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## Carbon monofluorides derived from sponge and shot cokes

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**Abstract** Carbon fluoride compounds,  $CF_x$ , are used as cathode materials in commercially important primary  $Li/CF_x$  electrochemical power sources. New  $CF_x$  compounds were prepared, apparently for the first time, from sponge and shot cokes by direct fluorination. The carbon starting materials and  $CF_x$  products were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, and elemental analysis for total fluorine. The discharge capacity of shot coke  $CF_x$  was unexpectedly low and is probably related to the heterogeneous nature of that form of coke.  $CF_x$  prepared from sponge coke that had been heated to 1930 °C exhibited the highest capacity, exceeding the capacity of a commercially available, battery grade  $CF_x$ . The discharge results show that  $CF_x$  from heated sponge coke has favorable electrochemical properties that render it attractive for lithium electrochemical power sources.

**Keywords** Carbon monofluoride · Lithium cells · Sponge coke

### Introduction

Lithium carbon monofluoride ( $Li/CF_x$ ) electrochemical power sources embody an important cell system that is used to operate a diverse array of devices because of its safety and performance characteristics under a wide range of operating conditions [1, 2, 3, 4]. For example,  $Li/CF_x$  coin cells are typically used in electronic devices for clock and memory backup applications, which take advantage of their relatively constant discharge voltage profiles. The long-term reliability of  $Li/CF_x$  cells has been recognized recently as a promising power source

for cardiac pacemakers. Additionally,  $CF_x$  has a high discharge capacity based on mass, significantly greater than the capacities realized for other commercially manufactured  $Li$  primary cell cathode materials [2, 3, 4].

The  $CF_x$  cathode material is key to providing the combined performance and stability to the  $Li/CF_x$  system. The electrochemical reaction of  $CF_x$  in  $Li/CF_x$  cells proceeds through several steps, including  $Li^+$  insertion into  $CF_x$  followed by reductive dehalogenation to ultimately yield carbon and  $LiF$  [5, 6, 7, 8]. Just as the carbon structure is an important factor determining reactivity towards lithium intercalation [9], it may be anticipated that the structure of the carbon starting material influences the electrochemical behavior of the  $CF_x$  product.

The  $CF_x$  commonly used in  $Li/CF_x$  cells is derived from petroleum coke. Other carbon starting materials for  $CF_x$  have been investigated, including coal tar pitch coke (Root MJ unpublished results, [10]), synthetic [11] and natural graphites [12], carbon black [11, 12], activated carbon [11, 12], glassy carbon [13], carbon fiber [14, 15], fullerenes [16, 17, 18, 19, 20], and carbons derived from graphite oxide [21, 22], graphite fluoride [21], or graphite fluorine intercalation compounds [23].

In this work, two new types of carbon starting material, sponge and shot cokes, were investigated as starting materials for  $CF_x$ . These cokes are byproducts of delayed coking operations that use petroleum feedstocks to produce valuable needle coke [24, 25]. Sponge and shot cokes from various sources have wide-ranging properties [24, 25, 26, 27, 28]. Sponge coke can be used for fuel or to manufacture carbon anodes for electrolytic aluminum production. It is named after its open, spongy microscopic appearance. Shot coke is an undesirable product that forms as small spheres. No commercial use for shot coke has been identified.

The carbon and  $CF_x$  samples used in this work were characterized by elemental analyses, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The electrochemistry of the  $CF_x$  cathode materials were examined in  $Li/CF_x$  cells.

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## Experimental

### Materials

Calcined sponge and shot cokes were from Great Lakes Carbon (Port Arthur, Tex.). The cokes were calcined between 1290 °C and 1480 °C. A sample of the calcined sponge coke was further heated to 1930 °C. The shot coke was ground and passed through a 200-mesh screen.

All  $\text{CF}_x$  materials were synthesized by Advanced Research Chemicals (Catoosa, Okla.) using direct fluorination following literature procedures [6, 7, 8]. Synthesis conditions were adjusted to obtain a carbon to fluorine ratio near 1. A commercial, battery grade  $\text{CF}_x$  derived from petroleum coke was also obtained from Advanced Research Chemicals.

### Characterization

Elemental analyses for total F were obtained using the carbonate fusion method at Advanced Research Chemicals [29].

XRD spectra were obtained with a Bruker D8 diffractometer using a Cu target. Diffraction patterns were fit as Lorentzian peaks. Lattice parameters were determined for carbon and  $\text{CF}_x$  materials assuming hexagonal structures [9, 30, 31]. The  $a$  and  $c$  axis coherence lengths,  $L_a$  and  $L_c$ , respectively, were calculated using the Scherrer equation [32].

XPS results were obtained from Materials Interface (Sussex, Wis.). XPS experiments were made using a Physical Electronics model 5700 spectrometer equipped with an aluminum anode. Energy peak locations were calibrated using polyethylene powder as an internal standard in one of the samples [33].

### Electrochemical methods

Electrode materials were prepared by mixing  $\text{CF}_x$  samples with acetylene black and an aqueous styrene butyl rubber suspension, then drying at 60 °C. Pellets of the resulting mixture were made by compressing approximately 0.03 g of this electrode mix in a 1.0 cm diameter die. The pellets were subsequently dried in vacuo at 60 °C for at least 8 h.

Two electrode Li/ $\text{CF}_x$  cells were assembled using commercial BR2325 coin cell hardware. Each  $\text{CF}_x$  pellet was accurately weighed before use. An aluminum wire screen served as the cathode current collector and two sheets of nonwoven polypropylene separator were used. A large excess of Li foil was placed on a stainless steel disk which was placed on a Belleville washer, as described previously [34]. The electrolyte was 1.0 mol  $\text{dm}^{-3}$   $\text{LiBF}_4$  in 1:1 propylene carbonate (PC):1,2-dimethoxyethane (DME). Cells were closed with a hydraulic press. All assembly operations were done in a dry room.

Cyclic voltammograms were obtained using an EG&G PAR 273A potentiostat controlled by CorrWare software (Scribner Associates). The scan rate was 0.02  $\text{mV s}^{-1}$ . Constant current chronopotentiometry measurements were acquired with an Arbin BTS 2043 electrochemical test system. The current applied to each cell was adjusted according to the mass of  $\text{CF}_x$  in the electrode pellet. Electrochemical capacity data are reported as the mean of at least two discharge experiments. All reported errors are standard deviations.

## Results

### Carbon characterization

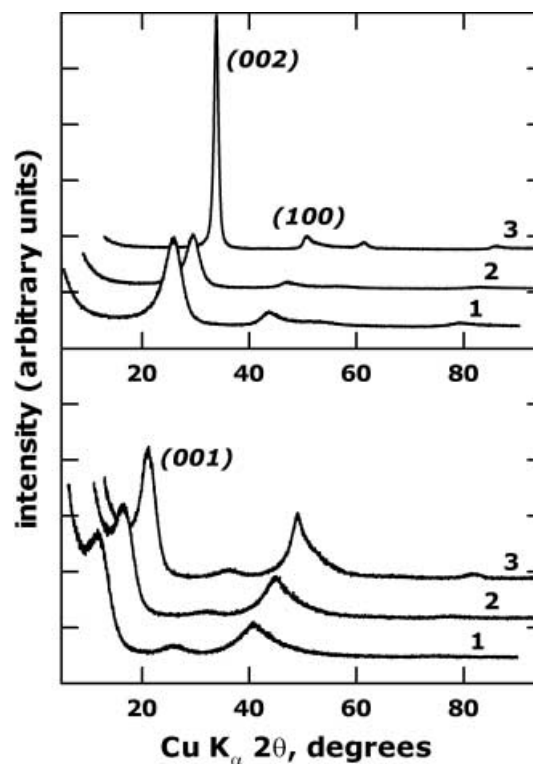
XRD patterns for the carbons used in this work are shown in Fig. 1. These spectra are typical of disordered carbons [9]. As sponge coke is heated to 1930 °C, the

diffraction peaks become narrower and more intense, indicating the carbon crystallites and structural ordering increase with heating temperature, i.e. the carbon becomes more graphitic [35, 36, 37].

Interlayer spacings between carbon sheets,  $d_{002}$ , calculated from the 002 peak near  $26^\circ 2\theta$  after correcting for the Lorentz-polarization factor, are 348.1 pm for the calcined sponge coke, 344.2 pm for the sponge coke heated to 1930 °C, and 347.7 pm for shot coke, compared with 335 pm for graphite [32]. The coherence lengths  $L_a$  and  $L_c$ , which estimate crystallite dimensions along the  $a$  and  $c$  axes, respectively, typically increase with carbon structural order [35, 36, 37]. Values for  $L_a$ , calculated from the (100) diffraction peak assuming a hexagonal structure, increase from 2.7 nm and 2.9 nm for shot coke and calcined sponge coke, respectively, to 4.6 nm for the heated sponge coke. Likewise,  $L_c$  values calculated from the (002) diffraction peak increase from 4.1 nm and 5.2 nm for shot coke and calcined sponge coke, respectively, to 18.3 nm for the heated sponge coke. These trends are expected as the sponge coke becomes more ordered (graphitized) with heating.

### $\text{CF}_x$ characterization

XRD patterns for the  $\text{CF}_x$  compounds prepared from the sponge and shot cokes, shown in Fig. 1, are typical



**Fig. 1** Top: X-ray diffraction spectra for (1) shot coke, (2) sponge coke, (3) sponge coke heated to 1930 °C. Bottom: XRD spectra for (1)  $\text{CF}_x$  prepared from shot coke, (2) sponge coke, (3) sponge coke heated to 1930 °C. The intensity axis scale of the upper plot is twice that of the lower plot. Spectra have been offset slightly for clarity

of this type of material [6, 7, 8, 31]. Peaks are sharper and more intense for the  $CF_x$  made from sponge coke heated to 1930 °C.

The  $CF_x$  XRD spectra in Fig. 1 were indexed according to literature reports [31, 38]. The values for the interlayer spacings,  $d_{001}$ , were calculated from the (001) peak found near  $13^\circ 2\theta$  after correcting for the Lorentz polarization factor. This dimension varies from 674.9 pm to 657.7 pm to 706.6 pm for  $CF_x$  prepared from the calcined sponge coke, sponge coke heated at 1930 °C, and shot coke, respectively. The analogous values for  $CF_x$  synthesized from other carbon types range from 585 pm and 590 pm for fluorinated natural graphite [30, 39] to  $\geq 700$  pm for  $CF_x$  prepared from petroleum coke or carbon derived from decomposed graphite oxide [21, 40].

The analytical results for the  $CF_x$  compounds are listed in Table 1. Each of the C to F ratios is near 1, which is the stoichiometric ratio for the bulk material.

The elemental surface compositions for  $CF_x$  derived from sponge coke found by XPS are given in Table 1. The peak positions are referenced to polyethylene. Alone or mixed with a  $CF_x$  sample, polyethylene exhibited a C 1s peak at 285.0 eV. This matches the generally accepted literature value [41]. Only small amounts of oxygen and nitrogen were detected, representing 0.2% to  $\leq 0.5\%$ , respectively, of the total elemental composition for atomic numbers larger than 2.

The surface F/C ratios measured by XPS were larger than the overall F/C ratios determined by chemical analysis (Table 1). This is anticipated since the edge sites located at the surface of  $CF_x$  consist of a larger proportion of  $CF_2$  and, to a much lesser extent,  $CF_3$  moieties [42].

Eight peaks may be resolved in the high-resolution C 1s XPS spectra of the sponge coke  $CF_x$  compounds. Both  $CF_x$  XPS spectra have a small C 1s peak at 285.2 eV, comprising 0.8–1.5% of the total carbon, ascribed to adventitious hydrocarbon contaminants [38, 43]. Two peaks centered near 286.4 eV and 287.7 eV individually account for 0.8–1.8% of the total carbon,

for a combined 2.1–2.8% of the total carbon. Similar peaks were previously attributed to defluorination of the  $CF_x$  surface during measurement [44].

The major C 1s peak at 290.4 eV, representing over 70% of the total carbon, is assigned to carbon bound to fluoride and surrounded by other CF groups [43, 44, 45]. This value indicates that the fluorine is covalently bound to carbon [41], as expected for high-temperature direct fluorination [6, 7, 8]. C 1s peaks on either side of the main \*CF peak (atom assignments are indicated by a preceding asterisk) are tentatively assigned to CF carbons as well, but in somewhat different environments. These peaks are included in the \*CF area percentages given in Table 1. The peak at 288.9 eV is shifted  $-1.5$  eV from the main \*CF peak and was previously assigned to edge (or perhaps lattice defect) CF groups, based on molecular orbital calculations and comparing the intensities of this peak with the \* $CF_2$  peak intensities [43]. The peak at 291.2 eV is  $+0.8$  eV from the main \*CF peak. A shift of this magnitude is anticipated if a neighboring carbon is bound to two F atoms [44]. This peak then may result from CF groups adjacent to  $CF_2$  moieties,  $F_2C$ -\*CF.

The second largest peak (9–16.5% of the total carbon) appears at 292.2–292.3 eV. The highest energy peak, corresponding to  $\leq 1.0\%$  of the total carbon, occurs at 293.8–293.9 eV. These peaks are attributed to  $CF_2$  and  $CF_3$  carbons, respectively [38, 43, 44, 45].

The peak assignments given in Table 1 compare favorably with those reported for other  $CF_x$  compounds [43, 44]. XPS peak positions for fluorinated fullerenes,  $C_{60}F_x$ , are similar, typically ranging from 289.3 eV to 290.5 eV for \*CF (although lower energies have been reported), from 291.5 eV to 292.3 for \* $CF_2$ , and 294.5 eV for \* $CF_3$  [19, 20, 46, 47, 48]. Published XPS results for the perfluorinated polymers poly(tetrafluoroethylene) and poly(hexafluoropropene) further support the assignments in Table 1. C 1s binding energies for  $CF_2$ -\*CF- $CF_3$ , \* $CF_2$ -CF- $CF_3$ ,  $F_2C$ -\* $CF_2$ , and  $CF_2$ -CF-\* $CF_3$  are 289.4–289.8 eV, 290.9–291.8 eV, 292.2–292.5 eV, and 293.3–293.7 eV, respectively [41, 49].

**Table 1** Total fluorine analysis, stoichiometry, carbon and fluorine content as determined from XPS measurements, C 1s and F 1s binding energies and relative peak areas for  $CF_x$  materials prepared by direct fluorination of sponge, shot, and petroleum cokes

Carbon starting material	% F <sup>a</sup>	F/C (x in $CF_x$ )	XPS elemental analysis			Binding energy in eV and area per cent (in parentheses) <sup>b,c</sup>								
			% C	% F	F/C ratio	*CF	* $CF_2$	* $CF_3$	C*F					
Sponge coke	63.4	1.09	44.2	55.2	1.25	288.9	290.4	291.2	(79.6)	292.2	(16.5)	293.8	(1.0)	689.1
Heated sponge coke	61.2	1.00	53.4	53.4	1.15	288.9	290.4	291.2	(82.3)	292.3	(9.0)	293.9	(0.8)	689.1
Shot coke	61.1	0.99												
Petroleum coke	62.2	1.04												

<sup>a</sup>Calculated % F for  $CF_{1.00}$ : 61.3%

<sup>b</sup>Polyethylene (C 1s binding energy = 285.0 eV) was used as reference

<sup>c</sup>The atom assignments are designated by a preceding asterisk

A single F 1s peak can be resolved in the  $CF_x$  spectra at 689.1 eV and is characteristic of covalent C-F bonding. This peak position is comparable to other  $CF_x$  materials previously reported, with F 1s binding energies between 689.2 eV and 690.5 eV [43, 44].

### Electrochemistry

Cyclic voltammograms for the sponge coke  $CF_x$  compounds are shown in Fig. 2. Only reduction peaks are observed under the conditions used in this work. No oxidation peak is observed because the reduction reaction is chemically irreversible, forming carbon and LiF as products. The peak potentials increase with increasing structural order of the  $CF_x$ , 2.13 V for the calcined sponge coke  $CF_x$  and 2.25 V for  $CF_x$  made from sponge coke heated to 1930 °C.

Electrochemical discharge capacities of Li/ $CF_x$  cells as a function of applied current are shown in Fig. 3. Capacities increase in the order shot coke  $CF_x$  < calcined sponge coke  $CF_x$  < petroleum coke  $CF_x$  < heated sponge coke  $CF_x$ . These results suggest that sponge coke heated to 1930 °C discharges more efficiently than the calcined sponge coke  $CF_x$ . The shot coke  $CF_x$  exhibited very low discharge capacities.

### Discussion

There are numerous literature reports regarding the electrochemistry of  $CF_x$  materials prepared from a diverse array of carbons [11, 12, 13, 14, 15, 21, 22, 23]. To our knowledge, this is the first example of  $CF_x$  prepared from sponge or shot cokes.

The overall discharge reaction for Li/ $CF_x$  cells may be written:

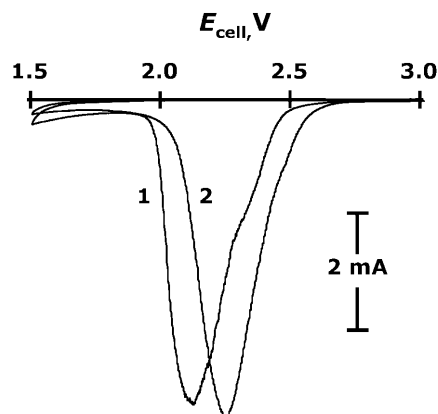
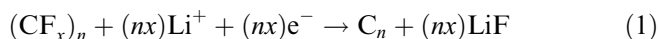


Fig. 2 Cyclic voltammograms for Li/ $CF_x$  cells containing  $CF_x$  materials prepared from (1) calcined sponge coke and (2) sponge coke heated to 1930 °C. Scan rate 0.02 mV s<sup>-1</sup>

The reaction proceeds with Li<sup>+</sup> intercalation into and diffusion within  $CF_x$  [5, 6, 7, 8, 50], followed by reductive defluorination. The structural characteristics of  $CF_x$  thus are expected to influence its electrochemical behavior.

Comparing the carbon  $d_{002}$  and  $CF_x$   $d_{001}$  values for the sponge cokes reveals that  $CF_x$  structural characteristics parallel the carbon starting materials. The relative structural order present in the carbon starting materials is retained during the fluorination process; more structurally ordered carbons yield more structurally ordered  $CF_x$ . The  $CF_x$  used here was prepared by direct fluorination of carbon with F<sub>2</sub> at temperatures between 370 °C and 390 °C, depending on the carbon starting material, to achieve a nearly stoichiometric composition. Much higher temperatures are required to induce structural ordering in the carbon materials. Thus, changes in layer stacking or further coalescence and expansion of the basal plane are unlikely.

The F 1s and C 1s peaks from the high-resolution XPS results in Table 1 clearly show that the C-F bonding in the  $CF_x$  compounds described here is covalent [38]. If the fluorination reaction temperature is too low, various carbons may retain adsorbed, unreacted fluorine. Intercalated fluorine may also be present in ionic or partially ionic forms ([51, 52] and references therein). These species are quite chemically reactive whereas covalent C-F bonds are stable under a wide range of conditions. For this reason,  $CF_x$  used in electrochemical power sources is prepared in such a way to form only covalent C-F bonds. No evidence for ionic or partially ionic fluoride was observed at the  $CF_x$  surface by XPS. F 1s peaks for partially ionic fluoride in carbon fluorine intercalation compounds occur 2.0–3.1 eV lower and the C 1s peaks appear at least 0.9 eV lower than observed for the compounds in Table 1 [51, 52].

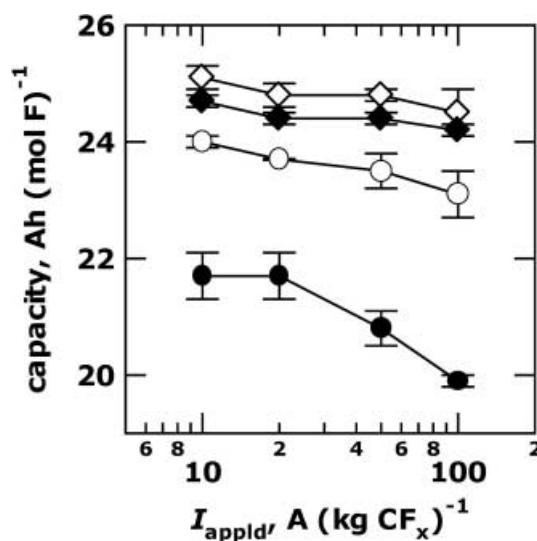


Fig. 3 Discharge capacities as a function of applied current density for  $CF_x$  materials prepared from shot coke (filled circles), calcined sponge coke (open circles), petroleum coke (filled diamonds), and sponge coke heated to 1930 °C (open diamonds). The lines connecting data points serve only to suggest data trends

The cyclic voltammograms of the sponge coke  $\text{CF}_x$  compounds (Fig. 2) show that the reduction peak potential at  $0.02 \text{ mV s}^{-1}$  for the heated sponge coke  $\text{CF}_x$  is over 100 mV higher than the calcined sponge coke  $\text{CF}_x$ . This is consistent with Li/ $\text{CF}_x$  cell potentials during chronopotentiometric measurements (not shown); the heated sponge coke  $\text{CF}_x$  is reduced at higher potentials in Li/ $\text{CF}_x$  than the calcined sponge coke  $\text{CF}_x$ . This contradicts literature reports that compare  $\text{CF}_x$  materials derived from different carbon sources. Electrochemical discharge potentials generally increase with  $\text{CF}_x$  structural disorder. Other factors may complicate direct comparisons among  $\text{CF}_x$  compounds synthesized from such diverse carbon sources, though. The two sponge coke samples used in this work were from a single source. The structural ordering of the coke was changed in a controlled manner by heating (vide supra). On the other hand, the more disordered shot coke  $\text{CF}_x$  follows the usual trend. It has a higher discharge potential than the calcined sponge coke  $\text{CF}_x$ .

Electrochemical discharge capacities do not appear to be a simple function of structural order when comparing  $\text{CF}_x$  materials from different natural and synthetic carbon types [11, 12, 21]. The shot coke  $\text{CF}_x$  had unexpectedly low discharge capacities (Fig. 3). It is anticipated from the XRD results that it would have a capacity similar to calcined sponge coke. However, shot coke comprises dissimilar carbon structural types [24, 25, 26, 27, 28]. It forms as spheres between 0.1 cm and 1 cm in diameter. The spheres comprise a smooth, dense external shell with low electrical conductivity, approximately 50  $\mu\text{m}$  thick. The core of these particles has a porous, fine-grained mosaic structure. It is likely that each constituent structural type has different electrochemical behavior. If one of these components has a low capacity, the overall discharge performance would be reduced.

The discharge capacity increases with increased structural order for  $\text{CF}_x$  prepared from sponge coke (Fig. 3). These data agree with another investigation using  $\text{CF}_x$  synthesized from a coal tar pitch coke sample that had been heated to different temperatures (Root MJ unpublished results), but only partially agree with the findings described in a US patent [10]. This disclosure teaches that  $\text{CF}_x$  electrochemical discharge capacity in a Li/ $\text{CF}_x$  cell increases as the coal tar pitch coke starting material is heated to 1800 °C, but decreases when it is heated to higher temperatures. The electrochemical discharge capacity of  $\text{CF}_x$  prepared from petroleum coke only decreases with increasing heating temperature of the starting material. The level of fluorination in the  $\text{CF}_x$  products was not considered, though. This is important because the  $\text{CF}_x$  synthesis conditions were not adjusted to account for the differences in carbon structure, which has a large effect on the fluorination reaction [6, 7, 8]. Since the electrochemical reduction reaction involves breaking C-F bonds, varying amounts of fluorine in the  $\text{CF}_x$  affect the overall cell discharge capacity. Care was taken during the fluorination reaction to obtain near

stoichiometric  $\text{CF}_x$  for the materials studied here and the F content was determined for each sample. Under these circumstances, capacity is observed to increase with the structural ordering of the  $\text{CF}_x$ , at least when the sponge coke starting material is heated to 1930 °C.

Figure 3 also compares the electrochemical discharge capacity of the new  $\text{CF}_x$  materials to a petroleum coke  $\text{CF}_x$  of the type commonly used in commercially available Li/ $\text{CF}_x$  electrochemical power sources. The  $\text{CF}_x$  prepared from heated sponge coke exhibited slightly higher discharge capacities than the petroleum coke  $\text{CF}_x$ . This shows that  $\text{CF}_x$  from sponge coke is an attractive cathode material for use in primary lithium electrochemical power sources.

The results from this investigation confirm that the electrochemical behavior of  $\text{CF}_x$  is at least partially, but significantly, dependent on the structural attributes of the carbon starting material. It is difficult to predict behavior when comparing  $\text{CF}_x$  materials prepared from different carbon sources. Still, it may be possible to deliberately tune the electrochemical properties of  $\text{CF}_x$  by modifying the structural ordering of the carbon starting material.

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