



Short communication

Analysis of hard carbon for lithium-ion batteries by hard X-ray photoelectron spectroscopy



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HIGHLIGHTS

- Lithium insertion mechanism into hard carbon is discussed.
- ⁷Li NMR, X-ray photoelectron spectroscopy, and hard X-ray photoelectron spectroscopy are used in this study.
- The existence of different Li insertion sites is proved by these spectra.

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ABSTRACT

Non-graphitizable carbon (hard carbon) as a negative electrode material for lithium-ion batteries is investigated by X-ray photoelectron spectroscopy, and hard X-ray photoelectron spectroscopy (HX-PES). HX-PES spectra have peaks of both the solid electrolyte interphase on the hard carbon surface and the hard carbon itself. The change in spectrum with state of charge is observed by HX-PES. Hard carbon has two types of lithium insertion site; between graphene sheets and into nano-scale voids. These spectroscopic results are consistent with the lithium insertion mechanism into hard carbon.

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1. Introduction

Lithium-ion batteries, which consist of a nonaqueous electrolyte with carbon as a negative electrode and transition metal oxides containing lithium ion as a positive electrode have been commercialized as power sources for portable electronic equipment, e.g., laptop computers, cellular phones and so on. Despite their associated high energy density, lithium metal electrodes have been plagued with a dendrite growth problem that can result in thermal

runaway, and thus carbon materials have come into practical use as negative electrodes [1]. Among the carbonaceous materials studied for use as negative electrodes in lithium-ion batteries, graphite has been widely used in commercial lithium-ion batteries owing to the resulting low working potential, high reversible capacity and other characteristics. Other carbonaceous materials have also been studied in an attempt to enhance the performance of lithium-ion batteries. Hard carbon is a promising candidate material for lithium-ion batteries in hybrid electrical vehicles, offering excellent cyclability and high input/output performances [2].

It is pointed out that the hard carbon should have many pores in the structure because its density is lower than that of graphite. Various structural models for hard carbon have been suggested by Shiraishi [3], Franklin [4] and Jenkins *et al.* [5]. Based on these models, representative lithium intercalation mechanisms of the

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hard carbon are known as the card-house model [6] and the wave model [7]. Although results of X-ray diffraction and transmission electron microscopic observations suggest that these structural models have a low crystalline and complex internal structure, their details and sites of lithium have remained unclear. Recently, Nagao *et al.* [8] reported their results of crystal structural analyses for hard carbon using X-ray and neutron diffraction-pattern simulation, neutron small-angle scattering and neutron total scattering techniques, showing that the state of lithium in hard carbon is very similar to the wave model. In the case of $E < 0.1$ V vs. Li/Li^+ , lithium occupies the nano-void formed by stacking faults in two-dimensional graphene layers, and a large capacity occurs. Lithium in hard carbon has at least two states: between graphene sheets, like graphite, and in nano-voids. The states of lithium in hard carbon have been characterized by ^7Li nuclear magnetic resonance (NMR) which reveals two kinds of lithium; ionic and metallic [9,10]. X-ray photoelectron spectroscopy (XPS) is a common tool to investigate the electronic state of elements in compounds. Electrochemically lithiated carbon has a solid electrolyte interphase (SEI) on the surface, which behaves a barrier to the XPS measurement. Although XPS using argon sputtering can be used to determine the depth profile of the SEI, the details of lithium in carbon materials have not been thoroughly evaluated.

The hard X-ray photoelectron spectroscopy (HX-PES) is a powerful tool to observe active materials directly under the SEI and/or the sediment because its probe depth is several tens of nanometers and insensitive to the surface condition. In the case of the positive electrode, decomposition products of the electrolyte also amass on the surface of electrodes [11,12]. These sediments are very thin but present a barrier to XPS measurement, like the SEI of the negative electrode. Argon sputtering is not suitable in case of the positive electrode because the whole product on the surface is blown away and active material is reduced very easily. We have already successfully observed its surface directly by HX-PES in a synchrotron facility [12] and clarified the superiority of HX-PES for the surface analysis of electrode. In this study, we report our direct observation of a negative electrode behind the SEI by HX-PES, and the lithium condition of hard carbon is discussed. ^7Li NMR measurements are also carried out for comparison.

2. Experimental

We used 18650-type cylindrical cells of capacity *ca.* 380 mA h for this study. These were designed to have a rate capability of more than 10 C. The cells were constructed from pressed double-side coated electrodes using a high-power design; the positive electrode was comprised of $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA, Toda Kogyo Corp.), acetylene black (AB, DENKA) and poly(vinylidene difluoride) (PVDF, Kureha Corp.) binder, and the negative electrode consisted of non-graphitizable carbon (hard carbon, Kureha Corp.) and PVDF (Kureha Corp.) binder. 1 mol dm^{-3} LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) with a volume ratio of 1:2 was used as the electrolyte.

The state of charge (SOC) for cells was controlled from 0% to 90% and disassembled in a glove box under dry argon. The electrodes were soaked for more than 2 min in DMC to remove remnant LiPF_6 , and then used as samples after drying *in vacuo* at room temperature for more than 10 h. A pristine electrode, never exposed to electrolyte, was prepared as a reference sample.

HX-PES was performed at BL47XU/SPring-8 with the approval of the JASRI. The X-ray photon energy was *ca.* 6.0 keV. The total energy resolution was estimated as 240 meV from Fermi edge of Au measurement. The peak position of the C1s with the highest binding energy was assumed to be caused by $-\text{CF}_2-$ of PVDF and set to 290.5 eV as a reference point for the sample charge-up

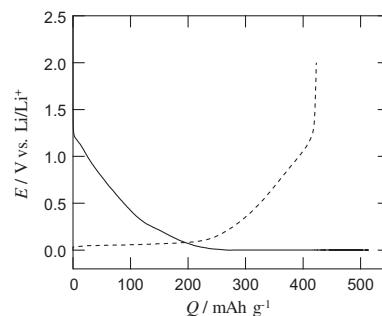


Fig. 1. First galvanostatic charge (lithium insertion process; solid line) and discharge (lithium extraction process; dashed line) curves of a hard carbon/lithium metal cell.

correction. The C1s profiles were decomposed into six peaks and Shirley's background by the curve-fitting software XPSPEAKS 4.1. Conventional XPS measurements were also performed on a PHI 5000 VersaProbe (ULVAC-PHI) with monochromatic $\text{Al K}\alpha$ (1.4866 keV). Charging effects by the poor surface conductivity were minimized by applying a 10 eV argon ion gun. In both cases, sealed vessels were used to transfer samples from the glove box to the analyzer chamber in order to avoid air exposure.

The lithiated hard carbons were examined by ^7Li NMR spectroscopy. The electrodes were put in NMR sample tubes in a dry box and set into a wideline probe of a ^7Li NMR spectrometer ($B_0 = 4.70$ T; $\nu_0 (^7\text{Li}) = 77.8$ MHz; CMX-200H, Chemagnetics Corporation). Line shift δ was measured with aqueous LiCl solution as an external standard.

3. Results and discussion

Based on previous studies [8,13,14], lithium occupies sites between graphene layers above 0.1 V vs. Li/Li^+ and in nano-scale voids below 0.1 V vs. Li/Li^+ . Fig. 1 shows an initial charge–discharge curve of a half-cell consisting of lithium metal and hard carbon electrodes. As shown in Fig. 1, a very large capacity is observed below 0.1 V vs. Li/Li^+ , and irreversible capacity accompanied by the formation of the SEI is observed. From this result, the relationship between the SOC of the 18650-type cylindrical cells and the potential (vs. Li/Li^+) of the hard carbon electrode can be evaluated as summarized in Table 1. For example, SOC = 70% means that the negative electrode is almost 0.1 V vs. Li/Li^+ .

Fig. 2(a) and (b) shows C 1s and Li 1s core-level spectra for hard carbon electrodes, respectively. The pristine sample has two peaks at 284.5 and 290.0 eV in the C 1s spectrum. The former peak relates to graphene layer parts in hard carbon [15,16] and the latter peak is assigned to $-\text{CF}_2-$ in PVDF [17,18]. A peak of $-\text{CH}_2-$ in PVDF, which can be observed at 286.0 eV [17,18], overlaps with the slope of the former peak. Samples of lithiated hard carbon have two peaks at 284.0 and 289.0 eV, which are almost independent of SOC. These peaks are assigned to the SEI, which consists of hydrocarbon, organic carbonates, lithium carbonate and so on [19–21]. The peak at 55.0 eV in the Li 1s spectrum corresponds to LiF and/or Li_2CO_3 in the SEI. It is very difficult to decompose these peaks because of the

Table 1
Relationship between SOC and negative electrode potential.

SOC/%	Electrode potential/V vs. Li/Li^+
0	0.540
30	0.283
50	0.204
70	0.096
90	0.072

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