Materials Science & Engineering B 226 (2017) 164–170

Contents lists available at ScienceDirect

Materials Science & Engineering B

journal homepage: www.elsevier.com/locate/mseb

Synthesis of functionalized graphite oxide films by three-dimensional self-assembly for lithium ion battery anodes

Shuai Sun[a,b,*], Chengyang Wang[b], Lei Wang[c], Mingwei Li[d]

[a] Department of Chemical Engineering, Chengde Petroleum College, Chengde 067000, PR China
[b] Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Synergetic Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin University, Tianjin 300072, PR China
[c] Department of Chemistry and Chemical Engineering, Hebei Normal University for Nationalities, Chengde 067000, PR China
[d] School of Science, Tianjin University, Tianjin 300072, PR China

ARTICLE INFO

Keywords:
Self-assembly
Graphite oxide
Film
Lithium ion battery

ABSTRACT

Functionalized graphite oxide films are synthesized by using $(NH_4)_2SO_4$ during self-assembly process of graphite oxide in water. Instead of stacking layer by layer, graphite oxide films with three-dimensional (3D) structure are obtained due to strong hydration of ions from $(NH_4)_2SO_4$. After low temperature treatment (400 °C) of the self-assembly films, $(NH_4)_2SO_4$ decomposes and N-doped films are obtained, the films can be used directly as anodes for lithium ion batteries. According to electrochemical test, the 3D self-assembly films exhibit enhanced lithium ion storage performances such as initial coulombic efficiency and specific capacity due to 3D structure and N atoms. Further studies show that owing to low chemical activities of graphitic structure in air, low temperature treatment (400 °C) under different atmospheres (N_2 or air) has little effect on structures and electrochemical performances of 3D self-assembly films, which is meaningful for producing the films on a large scale in the future.

1. Introduction

Owing to good lithium ion storage performance and conductivity after reduction, graphene oxide and graphite oxide [1] have been considered as excellent electrode materials for lithium ion batteries [2–6]. Although electrochemical performances of electrodes can be improved by adding mental elements, the electrodes using pure graphene oxide or graphite oxide as raw materials have drawn the attentions of many researchers because it is simple to produce them on a large scale in the future. The specific capacity of the electrode using reduced graphene oxide in lithium ion battery is ~710 mAh/g (the fifth cycle) at the current density of 35 mA/g [7] and the value is only ~350 mAh/g (the fifth cycle) at the current density of 50 mA/g if graphite oxide is used [8]. However, these values were obtained by using collector to assemble electrodes, the mass of collector was not taken into consideration. According to another research, the capacity value of electrode without collector tends to decrease (~300 mAh/g at the current density of 50 mA/g in the fifth cycle) [9]. Additionally, graphene oxide and graphite oxide can be self-assembled to synthesize film in water [10], which meets a growing demand for free-standing electrodes [11–14]. In the fields of electrochemical reactions and energy storage, multi-dimensional structure is useful for improving electrochemical performances of materials and thus have been studied by many researchers [15–21]. However, both graphene oxide and graphite oxide suffer from stacking layer by layer during self-assembly process, which leads to dense films and makes it difficult to prepare multi-dimensional structural materials. Though using inert templates can inhibit stacking and obtain three-dimensional (3D) structural electrodes [22], the templates increase the mass of batteries. According to our previous studies [23], salts have influence on movement of graphite oxide in water due to strong hydration of ions from salts in water. Thus, in this paper, salts were used during self-assembly of graphite oxide in water to inhibit formation of dense films and obtain 3D structure. $(NH_4)_2SO_4$ was chosen because it could decompose to form NH_3 and NH_4HSO_4 gas at relative low temperature (400 °C), which meets the demand for reducing graphite oxide at low temperature as electrode materials [24,25]. Additionally, N atoms from $(NH_4)_2SO_4$ were bonded to C atoms in graphite oxide during thermal treatment, which is useful for enhancing electrochemical performances of obtained materials [26–30]. It is easy to synthesize N-doped films by using the method reported in this paper, although new method such as using plasma for preparing N-doped carbon-based films has drawn the attentions of many researchers [31,32], it still needs further studies in order to prepare materials on a large scale for lithium ion batteries.

* Corresponding author at: Department of Chemical Engineering, Chengde Petroleum College, Chengde 067000, PR China.
E-mail address: happy6jerry@163.com (S. Sun).

http://dx.doi.org/10.1016/j.mseb.2017.09.018
Received 30 June 2017; Received in revised form 10 September 2017; Accepted 21 September 2017

Nowadays, graphene oxide and graphite oxide are usually reduced in inert atmosphere such as N_2 during thermal treatment, which may be not necessary due to the low chemical activities of graphitic structure in air [33,34]. Thus, in this paper, different atmospheres (N_2 or air) were used to reduce 3D self-assembly films and the structures and electrochemical performances of the films were studied.

2. Experimental

2.1. Preparation of graphite oxide hydrosol

Graphite oxide was prepared by a modified Hummers method. Briefly, graphite powder (12 g, 1200 mesh) and sodium nitrate (7.6 g) were mixed with sulfuric acid (320 mL, 98%) in an ice bath for 15 min. Then potassium permanganate (45.2 g) was slowly added to the mixture. After stirring for 2.5 h, deionized water (700 mL) was then gradually added to dilute the mixture and a bright-yellow suspension was obtained. The suspension was further treated with a H_2O_2 solution (60 mL, 30%), followed by centrifugation and careful washing to remove the salt remnants. After adding deionized water to the wet graphite oxide and stirring, a stable graphite oxide hydrosol with a concentration of 2.3 wt% was obtained. Graphite oxide was obtained by drying the hydrosol at room temperature for 1 day and then drying at 60 °C for 3 h.

2.2. Synthesis of functionalized films

Fig. 1a shows the diagram for the method to prepare functionalized films. As shown in Fig. 1a, graphite oxide hydrosol was mixed with a 42 wt% $(NH_4)_2SO_4$ solution at a weight ratio of 6:1 (Water was needed for mixing well, however, too much water from $(NH_4)_2SO_4$ solution resulted in more time for drying, the ratio 6:1 was appropriate according to experiment). The mixture was then treated at 95 °C for 5 h, during which graphite oxide was assembled gradually to obtain film with 3D structure and the mixture was dried. The film was then treated at 400 °C in N_2 or air for 1 h (the heating rate was 5 °C/min), during which $(NH_4)_2SO_4$ decomposed and N-doped graphite oxide film (NGM) was obtained. The films treated in N_2 or air were named as NGMN and NGMA, respectively, thickness of the films could be controlled by adjusting mass of the mixture (graphite oxide hydrosol and $(NH_4)_2SO_4$ solution). A graphite oxide hydrosol without mixing with $(NH_4)_2SO_4$ was also treated at 95 °C for 5 h and then treated at 400 °C in N_2 for 1 h, the obtained dense film without N atoms was named as GMN, thickness of the GMN could be controlled by adjusting mass of graphite oxide hydrosol. Different thicknesses of films by adjusting mass of raw materials are shown in Fig. 1b–d (magnified cross-sectional image of sample can be seen in Fig. 2c), it should be mentioned that it is difficult to determine the exact value of thickness by using scanning electron microcopy (SEM) due to the wrinkles and disordered sheets in 3D structure. Thus, the thicknesses of films shown in Table 1 were characterized using micrometer caliper.

2.3. Fabrication of lithium ion batteries and electrochemical measurements

The obtained GMN, NGMN and NGMA films were tailored to circle electrodes (13 mm diameter). After dried under vacuum at 120 °C, the electrodes were used as anodes for lithium ion batteries directly, mass and thickness of the electrodes are shown in Table 1. The thickness of each electrode is shown with a number in the name of sample (e.g. GMN-8 means GMN film with a thickness of 8 μm). Lithium ion coin cells were assembled in a glove box filled with argon. Lithium sheets were used as reference and counter electrodes, 1 M $LiPF_6$ solution in a 1:1 (V/V) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as electrolyte. The cyclic voltammetry (CV) analysis was investigated at a scanning rate of 0.1 mV/s within the range from 0 to 3 V using an electrochemistry working station (CHI660E). Galvanostatic charge/discharge analysis was carried out on a Land Battery Test System at different current densities (1 C = 372 mA/g) within the range from 0 to 3 V. All electrochemical measurements were carried out at room temperature.

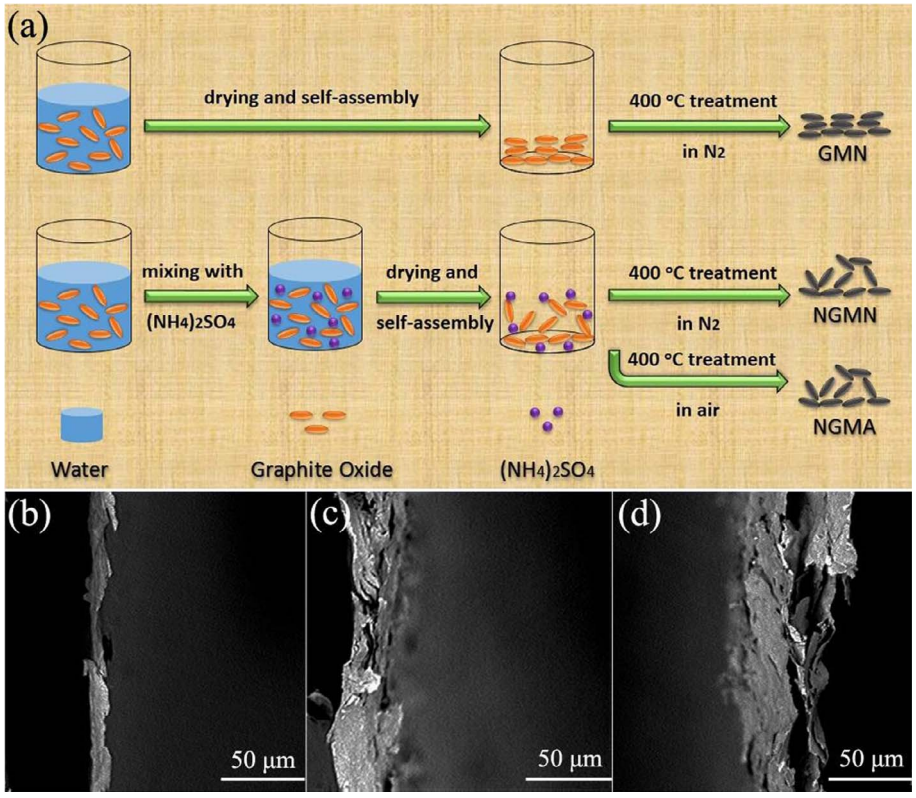

Fig. 1. (a) Diagram for the method to prepare functionalized films. Cross-sectional SEM images of (b) GMN-8, (c) NGMN-24 and (d) NGMN-54.