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Solid-State NMR Studies of Chemically Lithiated CF_x

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Abstract

Three types of fluorinated carbon, all in their original form and upon sequential chemical lithiations via *n*-butyllithium, were investigated by ^{13}C and ^{19}F solid-state NMR methods. The three starting CF_x materials [where $x = 1$ (nominally)] were fiber based, graphite based, and petroleum coke based. The aim of the current study was to identify, at the atomic/molecular structural level, factors that might account for differences in electrochemical performance among the different kinds of CF_x . Differences were noted in the covalent F character among the starting compounds and in the details of LiF production among the lithiated samples.

The lithium/carbon monofluoride (Li/CF_x) battery was one of the first lithium/solid cathode systems to be used commercially.¹ Its theoretical specific energy is about 2180 Wh/kg and is among the highest for the solid cathode systems. The open-circuit voltage is 3.2 V with an operating voltage of 2.5–2.9 V. Its practical specific energy and energy density range from 250 Wh/kg and 635 Wh/L for smaller cells to 590 Wh/kg and 1050 Wh/L for larger sizes. Because of the relatively high cost of CF_x compared to other solid cathodes such as manganese dioxide, its use is currently restricted to specialized applications such as biomedical and military, where its superior technical characteristics are required.

The active components of the cell are lithium for the anode and carbon monofluoride (CF_x) for the cathode where x is typically in the range 0.9–1.1 for commercial products. CF_x is synthesized by the reaction of fluorine gas with carbon powder at a high temperature (HT). CF_x is electrochemically active and stable up to 400°C, producing a cathode that resists self-discharge, resulting in a long shelf life for the Li/CF_x cell. Typically, the electrolyte consists of lithium tetrafluoroborate (LiBF_4) in gamma-butyrolactone or lithium hexafluoroarsenate (LiAsF_6) in a mixture of propylene carbonate and dimethoxyethane.

The simplified version of the discharge process is shown by the following reactions

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The carbon monofluoride is converted into carbon, which is more conductive than CF_x , thereby lowering the cell's internal resistance, improving the voltage regulation and cell efficiency while the LiF precipitates in the cathode structure.

Recent studies^{2,3} have shown that subfluorinated CF_x ($0.33 < x < 0.66$) materials exhibit a higher rate capability up to 25°C and an improved low temperature performance down to -40°C compared to a commercial CF_x prepared from coke with $x = 1.08$.

In practice, Li/ CF_x is a primary battery system in which lithium metal serves as the anode against a fluorinated graphite cathode in the presence of an electrolyte. Upon discharge, lithium is oxidized while fluorine is reduced, producing elemental carbon and LiF, which precipitates on the remaining CF_x structure. Certain facts about the mechanism of discharge of this system are known, such as the increase in electrical conductivity, attributable to the formation of conductive graphite from CF_x that occurs as the battery is discharged.⁴ However, the structure of the CF_x cathode during and after discharge, the mechanism of the defluorination process, and the exact location and form of the LiF remain unresolved.

The primary objective of this study is to investigate the three types of fluorinated graphite materials to determine any chemical and structural distinctions between the starting materials, and as they undergo lithiation. Electrochemical studies on these different types of CF_x have indicated significant differences in electrochemical performance. Ultimately, the aim is to correlate these findings with electrochemical data collected on the same materials to better understand the discharge mechanisms. The three starting CF materials were CF_xF , which is fiber based; CF_xG , which is graphite based, and CF_xC , which is petroleum coke based. These three compounds are of nominally the same composition, i.e., $(\text{CF})_x$, $x \sim 1$, but result from different preparation routes.

Each starting compound was subjected to a chemical reduction in *n*-butyllithium (nBL) under identical conditions to achieve several levels of lithiation followed by ^{19}F and ^{13}C NMR analyses. Both the solid powders and the liquid filtrates were studied. Though it is appreciated that chemical lithiation is only a relatively crude model for electrochemical reduction, in part because of the very rapid, highly exothermic, and far-from-equilibrium nature of the reaction compared to relatively slow discharge rates characteristic of CF_x cells, it does provide a useful means to characterize the samples in a timely manner. Therefore, although the spectroscopic details may somewhat differ between chemically and electrochemically reduced samples, it is expected that the main reaction species and the trends observed in their formation would be similar. The reactants were added very slowly, in a titration-like fashion, to allow the reaction to proceed uniformly, and the chemical reaction was closely monitored for drastic changes in temperature.

Experimental

Three different types of carbon, an amorphous coke, fibrous graphite, and standard graphite, were fluorinated at HTs (300–600°C) to provide starting materials CF_xC , CF_xF , and CF_xG , respectively. The starting materials were chemically lithiated in an effort to simulate electrochemical discharging on a shorter time scale. All of the starting materials were reduced by a 2.5 M nBL solution in hexane. The depth of discharge (DOD) was controlled by adjusting the nBL: CF_x mole ratio. The chemical procedure was as follows. Hexane (15

mL) was added to CF_x (1 g) in a reaction vessel to obtain the CF_x suspension. The vessel was closed and stirred at a moderate rate. Once the powders were thoroughly wetted with hexane, varying amounts of nBL were added at the rate of 1–2 mL/h, and the solution was stirred for 48 h until the reaction was completed. The solution was then filtered, washed three times with hexane, and dried overnight under vacuum at room temperature. All procedures were carried out under a controlled atmosphere in an argon-filled glove box.

Magic angle spinning (MAS) NMR measurements of both ^{13}C and ^{19}F in the direct detection mode were conducted on all three starting materials, G (graphitic carbon), F (carbon fiber), and C (amorphous coke), in addition to the lithiated materials. ^{19}F NMR was also conducted on the liquid effluents from the lithiation processes for some samples. The ^{13}C MAS NMR was conducted in an 11.7 T magnet with a Varian Inova 500 MHz spectrometer using a Doty low C/F background NMR probe, and the samples were spun at various speeds, from 8–12 kHz. The ^{19}F experiments were conducted using a 300 MHz Varian S Direct Digital Drive NMR spectrometer at various spinning speeds, from 18–25 kHz. For these experiments, a 90_x-180_y pulse echo sequence was used to minimize the probe background signal. An aqueous solution of lithium trifluoromethylsulfonate was used as an external reference for fluorine at -77.8 ppm relative to the common reference (CFCl_3 at 0 ppm), and tetramethylsilane (0 ppm) was used for carbon. All NMR spectral data were processed using Mestre-C, a standard NMR data processing software.

Powder X-ray diffraction (XRD) measurements were performed using a Shimadzu X-ray diffractometer XRD-6000, working with a $\text{Cu K}\alpha$ radiation. Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu Advantage 8400 instrument with the Pike EasiDiff diffuse reflectance accessory.

Results and Discussion

^{19}F NMR was conducted at a lower field (300 MHz) due to the capability of higher MAS speeds (20–25 kHz) on that instrument. Spectra for the starting materials C, F, and G are shown in Fig. 1. Generally, for homonuclear dipolar coupling, spinning speeds should be at least as great as half of the width of the spectral envelope, which, for ^{19}F , due to its strong dipolar interactions, is usually quite large. This properly separates out the side bands from the actual resonances. The width of all the fluorine peaks is attributed mainly to the large homonuclear dipolar coupling between the fluorine nuclei. So, at higher speeds, the main covalent C–F resonance, seen at approximately -184 ppm, narrows significantly. This allowed for the detection of a second component in the vicinity in the form of a prominent shoulder at approximately -166 ppm. When the spectral deconvolutions were performed, additional peak(s) from -171 to -178 ppm must be included to properly fit the spectra. These peaks have been identified as typical of fluorine in graphite intercalation compounds with C/F ratios of 4–6,⁵ that is, a more ionic or semi-ionic C–F interaction.⁶ The many small peaks seen in the region between -110 and -125 ppm⁷ (or between -116 and -120 ppm)⁸ are characteristic of $-\text{CF}_2$ sites. The differences in the CF_2 shifts are suggestive of different immediate environments, e.g., bulk vs edge sites. Some intensity is seen in the region from -40 to -80 ppm, which is where $-\text{CF}_3$ groups would resonate. However, the intensities of these resonances are too low to reliably quantify.

Upon lithiation, the LiF resonance is found near -200 ppm, as shown in Fig. 2 for the CF_x C series. Spectral deconvolutions were conducted to properly quantify the ratios of these resonances for all lithiation levels for all three types of materials, as presented in Fig. 3a–c.

The successive lithiation process can be tracked in the spectra through the obvious decrease in the C–F intensity and the accompanying increase in the LiF signal. Other trends were

made evident through the line deconvolutions, such as the reduction order of the different types of fluorine in the bulk. There appear to be approximately four different types of carbon–fluorine interactions, from covalent to semi-ionic/ionic. All three starting materials indicate significant percentages of semi-ionic C–F species, C, and G slightly more than F (33, 34, and 28%, respectively). This is significant for two reasons. One is that the starting materials were fluorinated at temperatures $>300^{\circ}\text{C}$ and are therefore considered HT CF compounds, and the C–F bonding in such compounds is expected to be almost, if not completely, covalent.⁹ Furthermore, with respect to the electrochemical behavior, ionic C_xF compounds tend to exhibit higher reduction potentials when compared to their covalent analogs.⁹ As far as the trend over the course of the lithiation, it appears through the deconvolutions that in F, the covalent fluorines are reduced at a faster rate than the semi-ionic fluorines in the initial stages (up to 23%). Then, there is a drastic reduction in the semi-ionic fluorines at the 69% level. A similar pattern is seen in C, although the starting material appears to lose some CF_2 intensity, and perhaps due to some restructuring of the layers over the course of the reaction, more semi-ionic species are apparently present in the first level of lithiation compared to the starting material. In G, it seems that the semi-ionic fluorines are reduced preferentially in the first stages, along with some restructuring of C–F interactions; the semi-ionic fluorines are greatly reduced by the 23% level and are not seen at all at 69% lithiation. In C and F, some ionic fluorine intensity remains even at the 69% level. The counterintuitive order in which the semi-ionic vs covalent F is consumed could well be related to the rapid kinetics and possible structural reorganization associated with the chemical lithiation process as opposed to slow electrochemical discharge. Studies of electrochemically reduced CF_x are in progress, and preliminary results suggest that this order is sometimes different from that for the corresponding nBL reduced materials.

In series G, the production of LiF maximizes near 80%. This implies that the lithiation reaction does not reach completion. The question remains whether the remainder of the nBL stays unreacted and simply volatilizes off of the surface, or whether a different reaction takes place, such as lithium reacting with the carbons in the structure. Additional experiments such as ^7Li MAS NMR could give some insight into this and are planned for the future, including ^7Li measurements of the liquid filtrates. However, the narrow chemical shift range of all the possible additional Li compounds that might be formed would make their identification by ^7Li NMR somewhat challenging because they would be indistinguishable from the main reaction product, LiF, as verified in preliminary measurements (not shown). The main CF peak in C and F samples is close to 10% of the signal at the 92% lithiation. This is an indication that the reaction in these samples does basically reach completion, as expected.

The existence of $-\text{CF}_2$ sites in and of itself, in samples that were nominally fully fluorinated (CF_1), implies the existence of fluorine-free graphitic regions.^{10,11} Further evidence of these is found in the ^{13}C NMR data of these same samples, in which $-\text{CF}_2$ and $-\text{CF}_3$ resonances can be identified, as discussed below. Another phenomenon common to all three samples is the persistence of these CF_2 resonances throughout the lithiation. In fact, any perceived reduction in that group of resonances, except perhaps in the first stage of the lithiation of C, is small enough to be within measurement error. This is consistent with the hypothesis by Delabarre et al. that the CF_2 groups are electrochemically inactive.¹² A significant difference in the samples is that in CF_x C and G, 3–5% of fluorine is in $>\text{CF}_2$ groups. This number is greater by approximately a factor of 2 for the CF_x F material. If these groups were indeed located on the particle surfaces, this observation could be related to the approximately 2-fold difference in surface areas of the CF_x F starting material compared to C and G, although all materials are of relatively high surface area, $\geq 100\text{ m}^2/\text{g}$, as determined by the Brunauer, Emmett, and Teller method.

A very small resonance near -70 ppm is seen in sample F. This peak is in the $-\text{CF}_3$ region and remains throughout the lithiation process. This is also consistent with Delabarre's hypothesis for $-\text{CF}_3$ groups as these were also deemed to be electrochemically inactive.

A peak near -130 ppm is seen in the F and G starting materials. It is "consumed" immediately in G but remains up until the last level of lithiation in F. This peak is in the CF_2 region, but clearly in a different configuration from the CF_2 resonance at -115 ppm. Further studies (relaxation and cross-polarization) would be necessary to provide more information.

^{19}F NMR was also conducted on the liquid filtrate from the lithiation of the following samples: G 7.7%, G 23%, F 23%, and F 92%. The NMR was conducted within 2 days of the lithiation process to detect any short-lived intermediates. No signal was seen, indicating that no soluble fluorine-containing species remained in the filtrate at the lithiation levels for these samples.

The ^{13}C MAS NMR spectra were collected on the 500 MHz spectrometer at spinning speeds of 10–20 kHz. The spectra of sample C are shown in Fig. 4 to give an indication of the spectral resolutions achieved. The spectra of F and G, which are similar in nature, are not shown. Instead, the useful (quantitative) information derived from their spectra is presented as bar graphs in Fig. 5a–c. Due to the long relaxation times of carbon nuclei in these materials, most other studies conduct ^{13}C NMR via cross-polarization by fluorine, which shortens the relaxation time considerably. However, cross-polarization data are not accurately quantifiable, as resonances are excited unequally. In this study, directly observed ^{13}C NMR was conducted. However, due to the low natural abundance of ^{13}C nuclei and its relatively low gyromagnetic ratio, the directly observed carbon signal is quite weak, necessitating thousands of scans. Due to time constraints dictated by the long T_1 times (90–200 s), this was not possible for all the samples; therefore, the signal-to-noise ratio was low, increasing the error margin in the associated spectral deconvolutions depicted in Fig. 5a–c. The results for sample G 7.7% appear to be anomalous, as they are in the ^{19}F deconvolution (Fig. 3c).

Several peaks are seen in the starting and lithiated materials, most of which are readily identifiable. The covalent CF carbon resonates at 88 ppm. According to Sato et al., in a study of semi-ionic CF materials, the ^{13}C chemical shift of carbon in a semi-ionic/ionic interaction with fluorine is near 89 ppm.⁶ Therefore, this peak would not be distinguishable from the covalent resonance. A clear resonance is visible near 109 ppm in all C and F samples. Shifts in this region are assigned to $>\text{CF}_2$ groups.⁸ As seen in the ^{19}F NMR data, this resonance appears to decrease slightly but does not disappear, even at the 92% lithiation level.

A small resonance near 34 ppm is seen in sample C and remains constant throughout the lithiation process. Resonances in this vicinity are identified as sp^3 tetrahedral carbon, e.g., a diamond structure, which resonates at 35 ppm.¹³ Another small resonance is seen near 43 ppm in all samples and is also attributed to sp^3 carbon. They exhibit different trends, however. The 43 ppm shift increases in intensity throughout the lithiation in C and F; this same shift appears in the starting material of G yet appears to decrease in that sample.

Two peaks near 125 and 136 ppm appear over the course of the lithiation. These peaks have been identified as graphitic carbon, the former considered "bulk graphitic" (C_b) (two or more bonds away from CF) and the latter considered "interfacial graphitic" (C_i) (less than two bonds away from CF).^{14,15} The F and G series appear to contain graphitic domains in their starting material. As some amount of CF_2 is seen in F, this is consistent with the presumed 1:1 CF ratio. In sample G, the existence of the graphite at the outset, with no recognizable CF_2 or CF_3 resonances, implies a C:F ratio greater than 1:1. As the lithiation

progresses, more bulk than interfacial graphite is observed in both C and F. This suggests that the initial graphitic domains are larger and perhaps more localized near the surfaces of the particles (i.e., not close to the remaining C–F regions). By the 69% lithiation step in both, the interfacial graphitic components are more significant, implying the creation of a greater number of smaller graphitic domains within the particles. In sample G at 69% the bulk graphitic carbon is quite large and then decreases upon further lithiation to 92%. A possible explanation for this unusual result is that the graphitic domains are large and continuous at 69% lithiation, and the subsequent increase in the interfacial component in the 92% sample would then suggest that these regions are broken up into smaller subdomains. There is also some uncertainty in the deconvolutions, which may exaggerate the intensity of the broad graphitic component. The overall increase in graphitic domains, in general, is also confirmed in the XRD data taken of these samples at different stages of lithiation. Figure 6 shows the XRD spectra of CF_xC samples at various levels of lithiation. The CF_x peaks at 13 and 42° are seen to deplete with increasing lithiation coincident with the increase in the prominence of the LiF peaks observed at 38, 45, and 65° and the carbon peak at 21°. A diffraction peak near 26°, which increases continuously with increasing lithiation, is assigned to graphite in a recent study of similar compounds.¹⁶ The carbon peak in our XRD study is at lower 2θ (21°) than expected for a typical carbon–graphite material (26°), indicating a larger interplanar spacing between layers of carbon in the product. The observation of the larger interplanar spacing carbon strongly suggests the possibility of solvent co-intercalation under our sample preparation conditions. This could be an artifact of the nearly instantaneous discharge achieved with chemical lithiation compared to the long, slow discharge characteristic of a typical battery discharge.

A simple calculation to monitor the F:C ratio over the course of the lithiation is indicated in Eq. 1¹⁵

$$\frac{F}{C} = \frac{CF + 2CF_2}{C_i + C_b + CF + CF_2} \quad [1]$$

These results are displayed in a bar graph format in Fig. 7. Some source of error is expected due to the poor signal-to-noise ratio of the ¹³C NMR spectra; however, samples C and F still indicate reasonable trends, while the data from sample G remain inconclusive. Samples C and F both indicate an F:C ratio close to 1 initially, and this does not significantly decrease until the second state of lithiation at 23%. As the semi-ionic intensity is included in that of the covalent because of the spectral overlap, the fact that this ratio changes only slightly could be supportive of the ¹⁹F data, which seemed to indicate that the production of LiF (and the accompanying removal of F from the bulk) was not the major event initially and rather that the first stage of lithiation mostly induced a rearrangement of the C–F atoms in the main structure.

The set of peaks in the region 10–32 ppm (see Fig. 4) likely arises from nBL, hexane, and derivatives of these compounds, as this is where they are known to resonate.^{17,18} As the species alone are volatile, and therefore not likely to remain on the surfaces over time, in addition to the fact that these resonances increase in intensity with increasing lithiation, it is highly probable that these compounds are co-intercalating into the graphite layers. Sample C does not indicate any of the 30 ppm resonance. This could be evidence of the different intercalation phenomena, perhaps due to the differences in lattice spacing/size of the intercalated specie. Additional evidence of intercalation is also shown in the XRD (see Fig. 6) and in the FTIR data taken of the lithiated samples in which vibrational modes

characteristic of organic hydrocarbon solvents at wavenumber ~ 2800 to 3100 cm^{-1} are shown (Fig. 8).

Figure 8 shows the FTIR spectra of chemical lithiated CF_xC at 0, 50, and 90% DOD. The peak at $\sim 1220\text{ cm}^{-1}$ is assigned to the covalent C–F bond vibration.¹⁹ The semi-ionic C–F bond vibration at $\sim 1130\text{ cm}^{-1}$ is not visible in these spectra, but this may be due to mode broadening resulting from a relatively large distribution of environments (as suggested by the NMR). With the increase in percent DOD, the covalent C–F bond vibration gradually decreases, while the doublets at ~ 1458 and 1579 cm^{-1} increase. In the mean-time, the triplets at ~ 2876 to 2961 cm^{-1} keep increasing with increasing percent DOD. These signals were unchanged even after the samples were stored at room temperature for several months. The enhanced triplets at $\sim 2900\text{ cm}^{-1}$ are an indication of hexane solvent or *n*-butyl group (or its derivatives) co-intercalation due to vigorous reaction conditions, in support of ^{13}C NMR and XRD observations. The pronounced doublets observed at ~ 1458 and 1579 cm^{-1} are tentatively assigned to aromatic perfluorinated graphene compounds (C_xF_y), which is likely formed due to solvent co-intercalation into the carbon layers during chemical lithiation.

A quantitative analysis of ^{13}C NMR for the peak region 10–32 ppm is shown in Fig. 9. As is clear in the quantitative deconvolutions in Fig. 9a–c, the resonances do not increase evenly, strongly suggesting intercalation of the hexane and nBL derivatives. (These resonances are not included in the ^{13}C NMR deconvolution graphs, to accurately compare the fates of structural carbon alone.) Additional details on possible Li-cointercalant interactions could be obtained from ^7Li – ^1H double resonance experiments, which are planned for the future.

Conclusions

The data collected provided insight into structural and chemical differences in these materials. The detection and quantification of several semi-ionic/ionic C–F interactions, in addition to the expected covalent CF interactions, were interesting, as HT ($>450^\circ\text{C}$) CF_x compounds have previously been presumed to be composed only of the latter. It was also then possible to track the order of reduction of the different fluorines over the course of the lithiation and to determine that in samples F and C the covalent fluorine is reduced in advance of the semi-ionic species. In sample G, the ionic interactions disappear more quickly and are entirely consumed by the 69% lithiation level. It was also evident in both the ^{19}F and the ^{13}C NMR that at least one type of CF_2 species remained as such throughout the entire lithiation process, indicating either electrochemically isolated regions or an electrochemically inactive bonding configuration. There appears to be a greater amount of LiF production in samples F and C compared to sample G at the highest DOD (nominally 92%). It was also confirmed that there is some amount of intercalation of the solvent and solvent breakdown products into the bulk structure that increased with successive lithiation.

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Figure 1.
(Color online) ^{19}F NMR of starting materials CF_xC , F, and G on a 300 MHz spectrometer at 26–32 kHz spinning speeds.

Figure 2.
(Color online) ^{19}F NMR of lithiated CF_xC series at 23 kHz spinning speed.

Figure 3.

(Color online) ^{19}F NMR (300 MHz) comparative quantitative line deconvolutions of lithiated (a) $\text{CF}_x \text{ C}$, (b) $\text{CF}_x \text{ F}$, and (c) $\text{CF}_x \text{ G}$. The numbers next to the species identifications refer to the chemical shift in parts per million, and the percentages on the horizontal axis describe the equivalent DOD.

Figure 4.

(Color online) ^{13}C NMR spectra of the lithiated CF_x C series, shown as a representative example of the ^{13}C NMR of the materials. The critical information is in the spectral deconvolutions, which are shown for all three samples.

Figure 5. (Color online) ^{13}C NMR (500 MHz) comparison of quantitative spectral deconvolutions of (a) CF_xC , (b) CF_xF , and (c) CF_xG . The numbers next to the species identifications refer to the chemical shift in parts per million, and the percentages on the horizontal axis describe the equivalent DOD.

Figure 6.
(Color online) XRD of chemically lithiated CF_x C.

Figure 7.
(Color online) F/C ratio throughout lithiation of C and F series. The percentages on the horizontal axis describe the equivalent DOD.

Figure 8.
(Color online) FTIR spectra of chemical lithiated CF_xC at 0, 50, and 90% DOD. The doublets at $\sim 2350\text{ cm}^{-1}$ are the CO_2 background.

Figure 9.
(Color online) ^{13}C NMR (300 MHz) of solvent derivative species in (a) $\text{CF}_x \text{C}$, (b) $\text{CF}_x \text{F}$, and (c) $\text{CF}_x \text{G}$.