Analysis of bis(trifluoromethylsulfonyl)imide-doped paramagnetic graphite intercalation compound using ^{19}F very fast magic angle spinning nuclear magnetic resonance

Kazuma Gotoh [a], Kazuyuki Takeda [b], Michael M. Lerner [c], Yoshimi Sueishi [a], Shinpei Maruyama [a], Atsushi Goto [d], Masataka Tansho [d], Shinobu Ohki [d], Kenjiro Hashi [d], Tadashi Shimizu [d], and Hiroyuki Ishida [a]*

[a] Graduate School of Natural Science & Technology, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan

[b] Division of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

[c] Department of Chemistry, Oregon State University, Corvallis, OR 97331-4003, USA

[d] National Institute for Materials Science, Tsukuba, Ibaraki 305-0003, Japan
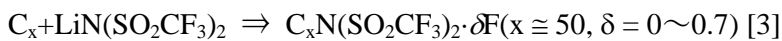
(Abstract) F atoms bonding to paramagnetic/conductive graphene layers in accepter-type graphite intercalation compounds (GICs) are analyzed using very fast magic angle spinning nuclear magnetic resonance, which is applied for the first time on ^{19}F nuclei to investigate paramagnetic materials. In the bis(trifluoromethylsulfonyl)imide(TFSI)-doped GIC, C-F bonds between fluorine atoms and graphene layers conform to a weak bonding of F to the graphene sheets. TFSI anions intercalated in the GIC do not show overall molecular motion; even at room temperature only the CF_3 groups rotate.

*Corresponding author. Tel/Fax: +81 86 251 7776

E-mail address: kgotoh@cc.okayama-u.ac.jp (K. Gotoh)

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(**Article**) Fluorination of carbon materials is one of the most powerful and effective methods to generate new properties for potential applications [1]. For example, one highly-fluorinated material, polycarbon fluoride $(C_xF)_n$ is used as a high energy density cathode material in primary lithium batteries.

Several novel accepter-type graphite intercalation compounds (GICs) containing fluorine compounds have been reported by Lerner et al. [2-4]. Their synthesis methods based on the oxidation of graphite using K_2MnF_6 oxidant in hydrofluoric acid could provide a relatively mild and safe fluorination approach compared to the traditional reaction using F_2 gas. One feature of these reactions is that additional fluorine atoms are believed to bond directly to the graphene sheets in the GICs, and the abundance of these C-F groups increases with reaction time. For example, in the reactions:

$C_x+LiN(SO_2CF_3)_2 \Rightarrow C_xN(SO_2CF_3)_2 \cdot \delta F(x \cong 50, \delta = 0 \sim 0.7)$ [3]

$C_x+KC_8F_{17}SO_3 \Rightarrow C_xC_8F_{17}SO_3 \cdot \delta F$ $(x \cong 18, \delta = 0 \sim 4)$ [4]

The notation δF indicates the additional fluorine atoms bound to the graphene sheets of the GICs. Although the presence of the additional fluoride can be confirmed by elemental analyses, further information on the nature of the C-F bonds generated has not been obtained to date.

^{19}F solid state NMR is one of the most powerful tools for investigating the electronic state of F atoms in carbon materials. Several states of F atoms on carbon materials such as carbon nanotubes (CNT), fullerenes, and polycarbon fluorides (CF, C_2F, $C_{2.5}F$) [5-7] have been reported; the C-F bonding can be covalent, ionic, or semi-covalent. However, the small amounts of fluorine in accepter-type GICs have not been observed by NMR because of peak broadening associated with paramagnetism of the GICs, specifically paramagnetic sites on the edges. Recently, a novel approach using very fast magic angle spinning (VFMAS) over 20 kHz has been shown to provide excellent resolution and sensitivity in both ^{1}H [8] and ^{13}C [9] NMR in paramagnetic materials. In

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present study, we investigated the state of F atoms bonding to graphene sheets for a bis(trifluoromethylsulfonyl)imide(TFSI)-doped GIC (C_xTFSI) by applying an ^{19}F VFMAS NMR technique. Perfluorooctanesulfonicacid(PFOS)-doped GIC (C_xPFOS) was also studied for comparison. TFSI is well-known as a component of ionic liquids proposed for use in batteries or capacitors. The anion can be intercalated into graphite using either chemical or electrochemical methods [10]. The spin-lattice relaxation times (T_1) were determined using ^{19}F NMR for the C_xTFSI in order to characterize the dynamics of intercalated TFSI molecules, which is relevant to the synthesis and reaction kinetics of storage materials in electrochemical devices.

C_xTFSI was produced from lithium TFSI ($LiN(SO_2CF_3)_2$, 3M corp. 0.6 g), 0.54 g of potassium hexafluoromanganate (K_2MnF_6, synthesized according to a literature [2]), and 0.3 g of graphite powder (Wako Chemical) in 48% w/o hydrofluoric acid by stirring for 10 days at room temperature [3]. C_xPFOS was produced by a literature method [4]. ^{19}F VFMAS NMR spectra were obtained at room temperature using a 7.0 T magnet and a home built MAS probe equipped with a Varian 3.2 mm spinning module. The data were acquired on a home built NMR spectrometer [11]. Trifluoroacetic acid was used as a standard with chemical shift at -76.6 ppm. ^{19}F NMR spin-lattice relaxation time (T_1) was measured using a 11.7 T magnet and a Thamway spectrometer. From the results of C, N, S, F elemental analyses and powder X-ray diffraction (XRD) patterns, the sample GIC's compositions and stages were established as follows: a) C_xTFSI $C_{40}N(SO_2CF_3)_2 \cdot 0.33F$, stage 2; b) C_xPFOS $C_{13}C_8F_{17}SO_3 \cdot 0.17F$, stage 3.

Electron spin resonance (ESR) spectrum of the C_xTFSI sample is shown in Fig. 1. The spectrum showed a broad and asymmetric signal (g = 2.0010(5)), which is explainable by an effect of conductive electrons (Dyson effect) [12] and anisotropy of the GIC. The density of paramagnetic spins in the C_xTFSI sample was estimated at 1.7×10^{18} spins g^{-1} (spin/C = $1/1.8 \times 10^4$) using a calibration by 4-Hydroxy-2,2,6,6-tetramethylpiperidinoxyl (TEMPOL) toluene solution.
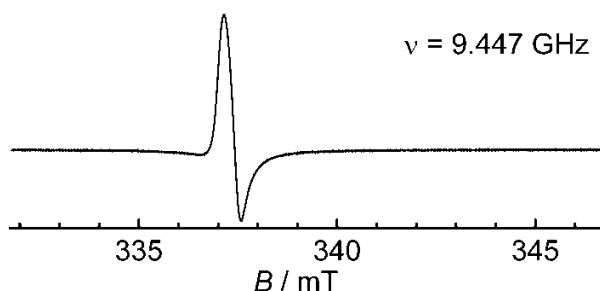
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$\nu = 9.447$ GHz

B / mT

Fig. 1 –ESR spectrum of C_xTFSI.

The ^{19}F VFMAS NMR spectrum of C_xTFSI is shown in Fig. 2(a). The prominent peak observed at -79 ppm is ascribed to the F atoms of CF_3 groups in the TFSI molecules. A second peak appears at -123 ppm at the spinning rate of 24.1 kHz, but is not observed by spinning frequencies under 20 kHz (Figs. 2(b) and 2(c)). This peak is ascribed to the fluorine atoms directly bonded to paramagnetic/conductive graphene layers in the GIC. Interestingly, the chemical shift for C_xTFSI at -123 ppm is similar to the value previously reported by Dubois et al [13] for "unusual weak bonding mode of F (-120 ppm)" in single-walled carbon nanotubes. CF_2 on polycarbon fluorides also show a peak at about -120 ppm [1,5]. However, it is less likely that only the peak of CF_2 on the edge of graphite appeared and no signal for CF was observed. The C_xPFOS sample showed a somewhat different ^{19}F response (Fig. 3). Signals at -124, -115, -84 and -74 ppm attributable to CF_3 or CF_2 of PFOS in the GIC were observed even under 20 kHz (Fig. 3(b)), and then a peak at -186 ppm appeared at 23.2 kHz spinning (Fig. 3(a)). The peak at -186 ppm can be assigned to the ionic fluorine atoms which intercalated into graphene sheets. The signal of weak-bonding F at C_xPFOS also should appear at about -120 ppm, however, it would overlap with CF_2 peaks and then could not be observed.
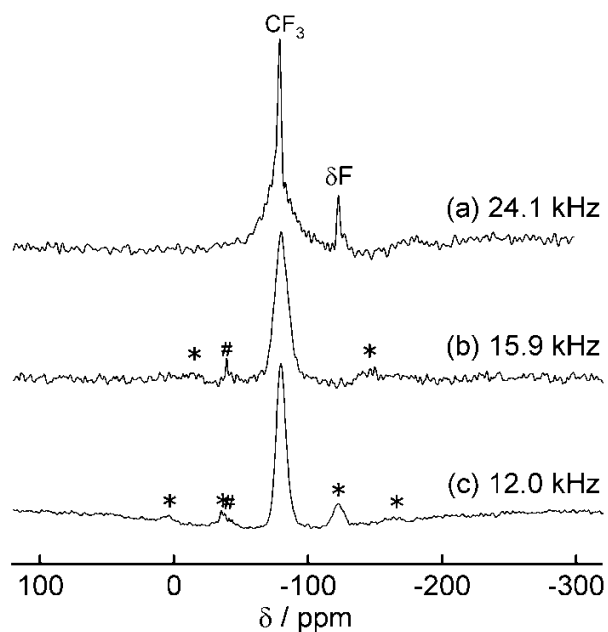
Fig. 2 – ^{19}F MAS NMR spectra of C$_x$TFSI at the spinning rate of 24.1 kHz (a), 15.9 kHz (b), and 12.0 kHz (c). ∗ and # denote spinning side bands and the offset frequency of the rf pulse, respectively.
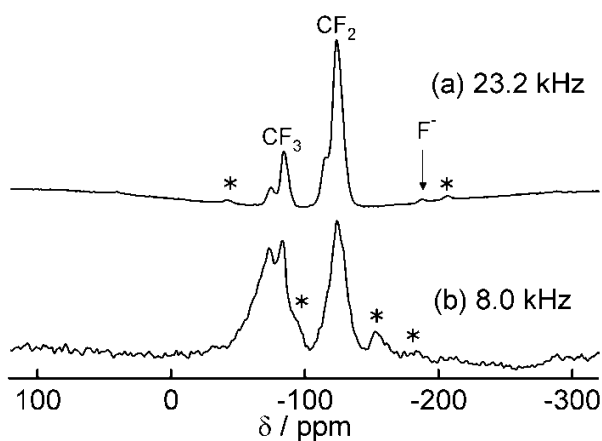

Fig. 3 – ^{19}F MAS NMR spectra of C$_x$PFOS at the spinning rate of 23.2 kHz (a), and 8.0 kHz (b). ∗ indicates spinning side bands.

Fig. 4 shows the temperature dependence of T_1 for C_xTFSI. A minimum of T_1 was observed, indicating that a molecular motion was thermally activated at the temperature. The T_1 data was fitted using following BPP equation [14] (1) and the Arrhenius equation (2);

$$T_1^{-1} = \frac{2}{3}\gamma^2\Delta M_2\left(\frac{\tau}{1+\omega^2\tau^2}+\frac{4\tau}{1+4\omega^2\tau^2}\right) \quad (1), \qquad \tau = \tau_0\exp\frac{E_a}{RT} \quad (2),$$

where γ, ΔM_2, τ, ω and E_a are the magnetogyric ratio of fluorine, the reduction of second moment of spectrum's line width through motion, the correlation time of the motion, the Larmor frequency, and activation energy of the motion, respectively. The T_1 curve fitted by the BPP equation is explained by a single molecular motion, which has parameters of E_a= 7.3±0.5 kJmol^{-1}, ΔM_2= 5.0±0.2 Gauss^2. This motion can be attributed to the rotation of CF_3 axis of TFSI molecules intercalated in the GIC because: (a) the value of activation energy and ΔM_2 are comparable with methyl rotations in typical amines, (b) the static NMR spectrum of C_xTFSI remains broad even at room temperature (not shown).
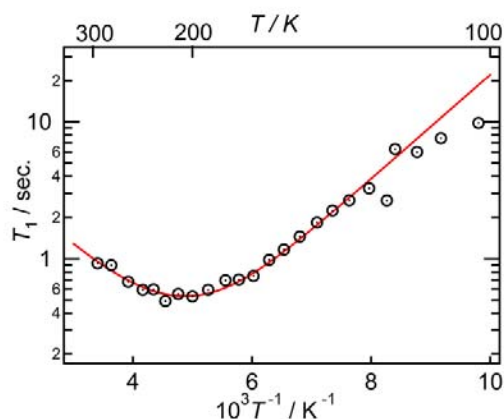

Fig. 4 – Temperature dependence of ^{19}F NMR T_1 in C_xTFSI and a fitting curve using the BPP equation [14].
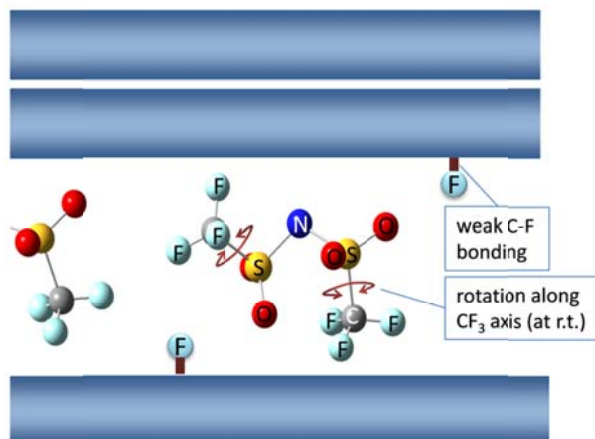
Fig. 5 – A structural model for C$_x$TFSI GIC.

In conclusion, a signal ascribed to F atoms or ions bonding to paramagnetic/conductive graphene layers in C$_x$TFSI and C$_x$PFOS could be observed using a VFMAS NMR technique. In the C$_x$TFSI, C-F bonds between F atoms and graphene layers conformed to a weak bonding of F to the graphene sheets. Additionally, TFSI anions in GIC are determined to not undergo overall molecular motion: even at room temperature only CF$_3$ groups rotate, as illustrated in Fig. 5.

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