EFFECT OF CURVATURE ON C-F BONDING IN FLUORINATED CARBONS : FROM FULLERENES AND DERIVATIVES TO GRAPHITE

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Introduction

Due to the polymorphism of carbonaceous materials and the versatility of the C-F bonding, the carbon/fluorine combination in fluorinated carbons is an unique association in chemistry. This results in interesting materials for many technological applications such as electrode materials for lithium batteries and solid lubricants. The resulting C-F bonding in fluorinated carbons could be classified into two categories with different application properties: covalent and ionic. For the first category i.e. covalent compounds, the graphite fluorides (CxF)n and (CF)n, prepared at 350 °C and 600 °C, respectively, are electronic insulators, the carbon skeleton consists of trans-linked cyclohexane chairs or cis-trans linked cyclohexane boats with sp3 bonding. The second category is composed of fluorine-graphite intercalation compounds (CxF), obtained at temperature lower than 100 °C, which have higher electronic conductivity. In this case the planar configuration of graphite is partially preserved. The nature of the C-F bond evolves from ionic for low fluorine content to “semi-covalent” for higher fluorine content. The carbon atoms are in almost sp2 hybridization.

When these fluorinated carbons are used as electrode material in primary lithium battery, the modulation of both the C-F bonding and the fluorine content allows either high capacities, high discharge potentials or high power densities to be obtained as a function of the required application [1-3].

The present work investigates the effect of the curvature of the C-F bond length could be obtained by NMR experiments performed at room temperature using a Tecmag spectrometer (working frequencies for 13C and 19F were equal to 73.4 and 282.2 MHz respectively). The 13C spectra were recorded using a solid echo sequence (two 5.5 µs/2 pulses separated by 25 µs); this sequence allows the acquisition of the whole signal without loss due to the electronic dead time followed by a quantitative determination of the different contributions.

In order to investigate the C-F bonding, five parameters were defined: the 13C and 19F NMR chemical shifts of the C-F bonds, the C-F bond length as seen by NMR, the wavenumber of the C-F vibration determined by infrared spectroscopy and the average discharge potential of fluorinated carbons in primary lithium battery. As a matter of fact, the discharge results in the irreversible breaking of the C-F bonds to form LiF and C. The change of the covalence leads to different discharge potentials.

Experimental

Fluorinated graphites were prepared using Madagascar natural graphite powder (particle size of 7.5 µm) at room temperature using synthesis methods already described elsewhere [2,4] which utilize a gaseous mixture of fluorine (F2), hydrogen fluoride (HF) and an inorganic fluoride (MF3).

Table 1 summarizes the synthesis and fluorination methods (by treatment with gaseous F2) for various nanocarbons. Fluorine level F/C is obtained by weight uptake.

Table 1. Synthesis methods of the nanocarbons and fluorination conditions using F2 gas

<table>
<thead>
<tr>
<th>Producer Method</th>
<th>Purity</th>
<th>&lt;Φs&gt; (nm)</th>
<th>t (h)</th>
<th>Tf (°C)</th>
<th>F/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HiPCO CVD</td>
<td>&gt; 95%</td>
<td>1.1</td>
<td>3</td>
<td>200</td>
<td>0.37</td>
</tr>
<tr>
<td>Electro-arc</td>
<td>&gt; 95%</td>
<td>1.5</td>
<td>5</td>
<td>190</td>
<td>0.32</td>
</tr>
<tr>
<td>SWCNTs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DWCNTs Helix CVD</td>
<td>90%</td>
<td>~4</td>
<td>3</td>
<td>300</td>
<td>0.42</td>
</tr>
<tr>
<td>DWCNTs Helix CVD</td>
<td>95%</td>
<td>50 +/-</td>
<td>3</td>
<td>380</td>
<td>0.43</td>
</tr>
<tr>
<td>MWCNTs Helix CVD</td>
<td></td>
<td></td>
<td>50</td>
<td>400</td>
<td>0.73</td>
</tr>
<tr>
<td>CNEs MER CVD</td>
<td>&gt; 90%</td>
<td>140 +/-</td>
<td>16</td>
<td>420</td>
<td>0.39</td>
</tr>
<tr>
<td>C60 MER</td>
<td>99.9%</td>
<td>3</td>
<td>300</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>C60 MER</td>
<td>99.9%</td>
<td>48</td>
<td>133</td>
<td>0.80</td>
<td></td>
</tr>
</tbody>
</table>

* chemical vapour deposition  ** average diameter (producer data)

NMR experiments were performed at room temperature using a Tecmag spectrometer (working frequencies for 13C and 19F were equal to 73.4 and 282.2 MHz respectively). The 13C spectra were recorded using a solid echo sequence (two 5.5 µs/2 pulses separated by 25 µs); this sequence allows the acquisition of the whole signal without loss due to the electronic dead time followed by a quantitative determination of the different contributions.

C-F bond length could be obtained by NMR measurements, since the C-F bond length correlates with the intensity of the dipolar interaction revealed by the Inverse Cross Polarization (ICP) sequence. This method was successfully applied to (CF)n and (C2F)n covalent graphite fluorides [6]. 19F and 13C chemical shifts were referenced to CFCl3 and tetramethylsilane (TMS), respectively. The recycle times were equal to 5 s for 19F and CP spectra and 100 s for 13C spectra.
The electrochemical procedure for the investigation of the discharge potential of CFx electrode in primary lithium battery is described elsewhere [1,3].

Results and Discussion

Single wall carbon nanotubes can be considered as intermediate between planar graphite and spherical fullerene, its 19F chemical shift should be included between ones of (CF)n (-190 ppm) and fluorinated C60 (-151 ppm). The δ value for fluorinated SWCNTs (produced by electro-arc method) of CF0.35 composition was equal to -168 ppm. This preliminary study underlines that the curvature could play a key role. To quantify the effect of curvature, various SWCNTs produced by different methods were fluorinated. The fluorine levels are given in Table 1. The MAS 19F spectra lines of fluorinated atoms involved in the C-F bond exhibit chemical shifts of -163 and -168 ppm for fluorinated HiPCO (of initial diameter 1.1 nm), and EA (of initial diameter 1.5 nm). The value for DWCNTs and MWCNTs fluorinated at 300°C (initial diameters of about 4 and 50 nm, respectively) are equal to -178 and -184 ppm. For all the studied samples the following dependence exists: decrease of curvature (or increase of the nanotube diameter) leads to decrease of a chemical shift and increase of the covalence of the C-F bond (Fig. 1). Moreover, the wavenumber values of the fluorinated CNTs (SWCNTs, DWCNTs and MWCNTs) are placed in between the two limits corresponding to the spherical fullerene and planar graphite fluorides. Another indicator of the C-F covalence is the wavenumber of the IR C-F vibration. Its strong correlation with 19F chemical shift was visualized in the Figure 1. The increase of the covalence results in a shift of the wavenumber to 1220 cm\(^{-1}\). For highly fluorinated fullerenes the wavenumber to 1220 cm\(^{-1}\) is observed by their thermally activated decomposition. Whereas a perfluorinated graphite plane remains unaffected, fluorofullerenes readily lose bonded fluorine above 350°C in the absence of a fluorine atmosphere. A quasi linear relationship of δ19F with the wavenumber is obtained for graphite fluorides, fluorine-GIC and fluorinated CNTs (see Fig. 1) in accordance with either the hyperconjugaison or the curvature effect. But the data set for C60 cannot be included in this relationship. The same remark can be done from chemical shifts dependence (13C and 19F). It could indicate that the curvature is not the only parameter which affects the C-F bonding in fluorinated C60 and the steric hindrance between fluorine atoms should be also taken into account.

Conclusions

The curvature prevents the formation of a pure sp\(^3\) hybridization for the carbon atom, since it requires an important local strain. The residual sp\(^2\) hybridized orbitals imply a weakening of the overlapping of the hybridized lobes of carbon and of the fluorine atomic orbitals. In other terms, this results in a weakening of the C-F bonding covalence. This covalence weakening affects the C-F bond strength and leads to a lack of robustness of the C-F interaction within fluorofullerene clusters. Such an effect can be experimentally observed by their thermally activated decomposition. Whereas a perfluorinated graphite plane remains unaffected, fluorofullerenes readily lose bonded fluorine above 350°C in the absence of a fluorine atmosphere. A quasi linear relationship of δ19F with the wavenumber is observed for graphite fluorides, fluorine-GIC and fluorinated CNTs (see Fig. 1) in accordance with either the hyperconjugaison or the curvature effect. But the data set for C60 cannot be included in this relationship. This remark can be done from chemical shifts dependence (13C and 19F). It could indicate that the curvature is not the only parameter which affects the C-F bonding in fluorinated C60 and the steric hindrance between fluorine atoms should be also taken into account.

References