

## Supporting Information

### Fundamentals of Li/CF<sub>x</sub> battery design and application

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In simple terms, the carbon source can affect the skeleton structure of its derivatives, which is important for conductivity; moreover, the defects of carbon increase reactivity and influence the fluorination degree and the strength of C–F bonds, which relate to the capacity and discharge voltage, respectively.

Since the fluorination progresses inwardly, the fluorine pattern of formed CF<sub>x</sub> is co-determined by the structure of the carbon and mechanism of F diffusion, which is under control of the fluorination method and condition. For the convenience of readers, we summarize the synthesis and properties of different types of fluorinated carbons in detail here.

Table S1 Detailed fluorocarbon synthesis and performance.

No.	CF <sub>x</sub>	Typical synthesis		structure		performance			Ref.
		Carbon source	Fluorination method	F/C	% sp <sup>2</sup> C	Capacity (mAh/g)	E <sub>1/2</sub> Voltage(V)	Current	
1	F-graphite	nature graphite	Direct fluorination, 390°C	0.61		670	2.35	0.5mA/cm <sup>2</sup>	1
2			Direct fluorination, 594°C	1		820	2.09		
3			Catalytic fluorination (RT)	0.65		~650	~3.08		2
4				1		~660	~2.4		
5			Mechanochemical fluorination	0.62		500	~3.0	25 mA/g	3
6		nanographite	Direct fluorination, 300°C	0.67		~800	2.83	10 mA/g	4
7			Direct fluorination, 400°C	0.82		~805	2.65		
8			Direct fluorination, 450°C	0.89		837.4	2.54		
9		Defective graphite	Catalytic fluorination (RT)	0.58		940	3.1	5.1 mA/g	5
10	F-graphene	graphene	Direct fluorination, 300 °C	0.67	7.5	632	2.35	10 mA/g	6
11		graphene oxide	Solvothermal fluorination 180°C	0.476					7
12	F-amorphous carbon	Ketjenblack	controlled fluorination 520°C	0.95		~770	~2.8	0.1C	8
13	F-hard carbon	calcinated macadamia nut shell	Direct fluorination, 250°C	1.1	12.11	898	3.05	10 mA/g	9
14			Direct fluorination, 280°C	1.12	10.47	949	2.97		
15		hard carbon	Direct fluorination,	1.03	20.45	774.7	~2.55	0.1C	10

No.	CF <sub>x</sub>	Typical synthesis		structure		performance			Ref.
		Carbon source	Fluorination method	F/C	% sp <sup>2</sup> C	Capacity (mAh/g)	E <sub>1/2</sub> Voltage(V)	Current	
		(purchased)	390°C						
16	F-carbon nanofibre	carbon nanofibre	Direct fluorination, 428°C	0.59		600	2.44	10 mA/g	11 12
17			controlled fluorination 450°C	0.56	46	613	2.34		
18			Direct fluorination, 435°C	0.68		510	2.27		
19			controlled fluorination 480°C	0.7	35	614	2.32		
20	F-carbon nanotube	carbon nanotubes	Direct fluorination, 350°C	0.74	8.9	640.76	~2.56	0.1 C	13
21			Direct fluorination, 400°C	1.28	6.4	705.02	~2.51		
22			Direct fluorination, 500°C	1.89	0.6	794.85	~2.26		
23			Direct fluorination, 525°C	2.11	0.5	727.2	~2.3	0.1 C	
24			Direct fluorination, 380°C	1	10.5	~695	~2.32		
25			Direct fluorination, 450°C	0.98	/	~790	~2.25		
26		plasma fluorination 300°C	1.14	7.46	819.3	~2.6	100mA/g	15	
27	F-carbon nanocage	Carbon Nanocages	plasma fluorination	0.98		850	~2.4	100mA/g	16

Several comparisons are conducted below to facilitate understanding.

Comparing fluorinated graphite and fluorinated hard carbon in line No.1 and No.15 of Table S1, they both fluorinated at 390°C by direct fluorination, while they have different F/C ratio as 0.61 and 1.03, respectively. Because the hard carbon is rich in defects which makes it easier to be fluorinated.

Comparing the fluorinated carbon nanofibers in line No.18 and No.19, the same carbon nanofibers are fluorinated by different methods, and different temperatures are demanded to obtain similar F/C ratio. The fluorinated carbon nanofibers exhibit considerable difference performance, indicating that fluorination method impact on the microstructure of formed CF<sub>x</sub>.

Comparing the fluorinated carbon nanotubes in line No.20-23, the carbon nanotubes are all fluorinated by direct fluorination, while the structure of fluorinated carbon nanotubes can be various because of the temperature difference. As a result, the visible structure difference leads to a considerable difference in batteries performance.

Table S2 Different fluorination methods and characteristics

Fluorination methods	Typical fluorinating agents	Advantages	Disadvantages	Ref.
direct fluorination	F <sub>2</sub> gas/F <sub>2</sub> -containing gas mixtures	suitable for large-scale synthesis	fluorination is uneven and damage the skeleton (high temperature)	17-21
controlled fluorination	TbF <sub>4</sub> , XeF <sub>2</sub> and NF <sub>3</sub>	dispersion of F is homogenous throughout the carbon matrix	fluorinating agent cost is high	22-27
catalytic fluorination	MF <sub>n</sub> (IF <sub>5</sub> , BF <sub>3</sub> , ClF <sub>3</sub> , AlF <sub>3</sub> , MgF <sub>2</sub> )-HF	low temperature, CF <sub>x</sub> contains non-fluorinated domains	subsequent high temperature treatment is needed	28-32
plasma fluorination	CF <sub>4</sub> , SF <sub>6</sub>	suitable for surface fluorination	F/C ratio is relatively low	33-35
solvochemical fluorination	HF	low temperature, convenient	only oxygen-rich carbon sources are recommended	36
mechanochemical fluorination	CoF <sub>3</sub>	room temperature fluorination	high-energy milling is needed	37

electrochemical fluorination	HF electrolyte	room temperature fluorination and easily control	F content is limited	38
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