



# $^7\text{Li}$ nuclear magnetic resonance studies of hard carbon and graphite/hard carbon hybrid anode for Li ion battery

H. Fujimoto\*, A. Mabuchi, K. Tokumitsu, N. Chinnasamy, T. Kasuh

Energy Technology Laboratory, Osaka Gas Co., Ltd, 6-19-9, Torishima, Konohana-ku, Osaka 554-0051, Japan

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## ABSTRACT

The hard carbon is attractive for the Li ion battery because of its higher capacity than the theoretical value of  $372 \text{ Ah kg}^{-1}$  based on the composition of stage 1 Li-intercalated graphite,  $\text{LiC}_6$ . However, since the Li-doping reaction occurs at the potential of around 0 V versus  $\text{Li/Li}^+$  reference electrode, it is often pointed out the possibility of Li metal deposition on the surface of anode. From the viewpoint of the safety, it may be a moot point. In the present study,  $^7\text{Li}$  NMR measurement was performed to estimate the degree of Li metal deposition on the surface of graphite and hard carbon anode. As a result, it is clarified that the Li metal deposition does not occur up to 110% over-discharge of the reversible capacity of hard carbon, whereas in the case of graphite anode, Li metal deposition occurred above 105% over-discharge of the capacity. From the  $^7\text{Li}$  NMR spectroscopy, the safety limit of hard carbon is rather superior to that of graphite.

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## 1. Introduction

About twenty years have passed since the Li ion battery using a carbon as an anode was commercialized. During the first few years, the electrochemical performance of most carbons was investigated. Nowadays, two types of carbons are commercially available. The first one consists of what are called “artificial graphites”, which are graphitized above ca.  $2500^\circ\text{C}$ . Since such carbons have high crystallinities, natural graphite should also be included in this group. In general, these graphites show excellent cycle performance, high capacities of  $350\text{--}370 \text{ Ah kg}^{-1}$ , and coulombic efficiencies higher than 90%. Therefore, graphite is commercially used as the anode of most Li ion batteries that are used in many electronic devices such as mobile phones, computers, and digital cameras. However, as the reversible capacity of graphite is limited to  $372 \text{ Ah kg}^{-1}$  base on the composition of the 1st stage Li-intercalated graphite,  $\text{LiC}_6$ , newly anode material with higher capacity such as graphite hybridized with silicon has been developed [1]. On the other hand, the hard carbon is the second candidate for the anode of Li ion battery. It was, for example, prepared by the heat treatment of isotropic pitch at  $1000\text{--}1100^\circ\text{C}$ , and shows a higher capacity than  $372 \text{ Ah kg}^{-1}$ . It was firstly reported by Takahashi et al. and Sonobe et al. [2,3]. After that, several groups also reported the carbons with similar structure and electrochemical performances [4–10]. The hard carbon materials have been recently received much attention as an anode for the

large scale Li ion battery for hybrid electric vehicles because of the excellent cyclability and high input/output performances. It is considered that such carbons accommodate the lithium species in the micro-pores as well as in the interlayer. Tatsumi et al. reported that the  $^7\text{Li}$  NMR signal observed at room temperature of fully lithiated hard carbon split into two peaks, high chemical shift signal above 100 ppm and low chemical shift at ca. 20 ppm at low temperature [4,6]. The former signal was explained by quasimetallic Li forming a lithium cluster in the pore of hard carbon structure and the latter was attributed to be the Li ion intercalated into graphene layers. After that, almost the same results were reported by several groups [7,8]. However, the  $^7\text{Li}$  NMR studies ever reported were only concerned for the hard carbon with the reversible capacity less than  $500 \text{ Ah kg}^{-1}$ . Dahn et al. reported that the hard carbons derived from sugar shows higher capacity than  $500 \text{ Ah kg}^{-1}$  [9]. We also succeeded the hard carbons with reversible capacity of  $520 \text{ Ah kg}^{-1}$  at the pilot plant level [10]. As a matter of fact, all hard carbons are not identical in composition, texture and structure. They may contain variable amounts of heteroatoms and have different open and closed pores. As a result, the sites available to lithium accommodation may differ from each other, which can lead to different  $^7\text{Li}$  NMR results. Hence, it is important to elucidate the pore structures in detail. Moreover, since the Li-doping reaction occurs at the potential of around 0 V vs.  $\text{Li/Li}^+$  reference electrode, it is often pointed out the possibility of Li metal deposition on the surface of anode. It may be a moot point from the viewpoint of the safety. In the present study, two kinds of hard carbons with high and low reversible capacities and the hybrid anode with graphite and hard carbon were investigated by means of  $^7\text{Li}$  NMR measurement in

\* Corresponding author. Tel.: +81 6 6205 3245; fax: +81 6 6462 3433.  
E-mail address: [hfujii@osakagas.co.jp](mailto:hfuji@osakagas.co.jp) (H. Fujimoto).

order to compare the state of Li species among them and to estimate the safety limit for the Li metal deposition by the over-charging of the Li-ion battery.

## 2. Experimental

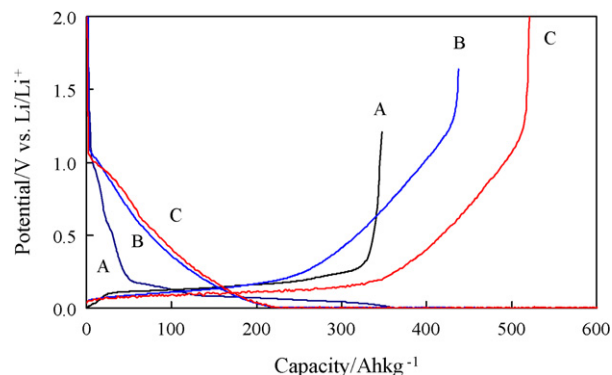
### 2.1. Preparation of carbons

As a starting material for the preparation of hard carbon, two kinds of pitches with different oxygen contents (9.4 wt% and 15.2 wt%, Osaka Gas Chemical Co., Ltd.) were used. The materials were milled and classified, so that the median diameter, D50 was adjusted to ca. 5–7  $\mu\text{m}$ . Thus obtained pitches were carbonized at 1100 °C. In the following, the hard carbons prepared from the pitches with 9.4 wt% and 15.2 wt% oxygen contents will be abbreviated as “HC-9” and “HC-15”, respectively. In order to compare the state of Li species in the hard carbon with that in graphite, synthetic graphite was also prepared from the naphthalene-based pitch (Mitsubishi Gas Chemical Company, Inc.) [11]. It was an anisotropic pitch having a softening point of 287 °C. The pitch was firstly mixed with 5 wt% of paraxylene glycol (PXG) as a cross-linking agent and 1 wt% boric acid as a graphitization catalyst under a coexistence of polymerization catalyst of 2 wt% of paratoluene sulfuric acid. Then, the mixture was heated up to 300 °C and polymerized for 3 h. Thus obtained carbon precursors were precarbonized at 800 °C in  $\text{N}_2$  atmosphere and graphitized at 2900 °C in Ar atmosphere. After that, they were milled and classified, so that the median diameter, D50 was adjusted to ca. 7  $\mu\text{m}$ . Hereafter, it is abbreviated as NBP-Graphite.

In order to enhance the electron conductivity and capacity of hard carbon anode, HC-9 was hybridized with graphite by the physical mixing method and chemical mixing method. In the former method, HC-9 and artificial graphite (SFG-15, TIMCAL Ltd.) were simply mixed with the weight ratio of 3:1, 2:1, 1:1. In the latter method, the precursor material of HC-9 was mixed with SFG-15 and carbonized at 1100 °C. The mixing weight ratio of them were determined considering the carbonization yield of the precursor, so that the final mixing ratio in hybrid carbon obtained become 3:1, 2:1, 1:1.

### 2.2. Electrochemical measurement of anode performance

Electrochemical measurements were performed using three-electrode test cells made of glass. A lithium metal was used as a counter and a reference electrode. The electrolyte used was a 1 mol  $\text{dm}^{-3}$   $\text{LiClO}_4$ /ethylene carbonate + diethyl carbonate (1:1). In order to measure the reversible capacity, the cells were discharged down to 0.001 V at a constant current density of 1  $\text{mA cm}^{-2}$  and then kept at a potential of 0.001 V, so that the total discharging time was 24 h. Then, the cells were charged in the potential range of 0.001 V to 1.3 V vs.  $\text{Li/Li}^+$  at a constant current density of 1  $\text{mA cm}^{-2}$ . The electrode density was adjusted to 1.1  $\text{gr cm}^{-3}$ , so that the degree of Li deposition was not affected by the deviation of current density among the samples.



**Fig. 1.** Charge/discharge profiles of graphite derived from naphthalene-based pitch (A) and hard carbons derived from coal tar pitch with 9.4 wt% oxygen content (B) and 15.2 wt% oxygen content (C).

### 2.3. Preparation of samples for the $^7\text{Li}$ NMR measurement

As the samples for the  $^7\text{Li}$  NMR measurement, the hard carbons were lithiated by the two method. First method was the constant current–constant voltage method (CC–CV method). In order to obtain the fully lithiated sample, the hard carbon was firstly discharged and charged to estimate the reversible capacity by the above-mentioned procedure and then, it was redischarged by the same condition in the second cycle. Another method was the constant current method (CC method). At the first cycle, the hard carbon was discharged and charged by the CC–CV method and then, it was redischarged in the range of 90–140% of reversible capacity at a constant current density of 0.2  $\text{mA cm}^{-2}$ . In the case of lithiated graphite, the graphite was firstly discharged and charged, and then redischarged by the CC method in the range of 95–105% of the reversible capacity. After that, the cell discharged was disassembled in the Ar dry box and the lithiated sample was extracted from the cell and was put into NMR tube. All the  $^7\text{Li}$  NMR spectra were measured by the MAS method with a Bruker FT-NMR (ASX-200) at 77.8 MHz at room temperature (280 K) and low temperature (150 K or 180 K). The rotational frequencies were fixed at 5 kHz for HC-9 and HC-15 and at 8–10 kHz for other samples. LiCl solution was used as an external standard.

### 2.4. Other measurements

The specific surface area (SSA) was measured with NOVA2000 (Quantachrome Co. Ltd.).

## 3. Results and discussion

### 3.1. Charge/discharge profiles of hard carbons

Fig. 1 shows the charge/discharge profiles of NBP-Graphite and two kinds of hard carbons, HC-9 and HC-15. The electrochemical characteristics are summarized in Table 1. NBP-Graphite showed a typical electrochemical performance of graphite, and its initial coulombic efficiency and reversible capacity were 84.6% and 345  $\text{Ah kg}^{-1}$ , respectively. HC-9 and HC-15 also showed a typical

**Table 1**  
Electrochemical characteristics of graphite derived from naphthalene-based pitch and two types of hard carbons.

Sample	Total reversible capacity ( $\text{Ah kg}^{-1}$ )	Reversible capacity below 0.2 V ( $\text{Ah kg}^{-1}$ )	Reversible capacity above 0.2 V ( $\text{Ah kg}^{-1}$ )	Initial coulombic efficiency (%)
NBP-graphite	345	–	–	84.6
HC-9	435	231	204	83.5
HC-15	521	331	190	84.5

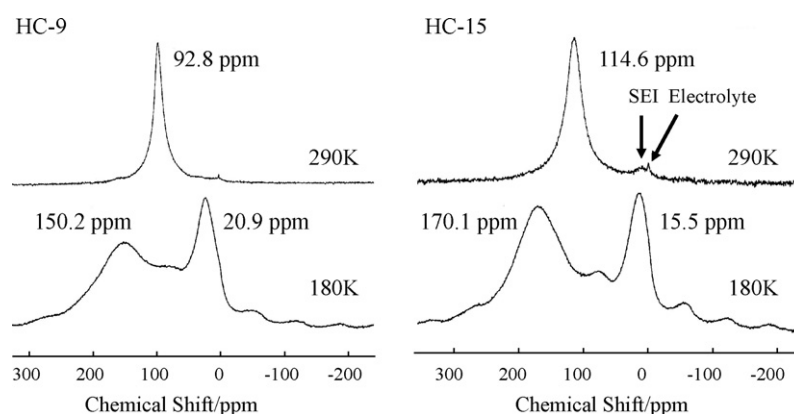


Fig. 2.  $^7\text{Li}$  NMR spectra of fully lithiated hard carbons derived from pitches with different oxygen contents at 290 K and 180 K.

profile of hard carbon. That is, the plateau below 0.2 V and turning point at ca. 0.2 V were observed in the discharge profile. The initial coulombic efficiencies and reversible capacities were 83.5%, 435 Ah kg $^{-1}$  for HC-9 and 84.5%, 520 Ah kg $^{-1}$  for HC-15. In general, the discharge profiles below and above 0.2 V are considered to be related to the Li-doping reaction into pores and interlayer, respectively. The carbon derived from the higher oxygen-containing pitch yielded a higher reversible capacity and longer plateau below 0.2 V.

### 3.2. Results of $^7\text{Li}$ NMR measurement of fully lithiated hard carbons

Fig. 2 shows the  $^7\text{Li}$  NMR spectra measured at 290 K and 180 K of fully lithiated hard carbons prepared by CC-CV method. The broad and sharp signals with very weak intensities at around 0 ppm are assigned to the Li species in the solid electrolyte interface and electrolyte, respectively [4]. Comparing the spectra of HC-9 and HC-15 at 290 K, the chemical shifts of main signals were 92.8 ppm and 114.6 ppm, respectively and the peak width of HC-15 was broader than that of HC-9. It suggests that the state of Li species doped in the carbon was somewhat different from each other. The spectra at 180 K show several spinning side bands in the range of  $-200$  to  $-110$  ppm and of  $50$ – $100$  ppm, which makes difficult to analyze the spectra. However, it is roughly concluded that the main signal observed at 290 K was separated into two signals at 180 K as reported by Tatsumi [4,6]. In the case of HC-9, the signal at 92.8 ppm at 290 K splitted into a signal with a high chemical shift of 150.2 ppm ( $S_H$ ) and a signal with low chemical shift of 20.9 ppm ( $S_L$ ) at 180 K. In the case of HC-15, the signal at 114.6 ppm splitted into two signals at 170.1 ppm and 15.5 ppm. As a result of decomposition of spectra, the signal intensity ratio of  $S_H/S_L$  for HC-9 and HC-15 were 1.47 and 2.17, respectively. Several groups reported that the low chemical shift signal at around  $0$ – $50$  ppm is due to the Li species doped between the interlayer, and the high chemical shift one is assigned to the Li species doped in the micro-pores [4,6,7]. Hence, it indicates that the amount of Li doped in the pores of HC-15 is larger than that of HC-9 being in agreement with difference of capacity of plateau region in discharge profile. That is, the sample with a longer plateau shows a larger signal intensity ratio of  $S_H/S_L$ .

### 3.3. Safety estimation for Li metal deposition by the over-discharging of graphite and hard carbon

Figs. 3 and 4 show the  $^7\text{Li}$  NMR spectra at 280 K of HC-9 and HC-15 over-discharged in the range of 90–130%. The main signal due to the Li-doping shifted from 77.6 ppm to 103.1 ppm for HC-9 and from 110.7 ppm to 124.7 ppm for HC-15 as the lithiation proceeded. Moreover, no Li metal deposition was observed up to 110% over-

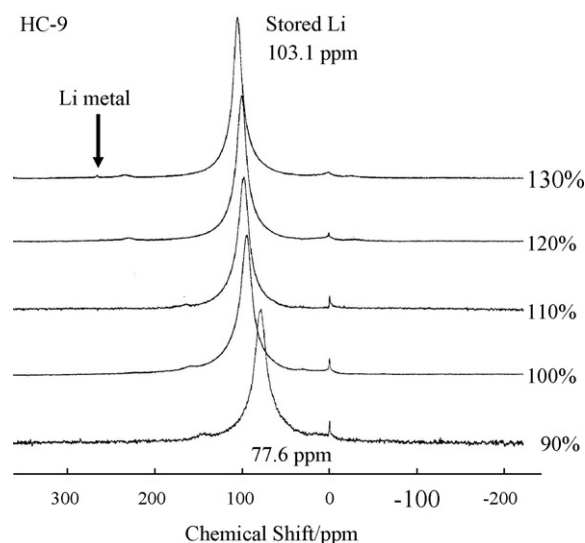


Fig. 3.  $^7\text{Li}$  NMR spectra at 280 K of HC-9 lithiated in the range of 90–130% against the reversible capacity.

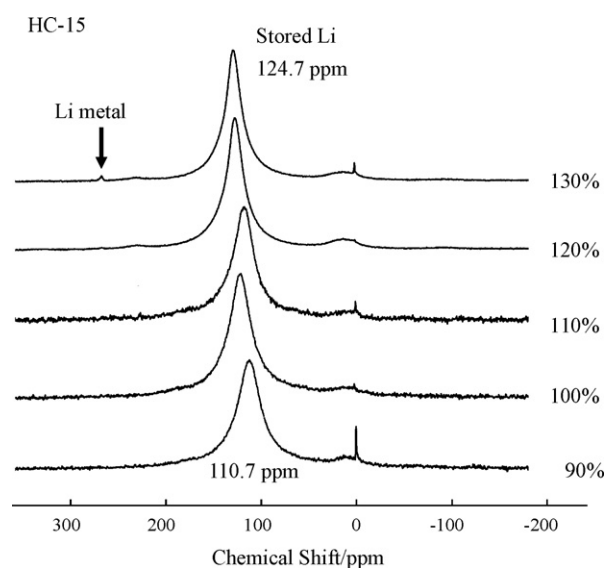


Fig. 4.  $^7\text{Li}$  NMR spectra at 280 K of HC-15 lithiated in the range of 90–130% against the reversible capacity.

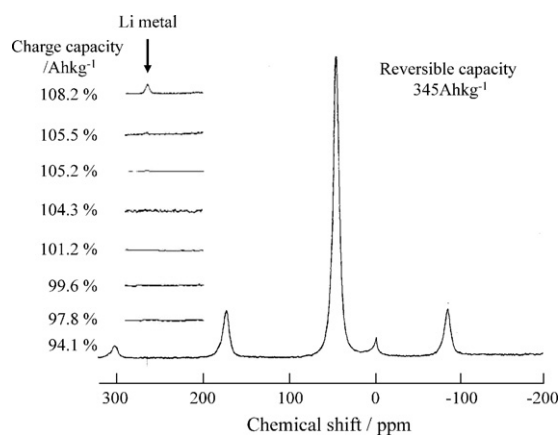


Fig. 5.  $^7\text{Li}$  NMR spectra at 280 K of naphthalene-based pitch graphite lithiated in the range of 94–110% against the reversible capacity.

discharge, whereas the samples with 120% or 130% over-discharge seems to show a very weak signal at 270 ppm corresponding to the Li metal. On the other hand, in the case of NBP-Graphite, the Li metal deposition was observed above only 105.2% over-discharge as shown in Fig. 5. These are very interesting results. The possibility of Li metal deposition for the hard carbon has been pointed out because the Li-doping reaction occurs at around 0V vs. Li reference electrode. In the case of over-discharge by CC method, the anode potential achieved to ca.  $-0.05$  V corresponding to the over-potential. Nevertheless, no Li metal deposition occurred. From the viewpoint of the  $^7\text{Li}$  NMR spectroscopy, the safety limit of hard carbon is superior to that of graphite. In the case of graphite, once saturated in-plane structure of  $\text{LiC}_6$  is formed, there are no more sites for Li storage. Hence, Li metal deposition occurs rapidly. On the other hand, the hard carbon contains extra sites to accommodate the Li species that does not contribute to the reversible charge/discharge reaction. The volume of such extra irreversible sites of HC-9 and HC-15 are estimated to be around 20–30% of the reversible capacity from the results of  $^7\text{Li}$  NMR spectra. In order to specify the irreversible sites,  $^7\text{Li}$  NMR spectra of lithiated hard carbons were measured at low temperature. Fig. 6 shows the  $^7\text{Li}$  NMR spectra at 180 K of HC-9 and HC-15 lithiated in the range of 90–110%. As the lithiation proceeded, the intensity of high chemical shift signal increased rather than the low chemical shift signal. It indicates that the Li species doped by the over-discharge would be stored in the extra micro-pores rather than in the interlayer.

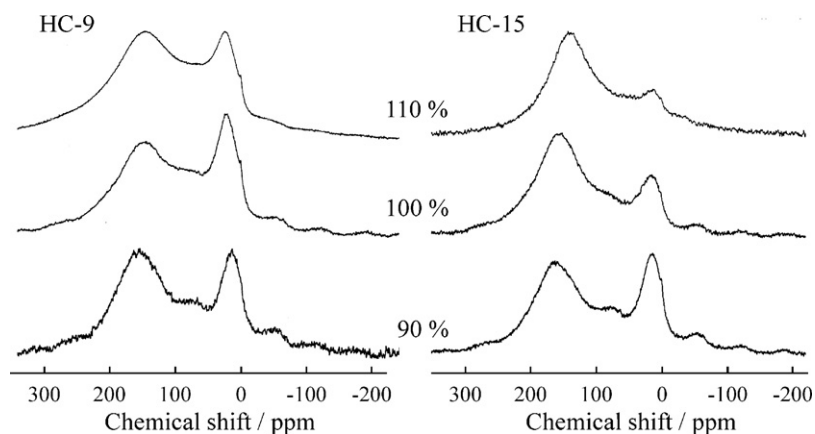


Fig. 6.  $^7\text{Li}$  NMR spectra at 180 K of hard carbon lithiated in the range of 90–110% against the reversible capacity.

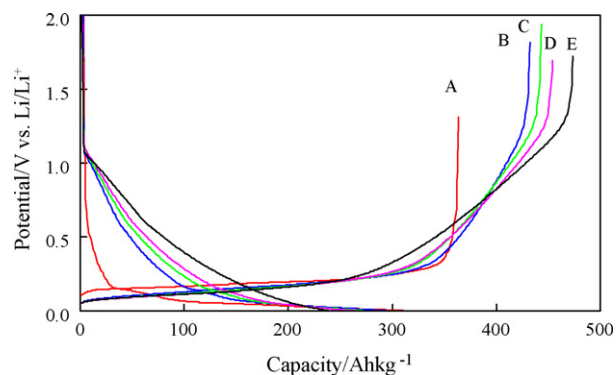


Fig. 7. Charge/discharge profiles of carbons hybridized by physical mixing method. The weight ratio of hard carbon/graphite is – A: 0/1, B: 1/1, C: 2/1, D: 3/1, E: 1/0.

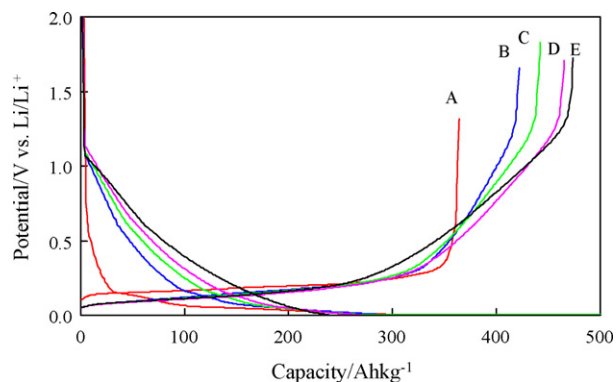
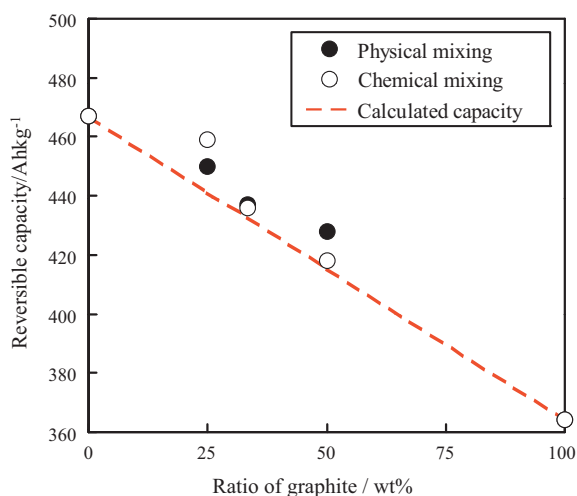


Fig. 8. Charge/discharge profiles of carbons hybridized by chemical mixing method. The weight ratio of hard carbon/graphite is – A: 0/1, B: 1/1, C: 2/1, D: 3/1, E: 1/0.

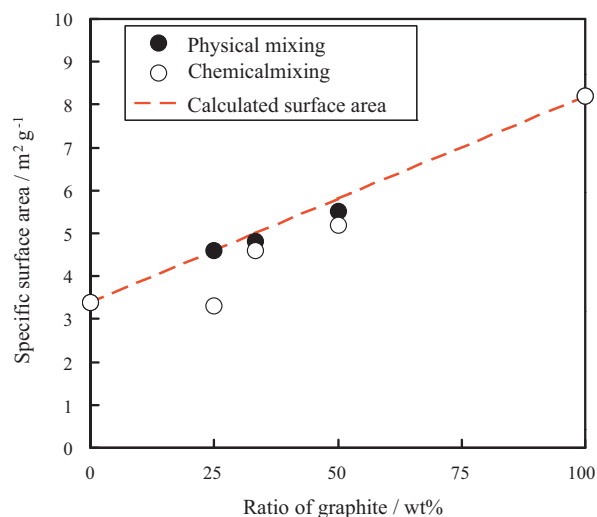
#### 3.4. Charge/discharge profile of the hybrid carbon anode

In the previous section, we discussed about the existence of extra pores that does not contribute to the reversible charge/discharge reaction. It is interesting to develop a method that makes such extra pores active for the charge/discharge reaction. Kida et al. and Yanagida et al. reported that the carbon anode hybridized by graphite and coke or hard carbon demonstrates a higher capacity than the weighted mean capacity of both samples in spite of the simple physical mixing [12,13]. Therefore, the hard carbon, HC-9 was hybridized with graphite, SFG-15 in order to enhance the electron conductivity and capacity of hard carbon. Figs. 7 and 8 show the charge/discharge profiles of the carbons





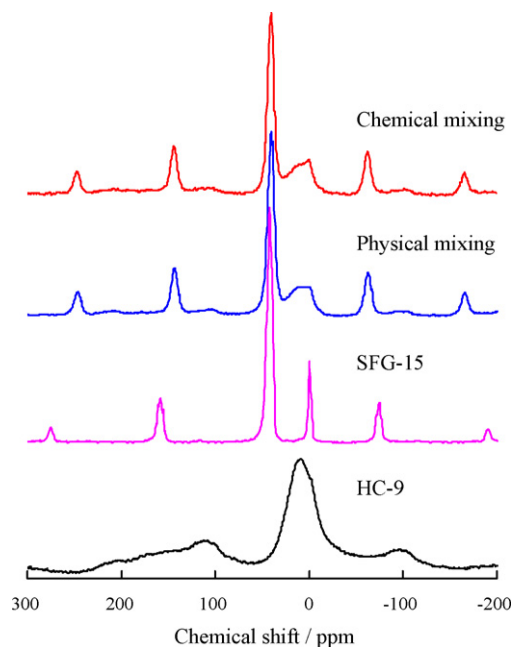
**Fig. 9.** Relationship between the graphite content in the hybrid carbon and reversible capacity.



**Fig. 10.** Relationship between the graphite content in the hybrid carbon and specific surface area.

hybridized by the physical and chemical mixing method, respectively. In both cases, the profiles of hybrid carbons changed from that of original hard carbon to graphite corresponding to the mixing weight ratio. Apparently, the results of the both mixing methods are almost the same. However, detail analysis revealed a slight difference in the reversible capacity and SSA. Fig. 9 shows the relationship between the graphite content in the hybrid carbon and its reversible capacity in both methods. The dashed line denotes the weighted mean capacity between the hard carbon and graphite. The most interesting point is that observed capacity was slightly larger than the calculated value. Especially, it is remarkable for the sample of 3:1 mixing (25 wt% content of graphite). It would be due to the enhancement of conductivity of HC-9 by the addition of graphite. We have already revealed by the density measurement that there are many ink-bottle type pores on the surface of hard carbon with high reversible capacity and that the entrance size of such pores are optimized for the Li-doping/dedoping [10]. The rate-determining step might depend on the entrance size. If the conductivity of hard carbon is improved by the addition of graphite, the some part of extra pores with slightly smaller size for Li-doping would begin to effectively function as a reversible charge/discharge pores. Moreover, in the case of chemical mixing method, another effect is also added. When the hard carbon precursor is co-carbonized with graphite, the various gaseous hydrocarbons such as CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, benzene-derived compounds evolved. As a result, the chemical vapor deposition was caused by such components, and amorphous carbon film was formed on the surface of graphite. Thus obtained carbon film is, in a sense, a hard carbon and has a capacity. The film formation is verified by the results of the SSA measurements as shown in Fig. 10. In the case of physical mixing, the plots of measured SSA lies on the dashed line based on the assumption of additivity between the mixing ratios of both carbons, whereas, in the case of chemical mixing, the SSA plots are below the estimated line. Especially, it is remarkable for the sample of 3:1 mixing ratio. The SSA value of 3:1 sample is nearly equal to that of original hard carbon. It indicates that most of the surface of graphite is covered with the hard carbon film by CVD.

Fig. 11 shows the <sup>7</sup>Li NMR spectra at 150 K of lithiated hybrid carbons. A clear difference between the hybrid carbons prepared by the physical/chemical mixing method was not observed, and both of spectra were almost the same. They consist in the graphite-derived and hard carbon-derived signals.



**Fig. 11.** <sup>7</sup>Li NMR spectra at 150 K of hybrid carbon prepared by physical and chemical mixing method. The mixing ratio of hard carbon and graphite is 1:1.

#### 4. Conclusion

As discussed above, the <sup>7</sup>Li NMR measurement revealed that the graphite can be discharged up to only 105% without Li metal deposition, whereas the hard carbon can be discharged up to 120–130%. It is concluded that the latter is superior to the former from the viewpoint of battery safety. Secondary, the hard carbon has multiple sites for Li storage, that is, reversible and irreversible sites for the Li-doping/dedoping reaction. The ratio of the irreversible sites is estimated to be 20–30% of reversible sites. The irreversible sites are effective for the inhibition of Li metal deposition, and such sites are partially promoted to the reversible sites by the hybridization with graphite.

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