

Note

STUDY ON THE OXIDIZED GRAPHITE MATERIAL COATED WITH N-DOPED PHENOLIC RESIN FOR LITHIUM ION BATTERIES

Yu-quan Zou, Chun-yang Wang, Qin-min Pan, Tong Zhao, Ling-zhi Wang* and Shi-bi Fang
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

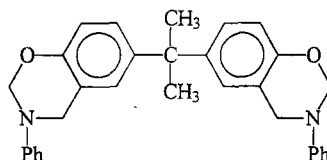
Abstract Carbon-coated oxidized graphite has been prepared by a liquid-state deposition method. Oxidized graphite was prepared by wet chemical oxidation. Oxidation increases the reversible capacity of graphite, but its initial charge and discharge efficiency was reduced. Phenolic resin was applied to form the disordered carbon layer on the oxidized graphite. The efficiency and reversible charge capacity were obviously increased. The morphology of carbon materials was investigated by SEM.

Keywords Lithium ion batteries, Phenolic resin, Oxidation

INTRODUCTION

During the past years, there has been much research work carried out on different kinds of carbonaceous materials used as anode in lithium-ion batteries. Among them, natural graphite seems to be the most promising candidate for anode material in lithium-ion batteries in terms of economy. Sanyo has already succeeded in applying natural graphite as the anode in the product^[1]. However raw natural graphite cannot be used for commercial purposes for it can seldom reach a capacity as high as the theoretical limit of lithium intercalated graphite. In order to increase the energy density, some researchers have reported about carbon materials produced by mild oxidation of natural graphite whose initial discharge capacity exceeded the theoretical discharge capacity of graphite (372 mAh/g)^[2-5]. At the same time, other groups investigated carbon material with a core-shell structure and a high energy density was obtained^[6-8]. In this study, wet oxidation was adopted to increase the discharge capacity. The efficiency and cyclic properties were improved by coating the oxidized graphite with disordered carbon produced from phenolic resin containing nitrogen.

EXPERIMENTAL



BA-a

The procedure for synthesizing BA-a is as follows: 0.2 mol aniline in 20 mL dioxane was added slowly to a mixture of 0.4 mol aqueous formaldehyde solution and 80 mL dioxane in a 500 mL three-necked flask, which was equipped with a thermometer, a condenser and a dropping funnel and cooled in an ice bath. The flask was cooled below 10°C by the ice bath. The mixture was stirred magnetically for 10 min before adding a solution of

* Corresponding author: Ling-zhi Wang (王玲治), E-mail: fangsb@infoc3.icas.ac.cn

Received April 17, 2001; Revised May 16, 2001; Accepted May 18, 2001

0.1 mol biphenyl-A in 100 mL dioxane. The reaction temperature was then raised, and the mixture solution was allowed to reflux for 6 h. The solvent was then removed under vacuum, and the resulted viscous fluid was dissolved in 200 mL ethyl ether. Purification of the precursor was accomplished by repeatedly washing its ether solution with NaOH solution^[9, 10].

The ordinary phenolic resin was prepared by the method of base-catalyzing.

The procedure of wet oxidation was performed as follows: 5 g graphite was treated with 120 mL H_2SO_4 (18 mol/L) and 40 mL HNO_3 (15.3 mol/L) at 110°C for 6 h followed by washing with distilled water until all the acid was removed, as indicated by pH titration of the filtered solution. The treated graphite was then placed in a tube furnace and heated to 800°C for 3 h under the protection of argon airflow.

The oxidized graphite coated with ordinary phenolic resin was prepared by the method of liquid-state deposition. The oxidized graphite and ordinary phenolic resin were stirred in the flask with alcohol as solvent. After 6 h stirring, the flask was heated at 50°C to evaporate the solvent. The treated sample was then solidified in an oven at 180°C for 4 h. The sample coated with solidified phenol resin was carbonized at 800°C for 3 h in a tubed-oven under protection of argon airflow.

The oxidized graphite coated with phenolic resin BA-a was prepared by the same method as described above. The oxidized graphite and BA-a were stirred in a flask with dioxane as the solvent. After stirring for 6 h, the flask was heated at 80°C to evaporate the solvent. The treated sample was then further reacted under fusion in the furnace at 200°C for 1 h. The sample coated with solidified phenolic resin was carbonized at 800°C for 3 h in the tube furnace under the protection of Ar airflow.

All electrochemical measurements were carried out using two-electrode test cells. The cells consisted of a lithium metal electrode and a graphite electrode. Graphite electrodes were prepared by spreading the graphite powder slurry (90 wt%) and poly (vinylidene fluoride) (10 wt%) dissolved in *N*-methyl-2-pyrrolidinone onto a copper foil substrate. The electrodes were then dried overnight at 105°C under vacuum and pressed between two flat steel plates at about 1 MPa pressure. Cells were assembled in an Ar-filled glove box. The cells were tested using computer-controlling constant-current cycles between 0.01 and 2.5 V at 25°C.

SEM measurements were performed using a Hitachi S-530. The surface areas of samples were determined by BET measurements ST-03.

RESULTS AND DISCUSSION

A sample designated as NG represents the natural graphite and that designated as OG represents the oxidized graphite. Phenolic resin A denotes the ordinary phenolic resin, while phenolic resin B denotes the phenolic resin prepared by the ring-opening polymerization of BA-a. OG-A and OG-B are the samples prepared by coating the oxidized graphite with phenolic resin A and phenolic resin B, respectively.

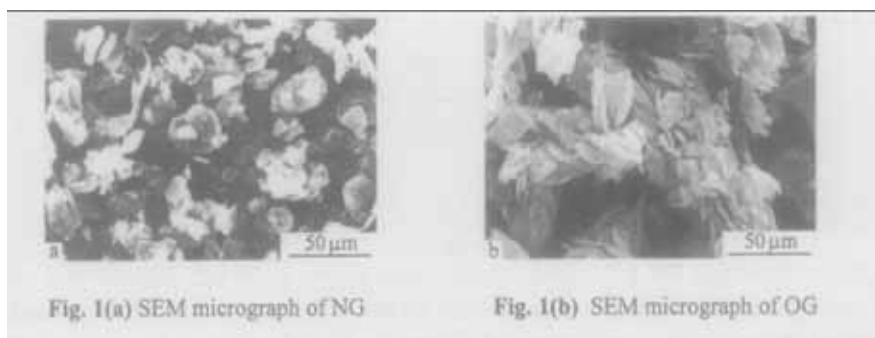


Table 1 presents some physical properties and corresponding electrochemical performance of graphite samples. From Table 1, it can be seen that the Q_1 and Q_R of sample OG were greater than natural graphite. It has been shown that oxidation can create nanoscopic cavities at the edge of planes of graphite^[4]. The increase of Q_1 and Q_R should be attributed to the creation of nano-voids. On the other hand, the efficiency of oxidized graphite

was decreased. Such phenomena should be due to the change of surface morphology and structure. Figures 1(a) and 1(b) present the SEM micrographs of graphite samples before and after oxidation. Compared with the dense particles of sample NG, sample OG shows a loose, thick, flake-like structure. Such a structure would result in an increase of surface area, which would consume the lithium ion irreversibly during the initial charge. So the initial charge and discharge efficiency was reduced.

Table 1. Comparison of NG and

	Q_1 (mAh/g)	Q_2 (mAh/g)	Efficiency (%)	Q_R (mAh/g)	Surface area (BET, m ² /g)
NG	370	296	80	220	2.20
OG	420	280	68	265	10.03

Q_1 : Initial discharge capacity; Q_2 : Initial charge capacity; Q_R : the 20th cycle capacity

Table 2 presents the electrochemical performances of sample OG, OG-A and OG-B. The efficiencies of OG-A and OG-B are higher than that of sample OG, which should be associated with the effect of coating. Figures 2(a) and (b) show the SEM images of oxidized graphite coated with disordered carbon. In Fig. 2(a), the particles of sample OG-A show dense and petaline structures. The oxidized graphite forms a core-shell structure. The shell is composed of disordered carbon created by the pyrolysis of phenolic resin. The shell could prevent the co-intercalation of solvent molecules, which is the main reason for low cycle efficiency of graphite.

Table 2. The electrochemical properties of graphite samples

	Q_1 (mAh/g)	Q_2 (mAh/g)	Q_R (mAh/g)	Efficiency (%)	Surface area (BET, m ² /g)
OG	420	280	265	68	10.03
OG-A	390	308	292	79	20.05
OG-B	395	323	318	82	20.18

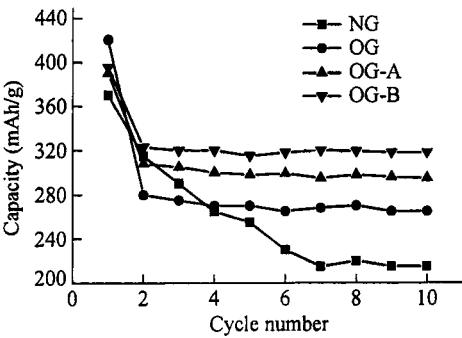
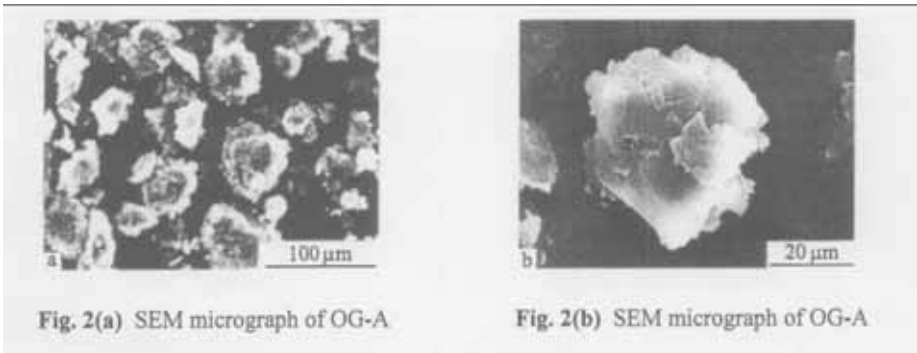


Fig. 3 Electrochemical properties of graphite

Figure 3 presents the cycle properties of graphite. In Fig. 3, the OG-A and OG-B show a higher Q_R than those of the NG and OG. On the other hand, the OG-B possesses a higher Q_R than that of the OG-A. The possible explanation for this is that the ratio of carbonization of phenolic resin BA-a (48%) is greater than that of ordinary phenolic resin (32%). The different degree of carbonization would affect the morphology of disordered carbon coated on the surface of oxidized graphite. Moreover the nitrogen atom in the phenolic resin BA-a is an electronegative element and lithium ion is electropositive. So the sample OG-B doped with nitrogen atoms would show stronger forces toward lithium ion and a higher energy density would be obtained during the process of charging and discharging.

REFERENCES

- 1 Fujimoto, M., Shouji, Y., Nohma, T. and Nishio, K., *Denki Kagaku*, 1997, 65: 949
- 2 Peled, E., Menachem, C., Bar-Tow, D. and Melman, A., *J. Electrochem. Soc.*, 1996, 143: 1
- 3 Ein-Eli, Y. and Koch, V.R., *J. Electrochem Soc.*, 1997, 144: 9
- 4 Robert, A.H., *J. Power Sources*, 1999, 81-82: 13
- 5 Menachem, C., Wang, Y., Flowers, J., Peled, E. and Greenbaum, S.G., *J. Power Sources*, 1998, 76: 180
- 6 Yoshio, M., Wang, H., Fukuda, K., Hara, Y. and Adachi, Y., *J. Electrochemical Soc.*, 2000, 147(4): 1245
- 7 Kuribayashi, I., Yokoyama, M. and Yamashita, M., *J. Power Sources*, 1995, 54: 1
- 8 Qiu, W.H., Zhang, G., Lu, S.G. and Liu, Q.G., *Chinese Journal of Power Sources*, 1999, 23(1): 7
- 9 Xin, N. and Ishida, H., *J. Polym. Sci., A1*, 1994, 32: 1121
- 10 Ishida, H. and Rodriguez, Y., *Polymer*, 1995, 36(16): 3151