Observation of micropores in hard-carbon using Xe-129 NMR porosimetry

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Abstract

The existence of micropores and the change of surface structure in pitch-based hard-carbon in xenon atmosphere were demonstrated using ^{129}Xe NMR. For high-pressure (4.0 MPa) ^{129}Xe NMR measurements, the hard-carbon samples in Xe gas showed three peaks at 27, 34 and 210 ppm. The last was attributed to the xenon in micropores (smaller than 1 nm) in hard-carbon particles. The NMR spectrum of a sample evacuated at 773 K and exposed to 0.1 MPa Xe gas at 773 K for 24 h showed two peaks at 29 and 128 ppm, which were attributed respectively to the xenon atoms adsorbed in the large pores (probably mesopores) and micropores of hard-carbon. With increasing annealing time in Xe gas at 773 K, both peaks shifted and merged into one peak at 50 ppm. The diffusion of adsorbed xenon atoms is very slow, probably because the transfer of molecules or atoms among micropores in hard-carbon does not occur readily. Many micropores are isolated from the outer surface. For that reason, xenon atoms are thought to be adsorbed only by micropores near the surface, which are easily accessible from the surrounding space.

Keywords: amorphous materials; microporous materials; NMR; hard carbon; xenon

1. Introduction

Carbon materials have generally been used as active materials in anodes of lithium ion secondary batteries (LIBs) from the dawn of LIBs' history [1]. One carbon material, non-graphitizable carbon (hard-carbon), after heating to temperatures greater than 1000°C, has been used as anode active materials. It is expected to be superior for use in batteries of large devices such as electric vehicles because of its excellent power and durability [2, 3]. Characteristically, cells using hard-carbon as an LIB anode provide greater charge capacity (500-600 mAh g^{-1}) than the theoretical capacity of a first-stage graphite anode (LiC_6: 372 mAh g^{-1}). The charge-discharge curve shows two stages: the stage proportional to charge voltage and the stage of constant voltage (CV). The cell can be charged (lithiated) rapidly by constant current (CC) in the former stage, but in the CV stage it is charged slowly while maintaining the potential at constant voltage. It has been reported that ^{7}Li NMR signals of fully lithiated hard-carbon showed two peaks at about 15 ppm and about 200 ppm, at the temperature range about 130-210 K [3-7]. The signals have been explained respectively by lithium ion intercalated into graphene layers and quasimetallic lithium forming a lithium cluster in the pore of hard-carbon. In a previous paper [3], we demonstrated that the CV capacity of some hard-carbon samples was nearly proportional to the intensities of the ^{7}Li NMR signals of quasimetallic lithium, which composes the Li cluster in the hard-carbon structure.

It is anticipated that hard-carbon has micropores because of the lower density of hard-carbon (≈1.5 g cm^{-3}) than that of graphite (2.26 g cm^{-3}) [3], [8]. The hard-carbon structure has attracted interest since its discovery in the early twentieth century by Franklin [9]. Some structural models including micropores have been proposed by others (Conard et al. [10], Jenkins et al. [11], Azuma [12]). Structural descriptions of micropores in hard-carbon are roughly classifiable into two: the space surrounded by edges of graphene sheets (based on the Franklin model [9]), and the void between graphene sheets [13] (based on the Conard model [10]). However, previously employed methods including microscopic observations (TEM & SEM), XRD, and N_2 gas isotherm measurements have not yielded accurate evidence of a porous structure. Nevertheless, results of neutron scattering and X-ray small angle scattering have suggested that a nanoscale void exists between graphene sheets [13]. It is needed to investigate the structures of the Li storage sites of hard-carbon for the developments of LIB anodes, as well as worthy for fundamental understanding about amorphous structure of carbon materials.

In fact, ^{129}Xe NMR is known as a useful method to investigate porous structures [14, 15]. The method was first proposed by Ito and Fraissard in 1980 [16] and has been applied [17] to myriad porous materials, including zeolites [14, 18-20], mesoporous materials [21-24], glasses [25], polymers [26-29], fullerenes [30], nanotubes [31, 32], activated carbons [33-36]. In ^{129}Xe NMR for xenon adsorbed in porous materials, the ^{129}Xe NMR chemical shift value (d) can be expressed as [15]

$$d = d_0 + d_\mathrm{S} + d_\mathrm{Xe\text{-}Xe} \cdot r_\mathrm{Xe} + d_\mathrm{SAS} + d_\mathrm{E} + d_\mathrm{M} \;, \qquad (1)$$

where d_0 is the reference (xenon gas at zero density). Also, d_S arises from collisions between xenon and the channels' surfaces, $d_{Xe\text{-}Xe} \cdot r_\mathrm{Xe}$ arises from Xe-Xe collisions and is expected to be linear with Xe density under low-loading conditions, d_SAS contributes at a very low level of xenon loading by the effect of strong adsorption sites (SAS), d_E and d_M account respectively for the presence of electric fields and paramagnetic species. The shift value at zero density is related to the pore size through the Xe-wall interaction term (d_S). The shift value in the high-loading region depends on the local density of adsorbed xenon. Ueda et al. [33] investigated the intermolecular interaction of xenon adsorbed in activated carbon fiber (ACF) according to the pressure dependences of ^{129}Xe NMR using an *in-situ* variable pressure NMR probe. For the present study, we intend to find the micropore of hard-carbon and investigate the inner-structure and surface in xenon atmosphere using ^{129}Xe NMR. Using that method, pressure dependences of xenon in hard-carbon were measured in addition to NMR spectra of hard-carbon in which xenon had been adsorbed at atmospheric pressure after evacuation at 773 K.

2. Experimental

2.1 High-pressure ^{129}Xe NMR measurement

Carbotron PS(F) (single point BET surface area is 7.0 m^2 g^{-1}; Kureha Corp.,) was used for all experiments as hard-carbon samples. The electrochemical properties of the sample were reported in ref. [3]. The ^{129}Xe NMR spectra at high pressure were recorded using a spectrometer (55.6 MHz, MSL-200; Bruker Analytik GmbH) with a home-built variable pressure NMR probe [28]. Before measurements, specimens (a) and (b) were evacuated (≈0.1 Pa) respectively at room temperature for 1 h and at 673 K for 72 h. The specimens were filled into pressure-resistant NMR cells and placed in a high-pressure NMR probe. The 0.1 MPa Xe gas signal was used as the 0-ppm standard for the ^{129}Xe NMR chemical shift. A single pulse sequence with a pulse delay of 5 s and a $\pi/2$ pulse of 3 *m*s, which were adjusted from the ^{129}Xe gas signal, were used for measurements.

2.2 ^{129}Xe NMR measurement at atmospheric pressure

Six specimens for measurements at atmospheric pressure (=0.1 MPa) were prepared as follows: heated at 773 K for 1-7 days under reduced pressure (≈0.1 Pa), then exposed to Xe gas at 0.1 MPa, annealed at 773 K for 1-7 days, and then sealed into 9 mmϕ glass sample tubes with Xe gas. The measurements were performed using the same NMR system with a normal probe for liquid samples. The 0-ppm-standard for the chemical shift and the pulse sequence were the same as those for high-pressure measurements.

2.3 XRD and Mercury porosimetry

After NMR measurements, powder X-ray diffraction (XRD) was measured of samples taken from NMR sample tubes for comparison of the structure with that of the sample before heat treatment. The samples' XRD patterns were measured using a diffractometer (RAD-C; Rigaku Corp.) with Cu-K_α radiation. A mercury porosimetry measurement was performed for the hard-carbon sample to investigate the distribution of pores larger than 2 nm, using a porosimeter (Autopore 9200; Micromeritics Instrument Corp.).

3. Results and Discussion

3.1 High-Pressure NMR

The ^{129}Xe NMR spectra of samples (a) and (b) with 4.0 MPa Xe gas pressure are shown in Fig. 1. For each sample, two strong peaks were apparent at 27 and 34 ppm, with a weak peak at 210 ppm. Although the intensity of the latter peak was less than 1/10 that of the 34 ppm peak, it was observed surely at the same shift values for plural samples, so that it could not be attributed to noises of the spectra. The shift values were equivalent in spite of their different evacuation temperatures and times. The pressure dependences of the 27 and 34 ppm peaks of (b) are respectively shown as closed circles and open circles in Fig. 2. The peak of 27 ppm for a sample at higher pressure (4.0 MPa) is attributed to free Xe gas because of its pressure dependence, which agrees with the previously reported result [28]. The 34 ppm peak can be assigned to xenon existing in large pores, i.e., macropores (larger than 50 nm) or mesopores (2-50 nm), of hard-carbon particles observed using mercury porosimetry (Fig. 3) through comparison with those reported for ACF [33]. That assignment can be made by referring to ACF signals because both Carbotron PS(F) and ACF have hard-carbon structures. Consequently, they are inferred to have similar surfaces. The increase in the shift value (open circles in Fig. 2) with lower pressure of less than 1 MPa is interpreted as the effect of paramagnetic radicals that are included in the hard-carbon framework. At low pressure, many of Xe atoms are adsorbed in pores of carbon, which have many paramagnetic sites. With increasing Xe gas pressure, Xe - wall interaction become relatively weaker because of the rising of Xe - Xe interaction; the shift closes to the essential value reflecting pore size.

It may be an evidence of mesopores because the shift of xenon in macropores can not be so far from 0 ppm at 0.1 MPa. The peak at 210 ppm for a sample at higher pressure (4.0 MPa), which was too weak to observe pressure dependence, is assignable to xenon in micropores (smaller than 1 nm) from ACF data [33]. Although micropores exist in the hard-carbon sample, as evidenced by the peak, the xenon atoms in the micropore are much fewer than free Xe gas or xenon in the large pores, in spite of the 4.0 MPa Xe gas pressure.

3.2 NMR at atmospheric pressure

Figure 4 shows the NMR spectra of samples that had been evacuated at 773 K and exposed to 0.1 MPa Xe gas at 773 K. The one-day evacuated and annealed sample (a) showed two peaks at 29 and 128 ppm (Fig. 4(a)), which are attributed respectively to xenon atoms adsorbed in the large pores and micropores (smaller than 1 nm) of hard-carbon, by referring to the pressure dependences of shifts in Fig. 2 and to those reported in [33]. The micropore peak (128 ppm) intensity was much stronger than that of the 210 ppm peak shown in Fig. 1, and was nearly equal to that of xenon in the large pores (29 ppm). But more than 20000 scans were needed to obtain the 128 ppm and the 29 ppm peaks. The weakness of the intensities implies that the amount of adsorbed xenon is much less than the total amount of a estimated from the space within the hard-carbon structure.

The micropore space in hard-carbon is expected to be filled with inert gas (for example, N_2 gas), which is involved in the growth process of the hard-carbon structure. The high-pressure NMR results imply that the inert gas is immediately replaced only slightly by xenon, even at 4.0 MPa Xe gas pressure, but evacuation at 773 K for 1 day allows the xenon to adsorb into the vacant micropores in hard-carbon after desorption of the inert gas. The results suggest that many micropores are isolated and are not accessible from the surrounding space. Xenon atoms are adsorbed only in the micropores near the surface, which are accessible from the surrounding space. For pores having an entrance to the surrounding space, evacuation with heating is effective only for desorption of some of the adsorbed nitrogen molecules.

Figure 5 shows XRD patterns for the following samples: (a) before heat treatment, (b) evacuation at 773 K for 7 days, and (c) the treatment in (b) followed by annealing at 773 K for 7 days in xenon atmosphere. All samples had equal (d_{002}) distances of 0.380 nm. Therefore, we inferred that the macroscopic structure (the framework composed of graphene and micropores) of hard-carbon was unaffected by heat treatment or a xenon atmosphere at 773 K.

Although the XRD results confirmed identical macroscopic structures of samples before and after heating and xenon adsorption, a gradual change of the NMR shift of adsorbed xenon was observed (Fig. 4). Regarding one-day evacuated samples (Figs 4(a)–4(c)), two peaks in (a) shifted and merged into one peak at 50 ppm, as shown in (c), with increasing annealing time in xenon gas.

The combination of two peaks in Figs. 4(a)–4(c) is explainable by the structural change of the path between pores. The widening of the path between a micropore and another micropore leaded to large average-size of micropores (the micropore peak shifted lower than 128 ppm). On the other hand, the widening between a large pore and a micropore gave the opposite shift (the larger-pore peak shifted higher than 29 ppm), while the structural change between large pores would hardly affect the shift value. At last the two peaks became to one peak, which means that Xe exchange between these sites could be occurred faster than NMR time scale. A similar interpretation is applicable to the spectrum (Fig. 4(d)) observed for the 7 days' evacuated sample, which shows a single peak, although the shift value of 81 ppm in (d) was different from the 50 ppm in (c). Seven days' evacuation at 773 K engendered ready diffusion between the large pores and micropores that were accessible from the surrounding space: the exchange came to take place faster than the NMR time scale. Interestingly, the peak at 81 ppm in (shifted further to about 50 ppm (Figs. 4(e) and 4(f)) with increasing annealing time in xenon gas, indicating that the microstructures of Xe-adsorbed hard-carbon samples came to have the same structure by taking sufficient annealing time in xenon gas of 7 days, in spite of dif evacuation time. From those results, we can conclude that evacuation at 773 K produces only a narrow path between the surface and micro sites through desorption of inert gases such as nitrogen, thereby yielding the single peak of 81 ppm, which is the average value of 29 and 128 ppm. We believe that annealing at 773 K in Xe gas widens that path and expands the pore entrances through diffusion of xenon, which revealed a larger apparent mean pore size of 50 ppm than 81 ppm. At least, the micropore elimination could not be confirmed from the change of NMR shifts and XRD. A linear correlation between the pore diameter and the ^{129}Xe chemical shift value has been generally reported for zeolites [37, 38]. Although it can not be applied for the carbon materials directly [35], the increased NMR shift from 29 to 50 ppm implies at least 1.5~a few- times-decreased pore size by evacuation (Figs. 4(a)–4(c)); the shift from 128 to 50 ppm indicates that the micropores (smaller than 1 nm) change to mesopores (over 2 nm). However, such an extraordinary change of the pore structure can be supported only slightly by these nearly identical XRD patterns.

As described in the *Introduction*, two micropore models for hard-carbon have been suggested for the adsorption of lithium ion: a space surrounded by graphene sheets and a void spreading between graphene sheets. For xenon adsorption, the adsorption site requires sufficient void space to accommodate a xenon atom, which has a radius of 0.22 nm, and which is far larger than a Li^+ ion. The stronger signal of adsorbed xenon by ^{129}Xe NMR would be observed if the most of latter void adsorbed xenon atoms. However, it would be difficult for a xenon atom to arrive at the void passing between graphene sheets as a Li^+ ion would. Additionally, the marked expansion of interplanar distance $d(002)$ which reflects a void between graphene sheets was not observed using XRD. Therefore, the micropore signal observed using ^{129}Xe NMR is explainable by the former micropore model. It was difficult to estimate the pore size distribution of the samples accurately using Xe NMR shift for two reasons: 1) the wide signals of the spectra that originated in the amorphous carbon structure, and 2) Xe atoms can intercalate only into sites larger than their own size (smaller pores were not evaluated). However, fine structural changes of the hard-carbon surface, which had not been observed by the nitrogen gas isotherm, were shown using ^{129}Xe NMR method. We are now challenging to have the more apparent NMR signals of xenon in micropores, and achieving. The results and investigation for the effect of xenon gas at heating process of carbon will be reported in near future as another work.

4. Conclusion

Sub-nanometer sized pores (micropores) and larger pores (mesopores or smaller macropores) were observed in a hard-carbon sample using ^{129}Xe NMR: the former cannot be observed using other porosimetric methods like nitrogen adsorption and mercury porosimetry. The respective xenon adsorption sites of the former and the latter are spaces surrounded by graphene sheets near the hard-carbon surface, which have pores that are larger than a xenon atom (≈0.43 nm), and the large pores' surface. When lithium is intercalated electrochemically into the hard-carbon, the lithium cluster might grow in the former space, i.e., it is the origin of the CV stage on the charge-discharge curve for LIB together with the void reported by Nagao et al. [13]. On the other hand, annealing at 773 K in Xe gas widens the path into hard-carbon and expands the pore entrances through diffusion of xenon, which revealed a larger apparent mean pore size of 50 ppm. The extremely weak NMR signal of micropores is attributable to the xenon adsorption that takes place only near the carbon surface, which might be improved by the refining of experimental method.

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Figure Captions

Figure 1.

^{129}Xe NMR spectra of the hard-carbon in 4.0 MPa Xe gas and enlargements of each spectrum. (a) and (b) respectively show samples evacuated (≈0.1 Pa) at room temperature for 1 h, and evacuated at 673 K for 72 h before introducing Xe gas.

Figure 2.

Pressure dependences of ^{129}Xe chemical shift values (open circles and closed circles) for a hard-carbon sample (b). The weakest peak observed at 210 ppm in Fig. 1(b) was not observed because of its extremely weak intensity.

Figure 3.

A pore diameter distribution for a hard-carbon sample measured using mercury porosimetry. Macropores (0.05–0.8 μm) and mesopores (2–50 nm) are observed.

Figure 4.

^{129}Xe NMR spectra for the samples: (a) evacuated at 773 K for 1 day and annealed at 773 K in xenon atmosphere for 1 day; (b) evac. 1 day, anneal. 2 days; (c) evac. 1 day, anneal. 7 days; (d) evac. 7 days, anneal. 1 day; (e) evac. 7 day, anneal. 2 days; and (f) evac. 7 day, anneal. 7 days. Vertical scales of the spectra are normalized with respect to each other.

Figure 5.

Powder XRD patterns of hard-carbon samples (a) before heat treatment, (b) evacuation at 773 K for 7 days, and (c) the treatment followed by annealing at 773 K for 7 days in xenon atmosphere.