a cell fragmentation instrument for 2 hours. Next, prepare additives and prepare 5 ml of ethylenediamine and ammonia solution in the ratio of 1:1 by volume. It was then added to 50 ml of graphene oxide dispersion and stirred with a magnetic stirrer for 30 minutes. Then add a certain amount of 0.2 M manganese chloride solution to the mixed liquid and stir for 15 minutes. Then transfer the solution to a hydrothermal kettle and heat it in an oven at 200 °C for 24 hours. Aging treatment shall be carried out after hydrothermal reaction. After aging, the hydrogel was put into the supercritical drying machine, and the carbon dioxide was used as a supercritical drying medium. Under the condition of 45 degree centigrade and a pressure of 7.5 MPa, the gel was dried for 24 hours, and the aerogels were obtained.

In the experiment, the amount of manganese chloride aqueous solution in hydrothermal reaction was taken as a variable to study the effect of the amount of manganese source on the material. The specific experimental setup is to add 5 ml, 7.5 ml and 10 ml of manganese chloride solution respectively. According to the different amount of manganese chloride added in the experimental group, they are named Mn5, Mn7.5 and Mn10 respectively.

2.2 Characterization and electrochemical test of materials
Then the materials were characterized by BET, XRD and SEM. The resistivity of the materials were tested by resistivity tester. The aerogels were then made into electrodes for supercapacitors. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and constant current charge discharge tests were carried out in a three-electrode system with 1m KOH solution as electrolyte. After completing the three-electrodes tests, the button capacitor was assembled. The electrochemical properties of the two electrodes were tested by CV, EIS and constant current charge discharge.

3. Results and discussion
The SEM test results of the material are shown in Figure 1. It can be seen from the figure that this material has a honeycomb like hole structure. Through comparison, it can be found that the structures of Mn5 and Mn10 materials are fluffy, while Mn7.5 presents a multi-layer structure with dense stacking. At the same time, the pore wall of Mn5 is thinner, and more aerogel sheets are attached to the Mn10 hole wall. Mn7. Although the stack is dense, there are holes between layers. In general, the material has a good pore network and can provide a path for ion transport in electrolyte.

Through the analysis of SEM images, we can see that Mn group materials can be divided into closely packed thick aerogels and relatively loose fluffy aerogels. In the loose structure, more graphene flakes are accumulated on the tube wall of Mn10. These different structures are bound to have different effects on the working process of capacitors, so it is necessary to further explore them. To further understand these two structures, BET test, resistivity test and XRD test were carried out for the aerogels of materials.
The test results of BET and conductivity are shown in Table 1. It is obvious from the table that the pore volume, specific surface area and resistivity of the material decrease with the increase of Mn addition. The specific surface area and pore volume decrease indicate that excessive manganese ions can inhibit the formation process of aerogels. At the same time, the reaction between manganese ions and graphene oxide will also destroy the existing pores, resulting in the decrease of pore volume. Although in general (compared to the three or four chapter), the addition of manganese ions will increase the resistivity of aerogels, but the resistivity of aerogels added with excess manganese ions is lower.

| Sample | Specific surface area (m²/g) | Pore volume (ml/g) | Resistivity (Ωcm) |
|--------|------------------------------|--------------------|------------------|
| Mn5    | 810.714                      | 2.727              | 4.24             |
| Mn7.5  | 766.172                      | 2.559              | 2.20             |
| Mn10   | 542.338                      | 1.802              | 1.865            |

Figure 2a can be obtained by using the adsorption and desorption data obtained from BET test. It can be seen from the figure that the adsorption curves of Mn group materials are type IV curves and the hysteresis curve is type H3. The results show that the holes in the manganese doped graphene aerogels are mainly mesoporous. The results show that there is no significant difference in the void structure between the three aerogels. The material was tested by XRD, and the results are shown in Fig. 2b. According to the diagram, Mn(CO₃) is found in the Mn materials, indicating that Mn is successfully incorporated into the aerogel structure. In addition, according to the obvious degree of peak shape, it can be known that the doping degree of manganese is directly proportional to the addition amount.
In order to further understand the material properties, three electrode tests were carried out. The impedance test results are shown in figure 3a-b. The oblique line with high inclination in the low-frequency part and the almost invisible semicircle in the high-frequency part show that the material has good capacitive properties. Cyclic voltammetry was carried out on the three electrodes, and the results are shown in Fig. 3c-f. It can be clearly seen from the CV diagram that the material has peaks at -0.1 V and -0.32 V. This peak is caused by the reaction of manganese. In addition, according to the Figure 3f, the pseudo capacitance reaction of the dense stacked aerogel Mn10 is more intense, indicating that although the manganese content is not as good as Mn10, this stacked and connected structure helps to pseudo capacitance reaction. In addition, from the overlap of CV curves, it can be seen that the loose porous structure aerogels of Mn10 and Mn5 have stronger cycling performance.

In order to explore the capacitance performance of the material, the constant current charge discharge test was carried out for the three-electrode system, and the specific capacitance values under different current densities (0.2 A/g, 0.5 A/g, 1 A/g, 2 A/g, 5 A/g, 10 A/g) were calculated. The charge discharge curve and rate performance of the three-electrode system of Mn group material under the current density of 1 A/g are shown in Figure 4. According to the charge discharge curve, Mn5 is a charge discharge curve similar to a triangle, and its pseudo capacitance is not obvious. The charge discharge curves of Mn7.5 and Mn10 deviate from the triangle, and there are obvious turning points in the charge and discharge curves, showing obvious pseudo capacitance characteristics.

Figure 3 Electrochemical measurement in three electrodes. EIS of (a) full spectrum (b) and high frequency area. CVs of (c) Mn5, (d) Mn7.5 and (e) Mn10 at the scan rate of 10 mV/s. (f) CVs of all samples at the scan rate of 10 mV/s.
According to the rate performance, it can be seen that two materials Mn10 and Mn7 with pseudo capacitance characteristics. The specific capacitance of Mn5 at low current density is much larger than that of Mn7 without obvious pseudo capacitance. And Mn7.5 aerogels with dense packing characteristics of aerogels exposed to electrolyte in a loose structure with an effective area greater than Mn10. Therefore, when the manganese content is low, Mn7.5 shows higher specific capacitance at low current density. However, with the increase of current density, the more abundant ion channels provided by loose structure play a role. The specific surface area of Mn10 is lower than Mn7.5. In the case, the capacitance of Mn10 exceeds Mn7.5. And the specific capacitance of Mn5 with loose porous structure is more stable. This shows that the loose porous structure formed when the amount of manganese is too high or too low is conducive to the performance of the material at high current density.

![Figure 4](image)

**Figure 4** Electrochemical measurement in three electrodes. (a) Charge discharge curve of materials at current density of 1A/g. (b) Rate capacities of Materials

In order to study the practical performance of the material, the material was assembled into a symmetrical water buckle capacitor, and the impedance, cyclic voltammetry, constant current charge discharge and cycle life were tested. The results of the impedance test are shown in Figure 5a. It is obvious from the figure that the inclination of Mn5 and Mn10 low-frequency areas is greater than Mn7.5. This shows that the diffusion rate of ions in Mn10 and Mn5 is faster than that in Mn7.5. The cyclic voltammetry test of button capacitor was carried out. The results are shown in Figure 5b-e. It can be seen from the figure that the capacitor presents a CV curve similar to a rectangle at this scanning rate. However, the overall capacitance is small, and the capacitance is completely proportional to the specific surface area of the material, and there is no corresponding peak on the CV Curve. It can be seen from the figure that the coincidence degree of the three is high, indicating that the structural change of the material is small during the cycle.

The cyclic charge discharge test of the capacitor and the magnification test results at current densities of 0.1 A/g, 0.2 A/g, 0.5 A/g, 1 A/g, 2 A/g, 5 A/g and 10 A/g are shown in Fig. 5f-g. It is obvious from the data in the figure that the performance of Mn10 is not reflected in the configuration of button capacitor, while Mn7.5 is only reflected at low magnification, while Mn5 is hardly affected. After that, the impedance test of Mn10 is carried out, and the results are shown in Figure 5h. It is found that the slope of the low frequency region of Mn10 impedance decreases after the test. This indicates that the structure of the material has changed. The structure of Mn10 is similar to that of Mn5, but there is no such change in Mn5. Therefore, this change may be due to the irreversible transformation of manganese in the process of charge and discharge, which destroys the structure of the material and makes the performance of Mn10 unable to be reflected.

The cycle life of materials was tested. The results are shown in Figure 5i. It can be seen from the figure that the order of cyclic stability of devices from high to low is Mn10 (retention rate 100%), Mn5 (retention rate 97%) and Mn7.5 (retention rate 93%). This result shows that the internal structure of Mn10 has been destroyed and has become a device that completely relies on electric double layers to provide capacitance. For other devices, the higher the manganese content, the lower the retention rate. This is because the irreversible reaction of manganese in the cycle leads to the decrease of device capacity.
Figure 5 Electrochemical measurement in cell batteries. (a) EIS spectrum of cell capacitor. CVs of (b) Mn5, (c) Mn7.5 and (d) Mn10 at the scan rate of 10 mV/s. (e) CVs of all samples at the scan rate of 10 mV/s. (f) Charge discharge curve of materials at current density of 1A/g. (g) Rate capacities of Materials. (h) EIS comparison of Mn10 before and after test. (i) Long cycle performance test.

4. Conclusion

In conclusion, manganese doped graphene aerogels were successfully synthesized by hydrothermal method using MnCl2 as manganese source. The aerogel has higher specific surface area, resistivity, pore volume and specific capacitance. It is found that within the setting range, the higher the addition of manganese, the smaller the specific surface area and pore volume of the material, and the larger the specific capacitance at low magnification. It is also found that the different aeration of manganese will lead to different aerogels. A porous porous aerogel structure will be formed if the amount is too high or too low, and a stacked aerogel structure will be added. At the same time, the influence of these structures on the capacitance performance is studied. It is found that the stacked aerogel structure is advantageous to provide capacitance at low current density while loose porous type performs well under medium current density. Then the button symmetrical capacitor is assembled and the practicability of the material is studied.
Acknowledgements
The authors gratefully acknowledge the support by Sichuan Science and Technology Program of 2021YFH0126, Quzhou Science and Technology Bureau Project (2021D006) and the Fundamental Research Funds for the Central Universities (A030202063008029).

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