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1

Strategic approaches to observing ^{39}K NMR signals from potassium–graphite intercalation compounds

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Abstract

Solid-state nuclear magnetic resonance (NMR) is an invaluable tool for potassium–graphite intercalation compounds (K-GICs), promising anode materials of K-ion batteries, but it has not yet been applied because of several issues. We attempted ^{39}K NMR measurements of K-GICs sealed in glass using an 18.8 T NMR spectrometer with an NMR probe adjusted to the samples. The first observed ^{39}K NMR signal of K-GICs showed the possibility of evaluating intralayer density, which cannot be ascertained from Raman measurements.

Keywords: Graphite intercalation compound, Solid-state nuclear magnetic resonance, Potassium

1   Carbon materials are known to take various forms and are used

19   Similarly, the intercalation–deintercalation of potassium into

Graphical abstract
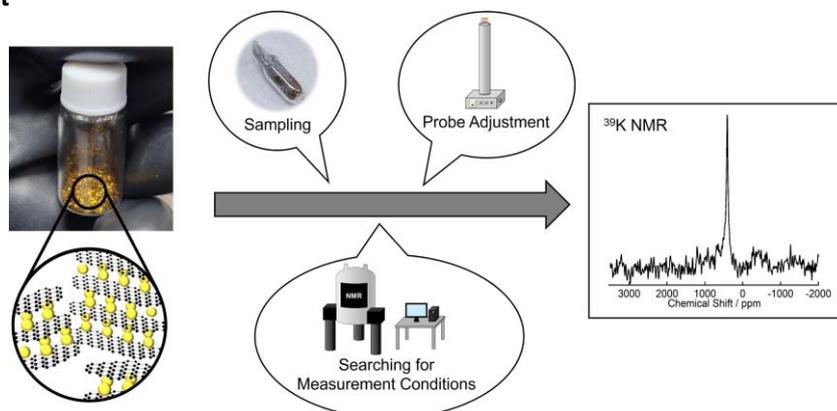
2   in a wide range of fields.[1,2] Development of new synthesis
3   methods and materials and evaluation of the properties of carbon
4   materials for various applications have been carried out.[3–6]
5   Graphite intercalation compounds (GICs) are interesting
6   materials in which several guest atoms or molecules are inserted
7   between the layers of graphite. GICs form various stage
8   structures described as stage n. The index "n" refers to the
9   number of graphene layers between the layers of intercalants.
10   Graphite and potassium form KC_8, KC_{24}, and KC_{36} GICs,
11   respectively, at stage 1, stage 2, and stage 3.[7,8] Since they were
12   first reported in 1841, GICs have long been studied because they
13   exhibit excellent physical and chemical properties including high
14   electrical conductivity, superconductivity, and hydrogen
15   storage.[9,10] Reversible intercalation–deintercalation of various
16   chemical species into graphite interlayers has been utilized as
17   electrode reactions for rechargeable batteries such as Li-ion
18   batteries (LIBs) and dual-graphite batteries (DGBs).[11,12]

20   graphite interlayers can be applied to K-ion batteries (KIBs).[13]
21   Actually, KIBs function according to the same mechanism as
22   LIBs and have some beneficial features including cost-
23   effectiveness and high energy density. These KIB
24   characteristics have accelerated the study of KIBs for
25   application to next-generation batteries.
26   In studies of LIBs and Na-ion batteries, solid-state nuclear
27   magnetic resonance (NMR) has played an important role in
28   elucidating the mechanisms.[14,15] Solid-state NMR can observe
29   target nuclei directly and reveal the structure and dynamics of
30   materials at atomic and molecular levels. Particularly, NMR
31   has contributed to the development of high energy density
32   and safer anode materials by revealing the states of quasi-
33   metallic clusters and dendritic alkali metals in carbon
34   materials.[16–18] Also in KIBs, NMR can be expected to contribute
35   to elucidating potassium storage mechanisms in carbon materials
36   such as graphite and hard carbon, which are promising anode

materials for KIBs. Despite growing demand for NMR analysis for the study of KIBs, no report of the relevant literature has described the use of potassium NMR for KIB research. This gap in the literature has occurred because potassium nuclei are difficult to measure as a result of their low sensitivity attributed to their small gyromagnetic ratio γ and a nuclear quadrupole interaction.[19] Potassium has three NMR active isotopes: ^{39}K, ^{40}K, and ^{41}K. Of these isotopes, ^{39}K has the highest potential for measurement because of its high natural abundance (93.3%) and relatively small nuclear quadrupole moment Q. However, the low Larmore frequency of ^{39}K (28.05 MHz in a static magnetic field of 14.1 T, which corresponds to ^{1}H resonance frequency of 600 MHz) leads to low sensitivity. Additionally, the high conductivity of K-GICs makes NMR measurement with general probes difficult because adjustment of a circuit in NMR probes (tuning and matching) might not match well. Reliable NMR spectra are not obtained using a standard sample rotor for Magic Angle Spinning (MAS) experimentation because K-GICs decompose during NMR measurement as a result of their high reactivity, even if nitrogen gas is used for driving and rotating for MAS. Because of these various difficulties, ^{39}K NMR measurements have not been applied to KIB research, although ^{39}K NMR can be expected to make an important contribution to KIB development.

For this study, we attempted to obtain reference ^{39}K NMR spectra of KC_8, KC_{24}, and KC_{36} as a first step toward using ^{39}K NMR in KIBs research. Samples were measured in the static magnetic field at 18.8 T to increase sensitivity. To reduce the effects of high conductivity and high reactivity, the samples were sealed in $\phi 8$ mm glass tubes with fluoropolymer. In addition, NMR probes were adjusted by changing the number of turns of the coil to match each sample. Optimal measurement conditions were explored. Among the results, ^{39}K NMR signals of potassium metal, KC_8, KC_{24}, and KC_{36} were observed. This report is the first of observed K-GIC signals showing different chemical shifts depending on the samples.

For this study, K-GIC samples were prepared by purchase or synthesis. The KC_8 sample was purchased from FUJIFILM Wako Pure Chemical Corp. The KC_{24} sample and KC_{36} sample were synthesized using the following procedure. Natural Graphite (SNO30; SEC Carbon Ltd.) and potassium metal (99.5% purity) were mixed at a stoichiometric ratio of KC_{24} or KC_{36} composition ratios. After these materials were placed into glass tubes, they were heated at 300 °C under vacuum for 1 week.

Raman spectra of the prepared samples were measured to confirm synthesis of the target compounds. Raman spectroscopy was carried out using a laser Raman spectrometer (NRS-5500; JASCO Corp.) with a 532 nm laser. The spot size of the laser for Raman measurement of KC_8, KC_8-air, KC_{24}, and KC_{36} samples was approximately 20, 20, 2, and 1 μm in diameter, respectively. Spectra were obtained at several locations per sample. For NMR measurements, 40–50 mg of a K-GIC sample were mixed with a similar volume of polyvinylidene difluoride (PVDF) to reduce the sample conductivity. Then they were placed in a $\phi 8$ mm Pyrex tube in an argon-filled glove box. After the Pyrex tube was taken out from the glove box without exposing the sample to air, it was sealed (Fig. S1(a)). In addition, a KC_8 sample degraded by air exposure was prepared for comparison: "KC_8-air" denotes the air-exposed sample. A potassium metal sample was also

prepared for NMR measurements. 27 mg of potassium metal was cut into 2–3 mm square pieces in an argon-filled glove box and was sealed in a $\phi 8$ mm Pyrex tube with PVDF. The ^{39}K NMR spectra were recorded using a spectrometer (18.79 T magnet, JNM-ECZ800R; JEOL/JASTEC or 18.79 T magnet, JNM-ECA800; JEOL/JASTEC). A general MAS probe was used to measure the potassium metal, KC_{24}, and KC_{36} samples. To measure the KC_8 samples, a resonance circuit of a homebuilt NMR probe was adjusted for the samples because of a mismatch between the resonance frequency of the MAS probe and the samples caused by the sample's high conductivity. All samples were measured under static conditions with a single pulse sequence with pulse length of 10 μs or 5 μs, a delay of 1 s, and overnight accumulation. KBr aqueous solution was used as a reference at 0 ppm.
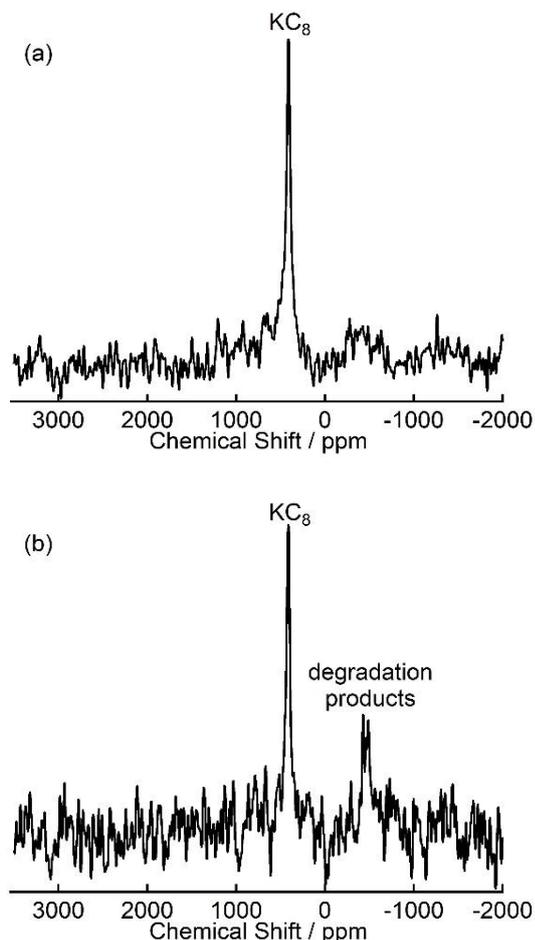
The prepared K-GIC samples were evaluated to determine if they were the desired samples before NMR measurements. K-GICs are known to exhibit characteristic colors depending on their composition. The samples used for this experiment were also colored: the purchased KC_8 sample was a golden powder, the synthesized KC_{24} sample was a bright blue powder, and the KC_{36} sample was a dark blue powder (Figs. S1(b–d)). Each sample was evaluated using Raman spectroscopy (Fig. S2). As shown in Fig. S2(a), the Raman spectrum of the KC_8 sample showed an asymmetric Fano-line at 1600 cm^{-1} with a C_z mode around 540 cm^{-1}, which shows good agreement with the reported Raman spectra of KC_8.[20,21] The Raman spectrum of the KC_{24} sample showed a single line around 1600 cm^{-1}, as presented in Fig. S2(b). This line corresponds to the G_c-line, related to the charged graphene layers next to an intercalant layer.[21] The Raman spectrum of the KC_{24} sample is similar to the reported Raman spectra of KC_{24}, confirming that the chemical composition of the synthesized sample is surely KC_{24}. For the Raman spectrum of the KC_{36} sample, two peaks were observed at 1580 and 1600 cm^{-1}, as shown in Fig. S2(c). These peaks at 1580 and 1600 cm^{-1} were assigned respectively to the G_{uc}-line, which is related to the uncharged graphene layers surrounded by the charged graphene layers, and the G_c-line. However, the intensity of the G_{uc}-line of the KC_{36} sample differed depending on the measurement spot, suggesting that the KC_{36} contains some compositionally different structures from KC_{36}. Because several particles of different colors were included in the KC_8-air sample, the Raman spectrum was obtained for each color particle. The Raman spectrum of the golden color particles in the KC_8-air sample is shown in Fig. S2(d). Signals observed at 1259 and 1550 cm^{-1} were assigned respectively to the D-band and E_{2g} mode or G-band, based on spectra similar to the Raman spectrum of stage 1 KC_8. Figure S2(e) shows that the Raman spectrum of the bluish particles in the KC_8-air samples was similar to that of KC_{24}. These results suggest that the KC_8-air sample has a stage 1 structure but that it is partially broken down into a stage 2 or higher stage structure.

The ^{39}K NMR spectrum of the potassium metal is presented in Fig. S3(a). Two peaks were observed at 2468 and 2637 ppm. The signal at 2468 ppm appeared even when the sample was not set, suggesting that the signal originates from the NMR probe (Fig. S3(b)). This signal is assigned to the spectral aliasing of silver because the NMR probe uses silver wire, which has a similar resonance frequency to that of potassium (Ag, 37.5 MHz; K, 37.3

3

1 MHz). In fact, the signal at 2468 ppm disappeared in
2 measurement with the homebuilt probe without silver wire. The
3 signal at 2637 ppm is regarded as that of potassium metal
4 because this signal was observed in measurements with both
5 probes. The Knight shift for potassium metal particles dispersed
6 in paraffin has been reported as 0.248% (2480 ppm),[22] which is
7 in reasonable agreement with results of this work.
8   Initially, we tried the NMR measurement of K-GICs using a
9 general ϕ8 mm MAS sample rotor. However, no reliable
10 spectrum was obtained because of sample degradation that
11 occurred during measurement. The certain spectra of the K-GICs
12 were obtained by sealing off the samples into the Pyrex tube to
13 keep them from degradation. Figure 1(a) presents that the NMR
14 spectrum of the KC_8 sample showed only one peak at 411 ppm.
15 The KC_8-air sample was also measured using ^{39}K NMR, which
16 is displayed in Fig. 1(b). The NMR spectrum showed three peaks
17 at -483, -429, and 413 ppm. Because the KC_8 signal was
18 confirmed to appear at 411 ppm, the signal at 413 ppm is
19 regarded as KC_8, whereas the signals at -429 and -483 ppm are
20 ascribed to degradation products. The Raman spectrum also
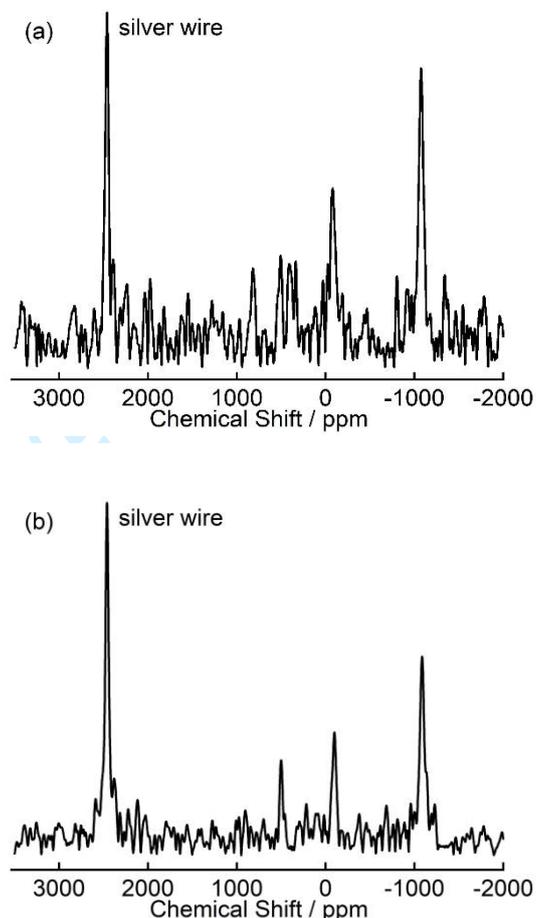21 suggests that the KC_8-air sample contains some KC_8 compound,

25 presence of stage 2 or higher stage compounds. In prior reports,
26 ^7Li NMR signals of lithium-stored carbon materials have
27 been also observed without MAS,[18, 23] and our results are
28 reasonable.
29   The ^{39}K NMR spectra of the KC_{24} and KC_{36} samples are
30 displayed in Fig. 2. The NMR signal of the KC_{24} sample was
31 observed at -1075, -80, 508, 817, and 2460 ppm (Fig. 2(a)),
32 whereas that of the KC_{36} was observed at -1087, -97, 500, and
33 2460 ppm (Fig. 2(b)). In Fig. 2(a), it seems that there are three
34 peaks at 336, 401, and 508 ppm around 500 ppm. However,
35 NMR measurements of another lot of KC_{24} samples showed only
36 a peak at 516 ppm (Fig. S4), suggesting that only the peak at 508
37 ppm is a signal of the sample and the other two peaks are noise.
38 The peak at 2460 ppm is assigned to the spectral aliasing of silver.
39 Although the KC_{24} sample was confirmed from Raman
40 measurements to have a stage 2 structure, the NMR spectrum
41 showed four signals aside from the silver signal. By contrast, for
42 the KC_{36} sample, the NMR spectrum was similar to that of the
43 KC_{24} sample, even though the Raman measurement confirmed
44 that the KC_{36} structure was partially heterogeneous. These
45 samples were not degraded by air. Therefore, the NMR spectra

Fig. 1. ^{39}K NMR spectra of (a) KC_8, and (b) KC_8-air.

Fig. 2. ^{39}K NMR spectra of (a) KC_{24}, and (b) KC_{36}.

22 which is consistent with NMR findings. These signals at -483
23 and -429 ppm are assignable to stage 2 or higher stage K-GIC
24 because the Raman spectra of the KC_8-air sample indicated the

46 of the KC_{24} and KC_{36} samples were more complicated than those
47 expected from the Raman measurement, suggesting that ^{39}K
48 NMR is likely to be a powerful tool for distinguishing

differences in the in-plane density of interlayer potassium that cannot be detected by Raman spectroscopy. Additionally, as noted earlier, the Raman results for the KC_8-air sample suggest that it contains stage 2 and higher stage compounds. However, the NMR spectra of the KC_{24} and KC_{36} samples differed from that of the KC_8-air sample. The causes for the different NMR signals of each sample might be the different host carbon types of the purchased KC_8 and the synthesized KC_{24} and KC_{36} samples. In fact, the chemical composition of the degradation products of K-GICs depends on the types of host carbon and the duration of exposure to air.[24] Further sample data acquisition is necessary for the accurate assignment of NMR signals.

In conclusion, we present the first observations of the ^{39}K NMR signals of K-GICs using an 18.8 T NMR system, by adjusting the resonance circuit of the NMR probe for each sample. The signal of stage 1 K-GIC (KC_8) is assigned clearly. Although some higher stage GICs, showed more complicated NMR spectra than expected from Raman measurements, our findings reveal that ^{39}K NMR can be a powerful tool for distinguishing differences in the in-plane density of interlayer potassium, which are not detected using Raman spectroscopy. The results are expected to contribute to the analysis of heterogeneous and disordered electrochemically intercalated carbon electrodes for KIBs.

Supplementary data

Supplementary material is available at *Chemistry Letters*

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5