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Effects of post-treatments on the performance of hard carbons in lithium cells

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Abstract

The main disadvantage of hard carbons when they are used for the negative electrode of lithium-ion batteries is a large irreversible capacity generally attributed to their important specific surface area. Our goals were to estimate the amount of residual lithium, i.e. not involved in the solid electrolyte interface (SEI) after a full deinsertion, and to reduce the irreversible capacity due to the SEI formation. Galvanostatic charge/discharge of carbon lithium cells was performed with carbon materials to which an additional pyrolysis has been applied in various conditions. Electrode materials made from as-received carbon have been analysed *ex situ* by electron paramagnetic resonance (EPR) at different steps of the insertion/deinsertion process. We found that 20% of the irreversible capacity is due to residual lithium trapped in the carbon matrix. Post-treatments up to 900°C resulted in decreasing the irreversible capacity from 260 to 65 mAh/g thanks to modifications of the surface functionality and possible improvement of the carbon network structure. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium-ion batteries; Irreversible capacity; Hard carbon; High temperature treatment

1. Introduction

During the last years, hard carbons have demonstrated promising properties for lithium-ion battery applications. Some of them are able to store more lithium than graphite and they do not exfoliate during cycling. However, their main disadvantage is a large irreversible capacity generally attributed to their important surface area [1]. Different studies have shown that this irreversible capacity could be due to several causes: reactions of lithium with the electrolyte to form a passivating layer called solid electrolyte interface (SEI) [2,3], reactions of lithium with the surface functional groups or the chemical species adsorbed on the carbon skeleton (essentially water) [4], lithium trapped in the porosity [5]. A surface treatment has been used in some cases to eliminate these groups in order to reduce the SEI and consequently the irreversible capacity [6–8].

Our objectives were to find out the proportion of lithium that remains inserted after the reversible part of deinsertion, and to reduce the irreversible capacity. For this purpose, we used electron paramagnetic resonance (EPR), which allows

the density of state at the Fermi level of the synthetic metal formed by the carbon host and the inserted lithium to be measured. In a second part of the paper, we will show that a further pyrolysis of the hard carbon at an appropriate temperature can depress the irreversible capacity by reducing the formation of the passivation layer. High resolution transmission electron microscopy (HRTEM) has been used to detect the subsequent structural modifications of the bulk.

2. Experimental

Hard carbon was formed by pyrolysis of cellulose under inert atmosphere for 15 min at 1000°C. For some cases, a second pyrolysis was performed during 24 h at temperatures ranging between 300 and 900°C, and the samples were transferred in a glove box filled with argon. All the electrochemical measurements were carried out using Swagelok[®] laboratory test cells. The electrolyte used was 1 M LiPF₆ in a 1:1 volume ratio of ethylene carbonate (EC) and diethyl carbonate (DEC). A microporous film separator (Whatman paper), wetted with the electrolyte, was sandwiched between the carbon electrode and a Li metal foil. The cells were assembled in an argon-filled glove box. A Mac Pile

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(Biologic, France) system operating in galvanostatic mode was used to perform the measurements. In all cases, a C/20 rate (corresponding to a capacity of 372 mAh/g in 20 h) was chosen to discharge the test cells in the potential range from 2 to -0.02 V. After insertion or deinsertion of lithium, the cells were dismantled in the glove box, and carbon samples were transferred in sealed quartz tubes. The EPR experiments were performed with a X-band spectrometer (Brüker, 9 GHz microwave frequency). For the HRTEM observations, we used a Philips CM20 microscope working at 200 kV. A small piece of each sample was finely ground, sonicated into alcohol and then deposited on a grid covered by a holey carbon film. Only fragments placed across the holes were studied to reduce the background noise. Quantitative structural data can be obtained thanks to a home made image analysis procedure.

3. Results and discussion

The galvanostatic charge/discharge curve of as-received carbon is shown in Fig. 1. The characteristics demonstrate an important part of the reversible capacity below 0.5 V versus Li, which is an important criterion for selecting an electrode material for lithium-ion batteries. However, the irreversible capacity is more significant (0.71 Li for 6 C) than it is usually for graphite (~ 0.1 Li for 6 C). It can be attributed to the important value of specific surface area for our samples ($250 \text{ m}^2/\text{g}$) as compared to graphite powders ($5\text{--}10 \text{ m}^2/\text{g}$). Moreover, the noticeable amount of oxygen still present in this carbon (C/O ratio of 33) suggests that surface functional groups might take part in the formation of the passivating layer [4].

Hard-carbons are constituted of short graphitic layers linked on the edges by heteroatoms and by C–C or C=C bonds. They are globally conjugated systems and, at least according to the EPR characteristics, their electronic behaviour is metallic when they are doped. In particular we verified that the spin susceptibility of the fully doped

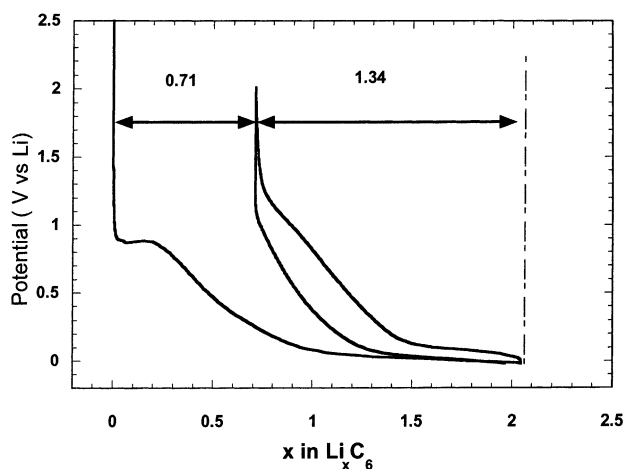
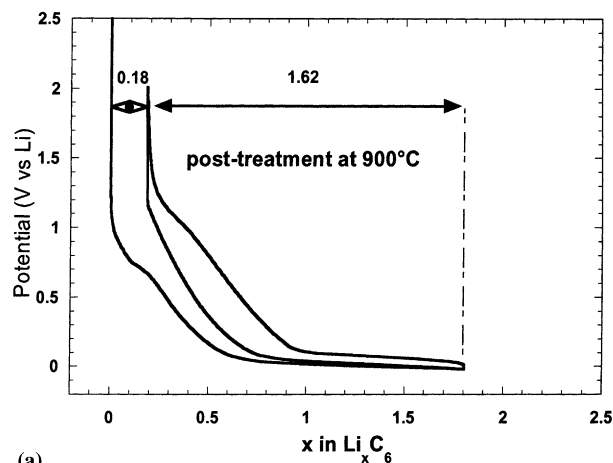


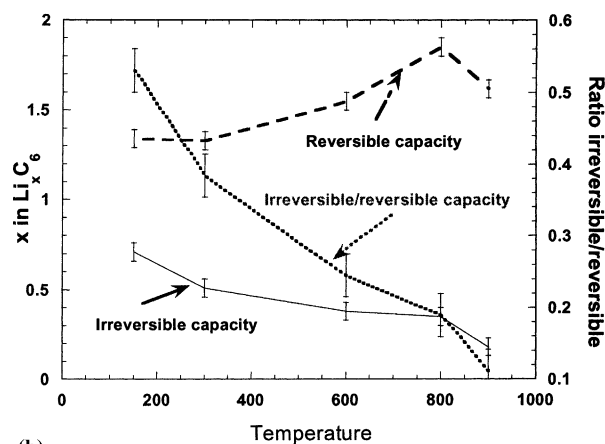
Fig. 1. Galvanostatic charge/discharge on as-received carbon.

samples follows a Pauli law as in a normal metal or in intercalated graphite. On the other hand, we measured that in the fully doped state the susceptibility is nearly equal to that of the graphite intercalation compound LiC_6 that suggests similar behaviour of disordered carbons and graphite [9,10]. We used this assumption to estimate the maximum concentration of lithium trapped in the carbon host after deinsertion. The susceptibility was compared to that of high stage intercalation compounds [10] and it appeared that no more than 20% of the irreversible part was due to lithium inserted in the carbon matrix. The rest of lithium is incorporated into the passivating layer or in the carbon matrix by reactions with dangling bonds. In both cases no signal is expected since there is no charge transfer to carbon.

Additional pyrolysis at 300°C of the carbon material induced a slight decrease of its irreversible capacity. At this temperature only adsorbed water is eliminated. The post-treatment at 900°C is very efficient in decreasing the irreversible capacity from 260 to 65 mAh/g (Fig. 2a). The plots of Fig. 2b illustrate the continuous evolution of the electrochemical capacities in the selected temperature range.



(a)



(b)

Fig. 2. Galvanostatic charge/discharge on the sample post-treated at 900°C during 24 h (a); and variation of the irreversible/reversible capacities and of their ratio with the treatment temperature (b).

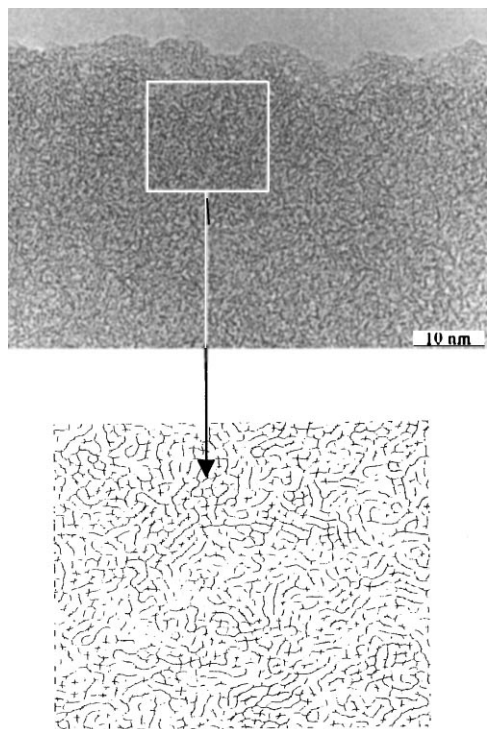


Fig. 3. HRTEM image of a hard carbon sample (inset: skeletonized image).

There are different interpretations for these results. It is well known that oxygenated groups are created at a carbon surface when it is exposed to air. Therefore, additional pyrolysis allows a surface to become almost free of any functionality that could react with the electrolyte. Another explanation came from gas adsorption measurements. The specific surface area drastically decreases from 250 to 4 m²/g for the post-treated material, which limits the SEI formation via the closure of micropores [11].

As-received and post-treated carbons have been observed by HRTEM in order to image the profile of the aromatic layers and to specify the multiscale organisation (structure, microtexture) [12]. Typically, for hard carbons obtained at about 1000°C, nanometric aromatic layers were detected. Approximately half of them were stacked in coherent domains called basic structural units (BSU) whereas the others were isolated. A noticeable heterogeneity of the samples was observed. Analysis of the skeletonised images [13] showed that the size and proportion of single layers depend on the analysed area (Fig. 3). Due to the release of functional groups, the post-treatment can be considered as a

second carbonisation. Indeed, locally, L_a and L_c , representing the diameter and the height of coherent domains, are slightly higher in the post-treated sample than in the as-received one. Hence, the post-treatment modified not only the microtexture, but also to a smaller extent the structure of the material. This explains why it can affect the reversible capacity as well as the irreversible one. However, because of sample heterogeneity, we cannot yet completely confirm this interpretation.

4. Conclusion

Electron paramagnetic resonance (EPR) experiments have demonstrated that the majority of lithium irreversibly inserted in hard carbons is located in the passivation layer. However, after a full de-insertion, there is still a slight charge transfer on carbon, showing that part of the lithium remains trapped in the carbon matrix. Irreversible capacities have been reduced by post-treatments that eliminate adsorbed molecules and oxygenated groups bonded to the carbon skeleton. Structural modifications of the bulk may occur along with surface cleaning, and thus may be also responsible for the improved electrochemical properties.

References

- [1] J.R. Dahn, T. Zheng, J.S. Xue, Y. Liu, *Science* 270 (1995) 590.
- [2] R. Fong, U. von Sacken, J.R. Dahn, *J. Electrochem. Soc.* 137 (1990) 2009.
- [3] Y. Matsumara, S. Wang, J. Mondori, *J. Electrochem. Soc.* 142 (1995) 2914.
- [4] W. Xing, J.R. Dahn, *J. Electrochem. Soc.* 144 (1997) 1195.
- [5] K. Guérin, A. Février-Bouvier, S. Flandrois, B. Simon, P. Biensan, *Electrochim. Acta* 45 (2000) 1607.
- [6] M. Kikuchi, Y. Ikezawa, T. Takamura, *J. Electroanal. Chem.* 396 (1995) 451.
- [7] E. Buiel, J.R. Dahn, *J. Electrochem. Soc.* 145 (1998) 1977.
- [8] S. Gautier, Ph.D. Thesis, Orléans, 1999.
- [9] P. Delhaes, J.C. Rouillon, J.P. Manceau, D. Guérard, A. Hérold, *J. Phys. Lett.* 37 (1976) 127.
- [10] J. Conard, H. Estrade, P. Lauginie, H. Fuzellier, G. Furdin, R. Vasse, *Physica* 99B (1980) 521.
- [11] E. Bueil, A.E. George, J.R. Dahn, *J. Electrochem. Soc.* 145 (1998) 2252.
- [12] J.N. Rouzaud, B. Duval, J. Leroy, in: J. Lahaye, P. Ehrburger (Eds.), *Fundamental Issues in Control of Carbon Gasification Reactivity*, Kluwer Academic Publisher, Dordrecht, 1991, p. 257.
- [13] J.N. Rouzaud, A. Galvez, O. Beyssac, C. Fontugne, C. Clinard, B. Goffe, in: *Proceedings of the 10th International Conference on Coal Science*, Vol. I, Taiyuan, China, 1999, pp. 25–28.