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Preparation and Properties of Oxidized Graphite Anode Doped with Metal Ion for Lithium Ion Batteries

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Abstract: Chemical oxidation and metal intercalation of natural graphite was utilized to increase the capacity and enhance the cycle property of graphite anodes in lithium ion batteries.

Keywords: Lithium ion batteries, oxidation, intercalation, interlayer distance.

During the past years, there have been a lot of interests in the research of carbonaceous material as anode in lithium ion batteries[1-3]. Among them, natural graphite seems to be the most promising candidate for anode in lithium-ion batteries in terms of economy.

Figure 1 The effect of Different Contents of Mixed Acid on Interlayer Distance

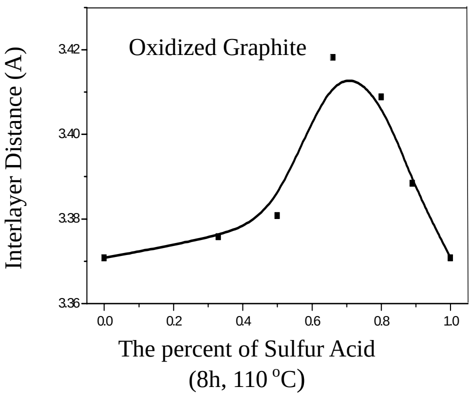
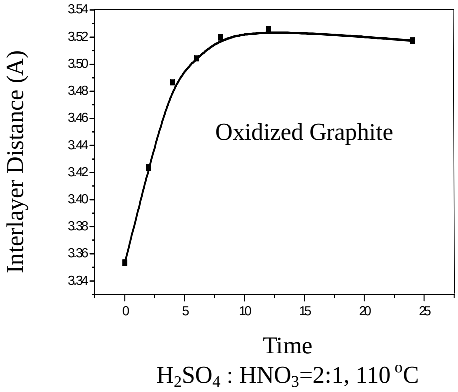


Figure 2 The Effect of Reacting Time On Interlayer Distance



However the raw natural graphite cannot be used for commercial purposes, because during process of charge and discharge, the solvent molecule would co-intercalate into the layers of natural graphite, which will result in the exfoliation of layers and the decrease of capacity. Some researchers have reported the carbon materials produced by mild oxidation of natural graphite whose initial discharge capacity exceeded the theoretical discharge capacity of graphite (372mAh/g)[4-6]. And other groups reported that the formation of KC_8 could increase the capacity of carbon anode[7-8]. In this paper, a new method of combining the wet oxidation with metal intercalation was introduced to increase the interlayer distance d_{002} and capacity of graphite anode in lithium ion batteries.

Figure 3 The effect of Temperature of Oxidation on Interlayer Distance

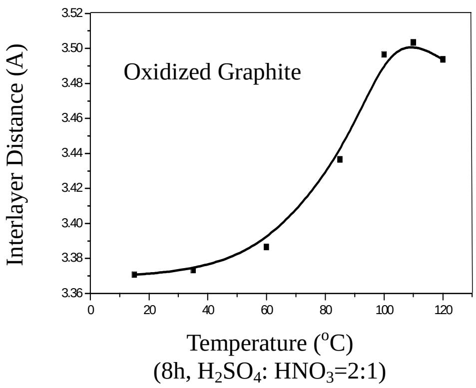
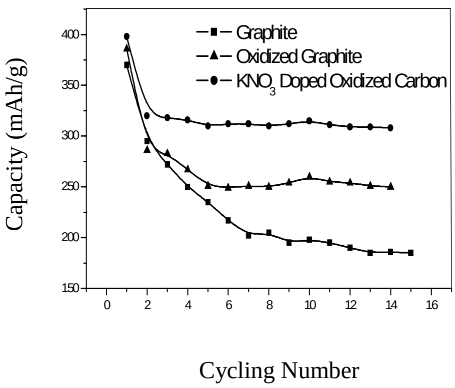


Figure 4 The Cycling Properties of Different Carbonaceous Materials

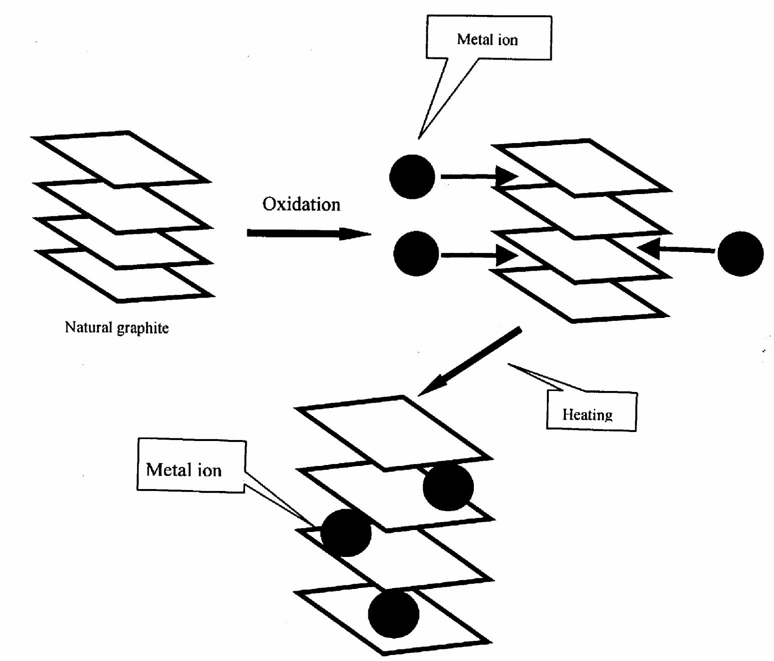


The oxidation of natural graphite was carried out by mixed acid of H_2SO_4 and HNO_3. Effects of experimental conditions on oxidation are presented by **Figure 1**, **2**, **and 3**. X-ray diffraction results show that optimum experimental conditions are: 100-110^{o}C, 6-8 hours, H_2SO_4 : HNO_3=2:1. Under such conditions, interlayer distance d_{002} is greatly increased, which will be helpful for metal ion to co-intercalate. Although the interlayer distance d_{002} of graphite was enlarged by oxidation, it returned to the original value of natural graphite 3.3558 Å when heated at 500^{o}C, which is a necessary step to prepare the usable oxidized material for anode of lithium ion batteries. The reason of such decrease is that heating makes intercalating molecules such as H_2O evaporate. In order to keep the interlayer distance, the metal salt KNO_3 was previously dissolved in HNO_3 and H_2SO_4. The interlayer distance of graphite was partially maintained after being heated. The mechanism is that the metal salt KNO_3 co-intercalated into the layer of graphite with other ions and molecules. And after heating at 500^{o}C, the KNO_3 was decomposed and existed in the state of K_2O, whose boiling point is >760^{o}C. The process of such co-intercalation was shown in **Figure 5** and the comparison of interlayer distance of different carbon materials was shown in **Table 1.**

Table 1 The Comparison of interlayer distance of different carbon materials

Carbonaceous Material	d_{002}(Å)	
	Unheated	Heated
Natural graphite	3.3558	3.3558
Oxidized graphite	3.5561	3.3558
Oxidized graphite doped with KNO_3	3.5174	3.3833

Figure 5 The process of metal ion co-intercalation



Oxidized Graphite doped with Metal Ion

The capacity and cyclic property of different materials were measured by constant-current cycling and result was shown by **Figure 4**, which indicates that the capacity of oxidized graphite doped with KNO_3 is greater than natural graphite and oxidized graphite. The possible mechanism is that the intercalation of K into graphite molecule increased both interlayer distance and space of lithium storage, which will result in the increase of capacity of graphite anode.

Figure 6(a) SEM Photograph of natural graphite (Untreated)

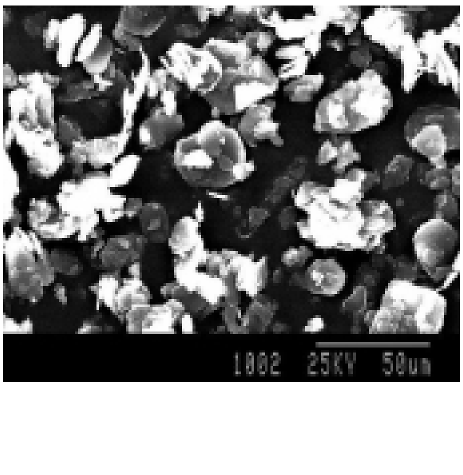
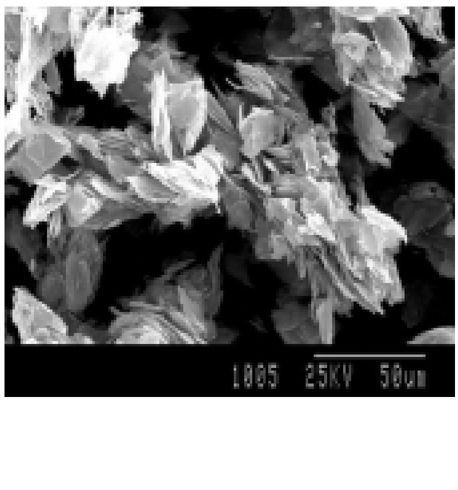


Figure 6 (b) SEM Photograph of oxidized graphite doped with KNO_3



At the same time, oxidized graphite doped with KNO_3 showed the good cycle property. **Figure 6(a)** shows the SEM photograph of natural graphite, which is mainly made of dense particles. **Figure 6(b)** shows the SEM photograph of oxidized graphite doped with KNO_3. From **Figure 6(b)**, we can see the dense particles of graphite became looser and showed three-dimensional layered structure. Such structure will increase the channels of lithium intercalation and therefore enhance the efficiency of charge and discharge.

References:

1. R. A. Huggins, *J. Power Sources*, **1999**, *81-82*, 13.
2. G. L. Che, B. B. lakshimi, C. R. Martin, E. R. Fisher, *Langmui*r, **1999**, *15*, 750.
3. R. A. Huggins, Solid State Ionics, **1998**, *113-115*, 57.
4. E. Peled, C.Menachem, D.Bar-Tow, A.Melman, *J. Electrochem. Soc.*, **1996**, *143*, L4.
5. E. E. Yair, Victor R.Koch, *J.Electrochem Soc.*, **September 1997**, *144*, 2968.
6. C.Menachem, Y.Wang, J.Flowers, E.Peled, S.G.Greenbaum, *J.Power Sources*, **1998**, *76*, 180.
7. R. Tossici, M. Berrettoni, M. Rosolen, R. Marassi, B. Scrosati, *J. Electrochem. Soc.*, **1996**,*143*, L64.
8. S. Sconocchia, R. Tossici, R. Marassi, F. Croce, B. Scrosati, *Electrochemical and Solid-State letters*, **1998**, *1* (4), 159.

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