

STUDY ON LITHIUM ION CHARGE AND DISCHARGE MECHANISM IN DISORDERED CARBON ELECTRODE

*C. Yamaguchi, S. Wang, J. Mondori, and H. Matsui
Fundamental Research Laboratories, Osaka Gas Co. Ltd, Osaka 554 Japan*

Introduction

Lithium ion rechargeable batteries using carbon materials as an anode have attracted a great deal of attention from both the scientific and industrial fields. Although considerable research has been conducted, the precise mechanism of the charging and discharging processes is still unclear. In the present study, in order to study the mechanism of the charging and discharging processes, the change of ^7Li -NMR parameters, for example, the Knight shift of the Li species was observed during the charging and discharging processes.

Experimental

Disordered carbon was obtained by heat-treating isotropic pitch at 1100°C . The resulting carbon exhibited a small crystallite size ($L_c=11\text{\AA}$) and large space distance ($d_{002}=3.7\text{\AA}$). The working electrodes were prepared by mixing the carbon powders with a polymer resin binder and compressed into a pellet. The electrochemical properties of the working electrodes were measured in a three-electrode cell that contained a counter electrode and a reference electrode. Details of the electrochemical condition are described elsewhere¹⁾.

^7Li -NMR measurements were performed with a Bruker, ASX 200 spectrometer. The spin-lattice relaxation times (T_1) were measured by means of the inversion-recovery pulse method ($\pi - \tau - \pi/2$).

Results and Discussion

The ^7Li -NMR spectrum of the discharged carbon electrode is shown in Figure 1. A broad peak at

-0.92ppm is observed, separated into a narrow peak at -0.83ppm and a broad peak at 0.60ppm by a curve fitting simulation. From FT-IR, X-ray diffraction, SIMS, ESCA¹⁾ and AFM, we confirmed that an irreversible capacity loss was caused by Li_2CO_3 forming on the surface and Li species formed in the bulk of the discharged carbon electrode because of side reactions during the first charging process. Therefore, the two peaks at -0.83ppm and 0.60ppm in Figure 1 are attributable to structures of Li_2CO_3 and Li species by the shift ($-1.5\text{ppm} \sim 0.9\text{ppm}$) of pure Li_2CO_3 which we measured. At the present stage, the detailed structures of these Li species are unclear.

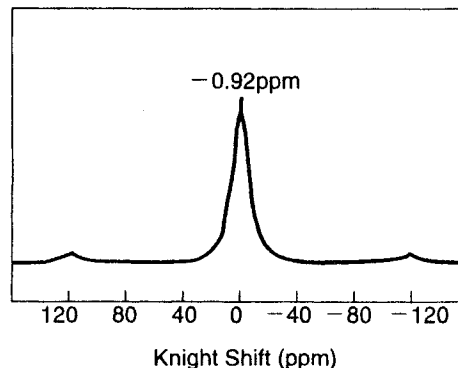


Fig.1 ^7Li -NMR spectrum of discharged carbon electrode

The ^7Li -NMR spectrum of the carbon electrode fully charged with Li is shown in Figure 2. Two peaks, at 71.95ppm and -0.92ppm , are observed. These results indicate that two lithium states exist at least in the Li-charged carbon electrode. We can assume that the broad peak (71.95ppm) corresponds to reversible capacity because this peak disappeared after the discharging process. The resonance frequency shift (71.95ppm) is different from those reported in literature, for example, 9.8ppm ²⁾, 20ppm ³⁾. This difference is probably related to the following two reasons. a)

One is the electronic spin density on the Li nucleus. b) The other is the crystal structure of the carbon electrode, such as the crystallite size and space distance.

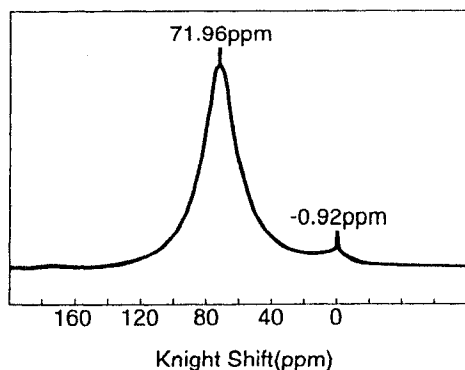


Fig.2 ^7Li -NMR spectrum of Li-charged carbon electrode

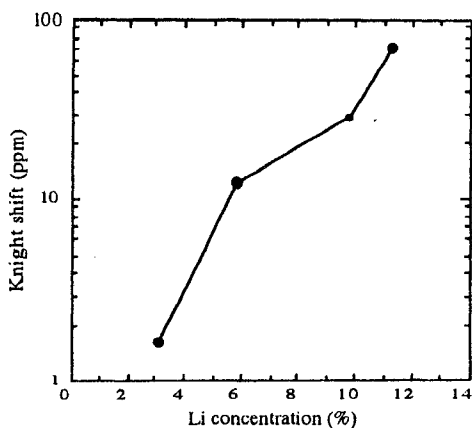


Fig. 3 Effect of Li species concentration on Knight shift

Next, the effect of Li species concentration in the Li-charged carbon electrode on the resonance frequency shift was studied. The results are shown in Figure 3. The resonance frequency of the peak shifted from 1.63ppm to 71.9ppm when the Li species concentration in the carbon electrode increased from about 3% to 11.3%. The resonance frequency shift appears to be a Knight shift because its range is very wide and proportional to the electron spin density at the Li nucleus. According to the above description, we can predict that the electron spin density at the Li nucleus increases with increasing Li species concentration during the charging process. In this study, the Knight shift of fully charged carbon electrodes is 71.95ppm and the shift is far from the Li metal shift (about 260ppm). Therefore, the electronic state of the fully Li-charged carbon electrode is still

ionic. The spin-lattice relaxation time(T_1) was obtained at various concentrations of lithium during the charging process as shown in Figure 4. The T_1 value decreases with increasing Li species concentration during the charging process. This result indicates that an interaction of Li ions with the lattice becomes strong with increasing Li species concentration in the carbon electrode. A T_1 value of this magnitude was reported for polyacetylene doped electrochemically with lithium, in which diffusive motion dominated the relaxation⁴. The Li ionic state and Li doping sites of the carbon electrode are still to be clarified and further systematic investigation, including measurement of the ^7Li -NMR at low temperature, is in progress.

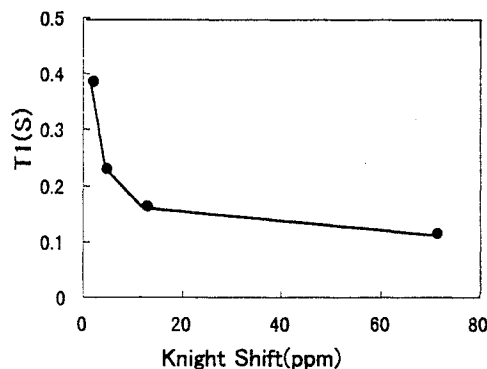


Fig.4 The variation of spin-lattice relaxation time (T_1) of Li with Knight shift

References

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