Investigation of Modified Nature Graphite Anodes by Electrochemical Impedance Spectroscopy

Li Wang, Jishi Zhao, Xiangming He[*], Jianguo Ren, Haipeng Zhao, Jian Gao, Jianjun Li, Chunrong Wan, Changyin Jiang

Institute of Nuclear and New Energy Technology, Beijing Key Lab of Fine Ceramics, Tsinghua University, Beijing 100084, PR China
[*]E-mail: hexm@tsinghua.edu.cn

Electrochemical impedance spectroscopy (EIS) is employed to investigate the modification of natural graphite. The pyrolytic resorcinol formaldehyde resin-coated natural graphite is characterized by BET analysis, electrochemical performance and EIS characterization. The electrolyte resistance, surface resistance and diffusion resistance are obtained by modeling the experimental Nyquist plots. The study reveals that, as the results of the modification on the NG surface and purification of NG, the modification can not decrease the resistance of NG anode; also enhance the stabilization of NG anode surface, leading to a better electrochemical performance.

Keywords: EIS; Natural Graphite; modification; Lithium-ion Battery

1. INTRODUCTION

Lithium-ion batteries are widely used in portable electronic devices such as cellular telephones, camcorders and notebook PC. There is also a strong interest in utilizing Li-ion batteries for transportation applications. Anode material is crucial for the high performance of lithium ion batteries. Many kinds of anode materials, such as graphitic carbon, amorphous carbon, composite, and so on, have been studied so far. However, synthetic graphite is still the dominant one available on the market because of the electrochemical properties of other kinds of anode materials are not viable for practical applications. Nature graphite (NG) has been paid much attention for its low cost compared to synthetic graphite [1]. NG is endowed with inartificial graphitic structure during the natural evolution instead of heat-treatment at high temperature (2800°C). Unfortunately, NG anodes cannot be applied for commercial lithium-ion batteries for its large irreversible capacity loss and poor cycling [2-4], which are mainly caused by the high anisotropy of the graphite surface [5], imperfect structures such as sp^3-

hybridized carbon atoms, carbon chains and edge carbon atoms [6] and some impurities [7]. These structural characteristics result in profound difference in chemical and electrochemical reactivity, interaction with the solid electrolyte interphase (SEI), kinetics for lithium intercalation and de-intercalation of the basal plane and the edge plane of the graphite [8], leading to the decomposition of electrolyte molecules to produce large irreversible capacity and cycling performance deterioration.

Recently, a lot of research findings [4, 9-14] have confirmed that the modification of graphite is an effective approach to improve its electrochemical performance. In previous reports [15-16], purification and carbon-film-coating of natural graphite as anode materials for Li-ion batteries have been studied to improve the performance of NG anodes, resulting in an admirable cycling performance and high initial columbic efficiency. Since knowledge of the kinetic properties of lithium transport in the anode host are important for determining the cycling performance, it is desirable to study about it with cycles increasing to know more how to improve the performance of NG anodes [17]. In another aspect, electrochemical impedance spectroscopy (EIS) technique is a powerful tool to understand the electrode process in Li-ion batteries [18-24]. In present study, we report the electrochemical investigations on NG/modified-NG anodes by electrochemical impedance spectroscopy (EIS) technique. Moreover, we demonstrate here that impedance of NG/modified-NG anodes changed with cycles increasing, which help us to understand more how the modification influences the electrochemical performance of the NG anodes.

2. EXPERIMENTAL

The resorcinol formaldehyde resin-coated powders (modified samples) are prepared as previous reported by zhao et al [15-16]. For electrochemical performance evaluation, half-cell studies are performed. C (acetylene black) powder and Teflon (PTFE) are used as conductive additive and binder, respectively.

The NG/modified NG powders are mixed with acetylene black and PTFE dissolved in ethanol in the weight ratio of 8:1:1 to form slurry. After solvent evaporation, the electrode is pressed round in shape and dried at $120^{o}C$ under vacuum over 24h. CR2025-type coin cells are assembled in a glove box (M. Braun GmbH, Germany) with H_2O and O_2 content below 1ppm. Metallic lithium foil is used as counter electrode. The electrolyte is 1.0M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1, v/v) and Celgard 2400 polyethylene is used as the separator.

EIS is done using the ZAHNER-IM6eX electrochemical workstation (Germany) at room temperature. The impedance spectra are recorded at each state allowing at least 5 additional hours for equilibration after each charge/discharge step, by applying a sine wave with amplitude of 10 mV in the 1 MHz-5 mHz frequency range. Data acquisition and analysis are done, respectively, using the electrochemical impedance software, ZSimpWin Version 3.00 (EChem Software, Ann Arbor, Michigan, USA.). All the electrochemical measurements are carried out at room temperature. The charge/discharge cycling is galvanostatically tested at a current of 0.1C with cut-off voltages from 0.002 to 2.00V.

3. RESULTS AND DISCUSSION

3.1. Structural characterization

The structural characterizations of natural graphite samples have been investigated [15]. The X-ray diffraction (XRD) results show that the modifying process of oxidation or encapsulation on graphite did not destroy the typical structure of graphite. However, it can be observed that the modification process decreases the relative peak intensity of the sample lightly, which seems to indicate that oxidation or encapsulation treatment leads to the decrease of the crystallinity. Some researchers [25] suggested that the decrease in crystallinity might imply that small change on surface morphology of the graphite takes place, i.e. the amorphous surface layer is formed.

Based on these SEM images [15], there are some sharp edges and chips on the edge section of untreated natural graphite. After modification, it can be found that an amorphous carbon film layer from pyrolysis of resorcinol formaldehyde resin coats on the surface of the graphite, resulting in improvement of the contact between graphite and electrolyte. Also, the presence of the amorphous carbon film layer might in some extent decreases the crystallinity of modified samples. Moreover, owing to better compatibility with electrolyte than highly ordered graphite, the amorphous carbon film coated on graphite is helpful to restrain decomposition of electrolyte and co-intercalation of solvated ions [26]. In addition, EDS and XPS analysis also indicate that the amorphous carbon layer coated the surface of pristine graphite.

3.2. Electrochemical characterization

Table 1 shows the charge/discharge performances and results of the BET surface areas of pristine natural graphite (NG) and modified natural graphite (modified NG). It can be observed that two graphite samples have similar initial discharge capacities but notably different initial charge capacity, and their initial charge capacities increase from NG to modified NG. Therefore, in comparison with 76.2% of the initial coulombic efficiency of NG, modified NG exhibits high initial coulombic efficiency, reaching 90.3%. From Table 1, one can notice that BET surface areas of NG and modified NG are 4.53 and 4.14 m^2 g^{-1}, respectively. Obviously, the BET surface area of modified graphite is fewer than that of pristine graphite. It is known that initial coulombic efficiency depends on the electrolyte decomposition and the formation of the SEI layer while the latter is usually proportioned to BET surface area of samples. Therefore, it is better understandable to observe that ordinal increases of the initial coulombic efficiencies of NG, modified NG correspond with ordinal reduces of their BET surface areas. At the same time, it can be estimated that the thickness of coated layer on graphite should be thinner from these results. After 70 cycles, the reversible charge capacities of NG, modified NG are 123.6 and 350.8 mAh g^{-1}, respectively, so the charge capacity retentions of two graphite samples differ remarkably.

The charge capacity retentions at 70th of modified NG are far more than that of NG, especially for that of modified NG reaching 96.4%, which indicates that the cycling performance of modified NG has reached a satisfactory and desirable result.

Table 1. The charge-discharge performance of graphite samples

Samples	BET surface area ($m^2\ g^{-1}$)	Initial charge capacity ($mAh\ g^{-1}$)	Initial discharge capacity ($mAh\ g^{-1}$)	Initial efficiency (%)	Charge capacity at 70th cycle ($mAh\ g^{-1}$)	Charge capacity retention at 70th cycle (%)
NG	4.53	318.5	418	76.2	123.6	38.8
modified NG	4.14	364	403	90.3	350.8	96.4

3.3. EIS characterization
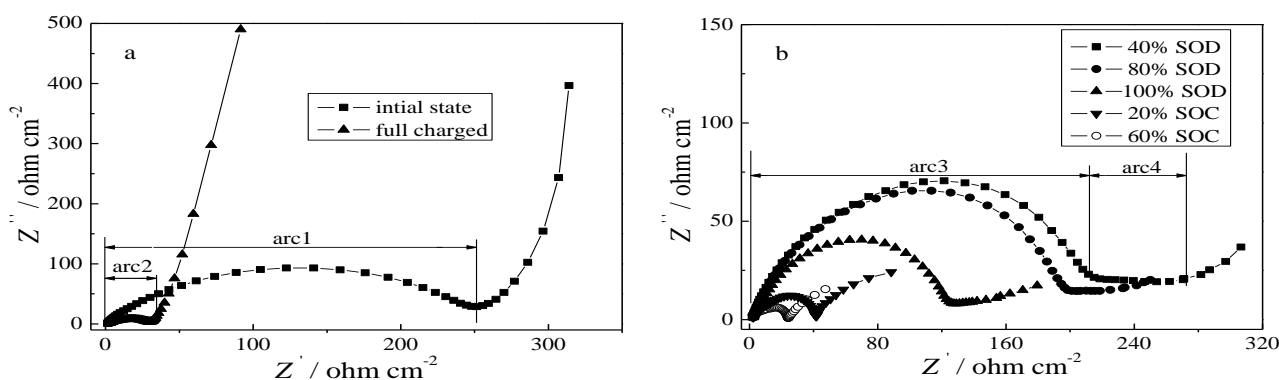
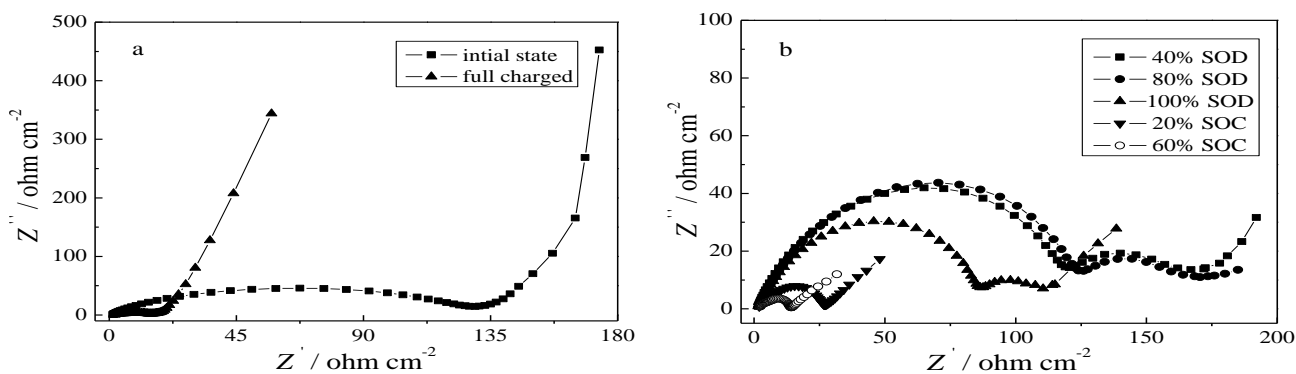**Figure 1.** Nyquist plots of NG in the first cycle

Figure 2. Nyquist plots of modified NG in the first cycle

Fig. 1 and Fig. 2 display the Nyquist plots of the electrochemical impedance spectra obtained from the NG and modified NG anodes at different state of charge/discharge (SOC/SOD) in the first charge/discharge process, respectively. As shown in Fig. 1a and Fig. 2a, the Nyquist plots of electrochemical impedance spectra consist of a compressed semicircle in high and intermediate frequency ranges and a straight line inclined at a constant angle to the real axis in the lower frequency

range. The plots with larger diameter belong to the initial state, another plots obtained at the full-charged state of first cycle. Furthermore, the electrochemical impedance spectra at other states displayed in Fig. 1b and Fig. 2b have different shape from those shown in Fig. 1a and Fig. 2a.

Fig. 3 shows the equivalent circuits used to analyze the Nyquist plots shown in Fig. 1 and Fig. 2. In present work, different equivalent circuits are applied according to the different shape of Nyquist plots. The equivalent circuit shown in Fig. 3a is used to analyze the plots shown in Fig. 1a and Fig. 2a; another equivalent circuit is used to analyze the other plots with different shape.
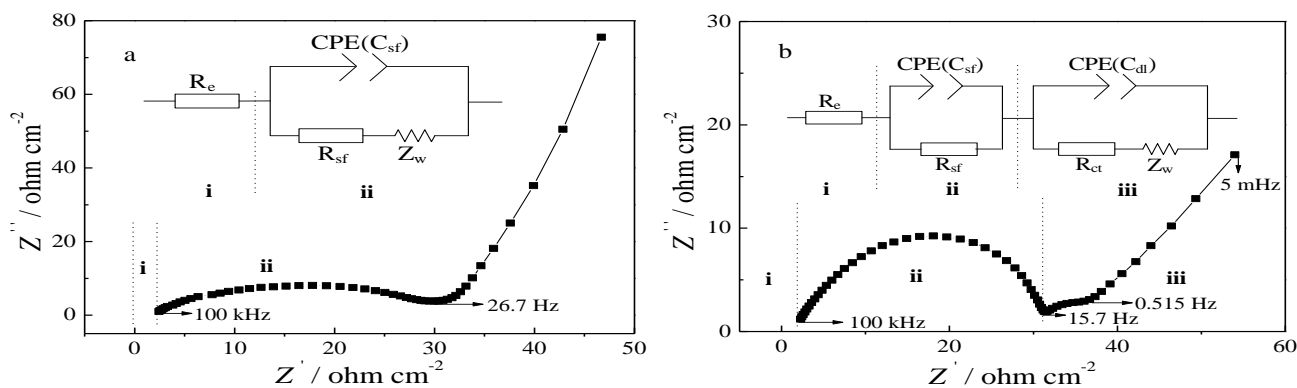

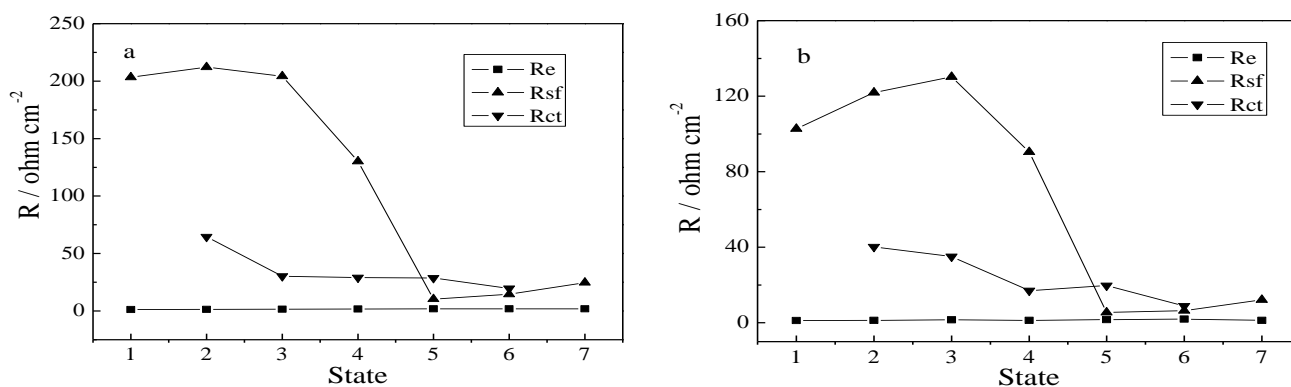**Figure 3.** Equivalent circuits used to analyze the Nyquist plots

Figure 4. Plots of R_e, R_{sf} and R_{ct} vs. different state in first cycle (1-initial state; 2-40%SOD; 3-80%SOD; 4-100%SOD; 5-20%SOC; 6-60%SOC; 7-full charged)

Fig. 4 displays the analysis results of electrolyte resistance (R_e), surface resistance (R_{sf}) and diffusion resistance (R_{ct}) obtained by modeling the experimental Nyquist plots shown in Fig. 1and Fig. 2 with the equivalent circuit, respectively. As shown in Fig. 3, for both NG and modified NG anode, the electrolyte resistance (R_e) is stable with different state during the first cycle. It also can be found that the modified NG anode has smaller charge/ion diffusion resistance (R_{ct}) and surface resistance (R_{sf}) than NG anode at every state during the first cycle, reflecting that the modification decreases the resistance of NG anode. The Nyquist plots of NG and modified NG anodes in the second and tenth

cycle also have been investigated. It reveals that the passivating film of NG anode is mainly formed in the first cycle. As the results of the modification on the NG surface and purification of NG, the modification can not decrease the resistance of NG anode; also enhance the stabilization of NG anode surface, resulting in better electrochemical performance, as shown in Table. 1.

4. CONCLUSION

The pyrolytic resorcinol formaldehyde resin-coated natural graphite is characterized by BET analysis, electrochemical performance and EIS characterization. The initial coulombic efficiency of natural graphite increases from 76.2% to 90.3% by modification due to the decrease of BET from 4.53 to 4.14 m^2 g^{-1}. After 70 cycles, the reversible charge capacities increase from 123.6 to 350.8 mAh g^{-1} by modification. The modified NG anode has smaller charge/ion diffusion resistance and surface resistance than NG anode at every state during the first cycle, reflecting that the modification decreases the resistance of NG anode. The study reveals that, as the results of the modification on the NG surface and purification of NG, the modification can not decrease the resistance of NG anode; also enhance the stabilization of NG anode surface, leading to a better electrochemical performance.

Reference

1. J. Shim, K. A. Striebel. *J Power Sources* 119–121 (2003) 955.
2. Y. P. Wu, C. Jiang, C. Wan, R. Holze. *Solid State Ionics* 156 (2003) 283.
3. J. J. Li, X. M. He, C. Y. Jiang, C. R. Wan. *J. New Mater. Electrochem. Syst.* 9 (2006) 21.
4. M. Yoshio, H. Wang, K. Fukuda, Y. Hara, Y. Adachi. *J Electrochem. Soc.* 147 (2000) 1245.
5. K. Guerin, F. B. Annie, S. Flandrois. *J. Electrochem. Soc.* 146 (10) (1999) 3360.
6. Y. P. Wu, C. R. Wan, C. Y. Jiang, J. J. Li, Y. X. Li. *Chinese Chem. Lett.* 10 (1999) 339.
7. K. Zaghib, X. Song, A. Guerfi, R. Rioux, K. Kinoshita. *J Power Sources* 119–121 (2003) 8.
8. J. P. Olivier, M. Winter. *J Power Source* 151-155 (2001) 151.
9. K. K. Guo, Q. M. Pan, S. B. Fan. *J Power Sources* 111 (2002) 350.
10. M. Yoshio, H. Wang, K. Fukuda, T. Umeno, T. Abe, Z. Ogumi. *J Mater. Chem.* 14 (2004) 1754.
11. M. Yoshio, H. Wang, K. Fukuda. *Angew. Chem. Int. Ed.* 42 (2003) 4203.
12. Q. M. Pan, K. K. Guo, L. Z.Wang, S. B. Fang. *Solid State Ionics* 149 (2002) 193–200.
13. E. Peled, C. Menachem, A. Melman, *J Electaochem. Soc.* 143 (1996) L4.
14. H. Buqu, P. Golob, M. Winter, J. O. Besenhard. *J Power Sources* 97-98 (2001) 122.
15. H. P. Zhao, J. G. Ren, X. M. He, J. J. Li, C. Y. Jiang, C. R. Wan. *Solid State Sciences* 10 (2008) 612.
16. H. P. Zhao, J. G. Ren, X. M. He, J. J. Li, C. Y. Jiang, C. R. Wan. *Electrochimica Acta.* 52 (2007) 6006.

17. M. Holzapfel, A. Martinent, F. Alloin, B. LeGorrec, R. Yazami, C. Montella. *J Electroanalytical Chemistry* 546(2003) 41.
18. M. A. Kiani, M. F. Mousavi, M. S. Rahmanifar, *Int. J. Electrochem. Sci.*, 2011, 6(7): 2581-2595
19. L. Wang, J. S. Zhao, S. H. Guo, X. M. He, C.Y. Jiang, C. R. Wan, *Int. J. Electrochem. Sci,* 2010, 5(8): 1113-1126
20. J. S. Zhao, L. Wang, X. M. He, C. R. Wan, C. Y. Jiang, *Int. J. Electrochem. Sci*, 2010, 5(4): 478-488
21. R. Santhanam, S. L. Ghatty, B. Rambabu, *Int. J. Electrochem. Sci*, 2010, 5(2): 189-199
22. N. N. Sinha, P. Ragupathy, H. N. Vasan, N. Munichandraiah, *Int. J. Electrochem. Sci*, 2008, 3(6): 691-710
23. S. Rajendran, M. R. Prabhu, M. U. Rani, *Int. J. Electrochem. Sci,* 2008, 3(3): 282-290
24. P. Periasamy, N. Kalaiselvi, S. H. Kim, *Int. J. Electrochem. Sci*, 2007, 2(9): 689-699
25. J. L. Shui, J. Zhang, C. X. Ding, X. Yang, C. H. Chen. *Mater. Sci. Eng*. B 128 (2006) 11.
26. Y. S. Han, J. Y. Lee. *Electrochim. Acta*. 48 (2003) 1073.