JOURNAL OF Materials CHEMISTRY

A green method for the preparation of anode materials for lithium ion batteries

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Received 7th September 2000, Accepted 17th January 2001
First published as an Advance Article on the web 21st February 2001

Here we demonstrate for the first time that an anode material for lithium ion batteries can be satisfactorily prepared by a green method. By selecting benign and easily recycled oxidants, solutions of H_2O_2 and $Ce(SO_4)_2$, the electrochemical performance of a natural graphite anode material can be markedly improved. Through thermogravimetric analysis, differential thermal analysis, X-ray photoelectron spectroscopy, high resolution electron microscopy and measurements of lithium capacity it was found that the surface structure of the natural graphite was modified with a dense layer of oxides, which could prevent the co-intercalation of solvent molecules. In addition, the stability of the graphite crystal was improved and the decomposition of electrolyte molecules was prohibited. Furthermore, a large number of nano-channels were introduced by oxidation, which favored lithium intercalation and de-intercalation. The reversible lithium capacity was enhanced from 251 to >330 mA h g^{-1}, and no capacity fading was observed in the first 10 cycles. This green method is also highly efficient and economical, the process can be performed below 60 °C.

Introduction

Since the first introduction of a lithium ion battery concept to the public in the early 1990s,[1] much research effort has been directed to its electrode materials, especially anodic ones. In combination with other advantages, lithium ion batteries avoid the environmental problems associated with the heavy metals used in traditional rechargeable batteries, *e.g.* Pb, Cd and Ni. To date, a wide variety of anode materials have been studied, including graphitic carbon,[1] amorphous carbons,[2–5] nitrides,[6] tin oxides[7–9] and novel alloys.[10] However, to our knowledge, graphitic carbon is still the only anode material which is commercially available, other materials developed have not been viable from the viewpoint of practical applications, cycle life being a particularly limiting factor.[9,11] In the case of graphitic carbon, it is known that its manufacture requires high temperature (>2000 °C) and produces some environmentally unfriendly gases such as CO, CO_2 and C_xH_y. It is natural, therefore, to seek new processes for the manufacture of anode materials which will have less adverse effects on the environment and require lower energy consumption.

Due to its high abundance, natural graphite was initially studied as a potential anode material for lithium ion batteries.[12] However, its poor cycling behavior, a consequence of the easy movement of the graphene planes along the *a*-axis direction during the intercalation and de-intercalation of lithium, in addition to the problem of solvated lithium intercalation, have since ruled this material out of practical lithium ion battery applications.[13,14] Other methods for modifying synthetic and natural graphites have been tested, *e.g.* gas-phase oxidation by oxidizing gases, for example oxygen, air and ozone,[15–17] but it is difficult to obtain satisfactory anode materials on a tonnage scale since the uniformity of the product is not easy to control. Recently, it was found that a liquid-phase oxidation, using solutions of strong oxidants such as HNO_3 and $(NH_4)_2S_2O_8$, can be empolyed to modify the electrochemical properties of graphite. It achieved the same goal as the gas-phase oxidation, and the reversible lithium capacity did not fade.[18,19] However, this method is still environmentally unfriendly.

The earlier work mentioned above suggests that the oxidation treatment is a good method for the modification of the electrochemical properties of carbonaceous anode materials. Here, for the first time, we tested two kinds of oxidants, H_2O_2 and $Ce(SO_4)_2$, which can be easily re-cycled by electrolysis, for the modification of a natural graphite. Our preliminary results showed that the products obtained had good electrochemical performance as an anode material in lithium ion batteries and this method would also be environmentally benign. Moreover, the modification can be performed at a low temperature ($\leqslant 60$ °C) with low energy consumption.

Experimental

A common natural graphite from China with a carbon content of $>99\%$, an interlayer distance, d_{002}, of 3.351 Å, a crystal size, L_c, of 120 Å and an average particle diameter of 17 μm (designated as A) was dipped into either an aqueous solution of 1 M H_2O_2 or a saturated solution of $Ce(SO_4)_2$. The samples obtained were then heated at 60 °C for 8 h, followed by rinsing with water and drying. The dried products were named as A1 and A2, respectively.

X-Ray photoelectron spectroscopy (XPS) was conducted on an ES-300 spectrometer, and the relative contents of O and C at the surface of the natural graphite were calculated on the basis of their photoionization cross-sections and the integrals of their X-ray photoelectron intensities. Thermogravimetric and differential thermal analysis (TG-DTA) was performed on a PCT-1 instrument (Beijing Analytical Instrument Co.) under air with a heating rate of 20 °C min^{-1}. High resolution electron micrographs (HREM) were obtained on a JEM-200CX (JEOL Ltd.) instrument under a high vacuum.

The reversible lithium capacity and the cycling behavior were

DOI: 10.1039/b007247h

tested using lithium foil as both the counter and reference electrode, with a 1 M $LiClO_4$ solution in a mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) (v/v = 3 : 7) as the electrolyte and a homemade porous polyproylene film as the separator. The anode was fabricated on a weight basis of 95% active anode material and 5% binder polyvinyl difluoride dissolved in *N*,*N*-dimethylformamide. After mixing, the paste was kneaded and rolled into a foil. Pellets with a diameter of *ca.* 1 cm were cut from the foil and dried at 120 °C under vacuum overnight prior to cell assembly in an argon box. The electrochemical measurements were performed with a Land cell test instrument (Land Company, Wuhan, China), and cells were cycled galvanostatically at a constant current density of about 40 mA g^{-1} between 0.0 and 2.0 V *vs.* Li^+/Li.

Results and discussion

It is known that there are a lot of imperfect structures present in graphite such as sp^3-hybridized carbon atoms,[20] edge carbon atoms[13,14] and carbon chains. These imperfections are especially prominent in natural graphite due to its incomplete graphitization during the natural evolution process. These kinds of structures are susceptible to attack by oxidants and will be removed during reaction with solutions of H_2O_2 and $Ce(SO_4)_2$. After the removal of these imperfections, the natural graphite will become much more stable. Fig. 1 shows TG and DTA curves for natural graphite before and after oxidation. At first, the weight decreased slowly because of the thermal decomposition of some oxides and a slight oxidation. Later, when the temperature exceeded 650 °C, extensive oxidation clearly occurred and the DTA curves increased. When the combustion reaction occurred rapidly, the DTA curves peaked. Exothermal peaks shifted from 742 to 752 °C, after oxidation by solutions of H_2O_2 and $Ce(SO_4)_2$, suggesting an improvement in the stability of the graphite crystal even though this shift is slight. In addition, this improvement in the stability was also reflected in the weight losses of graphite at the exothermal peak temperature. In the case of A1 and A2, the weight losses are 18 and 19%, respectively. In contrast, the weight loss for A is 23% at 742 °C. For sample A2, Ce^{4+} was clearly removed from the natural graphite after rinsing as any remaining Ce^{4+} would catalyze the exothermal combustion reaction and lead the exothermal peak to shift to low temperature, as observed for Ni and Co.[17]

Imperfect structures are usually located at the surface and surrounding graphite crystals, therefore, the surface structure will change after the oxidation treatment. XPS spectra of O_{1s} in the samples A, A1 and A2 are shown in Fig. 2 and partial results are summarized in Table 1. The spectra indicate that the oxygen atoms are present as four different species before and after oxidation: hydroxyl group oxygens, ether oxygens, carbonyl oxygens in –COOR (R = H and alkyl) and carbonyl oxygens in acetone. These species correspond to binding energy peaks at 534.1, 533.2, 532.3 and 530.9 eV, respectively.[21,22] X-Ray photoelectron spectra of C_{1s} in the samples A, A1 and A2 are shown in Fig. 3, which indicates that the carbon atoms also consist of four different of species: carbonyl carbons in acetone, carbonyl carbons in –COOR (R = H and alkyl), ether carbon and carbon atoms in graphene planes, which correspond to binding energy peaks at 288.9, 287.2, 285.9 and 284.4 eV, respectively.[21,22] In the case of natural graphite before the oxidation treatment, it is known that it will chemically and physically absorb water, oxygen and CO_2. Moreover, this kind of natural graphite was dipped into KOH solution to remove minerals and four kinds of oxides were consequently observed similar to the results for samples A1 and A2.[23] However, we could not obtain any clear indication as to which kind(s) of compound(s) was(were) mainly changed. One reason for this is that the oxidation reaction was complicated; another one is perhaps that the assignment and devolution of these kinds of species resulted in large errors. Perhaps the acetone groups play an important role since their relative content increased after the oxidation. One thing is clear, the loosely absorbed oxygen

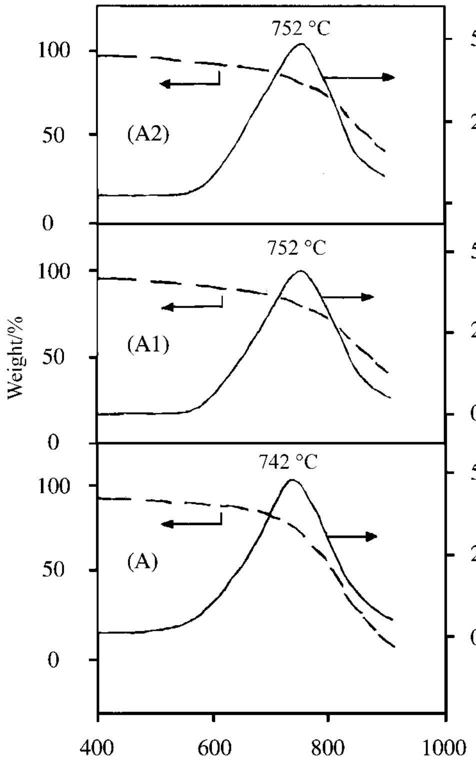


Fig. 1 Thermogravimetric (TG, dashed line) and differential thermal analysis (DTA, solid line) of the samples A, A1 and A2.

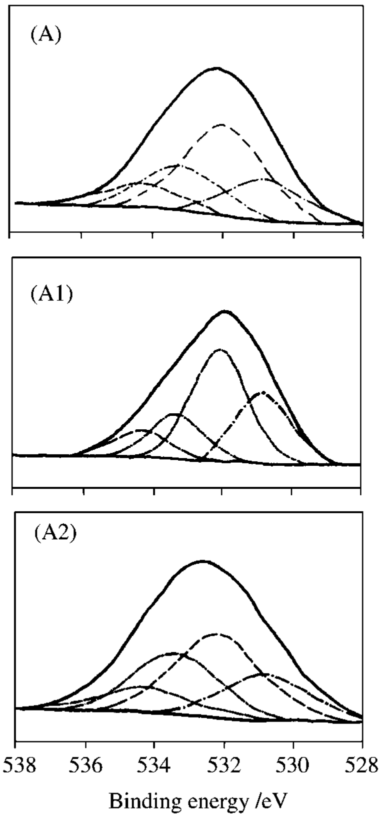


Fig. 2 X-Ray photoelectron spectra of O_{1s} in the samples A, A1 and A1.

Table 1 Results from XPS for samples A, A1 and A2

Sample	Oxidant	Weight loss (%)	O Content (%)	C Content (%)	Relative oxygen content (%) at different binding energy peaks (eV)[a]				Relative carbon content (%) at different binding energy peaks (eV)[a]			
					534.1	533.2	532.3	530.9	288.9	287.2	285.9	284.4
A	—	—	4.11	95.89	12.68	23.20	45.26	18.86	2.99	5.34	10.29	81.38
A1	H_2O_2	1.96	5.04	94.96	12.11	27.46	39.68	20.75	3.20	5.52	11.90	79.38
A2	$Ce(SO_4)_2$	2.09	4.61	95.39	10.67	17.57	44.13	27.63	3.29	5.63	7.19	83.38

[a] The peaks shown correspond to the four oxygen/carbon species discussed in the main text.

atoms were removed and refreshed with a layer of oxides that bonded more firmly with the carbon structure[15,17] since the results in Table 1 show that the oxygen content at the surface increased and there was a slight weight loss after the oxidation treatment. In another experiment, we attempted to re-oxidize the A2 sample and found that this time the weight loss was 0.90%, smaller than that from the first oxidation treatment, 2.09%. This clearly indicates that the active imperfect structures existed in the natural graphite and were removed during the above oxidation treatment though their amounts were small and no method has been found to effectively detect them.

HREM micrographs of the samples A and A1 are shown in Fig. 4. Before the oxidation treatment, there are micropores in the natural graphite A whereas none were observed in the STM of high quality natural graphite.[15] This difference is due to the purification process used to remove minerals. After the oxidation treatment, nanochannels could be clearly identified from sample A1. During the oxidation process, the pitting and channelling processes were initiated from imperfect structures, and later developed into the graphene structure from edge planes or basal planes.[24] This indicates that the number of nano-channels increased after oxidation with the H_2O_2 solution, which is consistent with the observation from the oxidation of an activated carbon.[25] This increase perhaps resulted from the elimination of some lattice vacancies and impurities similar to the gas-phase oxidation.[15,17] It will be also true for the oxidation by $Ce(SO_4)_2$ since their oxidation potentials (E^o) are almost the same, 1.78 and 1.61 V for H_2O_2/H_2O and Ce^{4+}/Ce^{3+}, respectively.

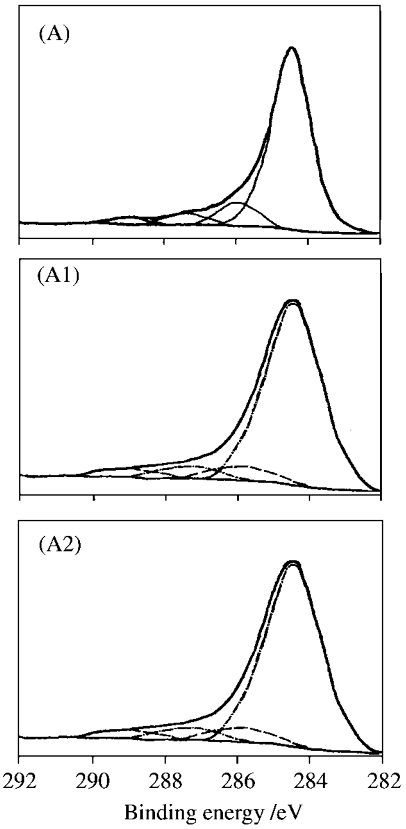
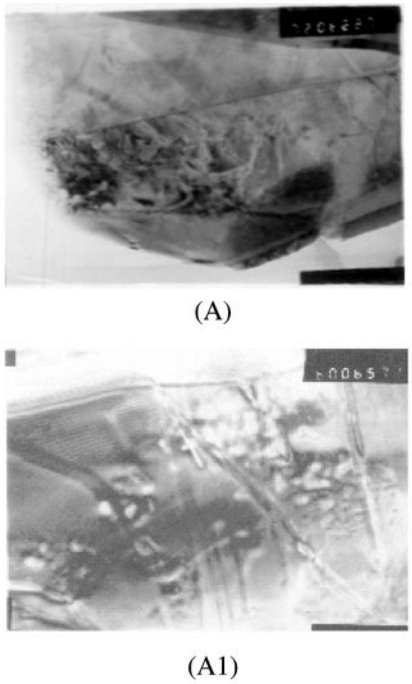


Fig. 3 X-Ray photoelectron spectra of C_{1s} in the samples A, A1 and A2.

After the oxidation treatment the reactivity of the natural graphite with organic solvents will be reduced due to an increase in the stability of the graphite crystal and the removal of some active imperfect structures, therefore, the irreversible capacity will decrease.[26,27] In addition, more nano-channels were introduced, which provides more inlets and outlets for lithium during the charge and discharge processes, and more lithium atoms can be stored in the inner micropores as lithium molecules or clusters.[11,15,28–30] Furthermore, a dense layer of oxides such as hydroxyl, ether and carbonyl groups formed at the surface during oxidation will produce a passivating film to prevent the co-intercalation of electrolyte molecules such as EC and DEC,[17] thus the exfoliation of the graphene planes and their movement in the *a*-axis direction will be prevented and the cycling behavior will be improved. Consequently, the electrochemical performance of the modified natural graphite as the anode material for lithium ion batteries will be much improved. Discharge and charge profiles in the first cycle and discharge profiles in the second cycle of the samples A, A1 and A2 are shown in Fig. 5. As mentioned above, the electrochemical properties of common natural graphite A before oxidation are very poor: its reversible lithium capacity is only 251 mA h g^{-1} while that of a high quality natural graphite such as NG-7 can be up to 372 mA h g^{-1}, *i.e.* the level of LiC_6.[12,15] In contrast, after the oxidation the reversible lithium capacity of the


(A)

(A1)

Fig. 4 High resolution electron micrographs of the samples A and A1 with sizes of 310 × 100 nm.

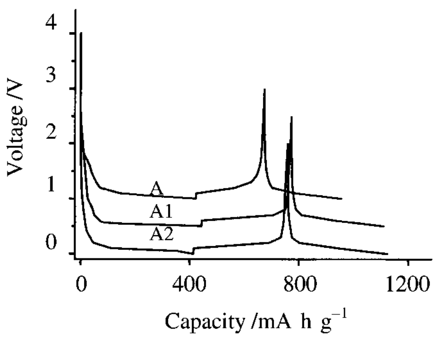


Fig. 5 Discharge and charge profiles in the first cycle and discharge profiles in the second cycle of the samples A, A1 and A2. For clarity, voltages of A1 and A are shifted upwards by 0.5 and 1.0 V, respectively.

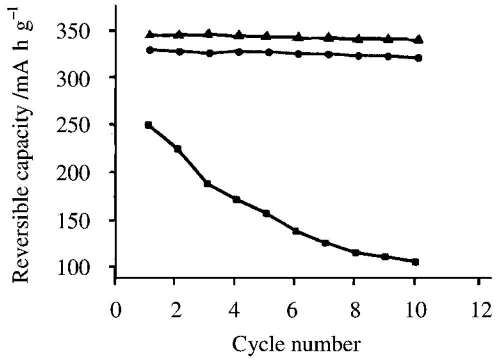


Fig. 6 Cycling behavior of the samples A (■), A1 (●) and A2 (▲) in the first 10 cycles.

common natural graphite is enhanced to 330 and 345 mA h g^{-1}, respectively. The capacity above 0.5 V in the first discharge process decreased markedly from 51 to 30 and 28 mAh g^{-1} after the oxidation. As to sample A, all lithium intercalated below 0.30 V could not be de-intercalated, suggesting that the solvent molecules co-intercalated during the intercalation process. In addition, the coulombic efficiency in the first cycle increased from 64 to above 80%. In the following cycles, the coulombic efficiency for the oxidized products A1 and A2 is close to 100%. On the other hand, that for the natural graphite A is only about 90%.

The cycling behaviors for the first 10 cycles of the samples A, A1 and A2 are shown in Fig. 6. In the case of A, its reversible lithium capacity faded very quickly due to the co-intercalation of the solvent molecules, the exfoliation of graphene planes and the movement of graphene molecules in the *a*-axis direction.[13,14] After the oxidation treatment, the reversible lithium capacity of samples A1 and A2 did not fade with cycle number.

Conclusion

We have found the use of H_2O_2 and $Ce(SO_4)_2$ as oxidants to be a reliable method for the modification of the electrochemical performance of a natural graphite. Both oxidants are highly effective for the removal of some imperfect structures, and thus improve the stability of the graphite crystal. The oxidation process which removes imperfect structures also introduces nano-channels into the structure. The surface of natural graphite was modified and covered with a dense layer of oxides to prevent the decomposition and the co-intercalation of electrolytes and the movement of graphene planes in the *a*-axis direction. Consequently, the reversible lithium capacity is enhanced from 251 to >330 mA h g^{-1}, and in the first 10 cycles, no capacity fading is observed. This method can be performed at a low temperature ($\leqslant 60$ °C), and is benign to the environment since both oxidants can be recycled. This green method is also exciting in terms of its economy and efficiency.

Acknowledgements

The financial support of the China Postdoctoral Foundation Committee and the Japan Sciences & Technology Corporation are much appreciated.

References

1 T. Nagaura, 4th International Rechargeable Battery Seminar, Florida, 1990.
2 K. Sato, M. Noguchi, A. Demachi, N. Oki and M. Endo, *Science*, 1994, **264**, 556.
3 S. Yata, H. Kinoshita, M. Komori, N. Ando, T. Kashiwamura and T. Harada, *Synth. Met.*, 1994, **62**, 153.
4 W. Xing, J. Xue, T. Zheng, A. Gibaud and J. Dahn, *J. Electrochem. Soc.*, 1996, **143**, 3482.
5 Y. P. Wu, S. B. Fang and Y. Y. Jiang, *J. Mater. Chem.*, 1998, **8**, 2223.
6 T. Shodai, S. Okada, S. Tobishima and J. Yamaki, *Solid State Ionics*, 1996, **86–88**, 785.
7 Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa and T. Miyasaka, *Science*, 1997, **276**, 1334.
8 W. Liu, X. Huang, Z. Wang, H. Li and L. Chen, *J. Electrochem. Soc.*, 1998, **145**, 59.
9 S. Machill, T. Shodai, Y. Sakurai and J. Yamaki, *J. Power Sources*, 1998, **73**, 216.
10 K. D. Kelper, J. T. Vaughey and M. M. Thackery, *J. Power Sources*, 1999, **81–82**, 383.
11 Y. P. Wu, C. R. Wan, C. Y. Jiang, S. B. Fang and C. Y. Jiang, *Carbon*, 1999, **37**, 1901.
12 T. D. Tran, J. H. Feikert, M. Y. Saidi and R. Koksbang, *J. Electrochem. Soc.*, 1996, **143**, 3466.
13 Z. Ogumi, S. K. Jeong, M. Inaba and T. Abe, IUPAC 8th International Symposium on Macromolecular-Metal Complexes, Waseda University, Tokyo, Japan, 1999, p. 45.
14 G. C. Chung, S. H. Jun, K. Y. Lee and M. H. Kim, *J. Electrochem. Soc.*, 1999, **146**, 1664.
15 E. Peled, C. Menachem and A. Melman, *J. Electrochem. Soc.*, 1996, **143**, L4.
16 T. Nakajima and K. Yanagida, *Tanso*, 1996, **174**, 195.
17 Y. P. Wu, C. Y. Jiang, C. R. Wan and E. Tsuchida, *Electrochem. Commun.*, 2000, **2**, 272.
18 Y. Ein-Eli and V. R. Koch, *J. Electrochem. Soc.*, 1997, **144**, 2968.
19 Y. P. Wu, C. R. Wan, C. Y. Jiang, J. J. Li and Y. X. Li, *Chin. Chem. Lett.*, 1999, **10**, 339.
20 L. C. F. Blackman, *Modern aspects of graphite technology*, Academic Press, London and New York, 1970.
21 Z. Wu and C. U. Pittman, *Carbon*, 1995, **33**, 597.
22 U. Zielke, K. J. Huttinger and W. P. Hoffman, *Carbon*, 1996, **34**, 983.
23 R. L. McCreery, in *Electroanalytical Chemistry: A Series of Advances*, vol. 17, ed. A. J. Bard, Marcel Dekker Inc., New York, 1991, p. 221.
24 C. Wong, R. T. Yang and B. L. Halpern, *J. Chem. Phys.*, 1983, **78**, 3325.
25 C. Moreno-Castilla, M. A. Ferro-Garcia, J. P. Joly, I. Bautista-Toledo, F. Carrasco-Marin and J. Rivera-Utrilla, *Langmuir*, 1995, **11**, 4386.
26 Y. P. Wu, C. Y. Jiang, C. R. Wan and E. Tsuchdia, *Electrochem. Commun.*, 2000, **2**, 626.
27 P. Yu, J. A. Ritter, R. E. White and B. N. Popov, *J. Electrochem. Soc.*, 2000, **147**, 1280.
28 A. Mabuchi, T. Katsuhisa, H. Fujimoto and T. Kasuh, *J. Electrochem. Soc.*, 1995, **142**, 1041.
29 Y. P. Wu, Y. X. Li, S. B. Fang and Y. Y. Jiang, *J. Mater. Sci.*, 1999, **34**, 4253.
30 Y. S. Han, J. S. Yu, G. S. Park and J. Y. Lee, *J. Electrochem. Soc.*, 1999, **146**, 3999.