

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

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**(Abstract)** F atoms bonding to paramagnetic/conductive graphene layers in acceptor-type graphite intercalation compounds (GICs) are analyzed using very fast magic angle spinning nuclear magnetic resonance, which is applied for the first time on  $^{19}\text{F}$  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  $\text{CF}_3$  groups rotate.

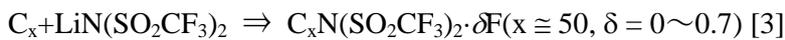
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**(Article)** Fluorination of carbon materials is one of the most powerful and effective methods to generate new properties for potential applications [1]. For example, one highly-fluorinated material, polycarbon fluoride ( $C_xF_n$ ) is used as a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

Several novel acceptor-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:



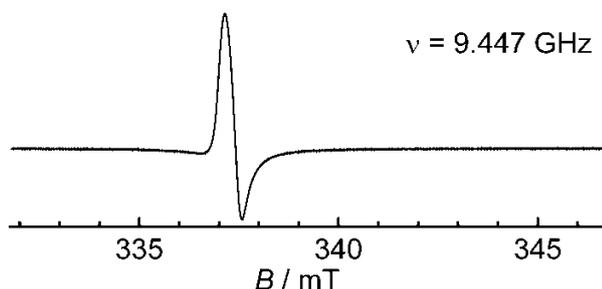
The notation  $\delta F$  indicates the additional fluorine atoms bound to the graphene sheets of the GICs. Although the presence of the additional fluoride can be confirmed by elemental analyses, further information on the nature of the C-F bonds generated has not been obtained to date.

$^{19}F$  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 acceptor-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  $^1H$  [8] and  $^{13}C$  [9] NMR in paramagnetic materials. In

present study, we investigated the state of F atoms bonding to graphene sheets for a bis(trifluoromethylsulfonyl)imide(TFSI)-doped GIC ( $C_x$ TFSI) by applying an  $^{19}\text{F}$  VFMAS NMR technique. Perfluorooctanesulfonicacid(PFOS)-doped GIC ( $C_x$ PFOS) 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  $^{19}\text{F}$  NMR for the  $C_x$ TFSI 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.

$C_x$ TFSI was produced from lithium TFSI ( $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ , 3M corp. 0.6 g), 0.54 g of potassium hexafluoromanganate ( $\text{K}_2\text{MnF}_6$ , 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].  $C_x$ PFOS was produced by a literature method [4].  $^{19}\text{F}$  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.  $^{19}\text{F}$  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)  $C_x$ TFSI  $C_{40}\text{N}(\text{SO}_2\text{CF}_3)_2 \cdot 0.33\text{F}$ , stage 2; b)  $C_x$ PFOS  $C_{13}\text{C}_8\text{F}_{17}\text{SO}_3 \cdot 0.17\text{F}$ , stage 3.

Electron spin resonance (ESR) spectrum of the  $C_x$ TFSI 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  $C_x$ TFSI sample was estimated at  $1.7 \times 10^{18}$  spins  $\text{g}^{-1}$  (spin/C =  $1/1.8 \times 10^4$ ) using a calibration by 4-Hydroxy-2,2,6,6-tetramethylpiperidinoxyl (TEMPOL) toluene solution.



**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.

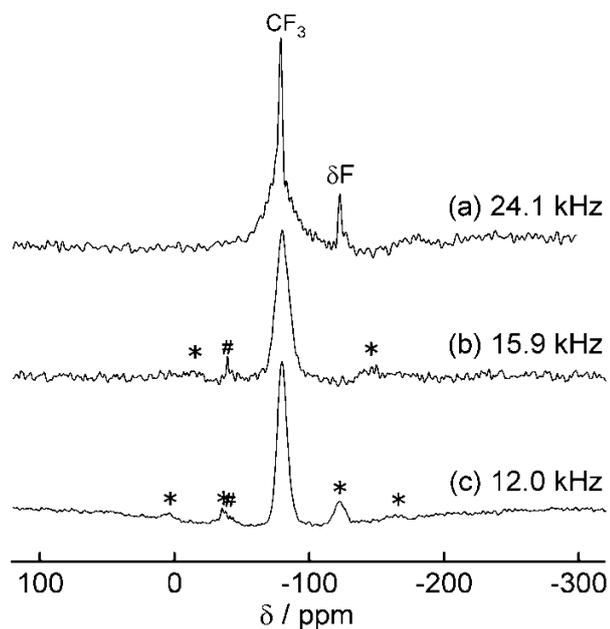


Fig. 2 –  $^{19}\text{F}$  MAS NMR spectra of  $\text{C}_x\text{TFSI}$  at the spinning rate of 24.1 kHz (a), 15.9 kHz (b), and 12.0 kHz (c). \* and # denote spinning side bands and the offset frequency of the rf pulse, respectively.

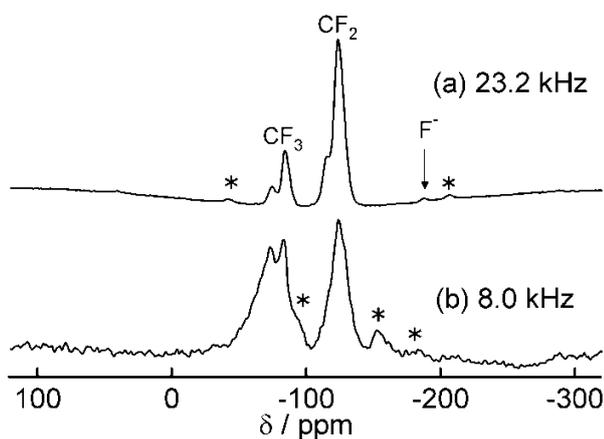
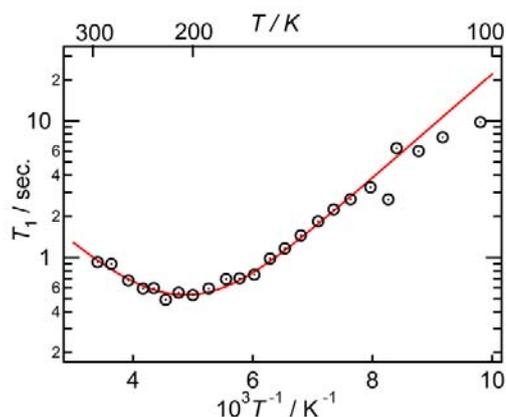


Fig. 3 –  $^{19}\text{F}$  MAS NMR spectra of  $\text{C}_x\text{PFOS}$  at the spinning rate of 23.2 kHz (a), and 8.0 kHz (b). \* indicates spinning side bands.

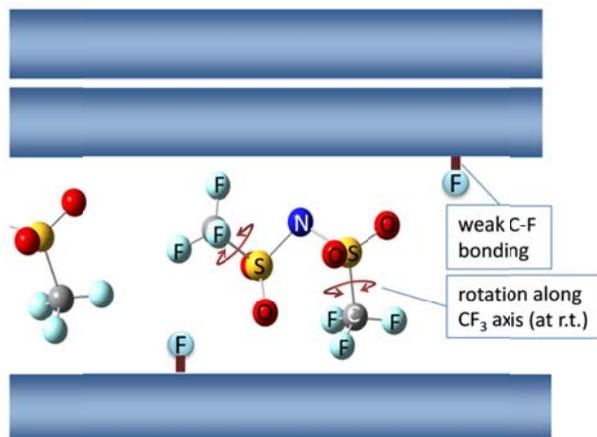
Fig. 4 shows the temperature dependence of  $T_1$  for  $C_x$ TFSI. A minimum of  $T_1$  was observed, indicating that a molecular motion was thermally activated at the temperature. The  $T_1$  data was fitted using following BPP equation [14] (1) and the Arrhenius equation (2);

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

where  $\gamma$ ,  $\Delta M_2$ ,  $\tau$ ,  $\omega$  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  $E_a = 7.3 \pm 0.5 \text{ kJmol}^{-1}$ ,  $\Delta M_2 = 5.0 \pm 0.2 \text{ Gauss}^2$ . 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  $\Delta M_2$  are comparable with methyl rotations in typical amines, (b) the static NMR spectrum of  $C_x$ TFSI remains broad even at room temperature (not shown).



**Fig. 4 – Temperature dependence of  $^{19}\text{F}$  NMR  $T_1$  in  $C_x$ TFSI and a fitting curve using the BPP equation [14].**



**Fig. 5 – A structural model for C<sub>x</sub>TFSI GIC.**

In conclusion, a signal ascribed to F atoms or ions bonding to paramagnetic/conductive graphene layers in C<sub>x</sub>TFSI and C<sub>x</sub>PFOS could be observed using a VFMAS NMR technique. In the C<sub>x</sub>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<sub>3</sub> groups rotate, as illustrated in Fig. 5.

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