

Supporting Information

A rechargeable room-temperature CF_x-sodium battery

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Experimental

Assembly and Electrochemical measurements

CF_x cathode was prepared with a composition of 80wt% CF_x (Jiangsu Zhuoxi Fluorination Technology Co. Ltd., x=1.0), 10wt% vapor-grown carbon fiber (VGCF) conductive additive and 10wt% polyvinylidene fluoride (PVDF) binder by mixing calculated amounts of CF_x, VGCF and PVDF in 1-methyl-2pyrrolidone (NMP) solvent and then was casted onto Al current collector, followed by drying at 60°C for 24h. These electrodes were prepared for physical characterization, such as XRD, SEM and EDX.

In order to avoid the side reaction of fluorine from PVDF, the preparation of electrode for electrochemical measurement was quite different. The CF_x power was dispersed into alcohol, than was casted onto the foam Ni, followed by drying at 60°C for 24h.

For electrochemical measurement, conventional home-made two-electrode cells and CR2016 coin cells were constructed in the argon-filled glove box with the CF_x as the cathode and one sheet of high-purity sodium foil as the anode, respectively. The home-made two-electrode cell consists of an H shape glass tube to separate positive and negative electrodes as well as two rubber plugs for sealing. The electrolyte was 0.25M NaPF₆ (Alfa Aesar) non-aqueous solution in 1,2-dimethoxyethane(DME) (Alfa Aesar). Weight of active material was directly obtained by subtracting the original substrate weight from total weight of the substrate and CF_x composite onto its surface, which were examined by electrobalance (BP 211D, Sartorius). The precision of the weight was ± 0.01 mg. Electrochemical measurements were performed at room temperature with a Land CT-2001A battery test system. The current density and capacity were calculated by dividing the current and capacity by the total mass of CF_x on the electrode.

Physical characterization

The XRD patterns of CF_x composite electrodes were investigated via a Bruker D8 advance diffractometer equipped with Cu-K α radiation ($\lambda=1.5406\text{\AA}$). SEM images and EDX spectra were captured using a field emission scanning electron microscope (HITACHI S-4800) operated at an accelerating voltage of 10kV. XPS analyses were carried out on a PHI 5000C ESCA system with monochromatic Al-K α X-ray source. For the *ex situ* measurements, care must be taken in the handling of samples at different states to avoid the exposure to oxygen or water. The cells were disassembled in the argon-filled glove box and the samples were rinsed in anhydrous DME to eliminate residual salts, the active materials were transferred into the chambers in several seconds for XRD, SEM and XPS measurements.

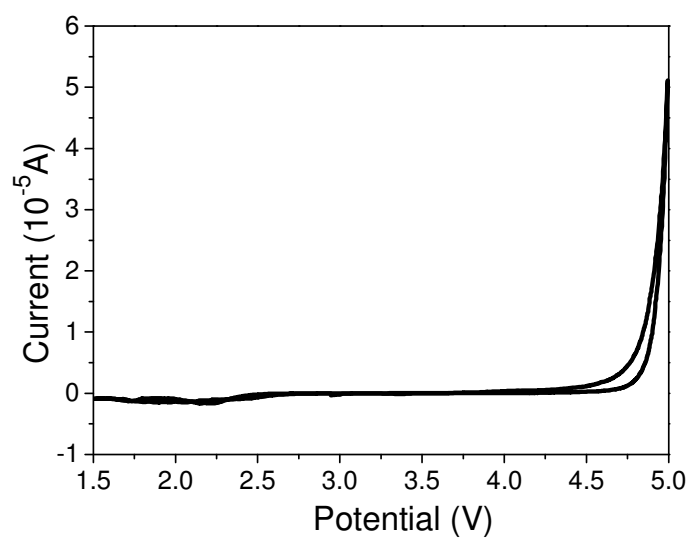


Figure S1 The CV curve of the electrolyte used in Na-CF_x cells.

From the CV curve of the electrolyte used in Na-CF_x cells, it can be sure that the electrolyte was stable from 1.5V to 4.4V. The electrolyte will be decomposed above about 4.4V.

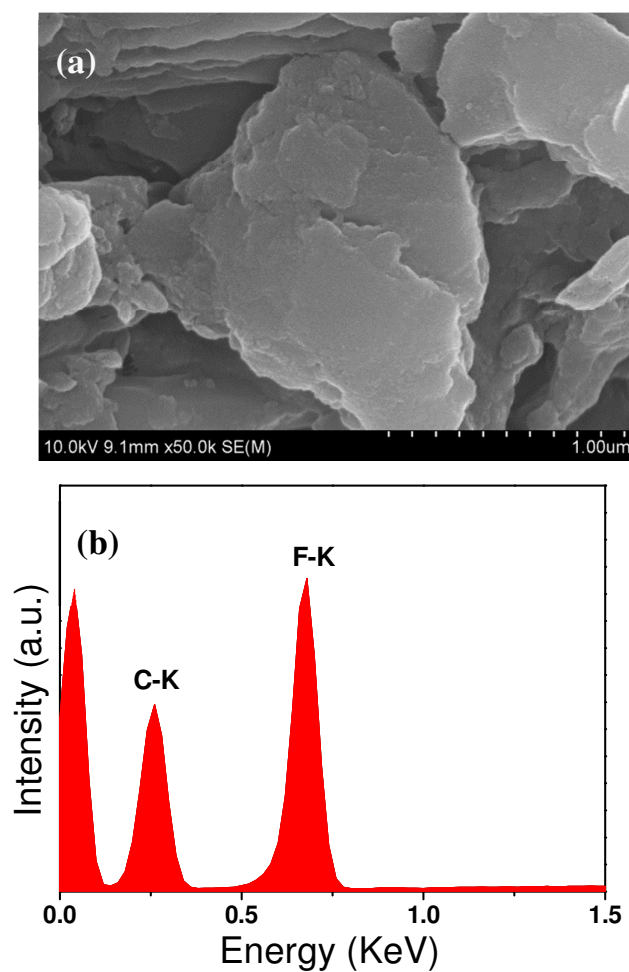


Figure S2 (a) SEM micrograph of a pristine CF_x electrode and (b) corresponding EDX spectra.

The surface of the pristine CF_x electrode is smooth macroscopically without any cubic shaped particles distributed on its surface as shown in Figure S2(a). The average molar concentration ratio of $\text{F/C}=0.83/1$ in pristine CF_x electrode which is composed of 80wt% CF_x ($x=1.0$), 10wt% VGCF and 10wt% PVDF.

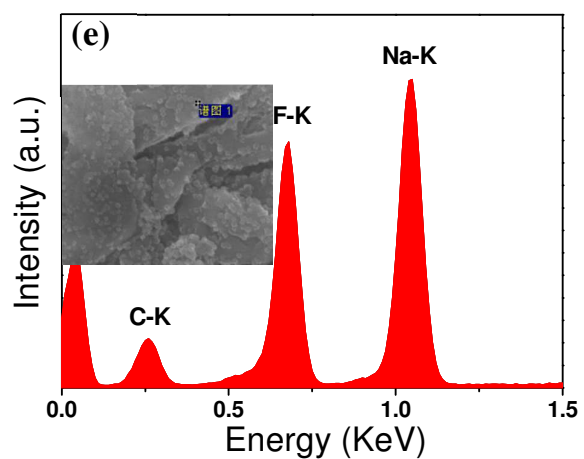
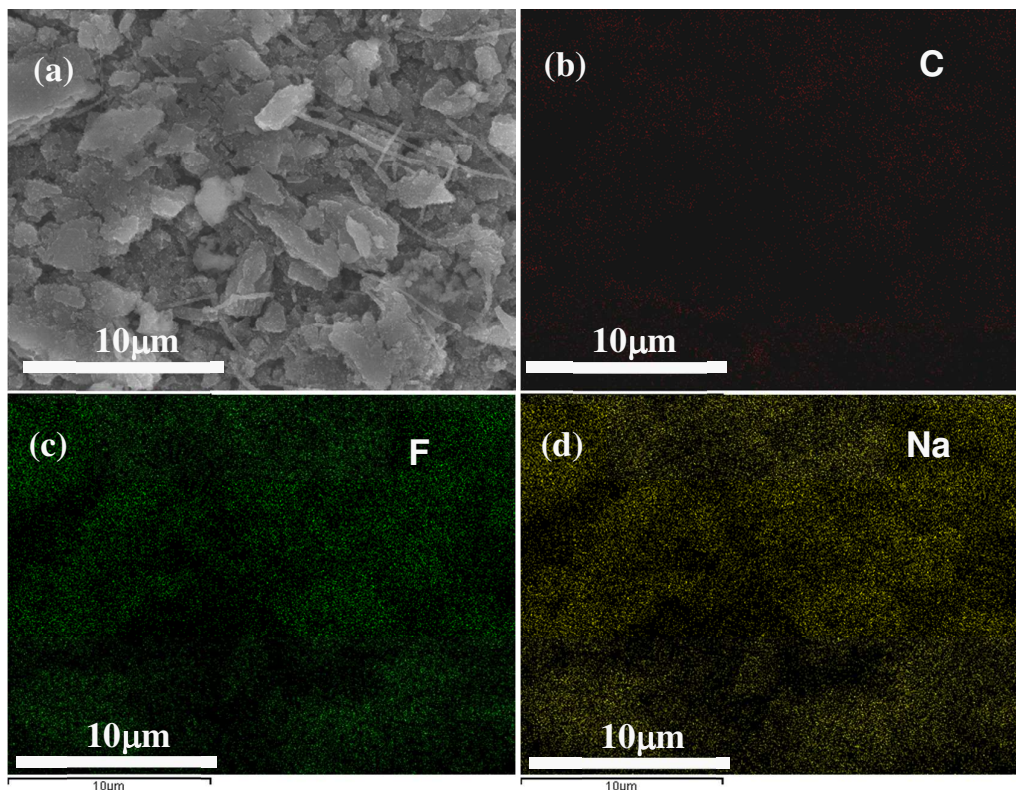


Figure S3 (a) SEM image of (a) CF_x electrode after the first discharging to 1.5V and corresponding elemental mapping of (b) C, (c) F and (d) Na; EDX spectra in the selected area (Insert).

The fluorine and sodium elemental mappings clearly exhibit the same distributions of Na and F atoms on the surface of the electrode after the first discharging to 1.5V, indicating that the chemical composition of the discharge product consist of F and Na

after the discharge process. EDX indicates that the average molar concentration ratio of F/Na/C=1.04:0.65:1. The amounts of the element fluorine are higher than that of sodium, which may be caused by the conducting salt (NaPF_6). These results suggest that the electrochemical reaction of CF_x with sodium to form NaF after discharge process.

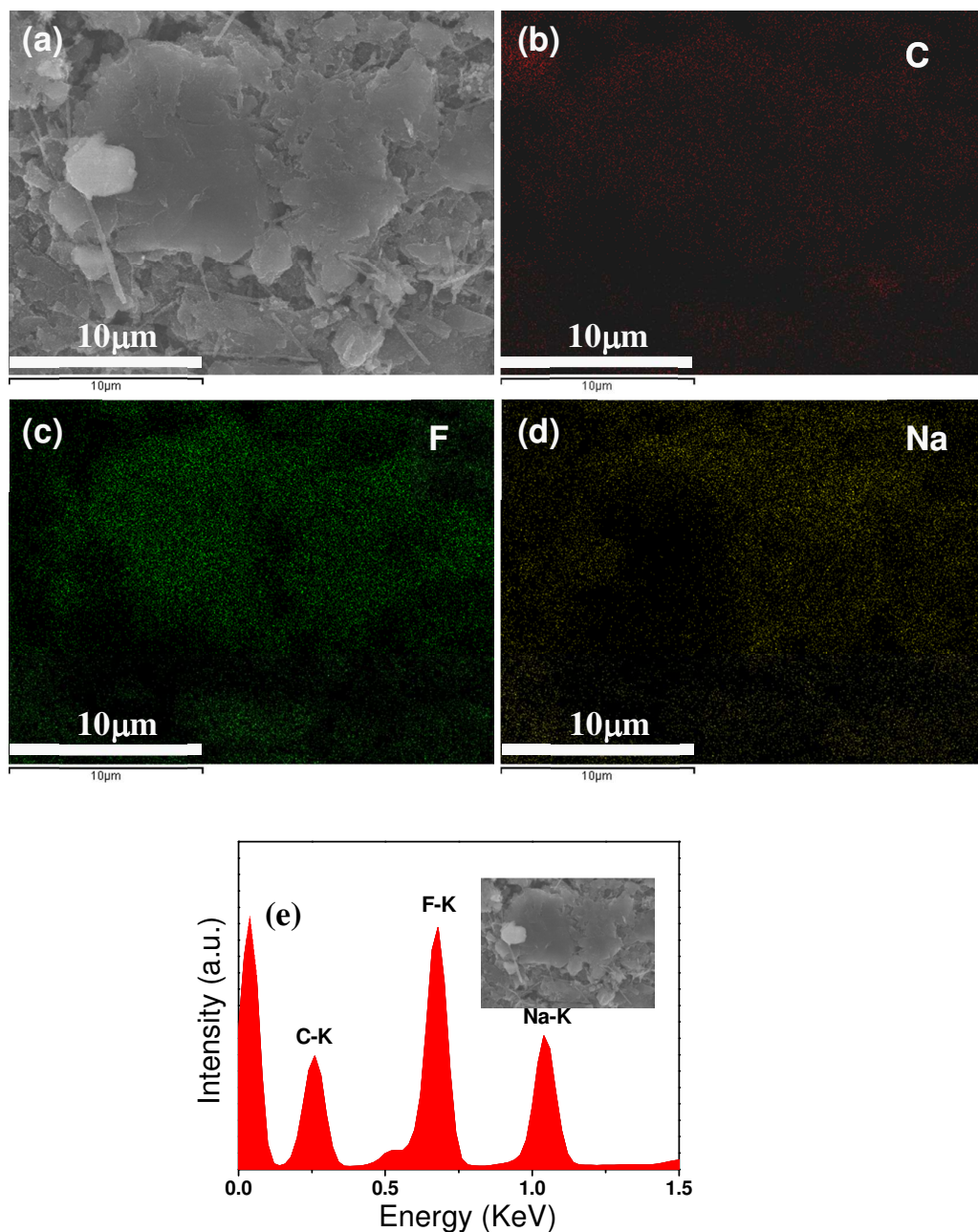


Figure S4 (a) SEM image of (a) CF_x electrode after the first charging to 4.4V and corresponding elemental mapping of (b) C, (c) F and (d) Na; EDX spectra in the selected area (Insert).

After charge process, the distribution of fluorin and sodium elemental are different (Figure S4(c-d)), and the amounts of sodium elemental are much lower than fluorin, indicating that the discharge products NaF are decomposed. EDX indicates that the average molar concentration ratio of F/Na/C=0.78:0.20:1.0. The exist of sodium may be caused by the incompletely decomposed or the conducting salt (NaPF₆).

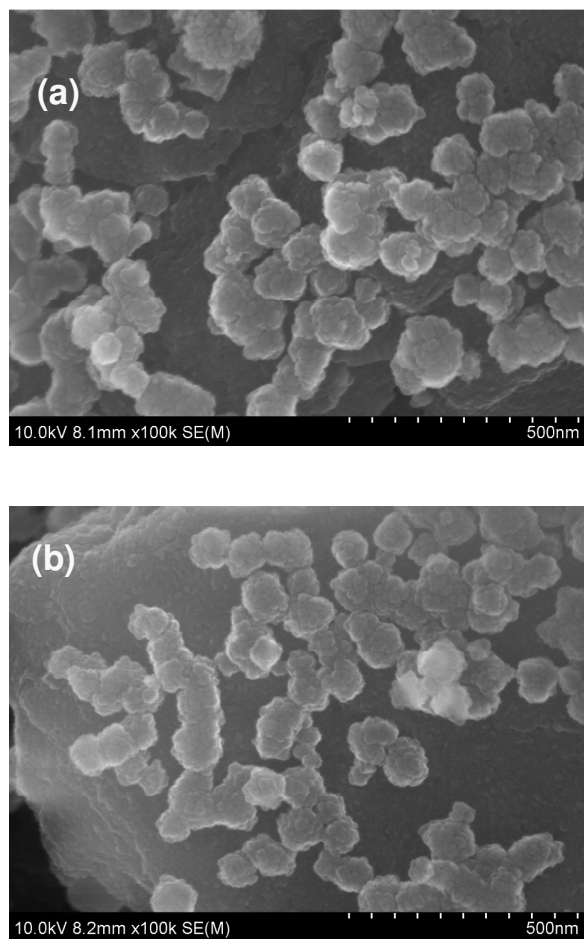


Figure S5 SEM image of CF_x electrode (a) after the first discharging of Li/CF_x cell to 1.5V; (b) after the first charging of Li/CF_x cell to 4.4V

Many cubic crystals were distributed randomly on the surface, with an average size of 150nm. Apparently, the sizes of the discharged products (LiF) are larger than those of NaF (70nm) as shown in Figure 2(b). After the first charging to 4.4V, these cubic particles remain on the surface of electrode as shown in Figure S5(b), indicating the irreversible reaction of Li/CF_x cell.

Table S1 Physical parameters of LiF and NaF.

	LiF	NaF
Gibbs free energy ΔG (KJ/mol)	-588.68	-545.17
Lattice parameter (nm)	0.40279	0.462
Ion conductivity(S/cm,44°C)	2.38×10^{-16} ^[1]	6.96×10^{-16} ^[2]
Bond length (10^{-12} m)	----	193
Bond energy (kJ/mol)	----	519
Dissociation energy (eV)	6.10	5.65

Li ion radius: 0.076nm

Na ion radius: 0.102nm

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Table S2 Sodium storage properties of CF_x and other materials reported recently.

Materials	Discharge Plateau(Range) Voltage(V)	Discharge Capacity (mAh/g)	Current Density	Reference
Na _{0.74} CoO ₂	2.7-3.6	107	0.1C	1
NaCrO ₂	2.9	110	0.05C	2
Na[Ni _{1/3} Fe _{1/3} Mn _{1/3}]O ₂	2.8-3.5	120	0.1C	3
Na _{2/3} [Fe _{1/2} Mn _{1/2}]O ₂	1.5-4.3	190	0.05C	4
NaVO ₂	1.5,2.2	120	0.05C	5
Fe ₂ (MoO ₄) ₃	2.5,2.6	91	0.1C	6
Na ₃ V ₂ (PO ₄) ₃	3.4	98	0.05C	7
KFe ₂ (CN) ₆	2.9, 3.7	100	0.05C	8
Na _{1.40} MnFe(CN) ₆	3.4	134	0.1C	9
NaFeF ₃	1.5-4.5	170-180	0.01C	10
SeS ₂	0.5-3.5	288	0.2C	11
MoSe ₂	0.3-3	106	0.1C	12
V ₂ O ₅	2.5-3.5	230	0.1C	13
Cu ₂ Se	1.9	253	0.1C	14
P	0.5-1.2	1764	0.1C	15
S	1.3-2.0	251	0.1C	16
Se	1.2-1.4	320	0.1C	17
Na ₂ FePO ₄ F	3.0-3.5	108	0.1C	18,19
NaFeSO ₄ F	2.5-3.5	83	0.1C	20,21
Na ₄ Co ₃ (PO ₄) ₂ P ₂ O ₇	4.1-4.7	95	0.2C	22
FeF ₃ 0.5H ₂ O	0.8-4.0	250	0.1C	23
BPOE	1.0-4.0	200	0.05C	24

O ₂ (air)	1.8-2.3	2030	0.1C	25
CF _x	1.5-2.3	786	0.1C	This work

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