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Review

Graphite intercalation compounds with large fluoroanions

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Abstract

Over the past 20 years, a number of relatively large, perfluorinated anions have been found to intercalate into graphite. This review will describe the background, some syntheses and structures of these graphite intercalations compounds (GIC's). The fluoroanion intercalates include perfluoroalkylimides, perfluoroalkylsulfonates, and perfluoroalkylborate esters. Synthetic methods can include either chemical oxidation, for example using K_2MnF_6 in anhydrous or hydrous hydrofluoric acids or electrochemical oxidation. These gallery structures present in these GIC's are larger and more complex than for most previously-known GIC's, and therefore may be important in advancing the known chemistry of graphite. In this review, the relationship of intercalate packing, orientation and conformation is discussed.

Keywords: Graphite; Intercalation; Fluoroanions

Contents

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1. Introduction

Graphite is a unique layered host in that it is electro-active and can be either oxidized or reduced to form intercalation compounds [1]. During oxidation, anions intercalate between the sheets, and the graphene sheets are separated and the structure expands along the stacking direction. The strong, aromatic carbon–carbon bonding remains intact in most cases, although the formation of graphite fluorides or graphite oxides can result in direct covalent bonding between intercalate and graphene carbon. Intercalation usually occurs to generate long-range order in the sequence of expanded galleries—this phenomenon is known as staging. Stage 1 has the greatest intercalate content, in this case the intercalate forms galleries between all the graphene sheets. In a stage 2 graphite intercalation compound (GIC), alternate galleries are occupied, in stage 3 every third gallery is occupied, and so on. The long-range ordering appears to be related to mechanical energy minimization, and requires a mechanical flexibility that is unique to graphene sheets [2].

Another difference between graphite intercalation and that of many other layered hosts is the very high potential required to oxidize graphite. The onset potential for graphite intercalation is above 4 V versus Li/Li^+, and this potential increases as a function of the extent of intercalation, so that potentials above 5 V can be required to achieve a stage 1 GIC. These very highly oxidative potentials greatly limit the synthetic approaches available, and candidate intercalate anions, in the formation of GIC's. It is for this reason that larger anions, containing alkyl groups, must be perfluorinated. To date there is not much evidence that the C–H bond can remain intact in an intercalate anion under the highly oxidative conditions found in acceptor-type GIC's.

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Even so, there has been a wide range of GIC's prepared containing oxidatively stable intercalate anions, these include the tetrahedral or octahedral fluoro-, chloro-, bromo- or oxo-metallates [3,4], trifluoroacetate [5], perfluoroalkyl-substituted sulfonyl imides or methides [6,7], perfluoroalkylsulfonates [8–11], and perfluoroalkylborate esters [12–13]. The gallery heights, or distance along the stacking direction between encasing graphene sheet centers, in these GIC's range from ≈0.6 nm for graphite bifluoride, C_xHF_2 and graphite nitrate, C_xNO_3, to ≈3 nm for $C_xC_{10}F_{21}SO_3$ [14]. The intercalation of the larger anions, forming highly expanded galleries, may well be the first step in developing a much broader range of graphite compounds where selective sorption, catalysis, and nanocomposite assembly are possible as for other layered hosts.

The first (and smallest) perfluoroalkylsulfonate intercalate, $CF_3SO_3^-$, has been produced with a gallery height of 0.8 nm, consistent with a monolayer arrangement of these intercalate anions. In contrast, electrochemical oxidation of graphite with the chemical series of perfluoroalkylsulfonates $C_nF_{2n+1}SO_3^-$ ($n = 4, 6, 8, 10$) produces GIC's with a bilayer arrangement of anion intercalates [8–11]. A chemical method was also employed to obtain new GIC's containing perfluoroalkylimides and methide $C(SO_2CF_3)_3^-$ [11]. A chemical method for some of these syntheses can readily generate multiple gram quantities without the need for binders or additives; and some of these GIC's show remarkable ambient stability. Due to these advantages, detailed structural analyses from relatively high-quality powder X-ray diffraction (XRD) data have been obtained in several cases. An example discussed below involves the study of helical twisting of fluorocarbon chains in the intercalate layer in $C_xC_8F_{17}SO_3$ [11]. This level of detail often cannot be obtained for GIC's that are difficult to obtain in gram quantities, high purity, or are very reactive/unstable in air.

This paper reviews recent results in the chemical intercalation of the perfluoroalkylsulfonate anions and the borate ester of $B[OC(O)C(O)O]_2^-$ [15] and the electrochemical intercalation of the borate esters $B[OC(CF_3)_2C(CF_3)_2O]_2^-$ [12], and $B[OC(CF_3)_2C(O)O]_2^-$ [13]. The GIC's obtained were characterized by a number of methods, with powder XRD being most important in order to develop detailed structural models for the compounds obtained.

2. Specific graphite compounds

2.1. Graphite borates

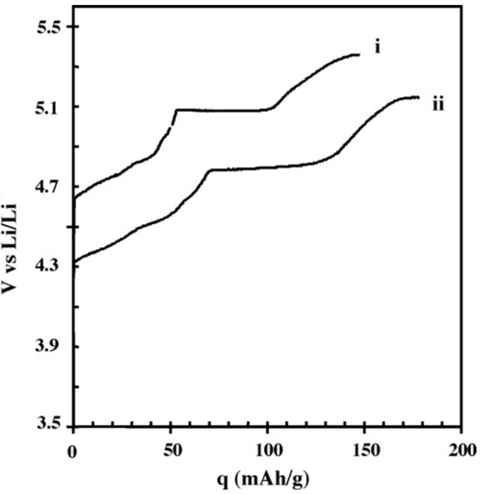

Fig. 1. Galvanostatic potential–charge curves for graphite electrodes oxidized in (i) 0.3 M $NaB[OC(CF_3)_2C(CF_3)_2O]_2/CH_3NO_2$ at a rate of 10 mA/g, and (ii) 0.3 M $LiN(SO_2CF_3)_2/CH_3NO_2$ at a rate of 50 mA/g [16].

During electrochemical preparation, the potential–charge curve obtained using the $B[OC(CF_3)_2C(CF_3)_2O]_2^-$ intercalate presents a series of plateaus and ascending regions that is highly characteristic of graphite intercalation (Fig. 1, line i). The required electrochemical potential increases during oxidation of a single phase, while the voltage plateaus occur where one stage in converted to another (during the preparation reaction this means that a higher stage is converted to one lower, for example stage 4 to stage 3). Fig. 1 also provides a charge curve where the intercalating anion is $N(SO_2CF_3)_2^-$ [16] As can be readily seen, the curve shapes and transition points are similar for these two electrolytes. The small difference in charge required to reach different transition points probably arises from different current efficiencies for the two electrolytes. This can associated with the different oxidative stabilities of these anions.

The GIC stage and gallery height were also found to be similar from XRD and electrochemical analyses of the products. [12–14] However, as is evident in Fig. 1, the potentials at the transition points differ significantly. In Fig. 2, a plot of the chemical potentials observed for the stage 2 GIC's versus $1/d_i$, where d_i is the gallery height, is shown for several GIC's. Since the lattice enthalpies for two-dimensional ionic structures are approximately inversely proportional to the separation of ionic charges, a somewhat linear relation would be expected. As is seen in Fig. 2, the utility of this very simple energetic model can be confirmed. This helps to explain the higher potentials required for intercalation of larger anions such as $B[OC(CF_3)_2C(CF_3)_2O]_2^-$ and $B[OC(CF_3)_2C(O)O]_2^-$ anions.

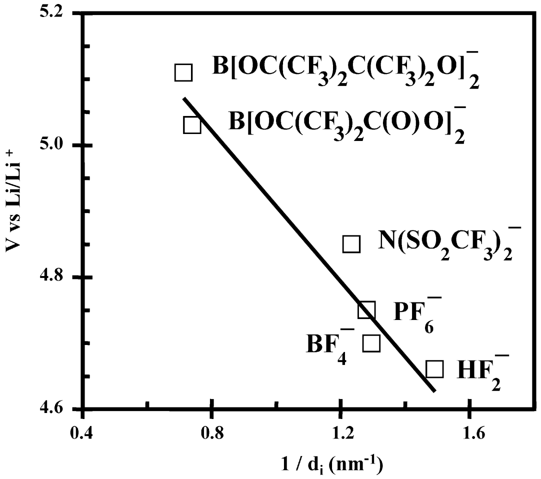

Fig. 2. Relationship between oxidation potential for stage 2 GIC's and $1/d_i$.

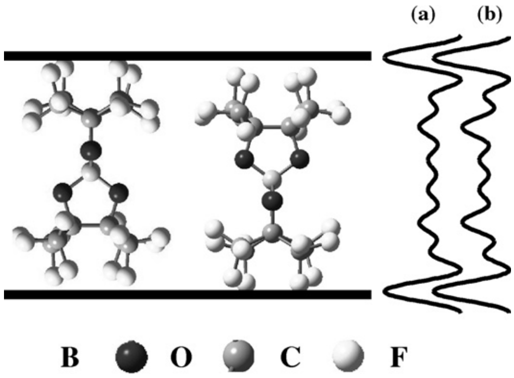

Fig. 3. One-dimensional electron density map generated from this structural model (a) closely agrees with that derived from the observed PXRD peak intensities (b) [12].

In addition, an extrapolation of the plot in Fig. 2 to infinite gallery height suggests that electrolytes stable above 5.2 V versus Li/Li$^+$ will be required in order to stabilize colloids containing isolated (delaminated) graphene sheets.

A geometry-optimized structural model for $C_xB[OC(CF_3)_2C(CF_3)_2O]_2$ is shown in Fig. 3. While the intercalate anions in GIC's normally are orientated so as to minimize gallery heights, and thereby have a minimal separation of positive sheet charges and anion centers, this is not the case for the borate chelate anions. For this and other large or asymmetric intercalates, it is important to consider packing effects within the galleries. In the anion orientation shown in Fig. 3, where the borate anions "stand up" in the galleries, the anions have a smaller "footprint" on the graphene sheet surface, and therefore can be more closely packed. A model using only steric effects indicates that these borate anions require $x > 72$ for the "lying down" orientation in a stage 2 compound, which is much greater than that observed or the typical value for small intercalate anions of $x = 48$ [17].

The bis(oxolato)borate anion, $B[OC(O)C(O)O]_2^-$, has never been intercalated into graphite using electrochemical methods, however, the GIC was recently prepared for the first time by chemical oxidation with F_2 in anhydrous hydrogen fluoride: [15]

$$C_x + [(\delta+1)/2]F_2 + B[OC(O)C(O)O]_2^- \rightarrow C_xB[OC(O)C(O)O]_2\cdot\delta F + F^- \quad (1)$$

In this case, both the chelate borate and fluoride intercalate. Elemental analyses to determine both x and δ in the product, $C_xB[OC(O)C(O)O]_2\cdot\delta F$, showed a low borate, and high fluoride, intercalate content as compared to related compounds prepared with electrochemical methods or smaller anions. The lower borate and higher fluoride contents are probably related – the fluoride anion requires space on graphene sheet surface and also charge transfer, so its presence in relatively high concentration should decrease the packing density of the larger borate chelate anions within the galleries.

2.2. Graphite perfluoroalkylsulfonates

GIC's with perfluoroalkylsulfonate anions can be obtained using either electrochemical or chemical oxidation methods.

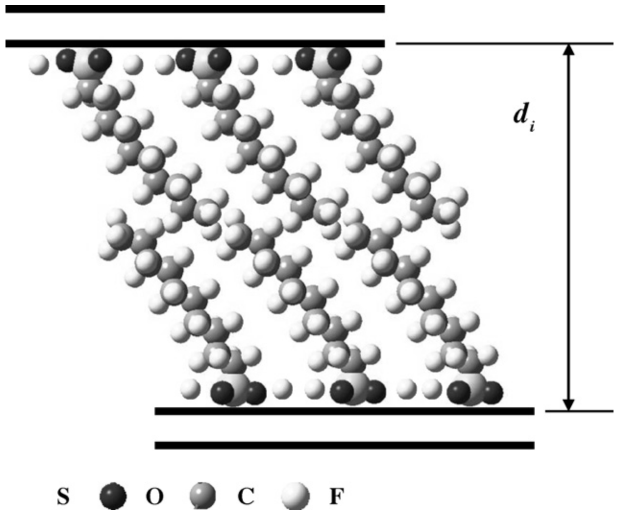

Fig. 4. Schematic diagram of stage 2 $C_xC_{10}F_{21}SO_3$, indicating the anion bilayer structure and intercalate orientation within galleries.

All the larger intercalate anions form bilayers in the expanded galleries (Fig. 4) where the sulfonate headgroups in each anion layer lying opposite the positive graphene sheet surfaces and the fluorocarbon chains extending towards the gallery centers.

Observed and calculated electron density maps for the $C_{10}F_{21}SO_3^-$ anion intercalate conformation are shown in Fig. 5. The peak labeled SO_3/F indicates the position of the anion SO_3 headgroups; these groups are oriented with the oxygen atom plane lying parallel to the graphene sheets. The structure models and chemical analyses indicate that fluoride co-intercalate is also present after chemical synthesis, and the F anion co-intercalate lies at a similar distance as the oxygen atoms. In another example of co-intercalation of fluoride, the values of x and δ for $C_xN(SO_2CF_3)_2\cdot\delta F$ were determined for different reaction times (Fig. 6) using K_2MnF_6 as an oxidant in 48% hydrofluoric acid. All the products

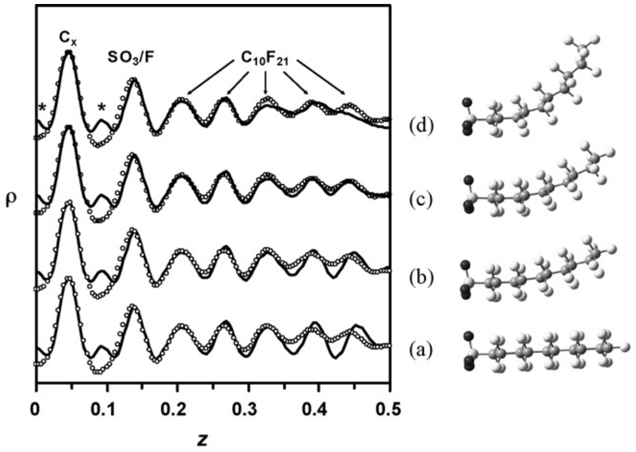

Fig. 5. Electron density maps for $C_{10}F_{21}SO_3^-$ linear anion (a), and with dihedral angles = 5° (b), 8° (c), and 15° (d). Open circles are from PXRD data, solid lines calculated from structure models. Asterisks show second-order peaks from the graphene plane.

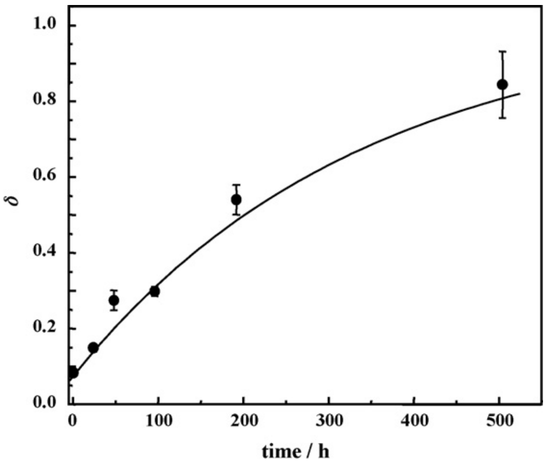

Fig. 6. Increase in fluoride content, δ, in $C_xN(SO_2CF_3)_2 \cdot \delta$ F vs. reaction time [18].

were stage 2, and x did not change greatly, however, the fluoride co-intercalate content increased significantly with reaction time [18].

For each larger intercalate anions, the fluorocarbon peaks were fit by adopting a single additional structural parameter that modifies anion conformations. For $C_xC_{10}F_{21}SO_3$, the best fit indicated a helical fluorocarbon chain with dihedral angle $\approx 8^\circ$. The anion conformation in this GIC is therefore changed markedly from the isolated anion calculation, which has a dihedral angle closer to 15°. The observed conformational change can be related to the steric requirements of intercalate packing. This represents an unusual case for GIC's, because anion packing effects can be ignored for smaller intercalate anions, and anion content can be related to the amount of charge transfer with the graphene sheets.

3. Conclusion

Graphite chemistry has expanded recently (literally and figuratively) to include larger and more complex anion intercalates between graphene layers. We can expect that along with these larger galleries, our ability to modify and re-organize graphene layers will also improve, as has been seen with other layered hosts.

Acknowledgement

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