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Properties of a novel hard-carbon optimized to large size Li ion secondary battery studied by ^{7}Li NMR

Kazuma Gotoh [a,*], Mariko Maeda [b], Aisaku Nagai [b], Atsushi Goto [c], Masataka Tansho [c], Kenjiro Hashi [c], Tadashi Shimizu [c], Hiroyuki Ishida [a]

[a] *Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan*
[b] *Research Center, Kureha Corporation, Iwaki, Fukushima 974-8686, Japan*
[c] *National Institute for Materials Science, Tsukuba, Ibaraki 305-0003, Japan*

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Abstract

The state of lithium in a novel hard-carbon optimized to the anode of large size Li ion secondary battery, which has been recently commercialized, was investigated and compared with other existing hard-carbon samples by ^{7}Li NMR method. The new carbon material showed a peak at 85 ppm with a shoulder signal at 7 ppm at room temperature in static NMR spectrum, and the former shifted to 210 ppm at 180 K. The latter at room temperature was attributed to Li doped in small particles contained in the sample. The new carbon sample showed weaker intensity of cluster-lithium signal than the other hard-carbon samples in NMR, which corresponded to a tendency of less "constant voltage" (CV) capacity in charge–discharge curves of electrochemical evaluation. Smaller CV capacity and initial irreversible capacity, which are the features of the novel hard-carbon, are considered to correspond to a blockade of the diffusion of Li into pore of carbon.
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Keywords: Hard-carbon; Lithium; Battery; ^{7}Li NMR; Anode; Electric vehicle

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1. Introduction

Carbon has been used as an anode active material in lithium ion secondary batteries (LIB) [1]. One of the carbon materials, non-graphitizable carbon (hard-carbon), was used as an attractive anode in the early days of LIB used practically; however, in the present days graphite is mostly used as anode because LIB is mainly used to small size instruments that need high energy density per cell volume, for instance, portable PC, cellular phone, etc.

Recently, hard-carbon has been reconsidered as a prominent anode active material of LIB with increasing an expectation of application to large size instruments. Its properties of high power and long durability are expected to be superior as the power source of large size batteries [2], for example, the battery used to pure electric vehicle (PEV) or hybrid electric vehicle (HEV).

The structure and the electrochemical property of hard-carbon have been investigated by various methods. The existence of void (micropore) in hard-carbon has been implied from the smaller density of hard-carbon ($\approx$1.5 g cm^{-3}) than graphite (2.26 g cm^{-3}) [3]. The pore is not thought to be connected easily to outer space because very slow adsorption of N_2 gas into hard-carbon for over 1 week is observed when the nitrogen adsorption isotherm is measured. Concerning the pore, some authors (Franklin [4], Conard and Lauginie [5], and so on [6,7]) proposed the structure of hard-carbon.

It was reported that the lithium fully-doped in hard-carbon showed a broad ^{7}Li NMR signal at about 85–120 ppm at room temperature [8–15]. Tatsumi et al. have shown that the signal for Li-doped non-graphitizable carbon splits to two peaks at 192 and 18 ppm at 143 K [9]. The 192 ppm signal was explained by quasimetallic lithium forming a lithium cluster in the pore of hard-carbon structure. The 18 ppm peak was attributed to the Li ion intercalated into graphene layers and the Li ion existing on the edge of carbon.

One of characteristic properties of LIB using hard-carbon as anode is that the charge–discharge curve shows two stages,

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[*] Corresponding author. Tel.: +81 86 251 7776; fax: +81 86 251 7832.
E-mail address: kgotoh@cc.okayama-u.ac.jp (K. Gotoh).

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viz. the stage proportional to charge voltage and the stage of constant voltage (CV). The cell can be charged (lithiated) fast by constant current (CC) in the former stage, while in the CV stage it is charged slowly with keeping the potential at 0 V. The CV stage has been noticed as the origin of higher capacity than 372 mAh g^{-1} of theoretical graphite anode of LiC_6, however, it is not preferred for large size battery. The power sources of large instruments like electric vehicles require a high charge–discharge rate (10–40 C) [2], which cannot be achieved at the CV stage of hard-carbon. On the other hand, the rate property of CC stage is generally superior to graphite. Still more, state of charge (SOC) of battery can be easily observed and controlled on the CC stage since it is proportional to the voltage of cell, and strong pulse-like input and output can be received because of the enough margin of electronic potential. Therefore, hard-carbon having little CV capacity is desired for large size battery. In general, heat treating of hard-carbon by high temperature can result smaller CV capacity but also leads to smaller CC capacity.

Recently, a novel hard-carbon having low CV capacity, Carbotron P(J) (Kureha Corporation), has been supplied. This carbon is expected to be good for large size battery because of smaller initial irreversible capacity and CC capacity same as normal hard-carbon. We intended to investigate the properties of the new carbon comparing the normal hard-carbons, Carbotron PS(F) and Carbotron P(F) (Kureha Corporation), and to make clear the state of lithium doped in the hard-carbon by ^{7}Li NMR method.

2. Experimental

The hard-carbon samples, (A), (B) and (C) are Carbotron P(J), Carbotron PS(F) and Carbotron P(F), respectively, which are prepared from a petroleum pitch and heat-treated in non-reactive gases [16,17]. The SEM observation on the surface of (A) is shown in Fig. 1. X-ray powder diffraction (XRD) patterns of three samples were measured on Rigaku RAD-C diffractometer with roter-flex and Cu Kα radiation. The particle sizes of samples were measured on Micromeritics Microtrac-FRA laser diffraction particle size analyzer.

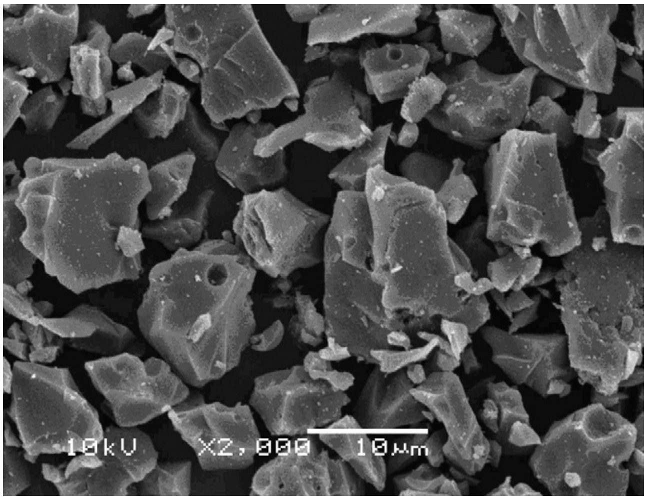

Fig. 1. The scanning electron micrograph of the carbon (A).

Test cells using carbon samples as anode active materials were made to evaluate the electrochemical properties as well as to obtain the specimens for NMR measurements. Lithium metal was employed as a counter electrode. The electrolyte of 1 mol dm^{-3} $LiPF_6$ solution in 1:1 (volume ratio) propylene carbonate (PC):dimethyl carbonate (DMC) was used. Electrochemical lithium insertion was performed at first with constant current density of 0.5 mA cm^{-2}. After the cell voltage reached to 0.0 V, the cell was kept at 0.0 V until the equilibrium current (the CV lithiation process). Electrochemical lithium extraction process carried out galvanostatically at 0.5 mA cm^{-2}.

The lithiated carbon electrodes were taken out from the cells and washed by DMC in an Ar atmosphere. After drying, the specimens were sealed into sample tubes with He gas for MAS NMR and static NMR measurements. ^{7}Li MAS NMR spectra were recorded on sample (A) to observe the dependence of insertion capacity by Bruker AVANCE 400 spectrometer at room temperature. The spinning rate was 5 kHz. Three spectra at the cell voltage of 0.1 V (155 mAh g^{-1}; the end of the CC lithiation process), 0.0 V (300 mAh g^{-1}; fully lithiation), and 0.0 V (500 mAh g^{-1}; the end of the CV lithiation process) were measured. Static ^{7}Li NMR measurements were performed by 11.7 T magnet and Thamway spectrometer at the temperatures between 30 and 293 K. The signal of saturated LiCl water solution was used as the 0 ppm-standard for the ^{7}Li NMR chemical shift above 273 K for both NMR measurements. Below 273 K, the center of the signal of LiCl powder was defined as 0 ppm. A single pulse sequence was adopted to the measurements.

3. Results

3.1. XRD and particle size analyses

XRD patterns of three samples are shown in Fig. 2. The interlayer distances and the crystallite size factors (L_c) calculated from XRD (0 0 2) reflection using Scherrer formula [18] are

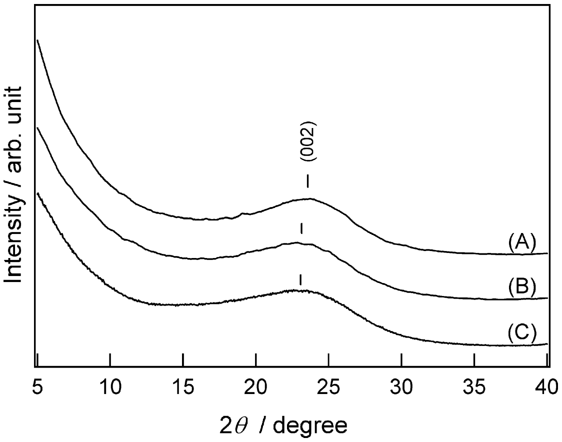

Fig. 2. Powder XRD patterns of carbon (A), (B) and (C).

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