Effects of Hydrothermal Oxidation Temperature on the Performance of Natural Graphite as an Anode for Lithium-Ion Cells

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Abstract: *Natural graphite (NG) was hydrothermally oxidized at room temperature, 100 ℃ and 200 ℃ respectively to analyze the effects of temperature on the electrochemical performance of the NG as an anode for lithium ion cells. Charge/discharge results showed that the sample treated at 100 ℃ exhibited the highest initial intercalation capacity of 340.1 mAh/g and a Coulombic efficiency of 89.9%, while the sample treated at 200 ℃ showed the highest capacity retention of 96.5% after 20 charge/discharge cycles. X-ray photoelectron spectra revealed that groups containing oxygen were present on the surface of all samples, which explains why the performance of the sample treated at room temperature shows slightly improved electrochemical performance that can be further improved by increasing the oxidation temperature.*

Keywords: Lithium-ion cell; Anode; Natural graphite; Surface oxidation; Coulombic efficiency

1. INTRODUCTION

The rapid development of electric vehicles (EV) and hybrid electric vehicles (HEV) drives the search for low-cost, safe, rechargeable batteries with high voltage, capacity, and rate capability [1]. The price of lithium ion cells is mainly determined by that of the raw materials (including the cathode, anode, current collector, electrolyte, separator and case) and the manufacturing process. The latter is difficult to be simplified because the battery packs for HEV and EV require cells packed in series and/or parallel, needing the lithium ion cells with high performance and consistency. The production of such cells dictates that the degree of accuracy and automation of machines for their manufacture should be much improved compared with those of normal lithium ion cells. Thus the raw materials have been concentrated on in extensive attempts to decrease the price of lithium ion cells. Because of its abundance and low price, natural graphite (NG) has attracted a lot of attention as a potential anode material for lithium ion batteries used in HEVs and EVs[2–6]. The combination of a NG anode and LiFePO$_4$ cathode is a promising approach to decrease the price of lithium ion cells [7,8]. However, NG anodes have exhibited disadvantages, such as low initial Coulombic efficiency and poor cycle performance. These performance may be improved by surface oxidation [5, 9-11], sulfuration [12], fluoration [13,14] or surface coating [15-17]. Wet oxidation is a simple, low cost method for modifying the surface of NG, and ammonium peroxydisulfate $((NH_4)_2S_2O_8)$ is a common oxidant to use [11]. The oxygen atoms in the air readily bind to dandling bonds on the edge of the NG face to form groups containing oxygen atom(s). Thus, oxidation at room temperature with $(NH_4)_2S_2O_8$ may not achieve the most effective modification. The oxidizability of an oxidant increases with temperature. Shui *et al*. [18] demonstrated that when HNO$_3$, H$_2$SO$_4$ and CH$_3$COOH were used as the oxidants, the oxygen content in NG could be increased from 3.89% in the raw material to 8.21% in the oxidized one if the temperature was increased to 98 ℃. In this study, the effects of hydrothermal temperature on the structure of graphite were analyzed and the charge/discharge performance of NG was discussed from the perspective of its application as an anode in lithium ion cells.

2. EXPERIMENTAL

2.1. Sample Preparation
2.1.1. Oxidation of NG

NG which was from the natural graphite mineral and not treated by any method, was supplied by BTR New Energy Material Co.

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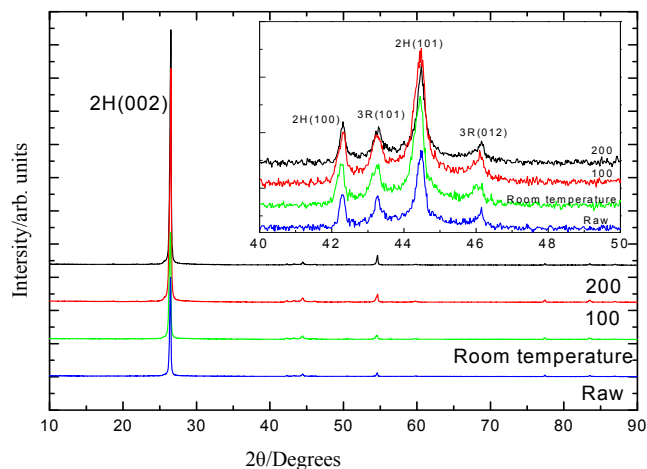Phone/Fax.: +86-543-3195583

Figure 1. XRD patterns of the NG samples

Ltd. (China). It was oxidized by adding the saturated solution of $(NH_4)_2S_2O_8$ into H_2SO_4 (1 M) and being treated in hydrothermal autoclaves at room temperature, 100 ºC or 200 ºC respectively for 24 hours. The product was purified by filtration, and rinsed with water until the pH reached 7 and then, it was dried with vacuum being lower than 2×10^4 Pa at 100 ºC.

2.1.2. Physical Characterization

The morphologies of the sample and electrode were observed using a scanning electron microscope (SEM) (S4800, Hitachi, Japan) operating at 15 kV. The surface disorder of the sample was then analyzed using a Raman spectrometer (LabRam I, Dilor, France) with the laser power of 4 mW and scanning time of 10 s. Subsequently, the structure of the oxidized graphite was measured by X-ray diffraction (XRD) (X'pert PRO, Panalytical, Netherlands). The surface functional groups containing oxygen were measured by X-ray photoelectron spectroscopy (XPS) using a PHI Quantum 2000 Scanning ESCA microprobe with monochromatic Al Kα radiation (1486.6 eV).

2.2. Electrochemical Measurement

A slurry of NG was prepared by ball-milling a mixture of 10 wt.% polyvinylidene fluoride (PVdF) together with an adequate amount of N-methyl-2-pyrrolidone (NMP) for 2 hours. The slurry was coated onto copper foil with an area of 1 cm^2 and then dried at 100 °C under vacuum being lower than 2×10^4 Pa for more than 10 hrs to obtain an electrode for measurement. CR2025 coin-type cells were assembled in an argon-filled glove box (Etelux 2000, China) where both moisture and oxygen levels were kept at less than 1 ppm. LiPF$_6$ (1 mol/L) in ethylene carbonate and dimethyl carbonate (EC-DMC, 1:1 v/v) was used as the electrolyte and lithium foil was used as the counter electrode. Charge/discharge cycles were performed using a Neware® instrument (China) with a stable current of 0.1 C (based on the theoretical capacity of graphite).

3. RESULTS AND DISCUSSION

XRD patterns of the NG samples (Fig. 1) show a characteristic of highly crystallized graphite [19]. Several peaks in the region from
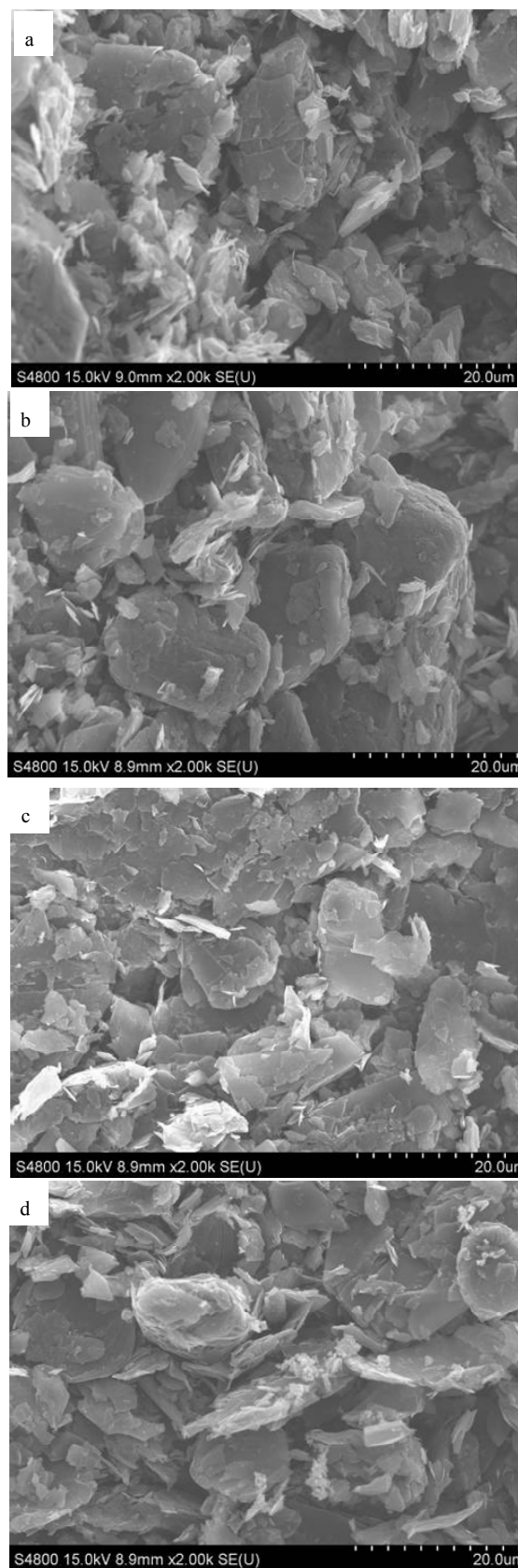

Figure 2. SEM images of the four NG samples (a) raw, and oxidized at (b) room temperature, (c) 100 ºC, and (d) 200 ºC

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40º to 50º are consistent with NG, including peaks at 42.5º H(100) and 44.5º H(101) that signal a hexagonal structure, and at 43.5º R(101) and 46º R(102) that indicate a rhombohedral structure [20]. The intensity of the peaks is almost constant for the four samples, suggesting that the content of the rhombohedral phase did not change significantly by oxidation.

SEM images of the four NG samples are shown in Fig. 2. The samples showed flake morphology but some flakes naturally aggregated to form spheres. Some small graphite particles filled the spaces between the spheres in the samples. Oxidation may cause exfoliation of the spherical samples due to the H_2SO_4 intercalation,
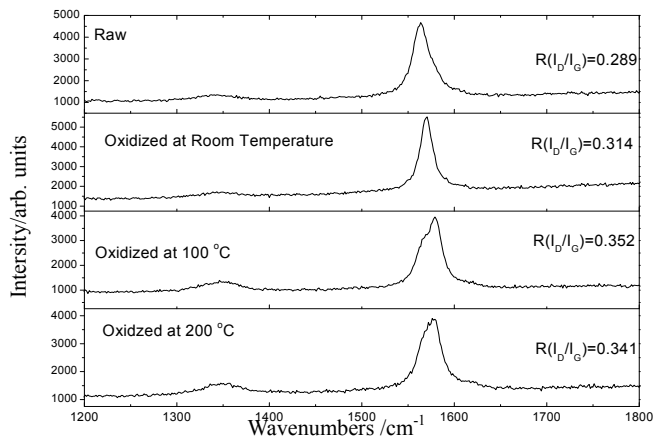

Figure 3. Raman spectra of the NG samples

especially when the oxidation is performed at 100 or 200 ºC. The small graphite particles resembled those arising from mild exfoliation, like from treatment with H_2SO_4 [20]. Increasing the proportion of small particles in the sample increases its specific surface area. The surface disorder in the samples was further analyzed by Raman spectroscopy (Fig. 3).

The Raman spectra of the four NG samples exhibit peaks at 1580 cm^{-1} (G band) and 1360 cm^{-1} (D band). The ratio of the intensity of D band divided by that of the G band reveals the surface disorder of the sample [17]. Calculated results show that the value of this ratio (R) has increased after oxidation. The ratio of the raw material, and samples oxidized at room temperature, 100 ºC and 200 ºC is 0.289, 0.314, 0.352 and 0.341, respectively. This indicates that the surface becomes more disordered after oxidation, which is consistent with the SEM observations shown in Fig. 2. The surface disorder of the sample oxidized at 200 ºC was less than that of the sample oxidized at 100 ºC because the oxidant $(NH_4)_2S_2O_8$ may be decomposed at 200 ºC. As a result, the actual oxidation time of the sample heated at 200 ºC is reduced to be less than that of the sample oxidized at 100 ºC.

In order to further analyze the groups forming on the surface of graphite, the samples were investigated by XPS and the oxygen spectra were further fitted by XPSPEAK software with a Lorentzian-Gassian value of 80% as shown in Fig. 4. Peaks at 534.1, 533.2, 532.3 and 530.9 eV correspond to the oxygen in hydroxyl groups, ether oxygen, carboxylic oxygen in –COOR (R=H and alkyl) and carbonyl oxygen atoms, respectively [9]. It was found that the peak corresponding to carbonyl oxygen atoms at 530.9 eV disappeared after oxidation. Relative percentages calculated from
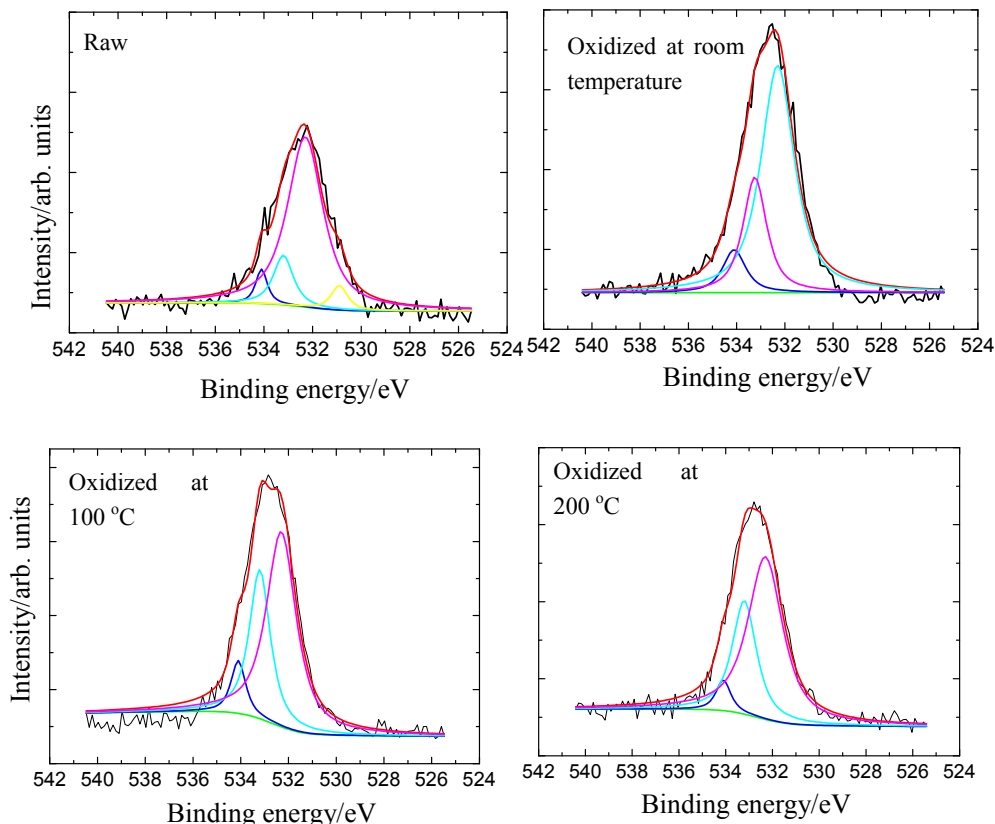

Figure 4. XPS O1s spectra of the NG samples and deconvolution of the corresponding broad peak between 526 and 540 eV
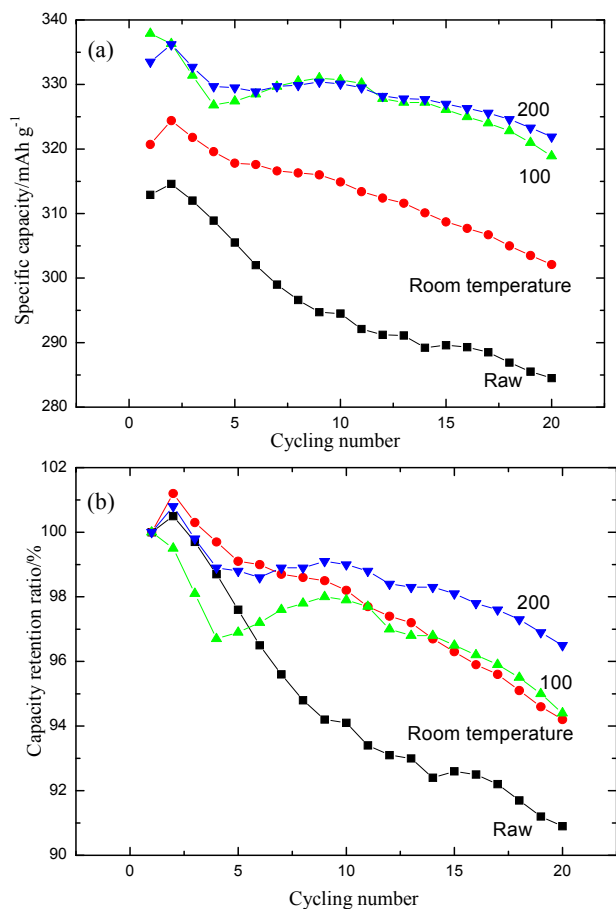
Figure 5. Cycling performance of the NG samples, (a) change in capacity with cycling number; (b) change in the capacity retention ratio with cycling number

of the area of the peaks are shown in Table 1. The percentages corresponding to ether oxygen have increased while those corresponding to –COOR have reduced after oxidation. The percentage corresponding to hydroxyl groups is relatively constant after oxidation.

The cycle performance of the four NG samples is shown in Fig. 5. The initial intercalation capacity of the samples has increased after oxidation. The raw material shows an initial intercalation capacity of 312.9 mAh/g, while that of the samples oxidized at room temperature, 100 ºC and 200 ºC is 324.8, 340.1 and 333.5 mAh/g, respectively. However, after 20 cycles their capacity has decreased to 284.5, 304.2, 309.3 and 321.9 mAh/g, respectively. The reversible capacity has been enhanced by oxidation because the oxidized samples have exhibited a third binding site; moreover, Li could bind to armchair, zigzag, or other edge sites in the carbon sample [11]. The sample oxidized at 100 ºC shows the highest initial capacity but the capacity of the sample oxidized at 200 ºC is the highest after 20 cycles. The capacity retention is shown in Fig. 5(b), indicating that the cycling stability has been improved by oxidation. The reason is that the wettability of the sample has been improved by oxidation, which could suppress the co-intercalation of solvent molecules into the layers of graphite, reducing the capacity decay caused by the changes of the crystal structure.

Table 1. Relative percentages of peaks in the O1s spectra of NG samples

Sample	O_{1s}			
	534.1	533.2	532.3	530.9
Raw	5.1	12.5	77.2	5.2
Oxidized at room temperature	9.5	23.8	66.7	0
100 ºC	7.9	32.2	59.9	0
200 ºC	5.1	30.9	64	0

The initial Coulombic efficiency has been increased after oxidation, from 83.2% for raw NG to 84.7%, 89.9% and 86.9% for the samples oxidized at room temperature, 100 ºC and 200 ºC, respectively. This improvement can be attributed to the increased content of surface groups containing oxygen. In particular, the content of ether oxygen has increased after oxidation (as shown in Table 1). Ether is one of the components of the solid electrolyte interphase (SEI) [21], therefore, the formation of ether groups by surface modification could naturally decrease the consumption of electrolyte, which accordingly has improved the Coulombic efficiency of the first cycles.

The above results show that increasing the oxidation temperature is an effective approach to improve the cycle performance of graphite anodes, but due to the decomposition of the oxidant, the cycle performance of the sample oxidized at 200 ºC is not significantly better than that of the sample treated at 100 ºC. The results also have confirmed that selectively increasing the content of components present in the SEI (i.e., the proportion of ether groups) could improve the electrochemical performance of NG.

4. CONCLUSIONS

NG was oxidized in solution at room temperature, 100 or 200 ºC. The sample oxidized at room temperature shows a reversible capacity and the initial Coulombic efficiency has been increased slightly compared with raw NG. The reason is that dangling bands on the surface of graphite can react with oxygen in the air to form surface groups similar to those formed upon oxidation by an oxidant. The reversible capacity and cycling stability can be further improved by increasing the oxidation temperature. The sample oxidized at 100 ºC shows the highest initial reversible capacity and Coulombic efficiency of 340.1 mAh/g and 89.9%, respectively. The sample treated at 200 ºC shows the best capacity retention of 96.5% after 20 cycles. The improved electrochemical performance is attributed to the increase of groups containing oxygen on the surface of graphite after oxidation, which could decrease the consumption and co-intercalation of electrolyte.

5. ACKNOWLEDGMENTS

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