INTRODUCTION

Although lithium-ion batteries (LIBs) are currently widely used, particularly in the portable electronics and automotive industries, there remains a strong demand for more advanced battery systems with higher energy and power densities, better safety properties, and lower prices.\(^1,2\) Recently, Na/CF\(_x\) batteries have been mentioned as a new rechargeable battery system with great potential.\(^3,4\) Fluorinated carbon (CF\(_x\)) as a cathode material for lithium batteries was developed in 1979\(^5\) and was mainly used in primary cells. Compared with conventional metal fluoride conversion materials, the Li/CF\(_x\) cathode system is known to have a much higher energy density (2180 W-h kg\(^{-1}\), supposing that \(x = 1\), the highest theoretical energy density among solid cathode systems\(^6\)). At the same time, when coupled with a Na metal anode and used in a rechargeable system, the resulting batteries could compete against the current performance of LIBs in terms of cost and energy density (Na/CF\(_x\) system, 1439 W-h kg\(^{-1}\), supposing that \(x = 1\)). However, research on primary Li/CF\(_x\) batteries has indicated that the reaction of CF\(_x\) with lithium is likely irreversible, because of the strong electronegativity of elemental fluorine, which makes the discharge product LiF difficult to decompose merely by charging.\(^7\) In addition, the discharge products of Na/CF\(_x\) batteries include NaF, and the dissociation energy of NaF (5.65 eV) is lower than that of LiF (6.1 eV). This may lead to the presence of a reversible reaction in a Na/CF\(_x\) battery system when the Na/CF\(_x\) battery charges and discharges. Recently, the reversible generation and decomposition of NaF has been claimed to occur in these batteries,\(^3,4\) yet the primary evidence (X-ray photoelectron spectroscopy) of the presence of these reactions is information taken from the surface of the materials. The reaction mechanisms of the reversible conversion between CF\(_x\) and NaF have remained unclear, especially regarding the process of Na-ion diffusion and the evolution of the structure, and thus more information is needed to describe them.

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It is believed that fully understanding the reaction mechanism is very important for developing the Na/CF system since most follow-up work depends on having knowledge of it, in particular, improving the electrochemical performance of the CF material. In primary Li/CF battery, the relevant discharge reaction mechanisms have been studied and discussed.8 There are two main competing reaction processes: the discharge process of CF or fluorinated carbon, graphite.10 Conductivity and the layered structure of the cathode precursor materials was assessed using 2025 type coin cells, remarked upon in previous studies.20 The cathode was prepared by mixing 80 wt % fluorinated carbon fiber, 10 wt % acetylene black, and 10 wt % binder. Two binders were used, poly(vinylidene fluoride) (PVDF) and a commercialized binder, that is, an aqueous solution of acrylonitrile-based polymer (fluorine-free, LA-132, Chengdu Indigo Power Sources Company, Ltd., Chengdu, China). Sodium metal discs were used as counter electrodes and the electrolyte was 1 M NaClO4 dissolved in ethylene carbonate/dimethyl carbonate/fluorinated ethylene carbonate in a 49:49:2 volume ratio. With use of a current density of 20 mA/g, galvanostatic charge/discharge tests were performed using a LAND CT2001A battery test system at 30 °C. Cutoff voltages were 1.5 and 4.7 V, with constant voltage charging used until the current was less than 10 mA.

The GITT was performed by applying an intermittent current to cells for 3 h, followed by an 18 h rest. The pristine cells were cycled between 1.5 and 4.7 V at a current density of 20 mA/g. All discharge voltage data came from the first titration points of the GITT curve during the discharge process. The Umax (experimentally measured voltage) and Ueq (equilibrium voltage) were defined as the voltage values before and after the standing process, respectively. The value of ΔU was defined as the difference between Umax and Ueq and indicated the overpotential. Commercial fluorinated graphite (CF0.9, SICONG Novel Material Development INC., Xiamen, China) was also tested under the same conditions for comparison purposes.

Characterizations. Fluorinated carbon fiber cathodes were characterized in both charged and discharged states using pieces of the electrode and material manually collected from the electrode pieces. The electrode pieces and materials were removed from the coin cells in an Ar-filled glovebox and then sealed in foil bags to prevent air exposure before characterization. Powder X-ray diffraction (XRD) patterns of the samples were collected with a Rigaku Ultima IV instrument with Cu Kα radiation. Scanning electron microscopy (SEM) was performed on a S4800. All NMR experiments were performed in a 9.4 T magnetic field with a Bruker Advance III spectrometer. The 13C NMR spectra were acquired using a 4 mm probe head at a spinning frequency of 60 kHz and with a single-pulse sequence. A recycle delay of 30 s and a 45° pulse length of 1.5 μs were applied. Both the 23Na and 19F NMR spectra were recorded using a 1.3 mm probe head at a spinning frequency of 60 kHz and with a single-pulse sequence. A recycle delay of 60 and 20 s and 90° pulse lengths of 1.7 and 2.1 μs were applied for the 23Na and 19F data, respectively. The chemical shifts of 13C, 19F, and 23Na were calibrated using Tetramethylsilane (0 ppm), LiF powder (~204 ppm), and 1 M NaCl solution (0 ppm), respectively. Soft X-ray absorption spectroscopy was performed at Beamline 8.0.1 of the Advanced Light Source in Lawrence Berkeley National Laboratory. Electrode samples were loaded into the ultra high vacuum SXAS characterization chamber with a special sample transfer tool to avoid any air exposure effects. The undulator and spherical grating monochromator supplied a linearly polarized photon beam with a resolving power of up to 6000. The experimental energy resolution was about 0.15 eV. Experiments were performed at room temperature and with the linear polarization of the incident beam 45° from sample surfaces. The SXAS spectra were collected using both total electron yield (TEY) mode with the probing depth around 10 nm and total fluorescence yield (TFY) mode with the probing depth larger than 100 nm. All the spectra were normalized to the beam flux measured by the upstream gold mesh.

Theoretical Calculations. The presented calculations were performed using the projector-augmented wave method within the density functional theory (DFT), as implemented in the Vienna ab initio simulation package.21–23 The generalized gradient approximation in the form of a Perdew–Burke–Ernzerhof functional24 was used to treat the exchange-correlation energy. Wave functions were expanded by plane waves up to a kinetic energy cutoff of 500 eV. Brillouin-zone integrations were approximated by using special k-point sampling of the Monkhorst–Pack scheme,25 with a k-point mesh resolution of 2π × 0.025 Å−1. The cell parameters and the atomic coordinates were fully relaxed until the force on each atom was less than 0.01 eV Å−1.

### EXPERIMENTAL SECTION

**Materials.** Fluorinated carbon fibers were prepared by high-temperature gas-phase fluorination as described in previous work, using amorphous carbon fiber and working under fluorine-containing inert gas conditions.14

**Electrochemical Test.** The electrochemical performance of the materials was assessed using 2025 type coin cells, remarked upon in the previous studies.20 The cathode was prepared by mixing 80 wt % fluorinated carbon fiber, 10 wt % acetylene black, and 10 wt % binder. Two binders were used, poly(vinylidene fluoride) (PVDF) and a commercialized binder, that is, an aqueous solution of acrylonitrile-based polymer (fluorine-free, LA-132, Chengdu Indigo Power Sources Company, Ltd., Chengdu, China). Sodium metal discs were used as counter electrodes and the electrolyte was 1 M NaClO4 dissolved in ethylene carbonate/dimethyl carbonate/fluorinated ethylene carbonate in a 49:49:2 volume ratio. With use of a current density of 20 mA/g, galvanostatic charge/discharge tests were performed using a LAND CT2001A battery test system at 30 °C. Cutoff voltages were 1.5 and 4.7 V, with constant voltage charging used until the current was less than 10 mA.

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RESULTS AND DISCUSSION

Disordered carbon fiber without high-temperature treatment is similar to soft carbon material. Organized regions (graphene structure) and unorganized regions (tetrahedral and highly buckled carbon) together make up a special three-dimensional disordered carbon structure. Both sp² and sp³ hybridized carbon exist in the carbon fiber, as shown in Figure S1, Supporting Information. The precursor as well as the pristine fabricated materials were characterized by SEM, XRD, and ¹³C NMR, as shown in Figure 1. As can be seen in the SEM imagery of Figure 1a,b, both precursor and CFₐ₀.₇₅ materials have rod-shaped, short fiber structures on the order of micrometers in size. Because of the strong corrosive effects of fluorine atoms at high temperatures, the carbon fiber rod structure is somewhat irregular in morphology and some smaller or roughly shaped particles are visible after fluorination, although the materials appear otherwise similar. Figure 1c shows the XRD patterns of precursor carbon fiber and fluorinated carbon fiber samples. The large peak width implies the disordered structure and the distances between carbon layers of the precursor carbon fiber and fluorinated carbon fiber were calculated to be 0.35 and 0.66 nm, respectively. An F/C ratio of 0.75 was derived from the peak areas of the ¹³C NMR spectra shown in Figure 1d. The spectra peak at 128 ppm corresponds to C, and the peaks from CF and CF₂ are located at 85 and 112 ppm, respectively.

Figure 1. Characterization of pristine materials (a) SEM imagery of the carbon fiber and (b) the fluorinated carbon fiber CFₐ₀.₇₅ (c) XRD patterns of the precursor carbon fiber and the fluorinated carbon fiber CFₐ₀.₇₅ and (d) solid-state ¹³C NMR spectrum of the CFₐ₀.₇₅ material.

Since the fluorine in the binder would contribute strongly to the background signal when analyzing samples with sXAS, two kinds of binders were used, PVDF and a commercialized binder, that is, an aqueous solution of acrylonitrile-based polymer (fluorine-free, LA-132). As can be seen in the electrochemical performance data (shown in Figure 2a), samples with different binders have similar first and second discharge capacities. This shows that the binder compound gives no substantial contribution to the performance of the material. Over the voltage range of 1.5−4.7 V, the material delivered a high reversible discharge capacity of 350 mA⋅h g⁻¹ and a long initial discharge voltage plateau at 2.75 V (the highest seen yet in this family of compounds). As shown in Figure 2b, during the charge process, the equilibrium potentials are almost identical. However, because of continually increasing charge overpotential, the voltage increased along with the charging progress. This implies that the conductivity of the material deteriorated with the generation of CFₓ during the charging process. Unfortunately, the electrolyte was unstable and seriously decomposed at high voltages, which hindered

Figure 2. Electrochemical performance (a) and (b) GITT measurements of the fluorinated carbon fiber CFₐ₀.₇₅.
further progress of the redox reaction and resulted in a low Coulombic efficiency. Reducing the charge overpotential and optimization of the electrolyte are thus the straightforward but key goal for our further research with this cathode material.

To further understand the charge and discharge mechanisms of the material and prove the existence of a reversible conversion reaction between CFₓ and NaF, sXAS and NMR were used to characterize the material at different charge and discharge states and to give the surface and bulk information, respectively. F K-edge sXAS is sensitive to the transformation of different chemical species and bonds in conventional reactions via the core electron excitation process. The two detection modes of sXAS, total electron yield and total fluorescence yield, provide 10 nm sensitive and 100 nm sensitive information, respectively.

As shown in Figure 3a, CF₀.₇₅ and NaF produce very distinguishable F K-edge sXAS spectra. The CF₀.₇₅ sXAS spectrum has no sharp features above the absorption threshold, reflecting the presence of C−F covalent bonds. By contrast, the ionic compound NaF displays multiple relatively defined features that are related to the strong core-hole effect. These dramatically different sXAS spectra enable the monitoring of the conventional reaction in the electrode. Figure 3b shows a sequence of F K-edge sXAS spectra collected from electrode samples at different states of charge. The transformation between CFₓ and NaF during electrochemical cycling is revealed by the reversible changes seen in the spectra. In addition, the surface-sensitive TEY spectra (Figure S2) show no essential differences compared with the bulk-sensitive TFY spectra. There is no signal from NaF at the charged state (4.7 V), which implies that the NaF to a depth of at least 100 nm is fully converted during the charging process. Electrochemical performance will suffer if the discharge mechanism in Na battery is merely a surface reaction, just like that of Li battery.

To get more information, particularly regarding the local environment of the fluorine in the samples during charge and discharge, ex situ solid-state NMR was used to analyze the CF₀.₇₅/Na system. As Figure 4c and Figure S3a show, the structure of CF₀.₇₅ is complex, and the ¹⁹F NMR spectra of the CF₀.₇₅ material can effectively determine that C−C−F structures and CF₂ groups predominated, which exhibit chemical shifts of −178 and −114 ppm, respectively. The fluorine in the PVDF binder is also represented in the NMR data. Its shift of −90 to −105 ppm (as shown in Figure S3b) is almost unchanged during the charge and discharge processes, further suggesting that no binder fluorine contributed to the electrochemical activity of the battery.

Because of the unique multidefect disordered structure of the carbon fiber, during the process of fluorination, the free diffusion of fluorine atoms was limited and caused an uneven distribution to develop. More fluorine gathered on the surface of the material, causing the CF₂ groups to be formed at the edges or in defects of the graphene structure. The F/C ratio of the interior material is lower than the calculated value of 0.75, which reflected the average value of the whole material, with the C−C−F structure predominating. The structure can be described as a fluorine atom bonded with a carbon atom, which is also bonded with the unfluorinated carbon atoms at the same time (namely, (CₓFᵧ)). Early reports in the literature suggested that these CF₂ structures are electrochemically inactive in LIBs due to a larger bond energy and thus larger energy barrier. However, as NMR spectra during the first discharge process show (Figure 4c), the CF₂ structures in the fluorinated carbon fiber must have reacted at the same time with other CF structures during the discharge process, contributing to the discharge plateau at 2.75 V. This implies that the CF₂ structures could have been active in this system and the different C−F structures were indistinguishable during the reaction sequence.

The NMR data in Figure 4b shows the reversible formation and decomposition of NaF, which can be detected from the changes in peak area. It corresponds well with the sXAS data. Furthermore, the generation of C−F bonds during the charge process can be clearly observed. The structure of the CFₓ generated during charge process was different from that in the pristine material, which is also reflected in two different equilibrium potentials (as shown in Table S1). As Figure 4c shows, two new peaks located at −163 and −191 ppm appear in the spectra during the first charge process. The peak located at a shift of −191 ppm corresponded well with the structure with parts of the graphene layers fully covered with fluorine (namely, (CFₓ)₀,). However, the peak found at a shift of −163 ppm is not well understood. The authors suggest it implies an intermediate state C−F bond, somewhat similar to semicovalent C−F and ionic C−F bonds, which exhibit chemical shifts of −147 and −171 ppm, respectively. This intermediate C−F bond would have a lower energy and be unstable, being first generated in the charge process. Then with more fluorine atoms being generated from the decomposition of NaF, the CFₓ generated in the charge process would transform into a relatively stable structure.

Figure 4b clearly shows that there is only a small increase in peak area corresponding to C−F bonds compared with a decrease in peak area for NaF, as cycling continues. This anomalous behavior may be due to the fact that the spin−spin relaxation time (T₂) of the CFₓ generated during the charging process was much shorter than that of the NaF. Calculations

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correcting for this factor were carried out to verify that the charge and discharge state specific integrated areas were in fact equal, as shown in Figure S.

The peak areas of the NMR spectra were integrated and corrected using Origin software, with corrections using the following formula,

\[ S' = S_0 \cdot \exp\left(\frac{33.33}{T_2}\right) \]

where \( S_0 \) is the integral area of the cathode material in a pristine state (here fit as “1”), \( S \) the corrected area, and \( S' \) the tested area. The areas of CF \(_x\) and NaF were calculated separately and the spin–spin relaxation times \( T_2 \) were used to correct them. The newly generated CF \(_x\) value was different from the original, with a spin–spin relaxation time \( T_2 \) of 0.937 ms, which was shorter than the pristine \( T_2 \) of 1.48 ms. In addition, the \( T_2 \) of both generated and decomposed NaF was the same value, 1.2 ms. The corrected areas of CF \(_x\) at different charge and discharge states were necessarily a little smaller than their actual values since the area coinciding with the PVDF peak was not included in the calculation producing the CF \(_x\) value (the integration from \(-105\) to \(200 \text{ ppm}\)). However, the change in fluorine between CF \(_x\) and NaF can be clearly observed.

As Figure 4d shows, there is only one NaF peak in the \(^{23}\text{Na}\) NMR spectra. There was no alternative process such as the reaction of sodium with carbon that could contribute to the discharge capacity. Thus, the second discharge capacity was primarily a result of the CF \(_x\) generated during the first charge process. Because of the smaller discharge overpotential (as shown in Table 1) and partly converted CF \(_x\), the discharge capacity was observed in the beginning of the second discharge process with the voltage and then decreasing gradually. The discharge curve is similar to that of fluorinated carbon CF \(_x\) materials with a low F/C ratio \((0.18–0.33)\), as reported in the literature.\(^{10,12,13}\)

Countering this and increasing the F/C ratio of charging production is possible by introducing a more suitable electrolyte, perhaps an ionic liquid electrolyte or solid electrolyte, or by somehow reducing the polarization voltage and letting the redox reaction be carried out to completion.

Table 1. Discharge Voltage of CF \(_x\) Measured by GITT Tests

<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>( U_{\text{meas}} ) (V)</th>
<th>( U_{\text{eq}} ) (V)</th>
<th>( \Delta U ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFG CF0.75-first cycle</td>
<td>2.26</td>
<td>2.95</td>
<td>0.69</td>
</tr>
<tr>
<td>FCF CF0.75-first cycle</td>
<td>2.79</td>
<td>3.30</td>
<td>0.51</td>
</tr>
<tr>
<td>FCF CF0.75-second cycle</td>
<td>2.90</td>
<td>3.26</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Note: CFG and FCF represent commercial fluorinated graphite and fluorinated carbon fiber, respectively.

Figure 4. Analysis of solid-state NMR spectra from the CF0.75/Na system with PVDF as binder, revealing changes in the material structure at different charge and discharge voltages. (a) The electrochemical profile of CF0.75 cycled at a current density of 20 mA/g. (b)–(d) Ex situ \(^{19}\text{F}\) and \(^{23}\text{Na}\) NMR spectra of samples cycled to various states of charge and discharge, as marked on the electrochemical profile, with (c) a magnification of the shift from 0 to \(-250 \text{ ppm}\) from (b) in order to more clearly view the peak intensities. In the figure, the abbreviations 1st D-1.5V and 2nd C-4.2 V correspond to discharge to 1.5 V in the first cycle and charge to 4.2 V in the second cycle, respectively.

Figure 5. NMR spectra integral areas of the materials at different charge and discharge voltages.
Unlike in the sXAS data, NaF remained observable in cells at a charged state in the NMR spectra. That data corresponded well to the electrochemical performance and implied the generation of NaF was not merely on the surface. For the conversion reaction process, there are only two possible mechanisms: fluorine ion outward diffusion or sodium-ion inward diffusion. Regarding the former, the generation of NaF mainly occurs on the surface of the material. In addition, the CF<sub>x</sub> material is different from traditional conversion materials, which form chalklike smaller particles during the cycling process. The carbon framework structures on the order of micrometers in size will remain since the C–C bond does not react during the charge and discharge processes (as shown in Figure S5). With this in mind, the difference between the sXAS and NMR data implies that NaF must be generated in the bulk of the materials and thus the mechanism of the reaction is more likely to be determined by sodium-ion diffusion. During the discharge process, the sodium ions could diffuse into the interior of the cathode material and generate NaF in the layer space of the carbon structure. This characteristic may benefit the regeneration of CF<sub>x</sub> upon charging.

The discharge voltage is always an important factor in determining the possible applications of the cathode material. For commercial fluorinated graphite materials, in LIBs, the discharge voltage (2.2 V, as shown in Figure S5a) is too low for wide use. However, the material prepared here shows a high discharge plateau at 2.75 V, which is even higher than that of commercial fluorinated graphite material performed in LIBs (2.7 V). That greatly expands the application range of the material and even makes Na/fluorinated carbon fiber systems a potential competitor with commercial Li/CF<sub>x</sub> cells in the field of primary batteries, considering the cost advantages.

To further understand the high voltage observed, DFT calculations were combined with galvanostatic intermittent titration technique (GITT) measurements. As shown in Table 1, the experimental measured voltage of fluorinated carbon fiber CF<sub>0.75</sub> (2.79 V) was far higher than that of fluorinated graphite CF<sub>0.9</sub> (2.26 V). In addition to a smaller discharge overpotential (0.18 V), there was also a large voltage difference of about 0.35 V. DFT calculations were undertaken to understand this substantial voltage difference. Compared with the commercial fluorinated graphite CF<sub>0.9</sub>, the fluorinated carbon fiber material CF<sub>0.75</sub> had a different F/C ratio and carbon structure. With use of graphite for an AB stacking model ([C + C]<sub>x</sub>), the calculated voltages of fluorinated graphite (stable structure) with different F/C ratios x are shown in Figure 6. Considering that the state of NaF generated in the discharge process was undefined, different kinds of NaF structural models (as shown in Figure S6) were adopted for the calculations, whose total energy was between that of an individual molecule and the bulk material. As shown in Figure 6a, fluorinated graphite with different F/C ratios had similar calculated voltages, especially when x was higher than 0.5. Their differences cannot explain the voltage gap of 0.35 V. In addition, fluorinated ordered carbon nanofibers with a similar layered structure also did not show as high a discharge voltage as the CF<sub>0.75</sub> material, which probably suggested that the high voltage was mainly caused by the special multiple-defect disordered structure of the carbon fiber.

In thermodynamics, the more stable the structure, the lower the voltage observed in electrochemical testing. For this family of CF<sub>x</sub> materials, a graphene layer fully covered with fluorine (namely, the (CF)<sub>x</sub> structure) is the most stable structure possible. When graphite or similarly layered carbon material is used as a precursor, fluorine atoms can diffuse evenly during the fluorination process and tend to fully cover one graphene layer with fluorine while other layers are left pristine<sup>18,31</sup> ([CF<sub>1</sub> + CF<sub>x</sub>]<sub>x</sub> or [CF<sub>1</sub> + CF<sub>x</sub>]<sub>x</sub> x < 1). Because of the high temperature and presence of excess fluorine involved in high-temperature gas-phase fluorination, which commercial production primarily uses, stable structures are more likely to be generated. However, when considering special carbon fiber materials, defects and a disordered structure hinder the free diffusion of fluorine atoms during fluorination. The kinetic factor may cause some metastable structures with higher energy ([CF<sub>1</sub> + CF<sub>x</sub>]<sub>x</sub> x < 1) to be generated and produce a pristine material that displays superior discharge voltage. However, during the discharge process, the fluorine converts into NaF and redistributes evenly. The kinetic factor will disappear and a stable structure will be generated during the charge process. This corresponds well with the NMR data mentioned previously, which determined that the (CF)<sub>x</sub> structure occupies most of the interior of the material rather than (CF), and the charge product possesses a (CF)<sub>x</sub> structure. Attempts have been made to identify several possible structural models of CF<sub>0.5</sub>, as shown in Figure S7. This unique structural
model is hard to determine because the structure of the disordered carbon fiber is complex and the influence of the kinetic factor is stochastic. However, as shown in Figure 6b, the metastable structures show a higher calculated voltage and the voltage difference between the stable structures and metastable structures could coincide with the observed voltage gap of 0.35 V.

Taken together, the high discharge voltage is primarily caused by the factors both in kinetics and thermodynamics. Compared with layered-structure fluorinated graphite, the three-dimensional carbon framework and lower F/C ratio improve the electronic conductivity of the material and thereby decrease the discharge overpotential. In addition, the disordered structure causes the generation of a metastable structure during the fluorination process, producing a discharge advantage from the thermodynamics.

Although this particular result holds for the CF0.75 material, the fact that the different NaF structures could also influence the discharge voltage should not be overlooked. As shown in Figure 6, the calculated voltages of CF3 producing a structure with 1–3 layers of NaF are closer to the equilibrium potential of experimentally tasted material, which corresponds well to the mechanism of sodium-ion diffusion. For the CF2 structures, which are active in this system and also contribute to the discharge capacity, the calculated voltage is lower than that of the CF structures which are modeled the same as produced NaF. The positive contribution of the CF2 groups may be only increasing the specific capacity, although the CF2 structures are mainly distributed on the surface of the materials and may cause the production of NaF with different structures. The discharge voltage and cycling performance will be further enhanced if the generation of similar structures is avoided in the fluorination process, and yet at the same time the specific capacity of the material will decline.

Combined with the experimental results mentioned previously which observed a certain amount of NaF being generated in the bulk of the material, a schematic of a Na-ion diffusion reaction mechanism in the Na/CF0.75 system can be proposed (as shown in Figure 7). The disordered structure of the pristine CF0.75 is complex and in a metastable state. Different kinds of metastable structures all coexist, with some associated with an ultra high discharge voltage. During the discharge process, sodium ions diffuse into the bulk of the material and generate NaF in the layer space of the carbon structure. All the carbon–fluorine structures react simultaneously and cause the material to perform with a high discharge voltage during the first cycle. During the charge process, the metastable structures do not reform, and limited by the large polarization voltage and a lack of suitable electrolyte, only a portion of the NaF decomposes. The reversible process is thus a cycle between partly converted CF3 with a relatively stable structure and NaF. Of course, this hypothesis needs further research to be shown conclusively.

**CONCLUSIONS**

Fluorinated carbon fiber CF0.75 is investigated as a novel cathode with high working voltage for rechargeable Na batteries. Because of the special three-dimensional disordered carbon structure of the precursor, the CF0.75 material contained metastable structures and displayed a smaller overpotential, which made it superior in discharge voltage to other members of its family of compounds. Unfortunately, the metastable structure was not reformed during the cycling process, although the improved electronic conductivity could be maintained. When coupled with a Na metal anode and cycled, the resulting battery showed a respectable amount of reversible capacity. Characterization from sXAS and NMR techniques are used to determine that the source of the capacity resulted from reversible reactions between CF3 and NaF. All the data implies a mechanism of Na ion diffusion during the cycling process, particularly in the bulk of the material. A schematic reaction mechanism of the Na/CF0.75 system is proposed based on our experimental and theoretical calculations. Limited by the large polarization voltage and a lack of suitable electrolyte, the reversible conversion as of yet only undergoes a partial reaction. Anyway, it is believed that the Na/CF3 system possesses the potential to become a high-energy density and low-cost battery, which has wide prospects for application, in particular, to large-scale energy storage.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b03762.

Detailed information involving the whole set of NMR spectra, sXAS spectra, SEM figures, and GITT curves as well as the theoretical calculation data (PDF).
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Author Contributions
Y.S. and H.Y. carried out the materials preparation and electrochemical testing. Y.S. acquired and analyzed the XRD and SEM data. G.Z. acquired the NMR data; G.Z. and Y.S. analyzed the NMR data. R.Q. carried out the sXAS experiments. R.Q., S.Y., W.Y., and Y.Y. processed and analyzed the sXAS data. J.H. carried out the DFT calculations; J.H., J.H., S.W., and Z.Z. processed and analyzed the DFT data. M.M., Z.G., and R.Q. modified the paper. Y.Y. and Y.S. proposed the research, and Y.Y. attained the main financial support for the research.

Notes
The authors declare no competing financial interest.

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