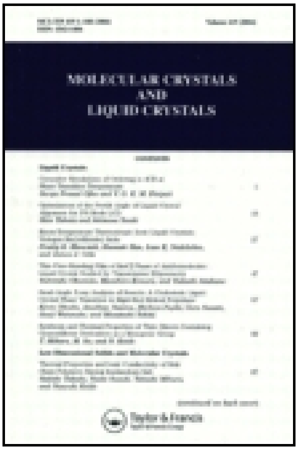

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A ^{7}Li NMR Study of a Hard Carbon as a Function of Temperature and Lithiation State

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To cite this article: K. Guerin, A. Fevrier-bouvier, S. Flandrois, M. Menetrier, B. Simon & P. Biensan (2000): A ^{7}Li NMR Study of a Hard Carbon as a Function of Temperature and Lithiation State, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 467-472

To link to this article: http://dx.doi.org/10.1080/10587250008025510

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 467-472
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Printed in Malaysia

A ^{7}Li NMR Study of a Hard Carbon as a Function of Temperature and Lithiation State

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Negative electrodes of lithium-ion batteries containing a hard carbon with different levels of lithiation were characterized by ^{7}Li NMR experiments. A dramatic effect of washing the lithiated electrodes with the solvent was observed. The spectra of unwashed electrodes in different states of lithiation show that three species seem to be present : covalently bonded, intercalated and pseudo-metallic lithium species, respectively.

Keywords: ^{7}Li NMR; Lithium-ion batteries; hard carbons

INTRODUCTION

Two types of carbon family are actually interesting for lithium-ion batteries: graphite and hard carbons. In order to study lithium insertion mechanism in these materials, ^{7}Li NMR is often used. Concerning graphite[1], ^{7}Li NMR spectra show a main band at 40 ppm corresponding to lithium intercalated between graphene layers (LiC_6 composition). Concerning hard carbons[2-4], ^{7}Li NMR spectra are different in position depending on the material studied which reflects the complexity of the insertion in this type of material. In this paper, we present the evolution of the ^{7}Li NMR spectra with the state of lithiation and upon cooling.

EXPERIMENTAL

The hard carbon studied was a sample from Mitsubishi Gas Chemical company, which has a low heteroatom content (C>96%), a low BET surface area (1.35 m^2/g) and a high closed porosity volume (0.111 cm^3/g) [5] .

Hard carbon powder was mixed with 5 w% Teflon aqueous dispersion and 5 w% acetylene black. The test cells were 20/25 Li/C coin cells with electrolyte 1M $LiPF_6$ PC/EC/3DMC (PC : propylene carbonate, EC : ethylene carbonate, DMC : dimethyl carbonate). A constant current density of 5 mA/g was used for all charge-discharge cycles on a galvanostatic MacPile controller. High reversible capacities (350 - 400 mAh/g) were reached. The cycling curves exhibit a classical low voltage plateau close to 0V which accounts for half the capacity.

For NMR measurements, the active material was extracted from the electrochemical cell in the dry box and was placed into NMR tubes without or after washing (with DMC or MeTHF). The aim of the washing process is to eliminate the Solid Electrolyte Interphase layer (SEI). ^7Li NMR spectra were recorded on a Bruker MSL200 spectrometer at 77.7 MHz, with static samples. A single-pulse sequence with phase cycling was utilised, with a 3μs pulse duration and a 1s repetition time. The spectrum width was 300 kHz, and the number of scans was in the 10000 range. The reference (0 ppm) was LiCl 1M in aqueous solution.

Three electrodes have been studied by NMR which have been extracted from cells discharged at -20 mV, charged at 0.08 V and charged at 2V vs Li^+/Li, respectively.

RESULTS AND DISCUSSION

Effect of washing

Fig. 1 shows the effect of washing on the ^{7}Li NMR spectra for materials recovered from the electrodes extracted from cells after discharge down to -20 mV. The peak with δ slightly negative for the unwashed sample is assigned to the SEI. After washing, this signal is eliminated, as expected. However, Fig. 1 shows that the other part of the signal is also greatly affected by the washing process.

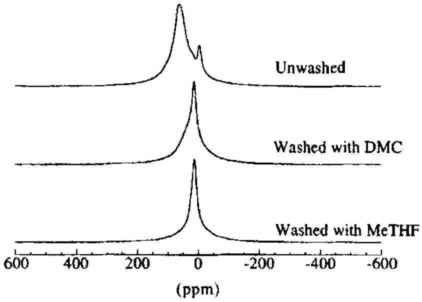

FIGURE 1 RT ^{7}Li NMR spectra of a fully lithiated hard carbon from an electrode unwashed, washed with DMC, washed with MeTHF

What happens is the transformation of the lithium species which give rise to the most shifted signal into other species with a smaller shift. This change is clearly more pronounced after washing with the more polar MeTHF. NMR measurements with decreasing temperature for the washed electrodes essentially show a broadening of the RT spectrum, which is rather different from the behaviour observed for the unwashed electrode (see below). We have no satisfactory explanation for this phenomenon. However, considering the changes that can be induced by washing, we have decided to perform no washing for the materials before the NMR characterisation discussed in the following. Therefore, one should keep in mind that slightly diamagnetically shifted signals must arise from the SEI, and maybe in part from a small amount of salt from the electrolyte, deposited during its evaporation.

Effect of the voltage of the battery

Fig. 2 shows the ^{7}Li NMR spectra obtained for an unwashed Teflon electrode from a cell discharged at -20 mV. Decomposition with lorentzian contributions shows that the main signal separates into three signals at low temperature. Two of these components shift to higher δ values , reaching 200 and 300 ppm respectively at 140K, whereas the third component seems to keep a constant position (~ 10 ppm) whatever the temperature. Furthermore, the signals widen at low temperature, and the SEI signal seems to disappear.

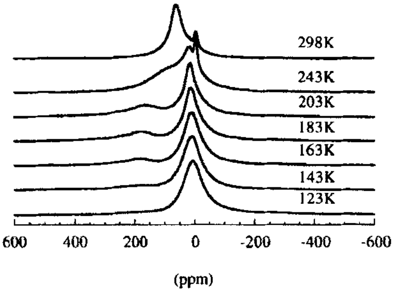

FIGURE 2 ^{7}Li NMR spectra of a fully lithiated hard carbon from an unwashed electrode at different temperatures

Fig. 3 shows the ^{7}Li NMR spectra obtained for an unwashed electrode from a cell charged at 0.08V, i. e. at the end of the low voltage plateau which accounts for half the capacity. Only one peak is clearly visible (in addition to that of the SEI). It seems that the main part of the signal is lost after a charge at 0.08V. Fig. 4 shows the effect of cooling on the ^{7}Li NMR spectra of the unwashed sample recovered in the charged state; only a strong broadening is apparent, although a small contribution remains around 250 ppm. We have recently proposed [5] an assignment of the three different signals present at low temperature (< 180K) for the discharged state.

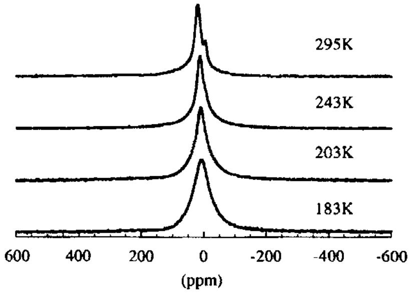

FIGURE 3 ^{7}Li NMR spectra of a hard carbon in half the charged state (0.08V) from an unwashed electrode at different temperatures

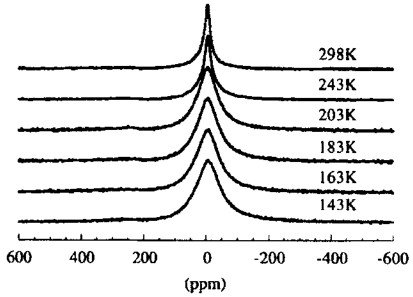

FIGURE 4 ^{7}Li NMR spectra of a hard carbon in the charged state from an unwashed electrode at different temperatures

The most positively shifted signal has been assigned to 'pseudo-metallic' lithium, the intermediate signal to 'intercalated' lithium and the rightmost signal to covalently bonded lithium ions. The lost of the most positively shifted peak after a charge at 0.08V can be interpreted as the disappearance of pseudo-metallic and intercalated lithium. In fact, it can be possible that 'intercalated' lithium species are still present but in fewer concentrations which induce a peak of weaker shift in comparison with 'intercalated' lithium in the fully lithiated materials. Also, it can be possible that the leftmost band is still present but widened and as a consequence lost in the background. Even for the fully lithiated materials, the leftmost band is no more visible under 160K. Moreover, the NMR spectra of a hard carbon in the charged state present a small contribution around 250 ppm. Based on the interpretation proposed above for the signals observed in the discharged state, the former may correspond to 'covalent' lithium, but with a smaller shift than in the discharged state since the carbon otherwise contains no 'intercalated' lithium, and therefore no charge transferred from it. In addition, the weak signal around 250 ppm visible at low temperature is reminiscent of what happens in the discharged state; it might therefore account for some pseudo-metallic lithium trapped within the porosity of the sample. Indeed, a correlation has been established between the closed porosity and the irreversible capacity in this type of material [6].

CONCLUSION

The ^{7}Li NMR characterisation of electrodes containing a hard carbon at different levels of lithiation reveals the complexity of the insertion phenomena in this type of material. Low temperature experiments show evidence for three different Li species in the fully lithiated state. An exchange process must take place at RT. However, we were not able to follow unambiguously the different signals above 200K. It was also the case during Li removal, as the quantitative study of NMR spectra is quite limited.

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