

# FLUORINATED ACTIVATED CARBONS FOR MECHANICAL ENERGY STORAGE

Sébastien Schlienger<sup>1</sup>, Julien Parmentier<sup>1</sup>, Marc Dubois<sup>2</sup>, André Hamwi<sup>2</sup>, Hayat Kharbache<sup>3</sup>, Francis Masin<sup>3</sup>

<sup>1</sup> Institut de Science des Matériaux de Mulhouse CNRS LRC 7228 Université de Haute-Alsace, CNRS LRC 7228, 15 rue Jean Starcky, Université de Haute Alsace, BP 2488, 68057 Mulhouse Cedex.

<sup>2</sup> Clermont Université, Université Blaise Pascal, Laboratoire des Matériaux Inorganiques UMR UBP-CNRS 6002, Clermont-Ferrand, France

<sup>3</sup> Matière Condensée et Résonance Magnétique, Université Libre de Bruxelles (U. L. B.), CP 232, Boulevard du Triomphe, B-1050 Bruxelles, Belgium

## Introduction

Porous materials are interesting candidates for applications devoted to storage or dissipation of mechanical energy. These applications are based on forced intrusion-expulsion cycles of water in hydrophobic or nonwetting porous media. In this context, various types of carbon materials were fluorinated using fluorine gas in order to decrease their hydrophilic character. They were then characterized by physico-chemical techniques and tested by water intrusion/expulsion experiments.

## Experimental

Different types of carbon materials were used for fluorination: i) *Mi* and *Pi* (with  $i=1,2$  or  $3$ ) are monolithic (*Mi*) or powder (*Pi*) mesoporous carbon samples obtained by various direct synthesis route inspired by Dai and al. and Zhao and al. [1-3], ii) RB3, R2030 and OPTI are commercial activated carbons (AC) in granules and powder form respectively obtained with different precursors. They were all steam activated. Fluorination was carried out for 12 h under  $F_2$  gas flow in a nickel reactor heated with a regulated furnace. The starting material was placed in a monel boat. Prior to the fluorination, the samples were outgassed for 2 h. at 200°C under  $N_2$  atmosphere in order to remove adsorbed water molecules; During the reaction with fluorine, these molecules form HF, which could catalyze the fluorination and result in inhomogeneous process. The temperature reaction was included in between room temperature and 50°C. The fluorine content  $x$  in  $CF_x$  composition, i.e. the molar F:C ratio, is determined from weight uptake. It is to be noted that, for such porous materials and whatever the synthesis conditions, the composition determined from weight uptake can be underestimated since a volatile fraction is probably swept away during fluorination. Additional characterizations are necessary to precise the true composition. Thermogravimetric analysis (TGA) performed under inert  $N_2$  atmosphere results in i) the desorption of HF and/or  $F_2$  from the porous fluorocarbon matrix and ii) the breaking of C-F bonds into either atomic fluorine or volatile  $CF_4$  molecules. The weight loss allows the initial composition to be estimated.

NMR experiments were performed at room temperature using a Tecmag spectrometer (working frequencies for  $^{13}C$  and  $^{19}F$  were equal to 73.4 and 282.2 MHz respectively). A special cross polarization/MAS NMR probe (Bruker) with fluorine decoupling on a 4 mm rotor was used. The  $^{19}F \rightarrow ^{13}C$  match was optimized on PTFE. For  $^{19}F$  MAS spectra, a simple sequence was used with single  $\pi/2$  pulse duration of 5.5  $\mu s$ . The  $^{13}C$  spectra were recorded using a solid echo sequence (two 5.5  $\mu s$   $\pi/2$  pulses separated by 25  $\mu s$ ); 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. Bond length might be an useful parameter to estimate the covalence. It could be obtained by NMR measurements, since the C-F bond length correlates with the intensity of the dipolar interaction. However, standard experiments using MAS spinning and Hartmann-Hahn cross polarization do not provide direct quantitative information on the dipolar couplings. The dipolar couplings can be reintroduced into the spectrum by means of the Inverse Cross Polarization (ICP) sequence. This method, extensively described in the corresponding papers, was successfully applied to  $(CF)_n$  and  $(C_2F)_n$  covalent graphite fluorides [4].  $^{19}F$  and  $^{13}C$  chemical shifts were referenced to  $CFCl_3$  and tetramethylsilane (TMS), respectively. The recycle times were equal to 5 s for  $^{19}F$  and CP spectra and 100 s for  $^{13}C$  spectra.

Water intrusion experiments were performed from 1 to 3700 bar. A cycle of intrusion-ejection of water was made for each sample using a mercury porosimeter (Micromeritics Autopore V) with an adapted measurement cell. These fluorinated materials were also study by nitrogen physisorption at 77 K before and after the water intrusion experiments. Specific surface area was obtained with the Brunauer-Emmett-Teller method for  $0.01 < P/P_0 < 0.05$ . Porous and microporous volumes were determined respectively at  $P/P_0 = 0.95$  and with the DFT method.

## Results and Discussion

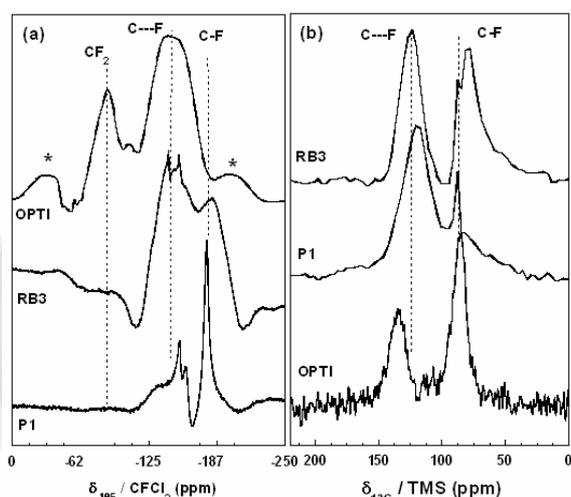
Table 1 summarizes the fluorination conditions and the resulting chemical composition using weight uptake during the reaction, TGA and NMR. The  $P_n$  series exhibits low fluorination rate (F:C < 0.18) contrary to the other samples. A good accordance between the various methods is obtained except for OPTI fluorinated at 50°C. The underestimation for this latter case underlines that decomposition occurred at 50°C during the fluorination and carbon atoms are lost because of their removal in  $CF_4$  or  $C_2F_6$  volatile molecules.

In order to identify the various fluorinated groups, i.e. C-F,  $CF_2$  or  $CF_3$  and the C-F bonding,  $^{19}F$  MAS NMR spectra were recorded with a spinning speed of 30 kHz (Fig. 1a). Regarding the weak intensities of the lines of  $CF_2$  and  $CF_3$  at, respectively, - 120 and - 80 ppm vs  $CFCl_3$ , their amounts are low after fluorination at room temperature (Fig. 1a). On the contrary, when the reaction temperature is increased at 50°C, the line of  $CF_2$  is broad and intense.  $CF_3$  groups are also present in low amounts. This fact is in accordance with the

decomposition underlined by the comparison between the composition obtained by weight uptake and NMR.  $\text{CF}_2$  and  $\text{CF}_3$  are located on the sheet edges. Further fluorination results in volatile  $\text{CF}_4$ . Presence of  $\text{CF}_2$  groups leads to a NMR line at 110 ppm vs TMS on  $^{19}\text{F} \rightarrow ^{13}\text{C}$  CP MAS spectra (not shown). The intensity is higher in the case of CA fluorinated at  $50^\circ\text{C}$  when compared to the samples obtained at RT.

**Table 1. Fluorination conditions and composition.**

Samples	$T_F$ ( $^\circ\text{C}$ )	Chemical composition		
		Weight uptake	TGA	NMR
P1	RT	$\text{CF}_{0.15}$	$\text{CF}_{0.09}(\text{HF})_{0.01}$	$\text{CF}_{0.11}$
P2	RT	$\text{CF}_{0.09}$	$\text{CF}_{0.04}(\text{HF})_{0.01}$	$\text{CF}_{0.05}$
P3	RT	$\text{CF}_{0.18}$	$\text{CF}_{0.07}(\text{HF})_{0.04}$	$\text{CF}_{0.08}$
RB3	RT	$\text{CF}_{0.42}$	$\text{CF}_{0.42}(\text{HF})_{0.01}$	$\text{CF}_{0.44}$
R2030	RT	$\text{CF}_{0.37}$	$\text{CF}_{0.38}$	$\text{CF}_{0.43}$
OPTI	50	$\text{CF}_{0.59}$	-	$\text{CF}_{0.74}$



**Fig. 1** (a)  $^{19}\text{F}$  MAS NMR (30 kHz) and (b)  $^{13}\text{C}$  echo solid-MAS spectra (12 kHz) of 3 representative cases of fluorinated ACs.

Different C-F bonds coexist in the CA whatever the fluorine content as revealed by the various lines observed in the -140/-200 ppm range on the  $^{19}\text{F}$  spectra (Fig. 1a). The lower the chemical shift, the higher the covalence. Weakened covalent (noted C---F) and purely covalent C-F bonds (C-F) in graphite fluorides result in chemical shifts of -170 and -190 ppm, respectively [5]. The C-F bonding is weakened because of the presence of non-fluorinated  $\text{sp}^2$  carbon atoms in their neighboring. The average C-F bond length, as seen by inverse CP NMR sequence, is of  $0.144 \pm 0.002$  nm. This value, which is longer than in covalent graphite fluoride, of  $(\text{C}_2\text{F})_n$  and  $(\text{CF})_n$  structural type ( $d_{\text{C-F}} = 0.138 \pm 0.002$  nm), is explained by the presence of non-fluorinated  $\text{sp}^2$  carbon atoms. Narrow lines are observed for P1 with low fluorine rate ( $\text{CF}_{0.11}$ ). The linewidth is related to the dilution of fluorine atoms in the carbon matrix, which results in the decrease of the  $^{19}\text{F}$ - $^{19}\text{F}$  homonuclear dipolar coupling.  $^{13}\text{C}$  spectra at 12 kHz recorded

with echo solid sequence (Fig. 1b) underline the different C-F bondings by the chemical shifts of both the C-F bonds at 80 and 87 ppm and the  $\text{sp}^2$  carbons (between 120 and 135 ppm). When the covalence increases the  $^{13}\text{C}$  chemical shift increases.

The textural evolutions of carbon materials before and after fluorination and water intrusion are reported in Table 2. When mild fluorination conditions are used (room temperature), the initial porosity of the carbon samples is hardly affected. Similarly, the micro- and mesoporosity of samples appear unchanged by the water intrusion experiments. The latter technique displays a hydrophobic character for the fluorinated carbon materials with the necessity to force water intrusion into the porosity.

**Table 2.** Textural properties of carbon materials submitted to fluorination and water intrusion experiments

Samples	Fluorination	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_p$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{hp}}$ ( $\text{cm}^3/\text{g}$ )
M1		298	0.41	0.06
M1	Yes	366	0.48	0.04
M1*	Yes	366	0.46	0.05
M3		409	0.43	0.15
M3	Yes	560	0.39	0.15
M3*	Yes	554	0.40	0.14
P1		237	0.38	0.30
P1	Yes	328	0.31	0.15
P3		582	0.43	0.15
P3	Yes	323	0.35	0.15
RB3		978	0.52	0.38
RB3	Yes	664	0.31	0.28
R2030		780	0.38	0.38
R2030	Yes	624	0.25	0.25
OPTI		1528	0.64	0.46
OPTI	Yes	316	0.18	0.18

\* : sample characterized after water intrusion experiments.

## Conclusions

The increase of the fluorination temperature results both in the decomposition into volatile  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  and the significant formation of  $\text{CF}_2$  groups. Whatever the condition and the precursor, different C-F bonds are formed when the fluorine content increases. The C-F bonding is found either purely covalent in highly fluorinated part or weakened covalence due to the hyperconjugation between non-fluorinated  $\text{sp}^2$  carbons and neighboring C-F bonds in non-saturated parts. These materials have potential applications to catch organic pollutants dissolved in water. The water intrusion can be also a method to classified materials by their hydrophobicity. To a lesser extend, hydrophobic porous carbons can be useful for energy storage in peculiar applications.

## References

- [1] Liang C, Dai S, J. Am. Chem. Soc. 2006;128:5316.
- [2] Wang X, Liang C, Dai S, Langmuir 2008;24:7500.
- [3] Huang Y, Cai H, Feng D, Gu D, Deng Y, Tu B, Wang H, Webley P.A, Zhao D, Chem. Commun. 2008; 2641.
- [4] Giraudet J, Dubois M, Guérin K, Delabarre C, Pirotte P, Hamwi A, Masin F, Solid State Nuclear Magnetic Resonance, 2007;31(33): 131-140.
- [5] Zhang W, Dubois M, Guérin K, Bonnet P, Kharbache H, Masin F, Kharitonov AP, Hamwi A, Phys. Chem. Chem. Phys. 2010;12:1388-1398.