Thermally oxidized graphites as anodes for lithium-ion cells

T. Prem Kumar, A. Manuel Stephan, P. Thayananth, V. Subramanian[*],
S. Gopukumar, N.G. Renganathan, M. Raghavan, N. Muniyandi

*Lithium Batteries Section, Advanced Batteries Division,
Central Electrochemical Research Institute, Karaikudi 630006, India*

Abstract

Lithium intercalation and deintercalation processes occur through solid electrolyte interfaces (SEIs) on the zigzag and armchair faces of graphite. Such SEIs are formed by reaction of surface groups on the graphite with lithium upon charging. The nature of this interface to a large extent determines the reversible and irreversible capacities of the graphite. We have investigated the influence of mild oxidation of samples of natural graphite and carbon nanotubes on the surface characteristics of the films formed on these materials upon lithium intercalation. The surface groups formed upon oxidation have been characterized using Fourier transform infrared (FT-IR) spectroscopy. The reversible and irreversible capacities of the thermally oxidized samples are discussed in terms of the surface film composition as well as enhanced surface area that contributes to increased number of sites for lithium intercalation. © 2001 Published by Elsevier Science B.V.

Keywords: Graphite; Carbon nanotubes; Lithium intercalation; Lithium-ion cells

1. Introduction

Graphites are particularly attractive candidates as anode materials in lithium rocking chair cells. In the recent past, Ohzuku et al. [1] reported that heat treatment at 700°C in the presence of acetylene black improved the performance of the graphite-fiber anode. Such thermal treatment was found to remove surface hydroxyl groups and water in addition to enlarging the surface area of the fibers [2]. Oxidation of graphite, both chemically and electrochemically, has been reported to result not only in enhanced anodic capacity but also to simultaneously reduce the irreversible capacity in the first cycle [3,4]. In this paper, we report the results of our study on the effect of thermal treatment on the electrochemical behavior of two graphitic carbons: natural graphite (NG-7) and carbon nanotubes.

2. Experimental

Natural graphite (NG-7) from the International Battery Association, Japan and in-house synthesized carbon nanotubes were chosen for this study. Carbon nanotubes were synthesized by catalytic decomposition of an acetylene–hydrogen mixture (5:95) over carbonyl nickel at 700°C for

1 h in a fixed-bed flow reactor (flow rate: 300 ml/min) [5]. The nickel in the as-formed carbon nanotubes was lixiviated in dilute nitric acid, washed with double distilled water, filtered and allowed to dry in an air oven at 150°C. Small samples of NG-7 and carbon nanotubes were subjected to mild oxidation in air at 550°C. Fourier transform infrared (FT-IR) examination (Perkin-Elmer FT-IR Spectrometer, model Paragon 500, UK) showed the presence of oxidized species on the anode surface after the heat treatment. Carbon electrodes were prepared by spread-coating a slurry of the carbon with 10% poly(vinylidene fluoride) (Sigma–Aldrich, USA) in *N*-methyl-2-pyrrolidone (Sigma–Aldrich, USA), on a copper current collector foil (0.05 mm thick, 18 mm dia) and drying the coat in an air oven. The loadings of the carbons in the discs were as follows: NG-7: 0.097 g; thermally oxidized NG-7: 0.140 g; carbon nanotubes: 0.133 g; and thermally oxidized carbon nanotubes: 0.053 g.

Standard 2016 type coin cell hardware was used for cell assembly with lithium (0.5 mm thick, 99.5%, Cyprus Foote Minerals, USA) and an electrolyte of 1 M $LiPF_6$ in a 30:70 (v/v) mixture of ethylene carbonate and diethyl carbonate. Celgard 2400 (Celgard, USA) was used as the separator. Carbon-limited cells were assembled in an argon-filled glove box (Mbraun, Germany) and crimp-sealed. Capacities were determined by cycling between 2.0 and 0.02 V. The rate of charge and discharge was 200 µA. In this paper, reversible capacity is defined as the second intercalation

---

*Corresponding author.

capacity and irreversible capacity as the difference between the first and second intercalation capacities.

3. Results and discussion

Several simultaneous processes occur when a graphitic electrode is cathodically polarized against lithium at potentials below 2 V [6]. Apart from lithium intercalation which may be accompanied by co-intercalation of solvent molecules, it is possible that partial or complete reduction of the solvent molecules and anions can also occur resulting in the formation of an insoluble layer on the carbon surface. This solid electrolyte interface (SEI) can influence the performance of the electrochemical couple.

3.1. FT-IR studies

The Fourier transform infrared (FT-IR) spectroscopic patterns of the heat-treated NG-7 and heat-treated carbon nanotubes samples showed absorption peaks corresponding to the oxidized functional groups such as C=O, COOH, etc. [7]. Typically, what we looked for were absorption peaks corresponding to the stretching vibrations of aryl carbonyl groups around the 1700–$1680\ cm^{-1}$ region. The absence of such absorption peaks on the thermally untreated carbons reveal the changes on the surface of the carbon. Weak absorption bands corresponding to aromatic C–H stretching could be noticed for the untreated carbons which, however, were completely absent in the absorption spectra of thermally oxidized carbon samples.

3.2. Characteristics of lithium–carbon cells

All carbons gave an open-circuit voltage of 2.8–3.0 V upon assembly. Fig. 1 shows the first discharge and charge curves of both untreated and thermally-treated carbons. It may be seen from the profiles for the NG-7 samples that the cell voltages drop rapidly to about 0.8 V where the discharge curve shows a plateau that spans more than 0.2 in the x-scale. This plateau has been attributed to the reaction between surface lithium and the electrolyte that leads to the formation of a protective surface film of reaction products [8–10]. The capacity corresponding to this plateau cannot be retrieved upon discharge [8]. The majority of the lithium intercalation reaction occurs below 0.4 V [9,11]. It may also be noted that the apparent total stoichiometry obtained in the first discharge process corresponds to approximately $Li_{1.2}C_6$, i.e. an x value of 0.2 more than the expected stoichiometry for complete lithium intercalation. This value of 0.2 in x is consumed in the reaction with the electrolyte. The first discharge capacity for NG-7 corresponds to 446 mAh corresponding to a stoichiometry of $Li_{1.19}C_6$, while the second discharge capacity is a paltry 219 mAh. Thus, the irreversible capacity in the first cycle amounts to 51%. The corresponding values for the thermally-treated NG-7 are
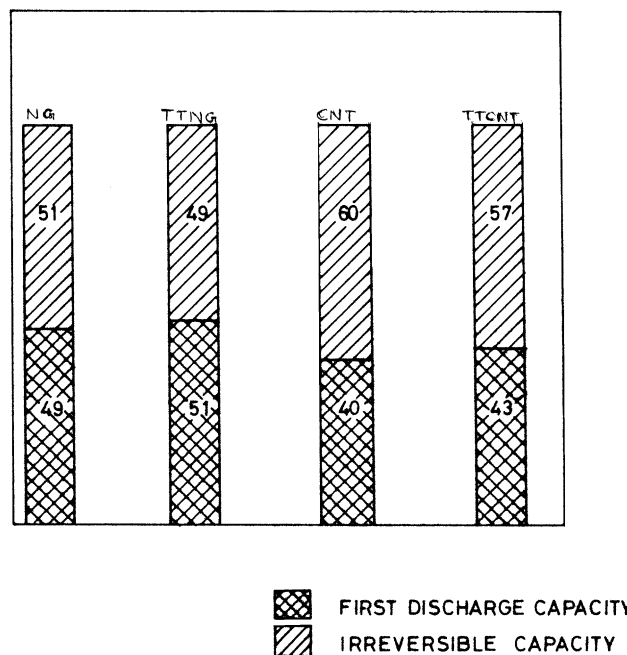

Fig. 1. The first discharge and charge curves of untreated and thermally-treated carbon samples. Na: natural graphite; TTNa: thermally-treated natural graphite; CNT: carbon nonotubes; TTNT: thermally-treated carbon nanotubes.

440 mAh ($Li_{1.18}C_6$) and 226 mAh with an irreversible capacity of 49%. For the untreated carbon nanotubes the first discharge of 1460 mAh ($Li_{3.92}C_6$) with a second discharge capacity of only 581 mAh (irreversible capacity: 60%). For the thermally-treated carbon nanotubes the values are 1444 and 620 mAh (irreversible capacity: 57%).

In Fig. 2 the irreversible capacity is presented as a fraction of the total capacity realized in the first discharge step. It can
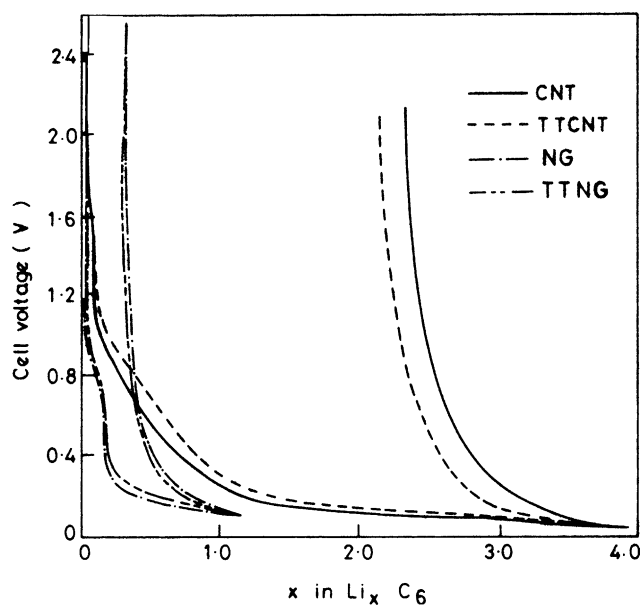

Fig. 2. Irreversible capacity as a fraction of the total capacity realized in the first discharge step.

be seen that the irreversible capacity gets marginally reduced upon heat treatment. This decrease in irreversible capacity is contrary to the results of Rubino and Tackeuchi [12] who in fact show that the increased irreversible capacity they observed with heat-treated graphites is due to increase in pore size of the graphite which in turn facilitates further attack of lithium on carbon surfaces with the electrolyte. In the case of carbon nanotubes both the untreated and heat-treated samples gave extremely high initial discharge capacities with attendant large irreversible capacities. Our values for carbon nanotubes may be compared to those obtained by Wu et al. [13] who report more than 1500 mAh for the first discharge capacity and 640 mAh for the second discharge capacity. The higher values for the irreversible capacities of carbon nanotubes may be explained as follows. As noted earlier, the region around 0.8 V in the discharge profile may be associated with the formation of a SEI on the carbon surface [9]. Carbon nanotubes have very large surface areas. The large irreversible capacities represent the loss due to the formation of a solid electrolyte interface over large areas on the carbon nanotube surface.

3.3. Cycling behavior

The discharge capacities recorded in the first five cycles are as follows: NG-7: 446-219-202-190-186 mAh; heat-treated NG-7: 440-226-216-212-206 mAh; carbon nanotubes: 1460-581-420-398-382 mAh; and heat-treated carbon nanotubes:1444-620-561-524-516 mAh. Thus, the capcities retained at the fifth cycle are 186, 206, 382 and 516 mAh for NG-7, heat-treated NG-7, carbon nanotubes and heat-treated carbon nanotubes, respectively. Translated as percentages of the first discharge capacity, they are NG-7: 42; heat-treated NG-7: 47; carbon nanotubes: 25; and heat-treated carbon nanotubes: 35. In other words, the number of lithium ions available per mole of Li_xC_6 for intercalation after 5 cycles are 0.50 for NG-7; 0.55 for heat-treated NG-7; 1.03 for carbon nanotubes; and 1.39 for heat-treated carbon nanotubes.

3.4. Effect of thermal treatment

Lithium intercalation and deintercalation into graphite take place through the zigzag and armchair faces rather than through the basal phase. Any solid electrolyte interface formed on the carbon can help in hindering co-intercalation of solvent molecules. It has been found that the oxidation of graphite by oxygen below 1000°C is facile along the zigzag faces and slow along the armchair faces; however, it is extremely slow along the basal planes [14]. During oxidation in air, acid groups are formed along the zigzag and armchair faces which can interact with lithium in the first intercalation step to form chemically bonded solid electrolyte interface as opposed to the solid electrolyte interface of the passive film type. During the first intercalation process, the acid groups are converted into surface lithium carboxylic
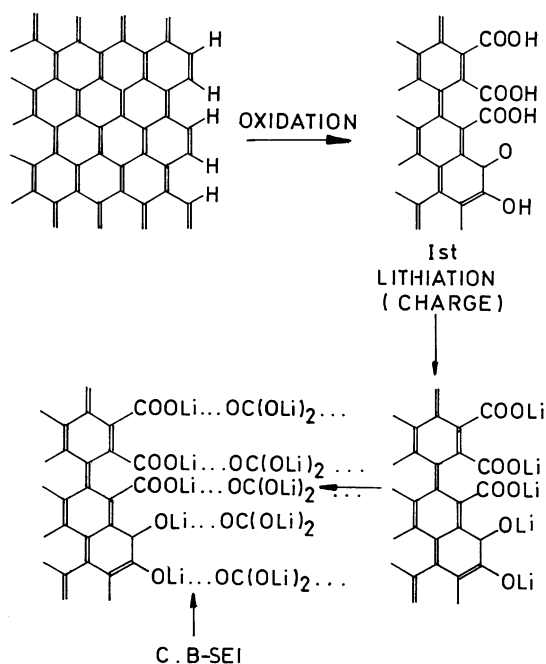

Fig. 3. Formation scheme for chemically-bonded solid electrolyte interface [3].

salt and surface –O–Li groups. Later, they can generate Li_2CO_3-based solid electrolyte interface upon contact with solvent molecules, such as ethylene carbonate, dimethyl carbonate, etc. This solid electrolyte interface may thus be expected to be chemically bonded to the –COOLi and –O–Li groups on the surface of the carbon (see Fig. 3).

The formation of molecular sieves on the surface of carbons by mild oxidation is well known [15–17]. The expected formation of chemically bonded solid electrolyte interface together with the molecular sieving properties of the same may account for the diminished access for solvent molecules to the carbon surface. Under such circumstances, co-intercalation of solvent molecules is greatly hindered which not only reduces the irreversible capacity but also degradation of the anode due to solvent co-intercalation during further cycling. This accounts for an increase in the reversible capacity of carbons as reported recently for NG-7.

4. Conclusions

The effect of mild air oxidation on natural graphite and carbon nanotube samples have resulted in marginal increase in the reversible capacities with attendant reduction in their irreversible capacities. The thermally-treated samples also seem to stabilize in terms of deliverable capacity upon cycling. Although the realizable capacities of carbon nanotubes (both untreated and thermally treated) are attractive in that they deliver more than the LiC_6 stoichiometric value of 372 mAh, their use in practical cells seem limited given the fact that their large irreversible capacities (of about

900 mAh/g) must necessarily come from the lithium-laden cathode material that must be coupled with them in practical lithium rocking chair cells.

References

[1] T. Ohzuku, Y. Iwakoshi, K. Sawai, J. Electrochem. Soc. 140 (1993) 2490.

[2] T. Takamura, M. Kikuchi, Y. Ikezawa, in: S. Megahead, B.M. Barnett, L. Xie (Eds.), Rechargeable Lithium and Lithium-Ion Batteries, PV-94-28, The Electrochemical Society, Pennington, NJ, 1995, p. 213.

[3] E. Peled, C. Menachem, D. Bar-Tow, A. Melman, J. Electrochem. Soc. 143 (1996) L4.

[4] C. Menachem, E. Peled, L. Burstein, Y. Rosenberg, J. Power Sources 68 (1997) 277.

[5] T. Prem Kumar, N.G. Renganathan, N. Muniyandi, Bull. Electrochem., submitted for publication.

[6] E. Peled, in: S. Megahead, B.M. Barnett, L. Xie (Eds.), Rechargeable Lithium and Lithium-Ion Batteries, PV-94-28, The Electrochemical Society, Pennington, NJ, 1995, p. 1.

[7] J.R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Prentice-Hall, Englewood Cliffs, NJ, 1965.

[8] R. Fong, U. von Sacken, J.R. Dahn, J. Electrochem. Soc. 137 (1990) 2009.

[9] M. Arakawa, J. Yamaki, J. Electroanal. Chem. 219 (1987) 273.

[10] Z.X. Shu, R.S. McMillan, J.J. Murray, J. Electrochem. Soc. 140 (1993) 922.

[11] J.R. Dahn, Phys. Rev. B 44 (1991) 9170.

[12] R.S. Rubino, E.S. Takeuchi, J. Power Sources 81/82 (1999) 373.

[13] G.T. Wu, C.S. Wang, X.B. Zhang, H.S. Yang, Z.F. Qi, P.M. He, W.Z. Li, J. Electrochem. Soc. 146 (1999) 1696.

[14] H.P. Pierson, Handbook of Carbon, Graphite, Diamond and Fullerenes, Noyes Publications, Park Ridge, NJ, 1993.

[15] M.M. Dubinin, O. Kadlee, I. Botlik, E.D. Zaverina, A. Zukal, B. Sumee, Dokl. Akad. Nauk USSR 157 (1964) 656.

[16] J. Koresh, A. Soffer, J. Chem. Soc., Faraday Trans. 1 (1980) 76.

[17] J. Koresh, A. Soffer, J. Chem. Soc., Faraday Trans. 1 (1980) 2457.