

# A New Porous Carbon via an Exfoliation of *n*-Octylammonium Tetrachloroferrate(III)-Graphite Intercalation Complex

Chai-Won Kwon, Dong-Hoon Kim, and Jin-Ho Choy\*

Department of Chemistry, Center for Molecular Catalysis(CMC), Seoul National University, Seoul 151-742, Korea  
Received July 29, 1998

A new graphite intercalation compound (GIC), *n*-octylammonium tetrachloroferrate(III)-graphite, has been derived from well-known ferric chloride graphite intercalation compound. X-ray diffraction study shows that the basal spacing of this new GIC is 20.8 Å. In order to investigate the local geometry around the iron atom in the graphite layers, X-ray absorption spectroscopy experiments were performed. The first discharge capacity of its exfoliated form is found to be 862 mAh/g, which is more than double the value of pristine graphite (384 mAh/g). Such a drastic increase implies that the exfoliated graphite is a promising electrode material.

## Introduction

Recently, many efforts have been made on the preparation of carbonaceous materials for anodes in Li-ion batteries.<sup>1-4</sup> Some of them exhibit very large capacities beyond the theoretical expectation of graphite, 372 mAh/g.<sup>5-8</sup> Such carbonaceous materials have been obtained by the pyrolysis of organic precursors at the temperatures of 550-1000 °C,<sup>5,6</sup> the mechanical milling of hard and soft carbons,<sup>7</sup> and the mild burning of graphites.<sup>8</sup> In this study, we describe a novel route to a porous graphite with high specific area through an exfoliation of graphite intercalation compound (GIC). A rapid thermal decomposition of guest molecules in GIC may induce the layered graphite host into individual graphite sheets. In order to maximize this effect, an effort has made to intercalate long chain organic molecules to expand the interlayer spacing of graphite layers. Here, we describe the synthesis and characterization of a new GIC, *n*-octylammonium tetrachloroferrate(III)-graphite, and the electrochemical discharge capacity of its exfoliated form.

## Experimental

The natural graphite (BG-39, Superior Graphite, USA) with the particle size of ~12 μm was used as a starting material. FeCl<sub>3</sub> (Aldrich, 97%) was purified by sublimation prior to use. As an organic intercalant *n*-octylammonium chloride was used.

At first, FeCl<sub>3</sub>-graphite intercalation compound was synthesized by conventional chemical vapor transport method,<sup>9</sup> and then washed with 1 M HCl solution to remove the excess FeCl<sub>3</sub>. A *n*-octylammonium tetrachloroferrate(III)-graphite was obtained by mixing FeCl<sub>3</sub>-graphite with excess *n*-octylammonium chloride in a pyrex tube, which was vacuum-sealed, and by reacting at 125 °C for 24 hours. For comparison, *n*-octylammonium chloride · FeCl<sub>3</sub> complex only was prepared. Stoichiometric amount of *n*-octylammonium chloride and FeCl<sub>3</sub> was put into the 1:1 (v/v) mixed solution of *n*-hexane and ethanol, and then the solvent was slowly removed under reduced pressure in a

rotary evaporator. Thermal decomposition of *n*-octylammonium tetrachloroferrate(III)-graphite was carried out at 400 °C in a tube furnace for 10 hours in air. The resulting compound was washed with 1 M HCl solution several times to remove iron-containing by-products such as Fe<sub>2</sub>O<sub>3</sub>.

The intercalation reaction and crystal structure of the samples were recorded by powder X-ray diffractometer (Phillips PW-1830) with Ni-filtered Cu-Kα radiation (λ=1.5418 Å).

BET specific surface area was calculated from N<sub>2</sub> adsorption isotherm measured at 77 K.

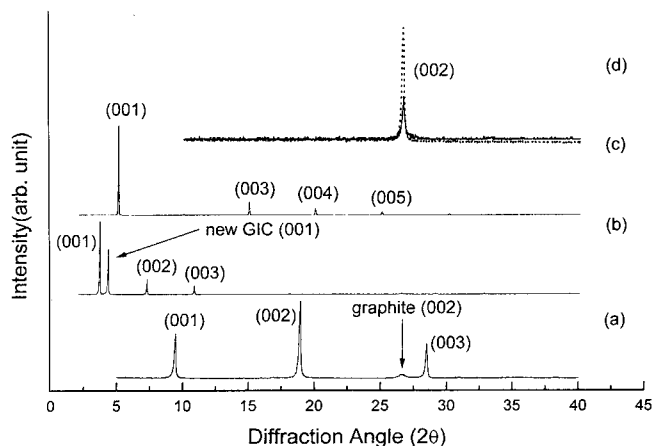
X-ray absorption experiments were carried out at the beam line 3C1 in Pohang Light Source (PLS), operated at 2.0 GeV with a ring current of 80-100 mA. All the data were collected in a transmission mode, and a Si (111) double crystal monochromator was used with N<sub>2</sub>-filled ionization detector. The data analyses were performed with the computer program UWXAFS2,<sup>10</sup> employing the curved wave theory using the scattering parameters obtained by FEFF6 code.<sup>11</sup> The used data ranges of k- and R-spaces were 2.7-11 Å<sup>-1</sup> and 0.5-3.0 Å, respectively.

Electrochemical measurements were performed in a two electrode test cell with the Li/1M LiPF<sub>6</sub> in EC-DMC (50:50 v/v)/graphite configuration. The galvanostatic discharge process was recorded at C/25 rate (at a constant current that can reach to Δx=1 in Li<sub>x</sub>C<sub>6</sub> in 25 hours) using Arbin BT 2043 multi-channel potentiostat/galvanostat. The cut-off voltage was set to 0.00 V for discharge (intercalation) and 2.00 V for charge (deintercalation), respectively.

## Results and Discussion

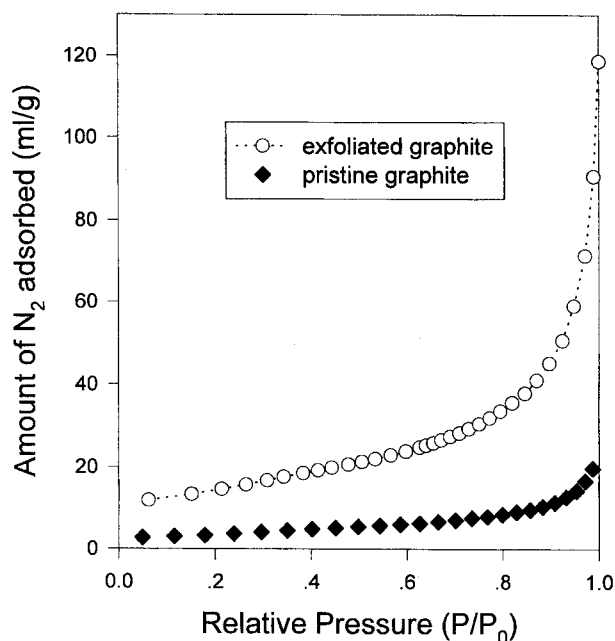
According to the powder XRD pattern for FeCl<sub>3</sub>-graphite, well-defined (00*l*) reflections corresponding to the 1st stage intercalation compound are observed (Figure 1(a)). The basal spacing of 9.4 Å is well consistent with the value reported previously.<sup>9,12</sup> The observation of a weak graphite (002) reflection is mainly due to the deintercalation of FeCl<sub>3</sub> during washing.<sup>12</sup> Upon intercalation of *n*-octylammonium chloride into FeCl<sub>3</sub>-graphite, the basal spacing expands to 20.8 Å (Figure 1(b)) to form a *n*-octylammonium tetrachloroferrate(III)-graphite(new GIC). This can be simply rationalized by the *c*-axis parameter (20.8 Å) of this new

\*Author to whom all correspondence should be addressed

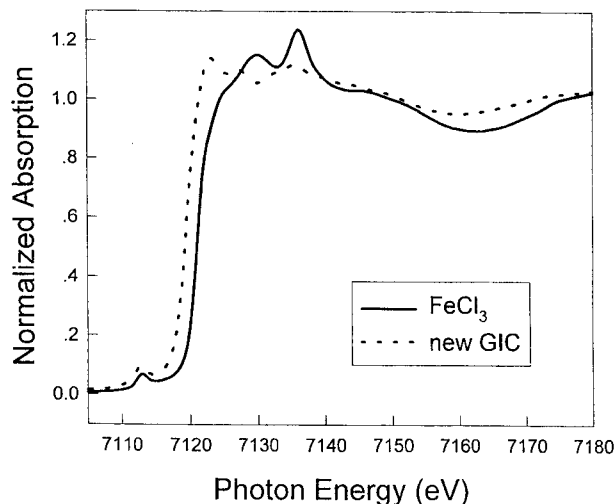


**Figure 1.** Powder X-ray diffraction patterns of (a)  $\text{FeCl}_3$ -graphite, (b) *n*-octylammonium tetrachloroferrate(III)-graphite (new GIC) together with remaining *n*-octylammonium chloride, (c) *n*-octylammonium chloride  $\cdot$   $\text{FeCl}_3$  complex and (d) the exfoliated graphite (—) compared with the pristine graphite (···).

GIC, which is the sum of the basal spacing of *n*-octylammonium chloride  $\cdot$   $\text{FeCl}_3$  (17.5 Å) (Figure 1(c)) and that of graphite (3.35 Å). The peaks of 24.1 Å correspond to the excess *n*-octylammonium chloride remaining on the surface of the GIC. It is worthy to note here that the separation of these two phases might be impossible by simple washing due to the unstability of the intercalated phase. Figure 1(d) shows the XRD pattern for the exfoliated graphite calcined at 400 °C. For comparison, the diffraction profile of the pristine graphite is overlapped in the figure as denoted with dotted line. It is evident from the line broadening and reduced intensity in diffraction profiles of exfoliated graphite that the resulting graphite is finely divided with turbostratic plates arrangement. The BET surface area obtained by  $\text{N}_2$  adsorption isotherm of the



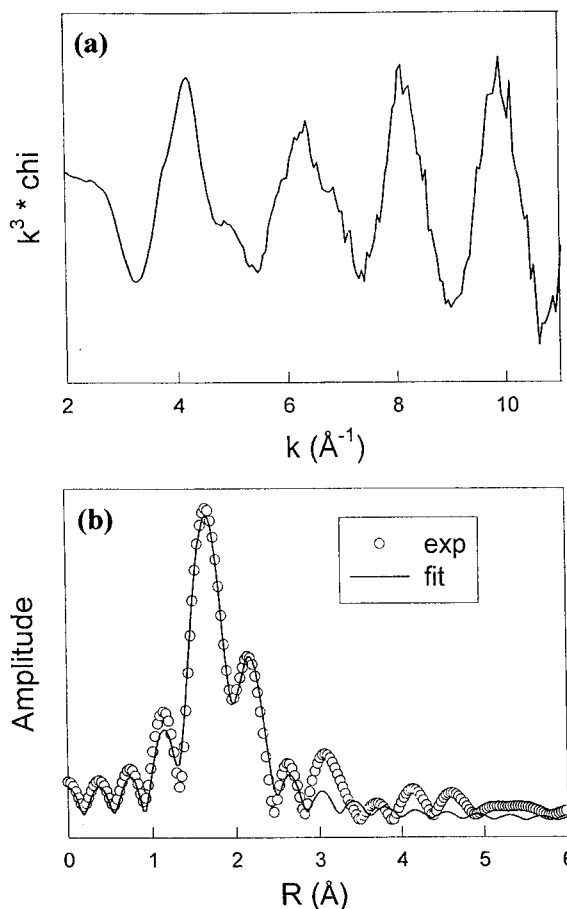
**Figure 2.**  $\text{N}_2$  adsorption isotherm measured at 77 K.



**Figure 3.** Fe K-edge XANES spectrum of *n*-octylammonium tetrachloroferrate(III)-graphite compared with that of  $\text{FeCl}_3$  as a reference.

exfoliated graphite is as large as 70  $\text{m}^2/\text{g}$ , while that of the pristine material is 10  $\text{m}^2/\text{g}$  (Figure 2). Such a drastic increase of surface area is mainly due to the graphite exfoliation.

In order to analyze the GIC structure, we carried out X-



**Figure 4.** (a) Experimental  $k^3$ -weighted EXAFS spectrum and (b) Fourier transforms (non-phase-shift-corrected) of experimental data (open circles) and model fits (thick line).

**Table 1.** The best fit results of the Fe K-edge EXAFS spectrum ( $\Delta\chi^2=149.15$ )<sup>a</sup>

	bond length	$\sigma^2$	$\Delta E_0$
Fe-Cl <sub>t</sub> (tetrahedral)	2.19(6) Å	0.00400 Å <sup>2</sup>	-1.9 eV
Fe-Cl <sub>o</sub> (octahedral)	2.44(2) Å	0.00789 Å <sup>2</sup>	-1.7 eV

<sup>a</sup>The fitting ranges for k- and R-spaces are  $2.7 \text{ \AA}^{-1} < k < 11 \text{ \AA}^{-1}$  and  $0.5 \text{ \AA} < R < 3.0 \text{ \AA}$ , respectively, and the fitting accuracy is about 0.02 Å for bond distance, and 25% for Debye-Waller factor ( $\sigma^2$ ).

ray absorption spectroscopy experiments. Figure 3 shows the Fe K-edge X-ray absorption near edge structure (XANES) spectra for the new GIC together with that of FeCl<sub>3</sub> used as the Fe<sup>3+</sup> reference. The pre-edge peak at around 7113 eV can be assigned to the 1s→3d transition.<sup>13,14</sup> It has been well known that the amplitude of this band is dependent on coordination number. Assuming that the edge jump height is unity, the normalized peak area (the height × FWHM) of 4-coordinated complexes is over 0.20 eV, and that of 6-coordinated ones is ranging from 0.04 to 0.09 eV.<sup>13,14</sup> The normalized pre-edge peak area of 0.16 eV in the new GIC corresponds to that of 5-coordinated Fe complexes ranging from 0.12 to 0.19 eV.<sup>13</sup> But, according to our knowledge, no iron compound, coordinated only with 5 Cl atoms, has been reported in the literature. It is therefore assumed that there exist two different kinds of iron atoms, namely, one from FeCl<sub>3</sub>-graphite with octahedral symmetry and the other from the new GIC with tetrahedral symmetry. Such an assumption was confirmed by extended X-ray absorption fine structure (EXAFS) analysis. The Fe K-edge k<sup>3</sup>-weighted EXAFS spectrum of the new GIC is shown in Figure 4(a). The first fit was carried out with only one Fe-Cl bond, which leads to a very small value of Debye-Waller factor ( $\sigma^2=0.00012 \text{ \AA}^2$ ) and a

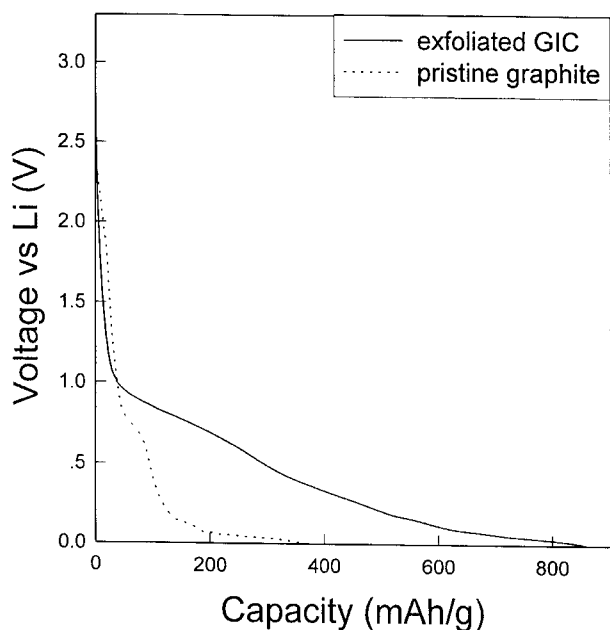
very large  $\Delta\chi^2$  value<sup>15</sup> ( $\Delta\chi^2=709.02$ ), indicating that this structure model is inadequate. As the shape of the first coordination shell (Figure 4(b)) indicates the existence of two Fe-Cl distances, the second fit should have been done with two Fe-Cl bonds. The best fit results are given in Table 1. The peaks at about 1.7 Å and 2.1 Å (non-phase-shift-corrected) can be assigned to the contributions of tetrahedral Fe-Cl<sub>t</sub> and octahedral Fe-Cl<sub>o</sub> bonding pairs, respectively. The bond distance of Fe-Cl<sub>t</sub> (2.19(6) Å) in this new GIC is close to that in [PCl<sub>4</sub>][FeCl<sub>4</sub>] (2.185 Å).<sup>16</sup> The bond length of Fe-Cl<sub>o</sub> (2.44(2) Å) is also reasonable compared with that in Co(NH<sub>3</sub>)<sub>6</sub>FeCl<sub>6</sub> (2.393 Å) and that obtained from theoretical calculation (2.38 Å).<sup>17,18</sup>

As shown in Figure 5, the voltage profiles of the exfoliated graphite and the pristine material during the discharge process are compared each other as a function of gravimetric specific capacity. The voltage plateaus of the pristine graphite are due to the specific staging phenomena during intercalation.<sup>2</sup> In contrast, the voltage profile of the exfoliated graphite gives no distinct plateau in the whole range, indicating that a surface grafting of lithium ions occurs during the discharge. It is worthy to underline that the capacity of the exfoliated graphite is twice larger than that of pristine graphite. Even though further electrochemical investigation should be done to improve the reversible capacity and the long term cycling behaviors the exfoliated graphite is expected to be a promising electrode material.

**Acknowledgment.** This work was supported by the Institute of Information Technology and Assessment (IITA) and S.N.U. Research Fund. Experiments at PLS were supported in part by the Korean Ministry of Science and Technology (MOST) and Pohang Iron & Steel Company (POSCO).

## References

- Fong, R.; von Sacken, U.; Dahn, J. R. *J. Electrochem. Soc.* **1990**, *137*, 2009.
- Dahn, J. R. *Phys. Rev.* **1991**, *B44*, 9170.
- Kanno, R.; Kawamoto, Y.; Takeda, Y.; Ohashi, S.; Imanishi, N.; Yamamoto, O. *J. Electrochem. Soc.* **1992**, *139*, 3397.
- Mabuchi, A.; Tokumitsu, K.; Fujimoto, H.; Kasuh, T. *J. Electrochem. Soc.* **1995**, *142*, 1041.
- Sato, K.; Noguchi, M.; Demachi, A.; Oki, N.; Endo, M. *Science* **1994**, *264*, 556.
- Dahn, J. R.; Zheng, T.; Liu, Y.; Xue, J. S. *Science* **1995**, *270*, 590.
- Disma, F.; Aymard, L.; Dupont, L.; Tarascon, J. M. *J. Electrochem. Soc.* **1996**, *143*, 3959.
- Peled, E.; Menachem, C.; Bar-Tow, D.; Melman, A. *J. Electrochem. Soc.* **1996**, *143*, L4.
- Metz, W.; Hohlwein, D. *Carbon* **1975**, *13*, 85.
- Frenkel, A.; Stern, E. A.; Voronel, A.; Qian, M.; Newville, M. *Phys. Rev.* **1994**, *B49*, 11662.
- O'Day, P. A.; Rehr, J. J.; Zabinsky, S. I.; Brown, G. E., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 2938.
- Hooley, J. G.; Soniassy, R. N. *Carbon* **1970**, *8*, 191.
- Roe, A. L.; Schneider, D. J.; Mayer, R. J.; Pyrz, J. W.; Widom, J.; Que, L., Jr. *J. Am. Chem. Soc.* **1984**, *106*,



**Figure 5.** Voltage profiles during the discharge of (a) the pristine graphite and (b) the exfoliated form as a function of gravimetric specific capacity.

- 1676.
14. Westre, T. E.; Kennepohl, P.; DeWitt, J. G.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1997**, *119*, 6297.
15. The  $\Delta\chi^2$  value is used as a measure of the goodness of fit, where  $\Delta\chi^2 = \frac{N}{n} \sum_{i=1}^N \left( \frac{\chi_{data}(R_i) - \chi_{theory}(r_i)}{\delta_i} \right)^2$ , where N is the number of independent data points,  $\chi(R_i)$  is the Fourier transform of  $\chi(k)$  at the point  $R_i$ ,  $n$  is the data points used, and  $\delta_i$  is the measurement uncertainty (see also ref 11).
16. Kistenmacher, T. J.; Stucky, G. D. *Inorg. Chem.* **1968**, *10*, 2150.
17. Beattie, J. K.; Moore, C. J. *Inorg. Chem.* **1982**, *21*, 1292.
18. Mehadji, C.; Chermette, H.; Cartier, C.; Verdager, M. *J. Phys. Chem.* **1995**, *99*, 5568.