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Characterization of structural heterogeneity in carbon fluorides

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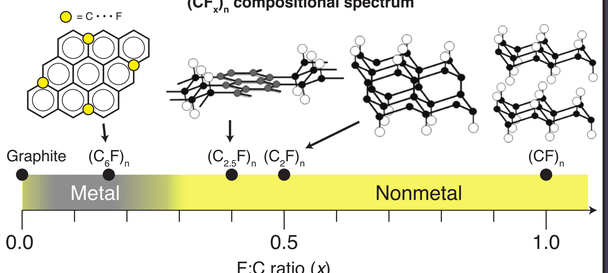
Introduction

Nonrechargeable, carbon fluoride "CF_x" conversion cathodes are a Li-primary battery chemistry that offer very high energy density and long cell lifetimes. The highest capacity is realized for $x = 1$, poly(carbon monofluoride), $(CF)_n$.

Chemistry	Representative Reaction	Voltage	Capacity	Energy density
Li-primary	$nLi + (CF)_n \rightarrow nLiF + (C)_n$	3.4 V	701 mA•h/g	2.18 W•h/g
Li-ion	$LiC_6 + FePO_4 \rightarrow C_6 + LiFePO_4$	3.5 V	117 mA•h/g	0.40 W•h/g

As a "CF_x" cell dischages the F:C ratio, x, of $(CF_x)_n$ drops to zero. The structural changes that accompany discharge are not well-understood.

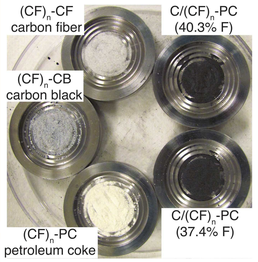
$(CF_x)_n$ compositional spectrum

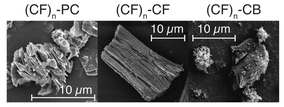


$(CF_x)_n$ exhibits a wide range of properties depending on F:C ratio, carbon source material, and synthesis. Variability of bonding motifs leads to polymorphism.[1-3] $(CF)_n$ is not polymorphic as the graphite sheets are fully fluorinated.[4]

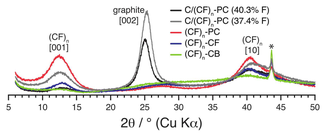
Real world poly(carbon monofluoride) samples, $(CF)_n$

Purchased from Advanced Research Chemicals, Inc.





- pXRD reveals graphitic component to black powders.
- No graphite signature for the "pure" samples.

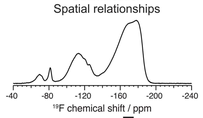


Why do samples of supposedly identical chemcial composition look so different? Do they differ on a molecular level?

Approach

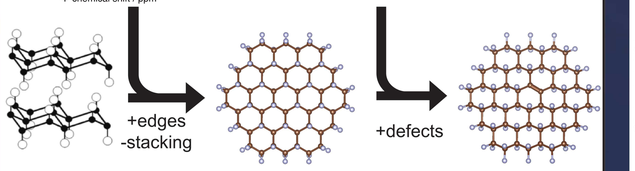
Develop a structural model to explain properties of $(CF)_n$.

Solid-state NMR
Functional groups
Quantification
Spatial relationships



DFT refinement
Structure-based prediction of NMR parameters
Bond dissociation energies
Analysis of periodically extended structures

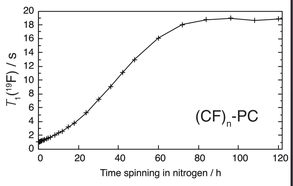
$$H\psi_i = \left\{-\frac{\hbar}{2m}\nabla^2 + V[\rho]\right\}\psi_i$$



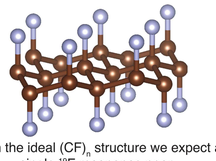
Experimental

All NMR data was acquired at 9.4 T and 33 1/3 kHz MAS using recycle delays between 1 s and 2.5 s. VT gas was regulated at 300 K (sample ~ 340 K). Fluorine-19 decoupling was applied during acquisition of ^{13}C signals. Proton decoupling had no effect on ^{19}F signals and was not used here.

The spinning gas was usually N_2. Over many hours this incurs a loss in sensitivity due to increasing $T_1(^{19}F)$ as intercalated O_2 exchages away. By spinning with air T_1 can be maintained below 2 s.



Defect analysis

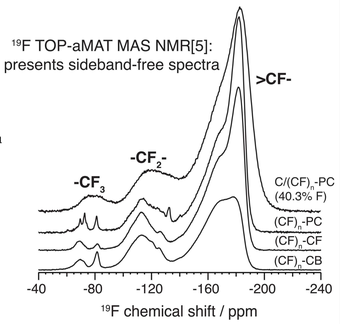


From the ideal $(CF)_n$ structure we expect a single ^{19}F resonance near δ_{iso}(>CF-) = -180 ppm

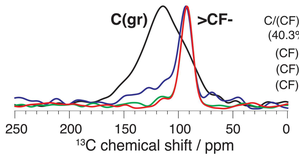
In reality, ^{19}F MAS NMR show:
- Variably broad resonances
- >CF-, -CF_2-, -CF_3 functional groups
- Shoulder/skewedness to >CF- peak
- Ambiguity in >CF-/-CF_2- overlap region

Real samples are represented by highly defective structures

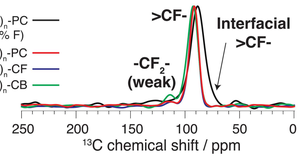
^{19}F TOP-aMAT MAS NMR[5]: presents sideband-free spectra



Direct excitation ^{13}C CPMG MAS NMR



$\{^{19}F\}^{13}C$ CP CPMG MAS NMR



- Graphitic carbon dominates C/(CF)-PC (40.3%)
- C(gr) also appears in other samples

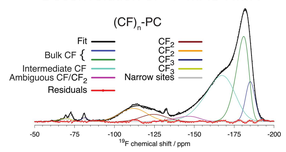
- C(gr) signal mostly lost
- Carbon at interface of fluorinated/graphitic domains suggested near 75 ppm

Sample	Carbon source	Color	Graphite fraction	F:C ratio (excluding graphitic carbon)	CF:CF_2 ratio (n)
$(CF)_n$-PC	Petroleum coke		< 0.3%	1.11	10.8
$(CF)_n$-CF	Carbon fiber		< 0.8%	1.11	9.8
$(CF)_n$-CB	Carbon black		3.3%	1.19	5.5
C/$(CF)_n$-PC (40.3% F)	Petroleum coke		90%	1.12	9.6

Residual, pXRD-invisible graphitic domains correlate well with color.

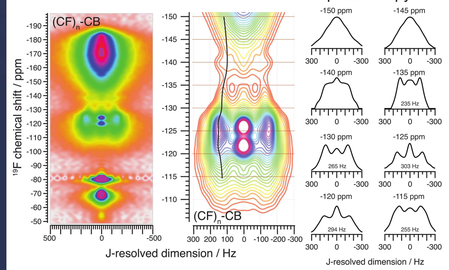
What is the nature of the other defects?

Deconvolution of ^{19}F MAS NMR



- Fit broad features common to all samples
- Skew-gaussian model
- Shift parameters constrained across samples
- Eight >CF-, -CF_2-, -CF_3 sites to capture line shape complexity (excluding narrow lines)
- Extensive overlap in -125 ppm to -150 ppm region; interpretation ambiguous

J-resolved ^{19}F spectroscopy



200 Hz – 300 Hz geminal F splittings are observed. -CF_2- extends to -140 ppm.

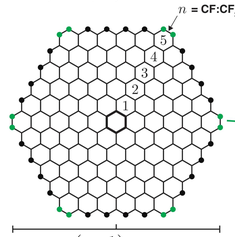
Not all -CF_2- are in weak coupling limit leading to 0 Hz peaks in *J* dimension.

Narrow peaks at -122 ppm and -126 ppm are unlikely the result of -CF_2- species.

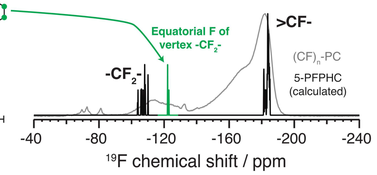
Part of -CF_2- region lost due to low T_2 values.

Spatial relationships

5-crown perfluoroperhydrocoronene (5-PFPHC)



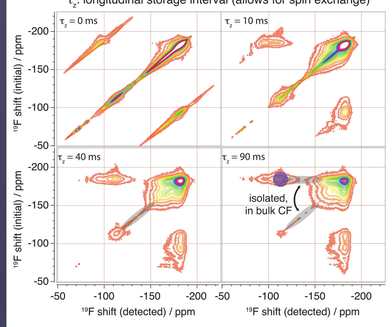
Crowned coronene platelet model
- Model system for fluorographene[6]
- Consistent with nm-sized platelets known to exist in many carbon sources.[7]
- n between 5 and 11 suggests $(CF)_n$ platelet diameters (d) between 3 nm and 6 nm

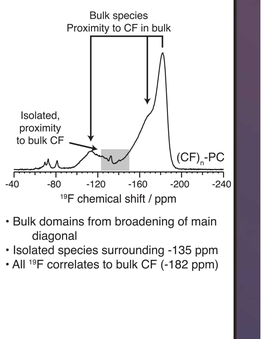


The crowned coronene platelet model does not explain many features in the ^{19}F MAS NMR spectra.

2D $\{^{19}F\}^{19}F$ spin diffusion EXSY experiments

τ_z: longitudinal storage interval (allows for spin exchange)

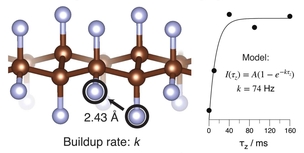




- Bulk domains from broadening of main diagonal
- Isolated species surrounding -135 ppm
- All ^{19}F correlates to bulk CF (-182 ppm)

From the buildup of the CF --> CF_2 transfer, ●, estimate a spin diffusion coefficient *D*. [8]

Assume initial build-up (short τ_z) is exclusively due to single transfer between edge groups:



Buildup rate: k

$D = (74\ \text{Hz})(2.43\ \text{Å})^2 = 4.3\ \text{nm}^2/\text{s}$

From the estimate of *D*, determine representative (rms) displacements of ^{19}F magnetization, *L*.

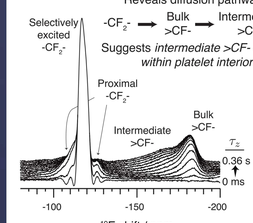
Diffusion in a plane: $L = \sqrt{4D\tau_z}$

$D = 4.3$ nm^2/s	
τ_z	L
10 ms	0.4 nm
40 ms	0.8 nm
90 ms	1.2 nm
360 ms (steady state)	2.5 nm (~platelet radius)

Extremely basic analysis ignores many factors. Nonetheless, suggests *all observable fluorinated domains exist within $(CF)_n$ platelets.*

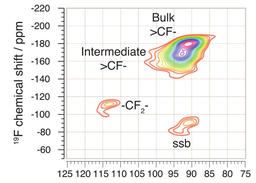
Selective 1D $\{^{19}F\}^{19}F$ spin diffusion EXSY

Reveals diffusion pathway:



$\{^{19}F\}^{13}C$ CP HETCOR CPMG

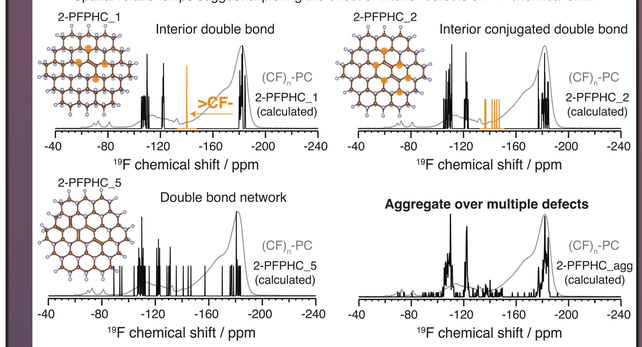
- 100 μs contact time for bonded >CF- correlations
- Bulk/intermediate >CF- distinction in ^{13}C shifts



Functional structural model

Defective platelet model

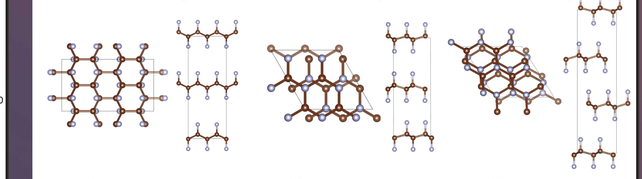
Spatial relationships suggest exploring the effect of interior defects on ^{19}F chemical shift.



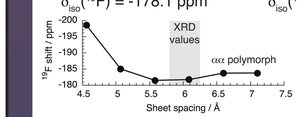
Double bond defects explain origin of "isolated" -135 ppm signal region.

Effects of sheet stacking

αα stacking | αβ stacking | αβγ stacking



$\delta_{iso}(^{19}F)$ = -178.1 ppm | $\delta_{iso}(^{19}F)$ = -178.2 ppm | $\delta_{iso}(^{19}F)$ = -178.7 ppm



Expected to effect shifts to < 5 ppm level.

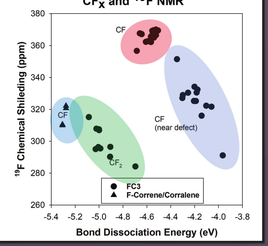
A detailed description of stacking is not essential for a functional structural model.

Defect correlation to electronic properties

- Correlations are known between ^{19}F shift,
  - C–F bond length,
  - C–F bond covalent character,
  - Half-cell discharge potential.[9]
- Signficant CF bond weakening is calculated for 2-PFPHC structures having double bond defects
- Correlation of bond energy with ^{19}F shielding (right)

The defective platelet model will be a servicable starting point for understanding electrochemical behavior.

CF_x and ^{19}F NMR



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