

Short Communication

Lithium doping/undoping in disordered coke carbons

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Abstract

The lithium doping/undoping behaviour of negative electrodes composed of heat-treated pitch coke with a disordered structure is investigated by using ⁷Li NMR and X-ray diffraction. A hysteresis is observed in the change in the average layer spacing $d(002)$ between the carbon sheets during the charge/discharge process. This change increases proportionally with the charge to a level of about 300 mAh/g but then stays nearly constant throughout the remainder of the charging to 773 mAh/g capacity. It decreases linearly, in proportion to the lithium undoping during the subsequent discharging. The ⁷Li NMR spectra suggest that two types of lithium doping sites exist in the coke: one type (S-site) has a wide range of spinning side bands while the other (C-site) has a narrower range. It is considered that C-site lithium atoms are located between the carbon sheets, while S-site lithium atoms are located at the surface of the microcrystallites formed by these sheets or at their microcavities. The C-site lithium atoms are far easier to dope/undope than the S-site counterparts.

Keywords: Lithium doping sites; Coke carbon; Lithium-ion batteries

1. Introduction

Interest is being directed towards carbonaceous materials as negative electrode materials for lithium-ion batteries of enhanced cell capacity [1,2]. Various carbons with disordered structures have been found [3–5] to exhibit higher charge capacities than graphite. These materials, however, exhibit a considerable irreversible capacity loss that leads to deterioration in the reversible cell capacity. In order to improve the charge/discharge of lithium-ion batteries, it is necessary to understand the mechanism of capacity loss in these disordered carbons. The present study examines the charge/discharge behaviour and lithium doping sites of negative electrodes that are composed of cokes heat-treated at relatively low temperatures.

2. Experimental

Carbon samples were obtained by heat-treating pitch coke in a nitrogen atmosphere at 750 °C (C-75) and 1000 °C (C-10) for 1 h. The carbon powders were sieved to under 40 μm. The working electrodes were prepared by mixing the carbon powders with 3 wt.% of organic polymer binder. The mixture was spread on to copper foil and then dried.

The electrochemical properties of the working electrodes were measured in a three-electrode cell that contained a counter electrode, a reference electrode, and a 1 M LiBF₄/propylene carbonate solution system. The charge/discharge characteristics were measured in the potential range of 0 to 2.0 V versus Li/Li⁺ at a fixed current density of 1.0 mA/cm².

⁷Li NMR measurements were performed with a Bruker, MSL 400P instrument (resonance frequency, 155 MHz). The average spacing between the carbon sheets $d(002)$ was calculated from the diffraction peak (near 24°) in the X-ray diffraction (XRD) profile with a Cu K α irradiation. The ⁷Li NMR and XRD analyses were conducted in an inert gas atmosphere.

3. Results and discussion

The XRD patterns of C-75 and C-10 are shown in Fig. 1. The broad diffraction peaks indicate a disordered structure in both carbons. The measured densities of the C-75 and C-10 carbons were 1.70 and 1.95 g/cm³, respectively.

The respective charge/discharge curves are presented in Fig. 2. In the first cycle, the C-75 had a charge capacity of 773 mAh/g, which is twice that of graphite, but a discharge

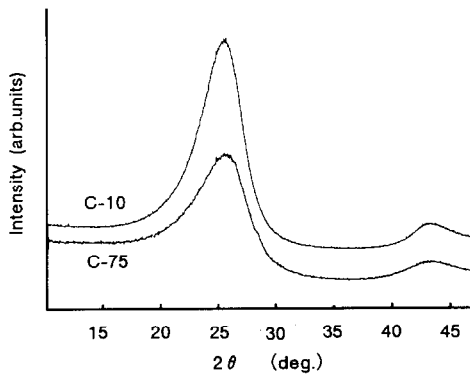


Fig. 1. X-ray diffraction patterns of C-75 and C-10.

charging to 773 mAh/g capacity. The change in the average layer spacing decreased linearly (in proportion to the lithium undoping) during the subsequent discharging process. A similar hysteresis in the $d(002)$ change has been reported for mesophase pitch carbon fibre that is heat-treated at 900 °C [6]. Throughout the second cycle, the $d(002)$ change in the C-75 carbon was more nearly proportional to the amount of lithium doping and undoping. These results indicate that two types of lithium doping sites exist in the C-75; both doping and undoping tend to occur more readily at sites that have a relatively strong influence on the carbon sheet alignment.

The ^7Li NMR spectra of the C-75 at various stages of lithium doping, in comparison with that of the C-10 at full charge, are presented in Fig. 5. Clearly, lithium is present in the C-75 in two distinct states in addition to that of the lithium salt. One is represented by the peak at a relatively high magnetic field strength (referred to as S-site Li), and the other

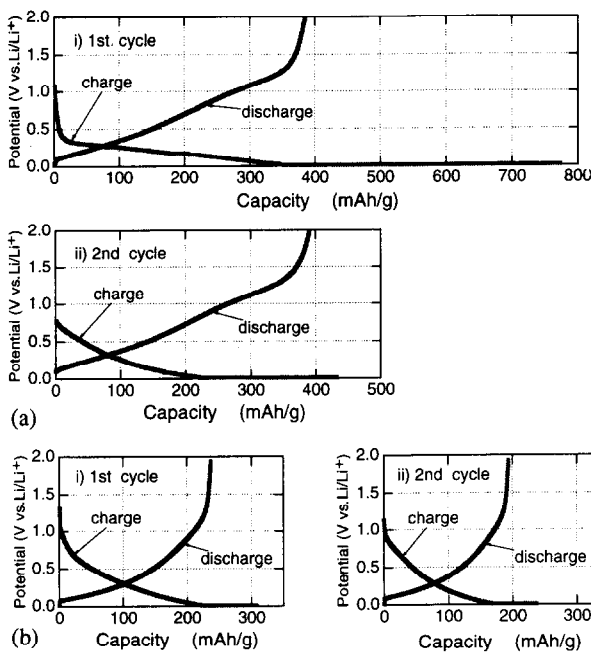


Fig. 2. Charge/discharge curves of C-75 and C-10: (a) C-75, and (b) C-10.

capacity of only 385 mAh/g, and thus an efficiency of less than 50%. In the second cycle, the efficiency increased to about 80%. For both cycles, its discharge curve exhibited a distinct plateau at about 1.2 V. The first cycle charge/discharge capacities of the C-10 (306 and 236 mAh/g, respectively) were both lower than those of the C-75, though the efficiency of 77% was substantially higher, and no plateau was present in the C-10 discharge curve.

The XRD patterns of the C-75 and C-10 at various stages of doping and undoping are given in Fig. 3. The characteristic stage structure of C_xLi intercalation compounds is absent; the only peak shift in evidence is that of the $d(002)$ diffraction peak. The change in the average layer spacing $d(002)$ between the carbon sheets of these carbons is shown in Fig. 4. For the C-10, it changed linearly with the charge throughout the first cycle. In the C-75, however, it increased proportionally with the charge to a level of about 300 mAh/g but then stayed nearly constant throughout the remainder of the

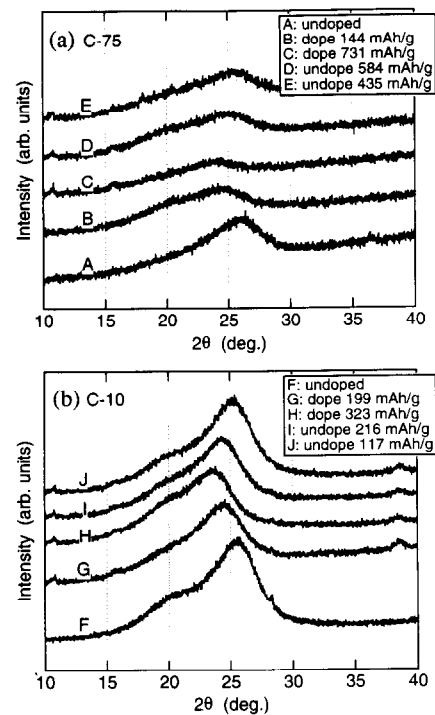


Fig. 3. X-ray diffraction patterns of C-75 and C-10 at various stages of lithium doping and undoping.

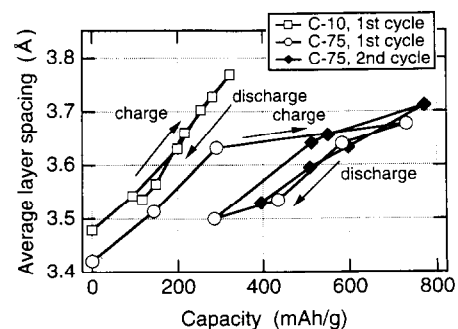


Fig. 4. Changes in average layer spacing of the C-75 and C-10 at various stages of lithium doping and undoping.

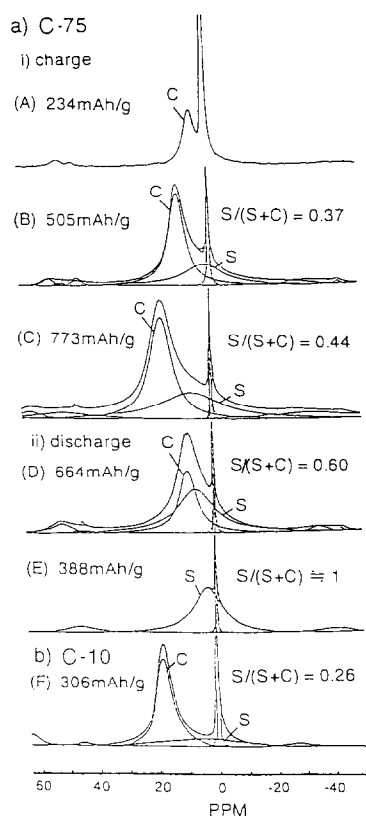


Fig. 5. ^7Li NMR spectra of C-75 and C-10 doped with lithium.

by the peak at lower magnetic field strength (referred to as C-site Li). Sato et al. [4] have similarly observed two different states of lithium in poly(*p*-phenylene) heat-treated at 700 °C, by ^7Li NMR analysis. As also shown in Fig. 5, the proportion of the S-site Li atoms in the C-75, as estimated from the NMR peak areas, increased from 0.37 to 0.44 during the late charging stage (505–773 mAh/g) and continued to increase throughout discharge, until it represented nearly all of the lithium remaining after full discharge (at 388 mAh/g). This doping pattern, together with the changes in $d(002)$ described above, indicate that the S-site is located in a region that does not strongly affect the carbon sheet alignment.

The NMR wide range spectra of the C-75 at early stage charging (Fig. 5, curve (A)) and final-stage discharging (curve (E)) are shown in Fig. 6(a) and (b), respectively. Spinning side bands are evident over a wide range in the latter, but not in the former. Such side bands generally imply the presence of a large electric field gradient [7,8]. This suggests electron state anisotropy in the region of the lithium atoms at final stage discharge. As these are predominantly S-site Li atoms, it therefore indicates that the S-sites are located either at the surfaces of the microcrystallites composed of several carbon sheets or in their microcavities, as opposed to the location of C-sites which lie between the carbon sheets and therefore strongly affect the sheet alignment, as shown by the change in $d(002)$ during early stage charging.

Taken together, the results of this study suggest that lithium doping and undoping in carbons such as C-75 that have a

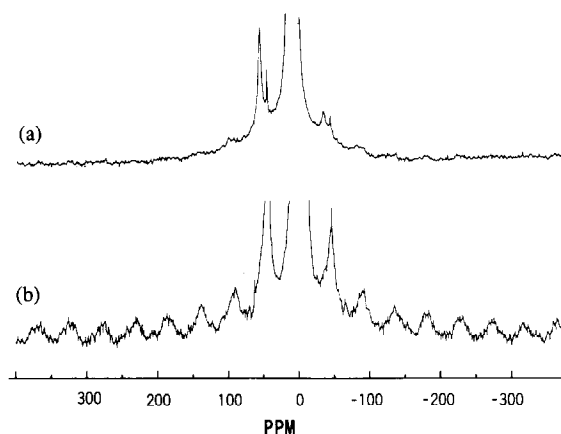


Fig. 6. Spectra of magic angle spinning NMR in the C-75 doped with lithium. (a) Early stage charging (343 mAh/g), and (b) final stage discharging (338 mAh/g).

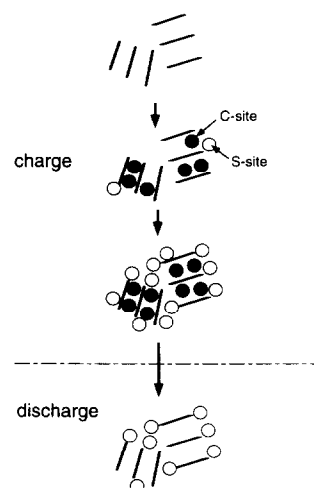


Fig. 7. Schematic representation of supposed lithium doping/undoping process in disordered carbon.

disordered structure proceeds as shown in Fig. 7. In this, doping the lithium atoms first occurs preferentially at the C-sites during the early stage charging and then occurs predominantly at the S-sites during late stage doping. Undoping initially involves C-site Li atoms during the early stage discharge followed by partial S-site Li undoping during late stage discharge. Most or nearly all of the S-site Li atoms remain in the carbon after full discharge. This model is also supported by comparison with the C-10, in which the number of S-sites is apparently much smaller and the irreversible charge is much lower.

4. Conclusions

It appears that two types of lithium doping sites exist in coke that has a highly disordered structure. One type (C-site) is located between the carbon sheets and the other (S-site) is located at the surface of the microcrystallites formed by these

sheets or at their microcavities. The nature and configuration of the S-sites are still to be clarified and further systematic investigations are in progress.

References

- [1] J.R. Dahn, A.K. Sleight, H. Shi, B.M. Way, W.J. Weydanz, J.N. Reimers, Q. Zhong and U. von Sacken, in G. Pistoia (ed.), *Lithium Batteries, New Materials, Developments and Perspective*, Elsevier, Amsterdam, 1994, p. 1.
- [2] A. Yoshino, K. Sanechika and T. Nakajima, *Jpn. Patent No. 90 863/87* (1987).
- [3] S. Yata, H. Kinoshita, M. Komori, N. Ando, T. Kashiwamura, T. Harada, K. Tanaka and T. Yamabe, *Synth. Met.* 62 (1994) 153.
- [4] K. Sato, M. Noguchi, A. Demachi, N. Oki and M. Endo, *Science*, 264 (1994) 556.
- [5] A. Mabuchi, K. Tokumitsu, H. Fujimoto and T. Kasuh, *Ext. Abstr., 7th Int. Lithium Battery Meet., Boston, MA, USA, 10–15 May 1994*, 1-A-11, p. 212.
- [6] A. Satoh, N. Takami, T. Ohsaki and M. Kanda, *Ext. Abstr., The Electrochemical Society, Fall Meet., Miami Beach, FL, USA, 9–14 Oct. 1994*, Proc. Vol. 94-2, p. 142.
- [7] C. Jager, in P. Diehl et al. (ed.), *Satellite Transition Spectroscopy of Quadrupolar Nuclei, NMR 31*, Springer, Berlin, 1994.
- [8] C.P. Slichter, *Principles of Magnetic Resonance, Third Enlarged and Updated Edition*, Springer, Berlin, 1989, p. 392.