NMR study for electrochemically inserted Na in hard carbon electrode of sodium ion battery

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Abstract

   The state of sodium inserted in the hard carbon electrode of a sodium ion battery having

practical cyclability was investigated using solid state ^{23}Na NMR. The spectra of anode

samples charged (reduced) above 50 mAh g^{-1} showed clear three components. Two peaks at

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9.9 ppm and 5.2 ppm were ascribed to reversible sodium stored between disordered graphene sheets in hard carbon because the shift of the peaks was invariable with changing strength of external magnetic field. One broad signal at about -9 ~ -16 ppm was assigned to sodium in heterogeneously distributed closed nanopores in hard carbon. Low temperature ^{23}Na static and magic angle spinning NMR spectra didn't split or shift whereas the spectral pattern of ^{7}Li NMR for lithium-inserted hard carbon changes depending on the temperature. This strongly suggests that the exchange of sodium atoms between different sites in hard carbon is slow. These studies show that sodium doesn't form quasi-metallic clusters in closed nanopores of hard carbon although sodium assembles at nanopores while the cell is electrochemically charged.

1. Introduction

Lithium ion batteries are used as common and indispensable power sources having high energy densities for consumer electronics nowadays [1]. The application of the batteries is not restricted to small electronic devices, but is expanding to large transportation such as electric vehicles (EV) or (plug-in type) hybrid electric vehicles (HEV). With the increasing demand for these battery's raw materials, the issue of the lithium resource and the cost are becoming increasingly prominent. Lithium is one of minor metals in the earth crust (concentration ca. 20 ppm), and the resource is distributed unevenly, mainly in South America. Thus, abundant sodium is expected to be an important new material for secondary batteries rather than lithium. Sodium is distributed everywhere on the earth, and the electrochemical potential and atomic weight of sodium are advantageous for batteries.

Graphite is mainly used as the anode in lithium ion batteries rather than other carbon materials because of the higher energy density per volume and the lower cost. Graphite and lithium form graphite intercalation compound (Li-GIC) easily and rapidly [2]. However, generally graphite does not form a GIC with sodium by electrochemical reduction. Although non-graphitazable carbon, such as hard carbon, containing closed nanopores in itself had been explored as an anode in sodium ion batteries, the durability and the cyclability of charge / discharge was not sufficient for real applications [3, 4]. Recently our group achieved a high capacity of sodium insertion and steady cycling performance using a cell containing $NaNi_{0.5}Mn_{0.5}O_2$ and hard carbon electrodes, and a relevant electrolyte [5-7]. Powder X-ray diffraction (XRD) for hard carbon electrodes showed expansion between disordered stacked graphene sheets. Small-angle X-ray scattering exhibited the reversible decrease of electron density contrast in nanopores, which was attributable to the reversible Na insertion into nanopores. However, the direct observation for sodium and its state analysis was not done in the previous reports.

Solid state nuclear magnetic resonance (NMR) is one of the most powerful tools to analyze the state of specific nucleus included within solid materials. Alcántara et al. reported [23]Na (magic angle spinning) MAS NMR of sodium intercalated in carbon in 2005 [8]. The pioneering research revealed that the state of sodium in disordered carbon microspheres is quite different from that of lithium. However, the cell had insufficient charge/discharge cyclability, and the influence of electrolyte was large because the NMR spectra of the samples made using EC:THF (ethyl carbonate : dimethyl carbonate) and EC:DMC (tetrahydrofuran) were quite different. These results suggested that the signal of irreversible Na created by decomposition of the electrolyte was not negligible.

It was reported that ^{7}Li NMR signal of lithium in hard carbon shifts from 9 to 80 ~ 120 ppm with increasing the concentration of lithium at ambient temperature [9, 10]. The signal split in two components at low temperature under 240 K; one is a narrower signal assigned to lithium between graphene layers, and the other is a broader component between 90 and 220 ppm [9, 11, 12]. The latter component has been ascribed to quasi-metallic lithium clusters in closed pore of hard carbon. In the present study, we measured ^{23}Na MAS and static NMR for sodium-inserted hard carbon anodes, and discuss the state of sodium in the carbon in comparison to lithium-intercalated carbon.

2. Experimental

Carbotron P(J) (Kureha Battery Materials Japan, Co, Ltd.), a hard carbon product, was used for the anode active material of the sodium ion battery. The results of characterization for the hard carbon using XRD, [129]Xe NMR, etc. were described in previous reports [9, 13].

Coin-type cells (20 mm diameter, 3.2 mm thickness) were assembled using hard carbon electrodes with poly(vinylidene fluoride) (PVdF) as a binder (carbon : PVdF = 90 : 10 in wt%) to prepare the specimens for NMR measurements. Sodium metal (Kanto Chemical Co., Inc.) was employed as a counter electrode. The electrolyte of 1.0 mol dm^{-3} $NaClO_4$ (Kishida Chem. Corp., Ltd., battery grade) solution in 98 : 2 (volume ratio) propylene carbonate (Kishida Chem. Corp., Ltd., battery grade) : fluoroethylene carbonate (FEC, Kanto Chem. Co., Inc.) was used. FEC addition is important for passivation of carbon electrodes [6]. Electrochemical sodium insertion was performed galvanostatically at a rate of 0.5 mA cm^{-2}. The Na cells were cycled for 5 times in a range of 2.0 – 0 V vs. Na metal, and then the cells were charged (reduced) to each composition. The carbon electrodes were taken out from the

cells and washed by propylene carbonate and diethyl carbonate in an Ar atmosphere. Seven specimens of Na-introduced carbon having different charge levels were prepared; A (0 mAh g^{-1}, fully discharged), B (30 mAhg^{-1}), C (50 mAh g^{-1}), D (100 mAh g^{-1}), E (150 mAh g^{-1},), F (200 mAh g^{-1}), and G (252 mAh g^{-1}, fully charged). After drying, each specimen was sealed into a 3.2 mmϕ sample rotor with argon gas to measure NMR. ^{23}Na MAS NMR spectra at room temperature were recorded using a 7.0 T magnet and a home built MAS probes equipped with a Varian 3.2 mm spinning module at the spinning rate of 23 - 25 kHz. MAS NMR spectra at low temperature between 200 to 300 K of sample G (252 mAh g^{-1}) were obtained using a 11.7 T magnet and a probe with Varian 3.2 mm spinning module. The spinning rate of 19 kHz was achieved by blowing cooled N_2 gas at temperatures between 210 - 300 K. Temperature dependence of a static NMR spectrum was performed using a 9.4 T magnet and a Thamway spectrometer at temperatures between 100 and 297 K. The signal of saturated NaCl aqueous solution was used for the 0 ppm reference. A single pulse sequence was adapted to all measurements. (*Caution!*: An intense ^{63}Cu signal at about +2000 ppm and the artifact signals appear in spectrum if copper NMR coil is used. The artifacts sometimes disturb the spectrum.)

3. Results and Discussion

Figure 1 shows ^{23}Na MAS NMR spectra of Na metal and sample A ~ F at room temperature. The state of charge (SOC) for each sample is plotted on the charge (reduction) process (sodium insertion) curve of the cell (Fig. 2). The metal ^{23}Na peak appearing at 1130 ppm and signals between 1130 and 60 ppm were not observed in spectra B ~ F. The spectrum of the completely discharged (oxidized) sample after sodium extraction (A in Fig. 1) showed relatively weak and broad peak between ±230 ppm, which should be assigned to sodium salts

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and/or compounds. The sodium salts/compounds are components of passivation film, namely, solid electrolyte interphase (SEI), formed by the irreversible decomposition of electrolyte at the surface of hard-carbon. The signal of the sodium salts/compounds was indiscernible in spectra B ~ F. Spectrum B (30 mAhg^{-1}) has a slight signal of electrochemically inserted sodium between +10 and -30 ppm although the line shape was not clear. Spectrum C (50 mAh g^{-1}) has clear three components; two peaks at 9.9 ppm and 5.2 ppm and one broad signal at about -9 ppm. The shifts of the former two peaks were the same in spectra C - F, while the intensity at 9.9 ppm increased greatly. The electrode potential for the hard carbon decrease gradually with the increase of SOC at the low Na concentration region (under 100 mAh g^{-1}, 40% charged), whereas the potential is almost constant at about 0 - 0.1 V for 100 mAh g^{-1} and higher SOC [5]. The line shape of the ^{23}NMR spectrum showed similar changes. The structure of the spectrum was almost invariant for 40% and higher SOC, except the gradual shifting of the peak of the broad signal from -14 to -16 ppm and increasing the intensity of the peak at 5.2 ppm. (D ~ F in Fig. 1). These results suggest that the potential variation of the hard carbon, such as sloped and plateau regions in Fig. 2, relates to the different state of sodium inserted into the stacked graphene and nano-pore sites for hard carbon.

According to Alcántara's report, the peak at 9 ppm and broad signal between -20 and -30 ppm for Na inserted carbon microspheres were assigned sodium inserted in void space between misaligned graphene layers and in nanocavities or surface films (SEI), respectively [8]. The peak at 9.9 ppm and the signal between -9 and -16 ppm of the specimens C ~ F are in good agreement with that assignment. However the peak at 5.2 ppm, which was ascribed to traces of sodium electrolyte or sodium impurities by Alcántara et al., also increased with the Na insertion. In the case of quadrupolar nuclei, each peak has second-order quadrupolar

broadening which is not completely removed by magic angle spinning [14]. If the additional 5.2 ppm peak was caused as an accompanied structure of the 9.9 ppm peak by the second-order broadening effect of ^{23}Na quadrupolar interaction, the shift value of the additional peak expressed by ppm unit would shift inversely proportional to external static magnetic field. The MAS NMR spectrum at higher magnetic field than in Fig. 1 of specimen G (252 mAh g^{-1}, fully charged) is shown in Fig. 3. The spectrum recorded at 300 K also had peaks at 9.8 ppm and 5.4 ppm, which are in good agreement with the peaks at B ~ F in Fig. 1. Because these peaks don't shift owing to the external magnetic field, we conclude that the peaks at not only 9.9 ppm but also at 5.2 ppm should be assigned to reversible sodium stored in hard carbon. Since the linewidth of the peak at 5.2 ppm is as narrow as the peak at 9.9 ppm, it should be assigned to another site between disordered graphene sheets, which may be a different stage structure. On the other hand, the shift of the broad component in Fig. 3 was a little different from the spectra D ~ F in Fig. 1, which is explainable by the difference of magnetic field and nuclear quadrupolar interaction of ^{23}Na. The broad signal implies not only the slow diffusion of sodium but also that the state of sodium ions is distributed because of the heterogeneous distribution of closed nanopores in hard carbon.

The behavior of sodium spectra is evidently different from lithium inserted in hard carbon. As mentioned in introduction, ^{7}Li NMR signals of lithium in hard carbon appears between 9 and 80 ~ 120 ppm proportional to lithium content at ambient temperature [9], whereas ^{23}Na signal doesn't shift depending on the sodium content. The behavior at low temperature was also different. The low temperature MAS NMR spectra at 19 kHz and static spectra for specimen G (252 mAh g^{-1}) are shown in Fig. 3 and Fig. 4, respectively. The lineshapes of MAS NMR spectra and static NMR spectra didn't change at all and peaks didn't

split in the temperature range studied. In the case of the Li ion battery, the peak at 9 ppm of the ^{7}Li NMR spectrum of anode hard carbon at room temperature split in two peaks, i.e., high-field shift at 10 ppm assigned to intercalated lithium between graphene layers and low-field shift at about 90 - 220 ppm attributed to quasi-metallic lithium clusters in closed nanopores by cooling the sample. The signal of the low-field shift becomes broader and disappears under 150 K because of inhomogeneous Knight shift of each Li nucleus caused by the size-distribution of clusters in closed nanopores. Na NMR didn't observe such a transition of spectra in Na inserted carbon samples at low temperature. These results strongly suggest that the exchange of sodium atoms between different sites in hard carbon is slow in NMR time scale. Also that sodium doesn't form quasi-metallic clusters in closed nanopores of hard carbon, although sodium assembles at nanopores while the cell is electrochemically charged.

4. Conclusion

Na NMR measurement was performed on hard carbon anodes of sodium ion battery. Because the component of the signal ascribed to the irreversible sodium including SEI layers on the surface of carbon was much weaker than that of reversible sodium ion, the reversible sodium could be distinguished distinctly. Sodium is inserted in two different sites between misaligned graphene sheets. Nanopores included in hard carbon also could store sodium reversibly like lithium. However, the sodium doesn't have quasi-metallic property in hard carbon.

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Figure Captions

Figure 1 ^{23}Na MAS NMR spectra of Na metal and samples A(SOC:0 mAh g^{-1}), B(30 mAh g^{-1}), C(50 mAh g^{-1}), D(100 mAh g^{-1}), E(150 mAh g^{-1}), and F(200 mAh g^{-1}) at room temperature obtained in a magnetic field of 7.0 T. The numbers of accumulation were 25000, 100000, 100000, 10000, 10000 and 8000 for A, B, C, D, E and F, respectively. The spinning speed was 23 - 25 kHz. # denotes a noise arising from the dc offset of the receiver.

Figure 2   Charge (reduction) curve of the Na cells after 5 cycles in the range of 2.0 – 0 V. The SOC of each sample used for NMR is plotted on the curve.

Figure 3   Low temperature ^{23}Na MAS NMR spectra of sample G (SOC: 252 mAh g^{-1}) obtained in a magnetic field of 11.7 T at a spinning speed of 19 kHz.

Figure 4   Low temperature ^{23}Na static NMR spectra of sample G obtained in a magnetic field of 9.4 T. # denotes a noise arising from the dc offset of the receiver.

Na metal

A (0 mAh g^{-1})

#

1200   800   400   0

δ / ppm

F (200 mAh g^{-1})

E (150 mAh g^{-1})

D (100 mAh g^{-1})

C (50 mAh g^{-1})

B (30 mAh g^{-1})

60   40   20   0   -20   -40   -60

δ / ppm

300 K

280 K

260 K

240 K

220 K

210 K

δ / ppm

297 K

260 K

220 K

180 K

\#

140 K

\#

100 K

ν / kHz

40   20   0   -20   -40