^{7}Li NMR studies on a lithiated non-graphitizable carbon fibre at low temperatures

K. Tatsumi,*[a] J. Conard,[b] M. Nakahara,[c] S. Menu,[b] P. Lauginie,[b] Y. Sawada[a] and Z. Ogumi[d]

[a] *Osaka National Research Institute, 1-8-31 Midorigaoka, Ideka, Osaka 563, Japan*
[b] *CRMD-CNRS, 1b, rue de la Férollerie, 45071 Orléans Cedex 2, France*
[c] *Institute for Chemical Research, Kyoto University, Gokasyo, Uji, Kyoto 611, Japan*
[d] *Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan*

^{7}Li NMR spectra of a lithiated non-graphitizable carbon fibre measured at temperatures below 200 K display three different signals and the NMR shift of one of the signals is larger than that of Li metal below 163 K.

Much attention has been focused on carbonaceous materials, *e.g.* graphite, petroleum cokes and carbon fibres, as a host for the Li^{+} ion, because carbon is one of the most promising anodes for secondary lithium batteries.[1,2] Both electrode potential and capacity of carbon anodes in organic electrolytes are dependent on the nature of the carbon used. Artificial carbon materials are classified into graphitizable (soft) and non-graphitizable (hard) carbons according to the degree of crystallinity by heat treatment.[3] In graphitizable carbons, graphite and carbons having the graphite-like stacking sequence of graphene layers to some extent give the lowest electrode potential (0–0.3 V *vs.* Li/ Li^{+}) during electrochemical insertion of Li^{+} ion.[4–7] The electrochemical capacity of graphite is limited to one lithium atom per six carbon atoms, *i.e.* LiC_6.[2,4]

On the other hand, non-graphitizable carbons heat-treated between 1000 and 1300 °C give a capacity higher than LiC_6. In addition, the carbons have a significant capacity in the potential range between 0 and 0.1 V, though the carbons have little amount of crystallites of the graphite-like stacking sequence.[8–10] Therefore, non-graphitizable carbons have been thought to have lithium storage sites different from the sites of lithium insertion into graphitizable carbons. ^{7}Li NMR methods have been used for analyses of Li in carbon materials.[5,8,11–13] Yamazaki *et al.* reported that lithium species in a non-graphitizable carbon, which showed a band at δ 90 in ^{7}Li NMR measurements at room temperature, consist of two species of lithium (δ *ca.* 190 and 20 at 140 K).[13] In the previous work,[8] it was shown that non-graphitizable carbon fibres also give capacity higher than LiC_6 with a significant capacity below 0.1 V. Here, we report the first ^{7}Li NMR data indicating three different lithium species in a non-graphitizable carbon fibre. Furthermore one of the lithium species gave a NMR shift larger than that of Li metal at temperatures below 163 K.

The non-graphitizable carbon fibre (FIP Petoca, nominal diameter 10 μm) prepared from an isotropic petroleum pitch was heat-treated at 1200 °C under a nitrogen atmosphere. The reversible capacity of the carbon fibre between 0 and 2.5 V was $x = 1.25$ for Li_xC_6 with a significant capacity, $x = 0.73$, between 0 and 0.1 V. The carbon fibre electrode was dried at 130 °C under vacuum for 24 h and then electrochemically reduced to 0 V in 1 mol dm^{−3} solution of $LiClO_4$† in ethylene carbonate (EC)–diethylcarbonate (DEC) (1 : 1, v/v) according to the procedure previously reported.[8] The carbon fibre fully lithiated to 0 V was washed with DEC and dried under vacuum for 15 min and then put into a NMR sample tube; the sample tube was sealed by an epoxy resin. All procedures for sample preparation were performed in an Ar-filled dry box. The sample was served for ^{7}Li NMR measurements using a wide line probe of a NMR spectrometer (CMX-200H Chemagnetics). NMR

shift was measured in ppm against LiCl (δ 0) used as an external standard.

The fully lithiated carbon fibre (reversible capacity $Li_{1.25}C_6$) showed a signal at δ 111 in the ^{7}Li NMR spectrum at 298 K [Fig. 1(a)]. The lithium species at δ 111 is quite different from those in graphitizable carbons, which give a peak between δ 7 and 45.[5,11] The shift of the signal at δ 111 (298 K) was independent of temperature from 298 to 243 K, whereas the shift increased with a temperature drop from 243 to 123 K. A new band appeared at δ 18 at temperatures lower than 243 K. The intensity markedly increased with lowering temperature. In addition, the spectra below 163 K showed a very broad signal at δ *ca.* 270.

The spectra below 203 K can be simulated by three Lorentzian peaks. The deconvoluted components for the spectrum at 143 K consisted of three signals at δ 18, 192 and 281 (Fig. 2). As seen in Fig. 1, the spectra showed high reversibility between cooling and heating; no spectral hysteresis was detected during a cyclic change of temperature. Moreover, all the signals were deconvoluted to Lorentzian line shapes. Since NMR peaks fitting to Lorentzian lines are observed for liquid- or gas-phase species, the present results suggest that
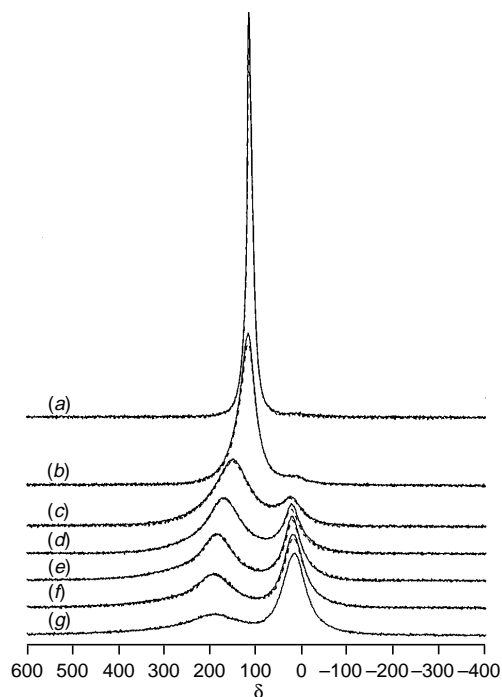

Fig. 1 ^{7}Li NMR (77.8375 MHz, relative to LiCl, δ 0) spectra for the fully lithiated carbon fibre recorded at (*a*) 298, (*b*) 243, (*c*) 203, (*d*) 183, (*e*) 163, (*f*) 143 and (*g*) 123 K; solid line, at the direction of cooling; dashed line, heating

lithium atoms in the carbon fibre are diffusive. These results thus indicate that the variation observed in the spectra is likely ascribed not to a crystalline phase transformation but to exchange of lithium nuclei among lithium atoms at different sites, and that the rate of exchange is slowed down on the timescale of NMR observation at low temperature, in agreement with the observed line broadening. The ^{7}Li NMR spectra at low temperature indicate that the fully lithiated non-graphitizable carbon fibre contains three different lithium species.

^{7}Li NMR shift of the signals determined by the curve fitting simulations is plotted as a function of temperature in Fig. 3. In general, ^{7}Li NMR shift for a lithium species in graphene layers is independent of temperature[11] as well as lithium metal,[14] and the shift for lithium in the fully lithiated graphitizable carbon heat-treated at 1000 °C was δ 18.[5] Although the peak position
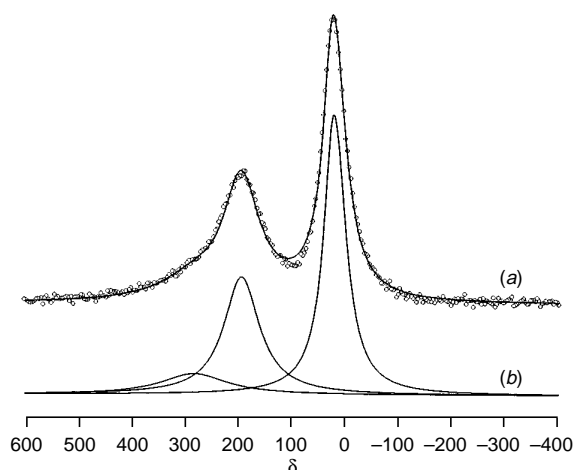

Fig. 2 ^{7}Li NMR spectra of the fully lithiated carbon fibre at 143 K: (*a*) experimental (○) and simulated (solid line) spectra; (*b*) deconvoluted spectra
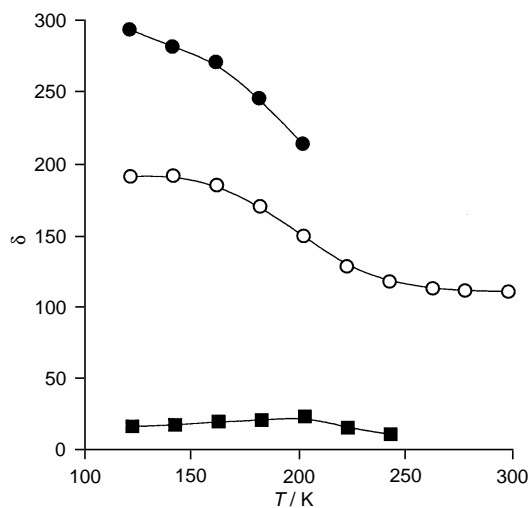

Fig. 3 ^{7}Li NMR shift of the signals determined by the curve fitting simulations as a function of temperature: the signals in the highest (●), the middle (○) and the lowest (■) fields in Fig. 2

in the lowest field in Fig. 2 showed considerable temperature dependence, the signal at δ 18 is inferred to be ascribed to the lithium species in crystalline graphene layers in the carbon fibre. On the other hand, the other signals are quite novel because NMR shift of the two signals increased with lowering temperature below 243 K. Furthermore, the shift of the signal in the highest field is higher than that of lithium metal (δ 262)[14] at low temperatures below 163 K. Although the structure of the lithium species of each peak is not clear at present, high shifts of the signals are explained as a Knight shift and correspond to lithium species with metallic character. Non-graphitizable carbons are considered to have microcavities between the crystalline grains.[3] Therefore, lithium species corresponding to the signals in the middle and the highest fields are inferred to be ascribed to lithium clusters formed in the microcavities of the non-graphitizable carbon fibre. The existence of the lithium species with metallic character is consistent with the result that the carbon fibre showed a significant capacity near 0 V. These features of the non-graphitizable carbon fibre are attractive as an anode material for advanced lithium-ion batteries.

Footnotes

References

1 J. R. Dahn, A. K. Sligh, Hang Shi, B. M. Way, W. J. Weydanz, J. N Reimers, Q. Zhong and U. von Sacken, in *Lithium Batteries: New Materials, Developments and Perspectives*, ed. G. Pistoia, Elsevier, Amsterdam, 1994, p. 1.
2 D. Billaud, A. Naji and P. Willmann, *J. Chem. Soc., Chem. Commun.*, 1995, 1867.
3 R. E. Franklin, *Proc. R. Soc., London, Ser. A*, 1951, **209**, 196.
4 T. Ohzuku, Y. Iwakoshi and K. Sawai, *J. Electrochem. Soc.*, 1993, **140**, 2490.
5 K. Tatsumi, T. Akai, T. Imamura, K. Zaghib, N. Iwashita, S. Higuchi and Y. Sawada, *J. Electrochem. Soc.*, 1996, **143**, 1923.
6 J. R. Dahn, A. K. Sleigh, H. Shi, J. N. Reimers, Q. Zhong and B. M. Way, *Electrochim. Acta*, 1993, **38**, 1179.
7 M. Inaba, H. Yoshida, Z. Ogumi, T. Abe, Y. Mizutani and M. Asano, *J. Electrochem. Soc.*, 1995, **142**, 20.
8 K. Tatsumi, T. Kawamura, T. Hosotubo and Y. Sawada, *J. Power Sources*, in the press.
9 J. S. Xue and J. R. Dahn, *J. Electrochem. Soc.*, 1995, **142**, 3668.
10 Y. Liu, J. S. Xue, T. Zheng and J. R. Dahn, *Carbon*, 1996, **34**, 193.
11 J. Conard and H. Estrade, *Mater. Sci. Eng.*, 1977, **31**, 173.
12 K. Sato, M. Noguchi, A. Demachi, N. Oki and M. Endo, *Science*, 1994, **264**, 556.
13 S. Yamazaki, T. Hashimoto, T. Iriyama, Y. Mori, H. Siroki and N. Tamura, *Proc. Soc. Solid-State NMR Mater.*, 1996, **20**, 39.
14 G. C. Carter, L. H. Bennett and D. J. Kahan, in *Metallic Shifts in NMR, Part I*, Pergamon Oxford, 1977, p. 239.