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# Mildly expanded graphite for anode materials of lithium ion battery synthesized with perchloric acid

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ABSTRACT

Mildly expanded graphite (MEG) was synthesized by using perchloric acid as both intercalating agent and oxidizing agent. Its performance as anode material for lithium ion battery was investigated. SEM, XRD, TEM, nitrogen adsorption and TGA/DSC were used to characterize the sample. Charge/discharge tests show that the MEG exhibits a rate capacity as high as 397 mAh/g at 0.2 C and 250 mAh/g at 1.6 C.

## 1. Introduction

Portable electronic devices, such as mobile phone and notebook computer, are becoming more and more popular, and even electrical vehicles have already been put into applications. They have more demands for lithium ion battery in all respects, such as the capacity, the performance under high charge/discharge rate, the stability under cycling, safety, cost, etc. Natural flake graphite has been playing a dominating role in the field of the anode material in lithium ion battery due to its excellent electrochemical performance and low cost. However, there are still two issues limiting its further development: poor cycle stability resulting from the volume change during the intercalation and deintercalation of lithium ions, and relatively low theory capacity (372 mAh/g) decided by its microstructure [1–3].

Up to now, all kinds of modification methods including mild oxidation [4–7], metals or metal oxides deposition [8], coating [9,10], expansion [11–14] and edge exfoliation [15], have been applied to improve the performance of natural graphite as anode material in lithium ion battery, among which mild expansion was an effective method put forward by our group [14]. By the process of intercalating reaction and deintercalating heat treatment, the cycling performance of the obtained mildly expanded graphite is greatly improved. However, the temperature of the heat treatment is as high as 360 °C and the time is as long as 28 hours because of the high boiling point of sulfuric acid, resulting in some trouble in its industrial manufacture. What's more, the sulfur remaining in the mildly expanded graphite is also pollutive.

In the present work, we synthesized mildly expanded graphite using perchloric acid as both intercalating and oxidizing agent. Because of its stronger oxidizing effect compared with sulfuric acid, perchloric acid can be intercalated to the graphite without other strong oxidizing agent. In addition, due to its relatively lower boiling point, the deintercalating process can be performed under lower temperature in less time. Moreover, the capacity of the obtained mildly expanded graphite is improved, indicating that the two limitations and other problems relating to the mild expansion were fundamentally solved.

## 2. Experimental

Raw materials were used as follows: spherical natural flake graphite (NFG) from Jixi, China with carbon content of 99 wt % and average particle size of 22.4 μm, commercially available perchloric acid (72 wt %). Some previous researches about expanded graphite [16–18] were referred to determine parameters chosen in the synthesis, but the treatment afterwards was quite different. In a typical synthesis, NFG was added into the solution of perchloric acid in a three-neck flask, and stirred at 120 °C. The mass ratio of graphite and perchloric acid was 1:4. After the reaction for 0.5 h, the mixture became glutinous slurry indicating that the reaction was completed. The obtained $HClO_4$–GIC was washed and centrifugally separated repeatedly until the pH value became 4 and then dried at

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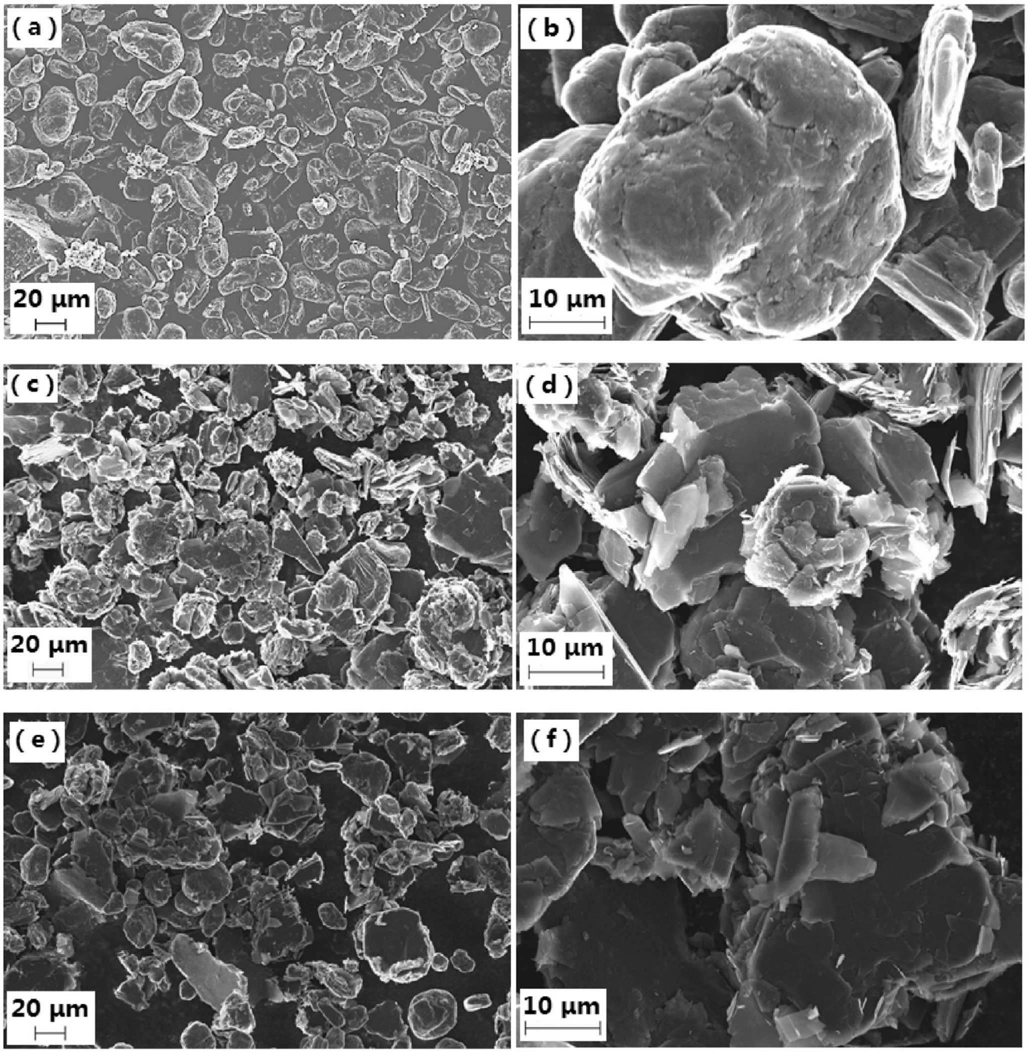

**Fig. 1.** SEM micrographs of NFG (a, b), washed $HClO_4$–GIC (c, d) and MEG (e, f).

100 °C. Finally, the mildly expanded graphite (MEG) was obtained by heating the $HClO_4$–GIC up to 200 °C with the ramping rate of 1.5 °C/min and the holding time of 2 h.

The working electrode was prepared by casting the slurry of mildly expanded graphite (MEG, 85 wt %), polyvinylidene fluoride (PVDF, 10 wt %) and carbon black (5 wt %) dissolved in *N*-methylpyrrolidone (NMP) on a copper foil. The foil was dried at 80 °C for 8 h and then dried in vacuum at 120 °C for 12 h. Lithium foil was used as the counter electrode and 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1, v/v) served as the electrolyte. The working and the counter electrodes were separated with Celgard 2400 separator. The cell was galvanostatically cycled between 0 and 1.50 V *vs.* $Li/Li^+$.

## 3. Results and discussion

Fig. 1 shows the morphologies of NFG, washed $HClO_4$–GIC and MEG. The particle of NFG is spherical and its surface is quite smooth. However, after the reaction, many folds and cracks appeared and still existed even after heat treatment, making the particles not only rough but also irregular. The specific surface area increases from 4 $m^2/g$ to 36 $m^2/g$ according to the result of nitrogen adsorption test, regardless of the contribution of closed pores which cannot be detected in this test [19]. The mean particle size and expansion volume also increase from 22.4 µm and 0.97 ml/g to 42.7 µm and 3.89 ml/g, respectively. Obviously, the surface of MEG is rougher. This change will influence its performance as anode material of lithium ion battery in two opposite ways. The first cycle columbic efficiency will be greatly decreased because there will be more surfaces covered by the solid state-electrolyte interface film. On the contrary, its capacity will be improved because more defects will be introduced to the particle, which will provide more space for lithium ions during charging and discharging.

TEM is used to further investigate the defects of the as-synthesized MEG. The TEM micrographs of NFG and MEG are shown in Fig. 2. It is easy to observe the nanopores with diameter about 3–5 nm in MEG. There is a great opportunity that during the process of mild expansion, the percloric acid was decomposed and finally deintercalated from the $HClO_4$–GIC. The deintercalation process is also verified by the result of TGA/DSC test, which is shown in Fig. 3. As we can see, there is a remarkable exothermic peak around 175 °C in the heating curve of the $HClO_4$–GIC, indicating the deintercalation of perchloric acid. In addition, the test of Energy Dispersive Spectrometer (EDS) shows that the weight percentages of chlorine in the $HClO_4$–GIC unwashed, $HClO_4$–GIC washed completely and mildly expanded graphite are 3.31%, 0.34% and 0.17%. This indicates that perchloric acid is suitable in this work due to its low boiling point, strong oxidizing property and high tendency to deintercalation. Comparing to other works using sulfur acid and other