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On the Choice of Carbon Materials at the Negative Electrode of Li-ion Batteries : Graphite vs. Hard Carbons

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We report on the two families of carbon materials (graphites and hard carbons) known to be the most attractive host structures in Li-ion batteries. Both present drawbacks related to the irreversible capacity. For graphites, it is due to exfoliation, which can be suppressed by the presence of the rhombohedral form. In fact, we show that some structure defects are responsible for this effect. For hard carbons, a clear correlation has been found between the irreversible capacity and the closed pore volume determined from helium pycnometry measurements.

Keywords: Lithium batteries; rhombohedral graphite; hard carbons; closed porosity

INTRODUCTION

The recent development of lithium rechargeable batteries results from the use of carbon materials as a lithium reservoir at the negative electrode. Reversible intercalation, or insertion, of lithium into the carbon host lattice avoids the problem of lithium dendrite formation and provides large improvement in terms of cycleability and safety.

As a matter of fact, all carbon materials can be lithiated to a certain extent. However, the amount of lithium reversibly incorporated in the carbon lattice (the reversible capacity), the faradaic losses during the first charge-discharge cycle (the irreversible capacity), the profile of the voltage curves during charging and discharging, all depend on the structure, texture and heteroatom content of the carbon material. Analysis of the published results^[1] shows that the best electrochemical performances are obtained at both ends of the structural evolution, for highly crystalline and highly disordered materials.

In graphitic materials, with a low degree of turbostratic disorder, generally designated as 'graphites', the LiC_6 stoichiometry (372 mAh/g) can be approached within the potential range 0 - 0.3V vs. Li^+/Li . However, very often, they suffer from large faradaic losses in the first cycle, especially with electrolytes containing propylene carbonate. Co-intercalated solvent molecules are reduced at low potential in gaseous products which exfoliate the graphite matrix.

Highly disordered carbons, especially hard carbons, may display large reversible capacities which can be more than twice the graphite value. However, the voltage profiles generally develop large irreversible capacities and some hysteresis. In this case, the irreversible capacity is not due to exfoliation, which does not occur, but is believed to result from large surface areas (leading to large volumes of passivating layer) and from the presence of surface functional groups and of heteroatoms left from the organic precursor, which can react irreversibly with lithium.

In this paper, we report on the irreversible capacities of both families of materials. We give evidence for the beneficial effect of some structure defects against graphite exfoliation and we show that the irreversible capacity of hard carbon anodes can result from an additional mechanism : lithium trapping in the closed porosity.

GRAPHITE EXFOLIATION : EFFECT OF CRYSTAL STRUCTURE

The usual structure of graphite is the hexagonal one (Bernal structure), where carbon layers are stacked with a sequence of the type "ABAB". Another less common form of graphite, that is also found to occur naturally or synthetically, but never in isolation, is known as rhombohedral graphite. The stacking sequence is "ABCABC". It is always obtained in association, mixed with the Bernal type. Using mechanical grinding or ultrasonics, the rhombohedral volume fraction can be increased up to about 40%^[2]. Recently, a clear correlation was found by Simon et al.^[3] between the rhombohedral phase content of numerous graphites and the faradaic losses induced by exfoliation. When a graphite sample contains at least 30% of rhombohedral form, no exfoliation is observed, even with electrolytes containing a large amount of propylene carbonate (up to 90 vol%)^[4]. However, when the graphite samples are heat-treated at temperatures higher than 1000°C, the faradaic losses due to exfoliation re-appear, even if the rhombohedral content remains higher than 30%. This is shown in figure 1 where the faradaic losses measured in the first cycle are plotted as a function of the heat treatment temperature (HTT) for three different graphite samples. These samples initially contained 40% (UF2, SFG6) and 34% (BF16A) of rhombohedral form. They were heat-treated under argon at

temperatures ranging from 500 to 2200°C. The rhombohedral content, estimated from X-ray diffraction measurements, diminished weakly as expected, because of the thermodynamic metastability of this phase, but remained higher than 30% even for the highest HTT. Galvanostatic cyclings in Li/C cells, using 1M LiPF₆ dissolved in a (1:1:3) mixture of PC, EC and DMC for the electrolyte, gave irreversible capacity values shown in Fig. 1. Clearly, above HTT = 1000°C, the faradaic losses due to exfoliation are restored.

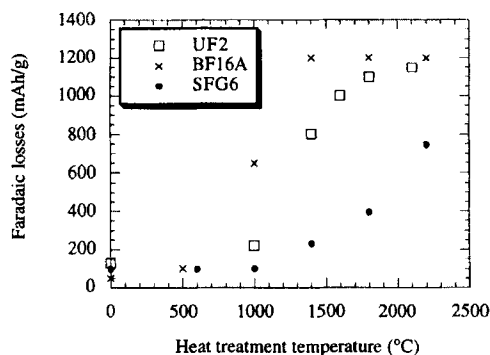


FIGURE 1 Evolution of faradaic losses as a function of heat treatment temperature

Raman spectroscopy experiments were carried out to understand this behaviour. Raman spectroscopy is a quite suitable method to study the microstructure of graphite materials. In the first-order spectrum of single crystal graphite, a main band appears at 1580 cm⁻¹ (E_{2g2} mode). This band is known as the G band and corresponds to displacements of carbon atoms strongly bonded within the graphene sheets^[5]. Two other bands appear in polycrystalline graphites or in unorganized carbons. The first one, at 1350 cm⁻¹, the so-called D band, is attributed to phonons out of the Brillouin zone center. Its activity is due to the breakdown of selection rules (k=0) resulting from disorder^[6]. Disorder causes also the appearance of a weak band, called D', near 1620 cm⁻¹, generally interpreted as resulting from a high density of phonon states for midzone phonons^[6]. The D band intensity, or the ratio $R = I_{1350}/I_{1580}$ of the integrated intensity of the disorder-induced line at 1350 cm⁻¹ to that of the Raman-allowed line at 1580 cm⁻¹, characterizes the degree of disorder in a graphitic material.

We found that graphite samples enriched in rhombohedral form always exhibit the D and D' bands. Figure 2 shows plots of the dependence on heat-treatment temperature of the ratio R for the three graphite samples of

figure 1. A strong decrease of R is observed for samples treated above 1000°C , which closely corresponds to the increase in faradaic losses.

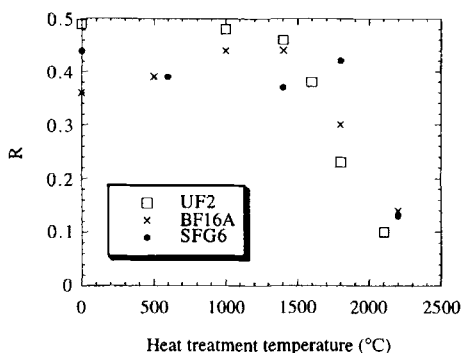


FIGURE 2 Evolution of R as a function of heat treatment temperature

Since there is no hint of reflexion broadening on X-ray diffractograms that could be related with the presence of disorder, we propose that the Raman band observed at 1350 cm^{-1} is mostly related to defects located at grain boundaries between rhombohedral and hexagonal domains. Such defects could hinder the layer opening necessary for the intercalation of solvated lithium species at the beginning of the first electrochemical cycle. They play the same role as the structure defects present in graphitizable carbons heat-treated below 2800°C , the treatment temperature which induces the beginning of exfoliation in these materials^[7]. But their nature is certainly different. For all the graphite samples investigated, the defects begin to disappear by annealing at about 1000°C , i. e. well below the rhombohedral-to-hexagonal transformation. This shows that the correlation previously found between the rhombohedral content and the irreversible capacity is an indirect one.

HARD CARBONS : ROLE OF THE CLOSED POROSITY

As mentioned above, large surface areas and heteroatom content are sources of irreversible capacity in hard carbons and, therefore, have to be minimized. But there is another important source of irreversibility, namely lithium trapping in the closed porosity, as we show below.

A series of hard carbon samples, with low heteroatom content and low specific surface area, that should therefore present low irreversibility, has been investigated by X-ray diffraction, helium pycnometry, complex impedance spectroscopy and galvanostatic cycling. The irreversible

capacities measured for the different samples ranged from 70 to 210 mAh/g. In a recent study of graphitic materials^[3], we have shown that the irreversible capacity due to the formation of the passivating layer is proportional to the double layer capacitance. Using the same electrochemical conditions as in the present study the proportionality coefficient has been found to be equal to 0.065 mAh/mF. In addition, the binder contribution to the faradaic losses has been estimated to be about 15 mAh/g of carbon. Both contributions can be assumed to be valid for the present samples. However, their sum is far from the measured values of irreversible losses. The remaining part amounts to 40 - 170 mAh/g.

Helium pycnometry measurements gave density values ranging from 1.75 to 1.99 g/cm³, much smaller than the density values (2.13 to 2.21 g/cm³) obtained from the average interlayer distance d_{002} given by X-ray diffraction. This means that the samples have a closed porosity inaccessible to helium. The closed pore volume, V_p , can be estimated from $V_p = 1/d_a - 1/d_t$, where d_a is the helium density and d_t the true density obtained from d_{002} .

Figure 3 shows the irreversible capacity corrected for passivation and binder effect as a function of the closed pore volume V_p , for the different hard carbon samples investigated. A linear relationship is observed with a slope of about 1400 mAh/cm³, which extrapolates to origin. Thus, in these materials, most of the irreversible capacity is due to lithium trapped in the closed porosity. Note that, if we assume a complete filling of the closed pore volume by lithium metal, the slope would be 2062 mAh/cm³, which means that the closed porosity is not completely filled up with lithium or that the closed porosity may also contribute to the reversible capacity to a certain extent.

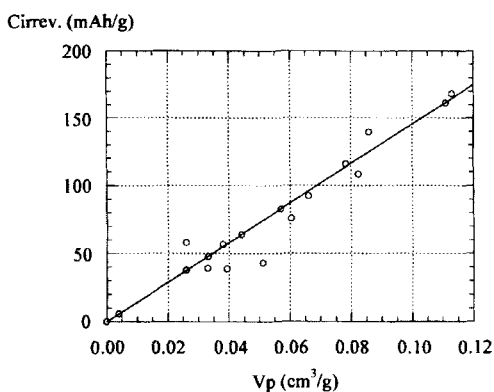


FIGURE 3 The irreversible capacity corrected for passivation and binder contributions as a function of the closed pore volume

CONCLUSION

Graphites enriched in rhombohedral phase do not experience exfoliation during the first lithium intercalation process, even in electrolytes containing a large amount of PC. In fact, we have shown that the beneficial effect of the rhombohedral phase against exfoliation must not be attributed to this phase itself, but rather to structure defects created during the formation of this phase. At the present time, such materials appear to have the best characteristics for the purposes of Li-ion batteries.

Nevertheless, some disordered carbons, with low surface area and low heteroatom content, could be of great interest, if it were possible to recover the lithium atoms trapped in the closed porosity, at least partly, for example by using mild oxidation or new cycling procedures. A few recent experiments in this line are encouraging.

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References

- [1] S. Flandrois and B. Simon., **37**, 165 (1999).
- [2] K. Guérin, S. Chehab, A. Février, J. Amiel, S. Flandrois and B. Simon, Proc. Eurocarbon '98. **vol. 1**, 27 (1998).
- [3] B. Simon, S. Flandrois, A. Février and P. Biensan, Mol. Cryst. Liq. Cryst., **310**, 333 (1998).
- [4] B. Simon, S. Flandrois, K. Guérin, A. Février, I. Ticulat and P. Biensan, J. Power Sources, in press.
- [5] R. Al-Jishi and G. Dresselhaus, Phys. Rev. B, **26**, 5414 (1981).
- [6] R. J. Nemanich and S. A. Solin, Phys. Rev. B, **20**, 392 (1979).
- [7] S. Flandrois, A. Février, K. Guérin, B. Simon and P. Biensan, Mol. Cryst. Liq. Cryst., **310**, 389 (1998).