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Graphene foam as an anode for high-rate Li-ion batteries

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Abstract. A foam-like graphene material can be prepared by freeze drying and thermal reduction of graphene oxide suspensions. The graphene foam has a much higher capacity than conventional graphite anode, and it possesses better rate capability comparing with powder-like graphene active materials reported previously. The influence of the annealing temperature on the charge-discharge performance of graphene foam has been investigated.

1. Introduction

The research on graphene has become one of the most attractive scientific topics at present, because this new carbon material possesses unique physicochemical properties which impart it with great potentials in various application areas.^[1,2] The application of graphene in energy storage materials, such as electrode active materials in Li ion battery^[3] or super capacitor^[4], is believed to be a promising field with a huge market. The ultra-thin graphene layers with graphitic basal structure may favor a higher accommodation sites and a faster migration rate of Li ions during charge-discharge processes while keeping high electron conductivity, comparing with conventional graphite anodes. Therefore, graphene offers a new option to carbon-based anode materials in Li ion batteries. Since 2008, several research groups have studied the electrochemical properties of graphene anode materials. It was found that graphene powders could deliver a higher specific capacity than graphite, which was suitable for high-capacity Li ion batteries.^[3,5-8] On the contrary, graphene paper with a much denser stacking of graphene sheets comparing with powders shows apparently lower storage capacity.^[9,10] Accordingly, it is speculated that the morphology and the 3D construction manner of graphene is crucial to its charge-discharge characteristics.

In this paper, foam-like graphene anodes were prepared by freeze drying and subsequent annealing of graphene oxide suspensions. The graphene foam with a high porosity showed a relatively large specific capacity and good cycle stability at high current densities. Furthermore, no conductive additive and binder were needed during the electrode preparation, since graphene foam with a certain degree of mechanical strength could be self supported.

2. Experimental

The preparation of graphene oxide (GO) followed the procedure of our earlier work.^[11] The obtained aqueous suspension of GO was centrifuged to reach a concentration of 2 wt.%, immersed in liquid nitrogen, and then freeze dried for 24 hours. The resultant brown GO foam was annealed at 600 °C in a tube furnace for 5 hours in Ar atmosphere, after which it was thermally reduced to graphene foam. The annealing temperatures of 400 °C and 800 °C were also applied while keeping other experimental conditions constant. The graphene foam was directly used as the anode with no conductive additive

and binder during the assembly of coin cells (2032). Lithium metal was applied as the anode, Celgard 2600 as the separator, and 1 M LiPF₆ (dissolved in ethylene carbonate and dimethyl carbonate with a 1:1 volume ratio) as the electrolyte. Cells were tested at room temperature using a LAND-CT2001A battery cycler (Wuhan, China) within the voltage range of 0-3.0 V (vs. Li⁺/Li).

3. Results and discussion

Figure 1a shows the macroscopic morphology of graphene foam obtained from freeze drying and annealing of GO suspension. Though graphene foam has a very low apparent density less than 0.1 g/cm³, it possesses a certain degree of structural flexibility and elasticity. As shown in Figure 1, graphene foam can quickly recover to its original morphology after being squeezed by tweezers. The SEM characterization (Figure 1b) reveals that graphene foam has an ultra-hollow internal structure with a high porosity. Micro-sized crystals of ice formed during the fast freezing of GO suspension in liquid nitrogen served as the templates,^[12] and large amounts of pores with dimensions of ~ 10 μm were generated after ice was completely sublimated in vacuum. Though the graphene framework is very thin, which is translucent under electron beams, the ultra-high mechanical strength of graphene sheets^[13] gives rise to macroscopic elasticity of the foam-like structure. Furthermore, highly conductive and continuous graphene framework provides a network for fast electron migration; while the pores ensure easy impregnation of electrolytes all over the sample. Such monolithic graphene foam thus can be directly used as the anode without addition of conductive additives and binder, as well as current collectors which are essential for powder-like active materials.

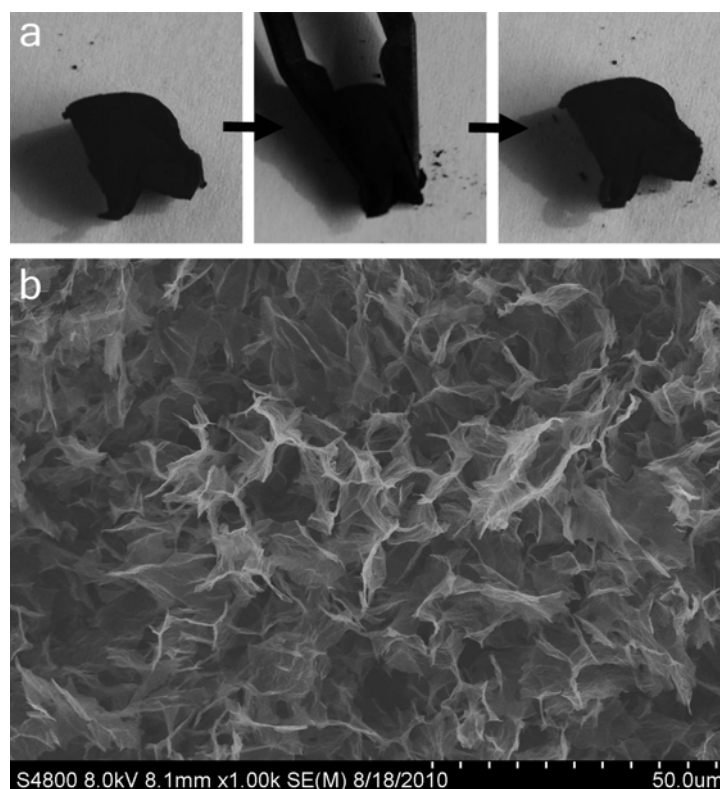


Figure 1 a) Digital photographs of a graphene foam. b) SEM image of the graphene foam.

The electrochemical properties of the graphene foam anodes were then evaluated. The initial discharge and charge capacity of graphene foam at a current density of 50 mA/g are 1059 and 732 mAh/g, respectively, which is much higher than conventional graphite anodes or paper-like graphene anodes, and is comparable to powder-like graphene anode materials reported previously. The rate

capability of graphene foam was tested by increasing the current density gradually from 0.1 A/g to 4 A/g as shown in Figure 2b and c. The charge capacity decreases, and the voltage raises along with the increasing of the current density. The reversible capacity at a current density of 1 A/g is ~ 230 mAh/g which is 57% of the reversible capacity at 0.1 A/g. Further increasing to an even higher current density of 4 A/g results in a reversible capacity of ~ 140 mAh/g, equivalent to 35% of the capacity at 0.1 A/g. In previous reports on graphene anode materials, relatively low current densities such as 50 mA/g were usually adopted to assess the charge-discharge performance.^[3, 7, 8] The ultrahigh current density of 4 A/g has never been used. Hence, the graphene foam material exhibits excellent rate capability. The cycle stability of graphene foam was also measured by charging and discharging the coin cell at a relatively high current density of 1 A/g. After 100 cycle times, the reversible capacity still retains 82% of the initial capacity (see Figure 2d). Consequently, the graphene foam material is a good candidate for high power Li-ion batteries that require fast charge and discharge.

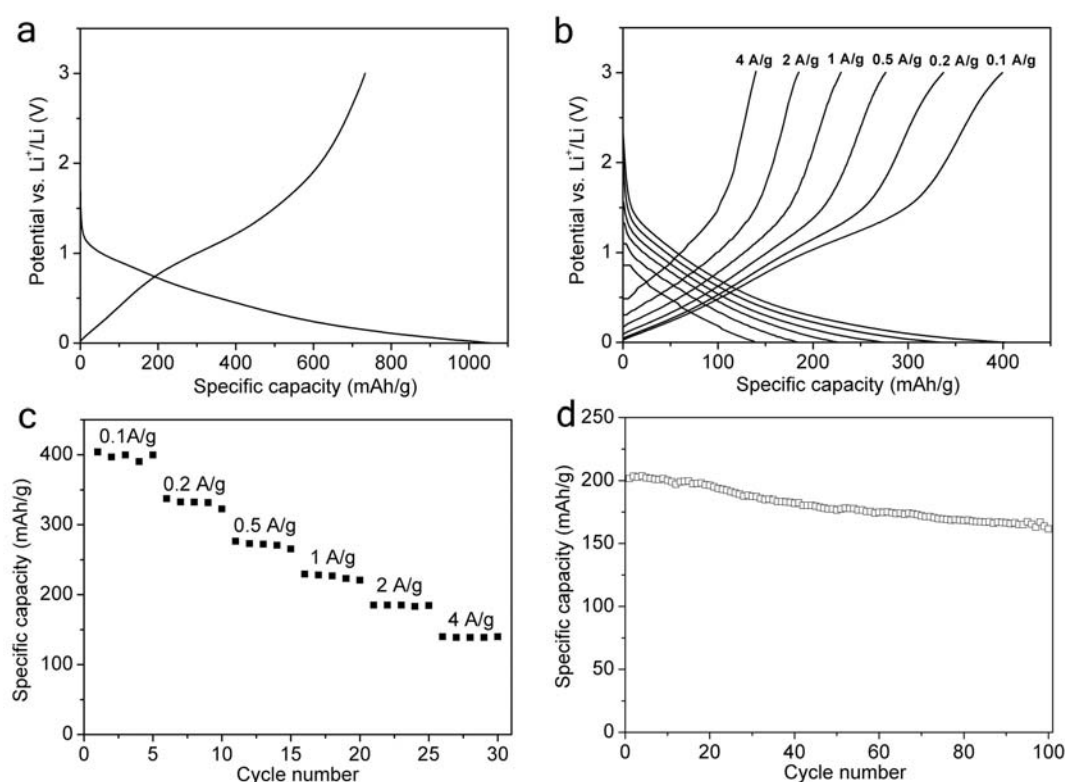


Figure 2 a) Initial charge-discharge curves at a current density of 50 mA/g, b) charge-discharge curves at different current densities, c) reversible capacity at different current densities and d) capacity retention at a current density of 1 A/g of graphene foam annealed at 600 °C.

The reduction degree and conductivity, as well as surface functional groups of thermally reduced graphene are closely related to the annealing temperature. Therefore, the charge-discharge performance of graphene foam materials annealed at different temperatures is systematically investigated. Figure 3a shows the initial charge-discharge curves of graphene foams annealed at 400, 600 and 800 °C, respectively, at a current density of 50 mA/g. It is apparent that the capacity decreases when the annealing temperature increases. Graphene foam thermally treated at 400 °C has a reversible capacity higher than 800 mAh/g at 50 mA/g, which is about 150 mAh/g and 500 mAh/g larger than samples annealed at 600 °C and 800 °C, respectively (figure 2b). It can be attributed to relatively higher content of functional groups such as carboxyl groups on graphene sheets when annealed at lower temperatures, which can have a reversible electrochemical reaction with Li ions and thus increases the capacity.^[14] However, the capacity of graphene foam annealed at 400 °C fades quickly

when the current density is increased. Its capacity at a current density of 0.2 A/g is, on the contrary, ~ 100 mAh/g smaller than that of the sample thermally treated at 600 °C at the same current density (figure 2c). The lower conductivity induced by a lower reduction degree at 400 °C might be the main reason that results in an obviously deteriorated rate performance. For comparison, though the capacity of graphene foam annealed at 800 °C is relatively low, its capacity retention along with the increasing of the charge-discharge current is comparable to that of the sample annealed at 600 °C. Considering both specific capacity and rate capability, 600 °C is the optimal annealing temperature to obtain graphene foam anode materials with an excellent charge-discharge performance.

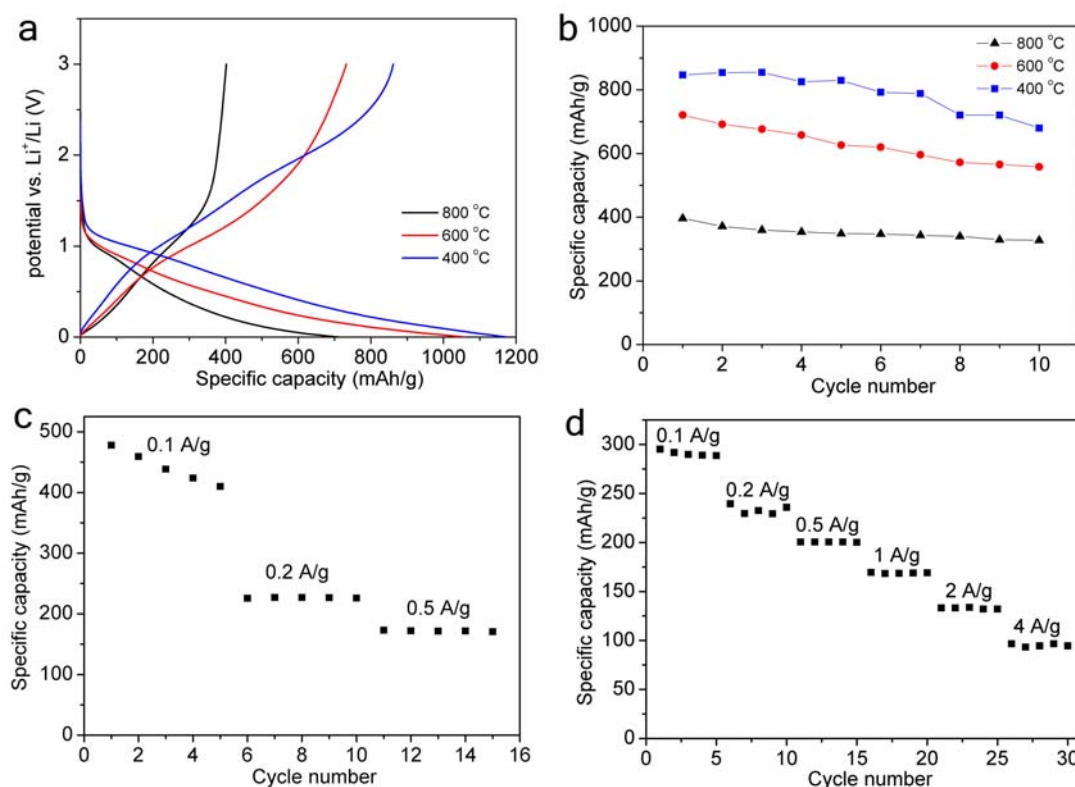


Figure 3 a) Initial charge-discharge curves and b) reversible capacity cycled at 50 mA/g of graphene foams annealed at different temperatures. c) Reversible capacity of graphene foam annealed at 400 °C at different current densities. d) Reversible capacity of graphene foam annealed at 800 °C at different current densities.

4. Conclusions

The graphene foam materials prepared by freeze drying and thermal reduction of graphene oxide suspensions were applied as an anode for Li-ion batteries, which shows a good rate capability and cycle stability. The unique morphology and structure of graphene foam impart it with a better charge-discharge performance than previously reported powder-like graphene anode active materials, which sheds some light on the potential application in high power Li ion batteries.

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