



Fluorination regulates heat generation in Ah-level lithium/fluorinated carbon pouch cells

Xia Xixian¹, Li Yu⁴, Sun Lidong⁵, Peng Cong⁴, Kong Lingchen¹, Wang Yong¹, Feng Wei^{1,2,3,*}

(1. School of Materials Science and Engineering, Tianjin Key Laboratory of Composite and Functional Materials, Tianjin University, Tianjin 300072, China;

2. School of Materials Science and Engineering, Key Laboratory of Advanced Ceramics and Machining Technology of

Ministry of Education, Tianjin University, Tianjin 300072, China;

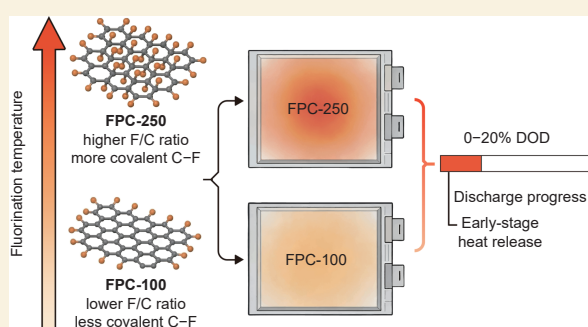
3. State Key Laboratory of Precious Metal Functional Materials, Tianjin University, Tianjin 300072, China;

4. Institute of Advanced Technology and Equipment, Beijing University of Chemical Technology, Beijing 100029, China;

5. Guangdong Provincial Key Laboratory of New Energy Materials Service Safety, Shenzhen Key Laboratory of Energy Electrocatalytic Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518071, China)

Abstract: Lithium/fluorinated carbon (Li/CF_x) batteries are among the most promising high-energy-density primary batteries. However, substantial heat generation during discharge remains a safety concern, particularly for high-mass-loaded pouch cells. Fluorinated porous carbon (FPC) samples with different degrees of fluorination were obtained by changing the fluorination temperature, and their effects on heat generation in Ah-level Li/FPC pouch cells were examined. The fluorination temperature not only influences the F/C ratio, but also the C–F bonding configuration, and physicochemical properties of the FPC. Pouch cells using the more highly fluorinated cathodes generated the most heat during discharge. The heat generated also has a clear stage dependence, with the largest difference appearing in the 0–20% depth of discharge range. Post-discharge structural characterization and kinetic analysis showed that the highly fluorinated FPC cathodes have more LiF accumulation concentrated in certain regions, together with a higher charge-transfer resistance, stronger polarization, lower Li⁺ diffusivity, and a higher nucleation overpotential. These factors collectively intensify the early-stage heat generation in the cells. This study shows that the fluorinated cathode structure, LiF evolution, and discharge kinetics jointly govern heat generation in Li/FPC pouch cells, possibly providing a way to improve their thermal safety.

Key words: Fluorinated porous carbon cathodes; Fluorination temperature; Pouch cells; Heat-generation behavior; Thermal safety



1 Introduction

Lithium/fluorinated carbon (Li/CF_x) primary batteries are widely used in aerospace, military equipment, emergency power supplies, and long-life electronic devices because of their high theoretical specific energy (2180 Wh/kg), low self-discharge rate, and excellent storage stability (> 10 years)^[1–2]. With the growing demand for high-energy-density primary batteries, the Li/CF_x system has attracted renewed attention^[3–4]. However, substantial heat generation during discharge remains a major safety concern, particularly under high-rate and high-mass-loading conditions. The discharge reaction is exothermic, and the

CF_x cathode is intrinsically poorly conductive^[1]. These factors can cause severe polarization and local heat accumulation, leading to a pronounced temperature rise and higher risks of electrolyte decomposition, separator shrinkage, and internal short circuit. Therefore, suppressing heat generation is critical for the safe application of Li/CF_x batteries.

The discharge behavior of Li/CF_x batteries is

Received: April 12, 2026

Revised: May 15, 2026

Accepted: May 15, 2026



closely related to the structural and chemical characteristics of the CF_x cathode^[5–6]. As the active fluorine reservoir, the cathode determines the available capacity through its fluorine content and C–F bonding configuration. At the same time, its carbon framework, pore architecture, defect structure^[7–8], and electronic transport capability affect electrolyte accessibility, charge transfer, and reaction uniformity during discharge^[9–10]. Therefore, the cathode structure is not only a capacity-determining factor, but also an important materials parameter that influences the discharge stability and thermal response of Li/ CF_x batteries.

Recent studies have examined the thermal behavior of Li/ CF_x batteries from several complementary perspectives. Chen et al.^[11] conducted calorimetric and simulation-based analyses of battery heat generation, thereby providing insight into the cell-level thermal response during discharge. Wan et al.^[12] developed embedded sensors for in situ thermal monitoring and safety warning in Li/ CF_x batteries. More recently, Du et al.^[13] identified LiF nucleation as a kinetic bottleneck for heat generation and demonstrated that LiF pre-nucleation can effectively mitigate the associated temperature rise. Concurrently, mechanistic studies by Sayahpour et al.^[5], Leung et al.^[14], and Zhang et al.^[15] have advanced the understanding of the discharge pathway, LiF evolution, and structural changes of CF_x cathodes during discharge. Nevertheless, the thermal consequences of fluorination-induced variations in cathode chemistry and microstructure have been examined less systematically.

In this study, the fluorination degree of fluorinated porous carbon (FPC) cathodes was systematically tuned by varying the fluorination temperature. The resulting FPC cathodes were assembled into Ah-level Li/FPC pouch cells. Unlike previous studies that mainly focused on cell-level heat analysis, safety monitoring, heat-mitigation strategies, or general discharge mechanisms, this work takes the fluorination-engineered cathode itself as the structural variable. The relationship between cathode properties and heat-generation behavior was investigated by correlating fluorination-induced changes in fluorine content, C–F bonding configuration, pore structure, and electronic

transport capability with heat generation in pouch cells. Pouch-cell thermal measurements, post-discharge structural characterization, and kinetic analysis were combined to identify the respective roles of LiF evolution and kinetic polarization in stage-dependent heat generation. These results demonstrate that fluorination-induced changes in cathode structure and kinetics are closely associated with heat generation in Li/FPC pouch cells.

2 Experiment

2.1 Materials

Porous carbon (PC, Jingwei Co., Ltd.) was selected as the carbon precursor. Gas-phase fluorination was carried out in a custom-made Monel alloy reactor using a 30% F_2/N_2 gas mixture as the fluorinating medium. The fluorination reaction of PC was conducted for 24 h at 100, 150, 200 and 250 °C, respectively, and the system pressure was maintained at 0.03 MPa throughout the process, as schematically illustrated in Fig. S1. By precisely controlling the fluorination temperature, a series of FPC samples with different fluorination degrees was obtained. The samples were denoted as FPC- x , where x is the fluorination temperature.

2.2 Characterizations

The sample morphology was examined by scanning electron microscopy (SEM) (JEOL JSM-7800F, Japan) and transmission electron microscopy (TEM) (JEOL JEM-IT800, Japan). Fourier-transform infrared (FTIR) spectra were collected in the range of 500–4000 cm^{-1} using an infrared spectrophotometer (Thermo Scientific Nicolet iS20, USA). X-ray diffraction (XRD) patterns were recorded with an X-ray flat-panel detector (Rigaku SmartLab SE, Japan) under Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, 40 mA) over a 2θ range of 5°–90°. X-ray photoelectron spectroscopy (XPS) was performed using a spectrometer equipped with an Al anode source (Thermo Scientific K-Alpha, USA) at 15 kV to analyze the chemical composition of the materials. Raman spectra were recorded on a Horiba LabRAM HR Evolution spectrometer (Japan). Nitrogen adsorption-desorption isotherms were meas-

ured using a Micromeritics ASAP 2460 gas adsorption analyzer, and the specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The conductivity of the samples was measured by a four-probe method using an ST2742B automatic powder resistivity tester (Jingge Electronic Co., Ltd.).

2.3 Electrochemical tests

FPC (80%), conductive carbon black (10%), and binder (10%, CMC2000 : PAA-Li = 1 : 1 by mass ratio) were first dispersed in ultrapure water to form a homogeneous slurry. The slurry was uniformly coated onto aluminum foil and dried in a vacuum oven at 120 °C for 8 h. The dried electrodes were punched into discs and transferred to an argon-filled glove box for cell assembly. The cathode active-material loading was 1.95–3.71 mg/cm². CR2032 coin cells were assembled using lithium foil as the anode, Celgard 2034 as the separator, and 1 mol/L LiFSI in propylene carbonate : DME (1 : 1 by volume) as the electrolyte, with an electrolyte volume of 40 µL. Constant-current discharge tests were carried out at 25 °C at 10, 20, 50, 100, 200, 500 and 1000 mA/g based on the mass of the cathode active material, with a cut-off voltage of 1.5 V. The tests were conducted on a Land Battery Test System (CT2001A, Wuhan Jinnuo Electronics Co., Ltd.). Electrochemical impedance spectroscopy (EIS) was performed on a PARSTAT 2263 electrochemical workstation (AMETEK SI) over a frequency range of 1 MHz to 0.01 Hz with an AC amplitude of 5 mV. For the galvanostatic intermittent titration technique (GITT), the cells were discharged at 10 mA/g for 30 min and then allowed to rest for 4 h; this cycle was repeated until the cut-off voltage of 1.5 V was reached. To evaluate practical performance, Li/FPC pouch cells were also assembled. Their cathodes contained 88% active material, 6% conductive additive, and 6% binder. The preparation process for the pouch cell is shown in Table S1. The pouch-cell cathode measured 5.8 cm × 4.2 cm, with Al tabs of 1.5 cm × 1 cm; the cathode active-material loading was 8.55–8.90 mg/cm², and the electrolyte filling quality was fixed at 1.2 based on the mass of the cathode active material.

2.4 Thermal tests

The temperature change during pouch-cell discharge was measured with a thermocouple calorimeter (YET-610, Luchang Co., Ltd.). The thermocouple was attached to the center of the pouch-cell surface during the thermal measurements. To ensure reproducibility and comparability among pouch cells with different FPC cathodes, the mass of cathode active material in each pouch cell was controlled within 2.45–2.53 g. Thermal tests were conducted in ambient air at 25 °C with a cut-off voltage of 1 V. Two discharge protocols were used: (1) constant-current discharge at 1 C and (2) constant-current discharge at 1 A/g, based on the mass of the cathode active material. During testing, the cell temperature was recorded in real time. The resulting temperature-time data were used for a quantitative comparison of the heat-generation behavior of FPC cathodes with different fluorination degrees under different discharge conditions. Detailed configuration parameters of the pouch cells are summarized in Table S2.

3 Results and discussion

3.1 Influence of fluorination temperature on the structure and properties of FPC cathodes

To clarify the effect of fluorination temperature on FPC cathode properties, the carbon precursor and the resulting FPC samples were systematically investigated in terms of structure, bonding states, and electronic transport properties. PC was selected as the precursor because its high specific surface area and rich pore structure provide abundant active sites, making it highly responsive to variations in fluorination temperature^[16–17]. In addition, the porous framework is beneficial for Li⁺ transport and exposing reaction interfaces during discharge. PC was fluorinated at 100, 150, 200 and 250 °C to produce 4 types of FPC samples, denoted FPC-100, FPC-150, FPC-200 and FPC-250, respectively.

The surface of pristine PC is relatively compact and exhibits a rich pore structure (Fig. S2). After fluorination, SEM images (Fig. 1a) show that fluorine penetrates the PC framework and damages both the

surface and internal pores, leading to numerous irregular defects on the FPC surface^[18–19]. As the fluorination temperature increased, the fluorination degree gradually increases, and the surface becomes more fragmented with finer particles. Pristine PC is amorphous and shows no obvious lattice fringes (Fig. S3). After fluorination, FPC retains a structure similar to that of PC (Fig. 1b and Fig. S4), indicating that a highly amorphous structure favors the fluorination of carbon materials by fluorine gas^[20–21]. This observation is consistent with the selected-area electron diffraction (SAED) patterns, which exhibit broad diffuse halos, confirming the predominantly amorphous nature of the samples^[19,22]. The XRD pattern (Fig. 1c) shows that pristine PC exhibits a broad peak associated with the graphite-like (002) plane, suggesting a certain degree of stacking order. After fluorination, this peak is no longer observed, indicating disruption of the ordered carbon structure^[19,22]. Raman spectra

(Fig. S5) further support this conclusion, as the I_D/I_G ratio increases from 0.79 to 1.12, indicating a gradual increase in structural disorder with increasing fluorination temperature^[22–23].

The evolution of fluorination degree and bonding state was further analyzed by FTIR and XPS. In the FTIR spectra (Fig. 1d), the peaks at 1150 and 1580 cm^{-1} are assigned to C–O and C=O stretching vibrations, respectively^[21]. After fluorination, these oxygen-related peaks are significantly weakened, while 2 strong peaks appear at 1217 and 1320 cm^{-1} , corresponding to the stretching vibration of covalent C–F bonds and the asymmetric stretching vibration of CF_2 groups, respectively^[21,24]. The increasing intensity of these peaks with fluorination temperature indicates a higher fluorination degree at higher fluorination temperature. The F/C ratio calculated from elemental analysis (Fig. S6) also follows the same trend with increasing fluorination temperature. In the

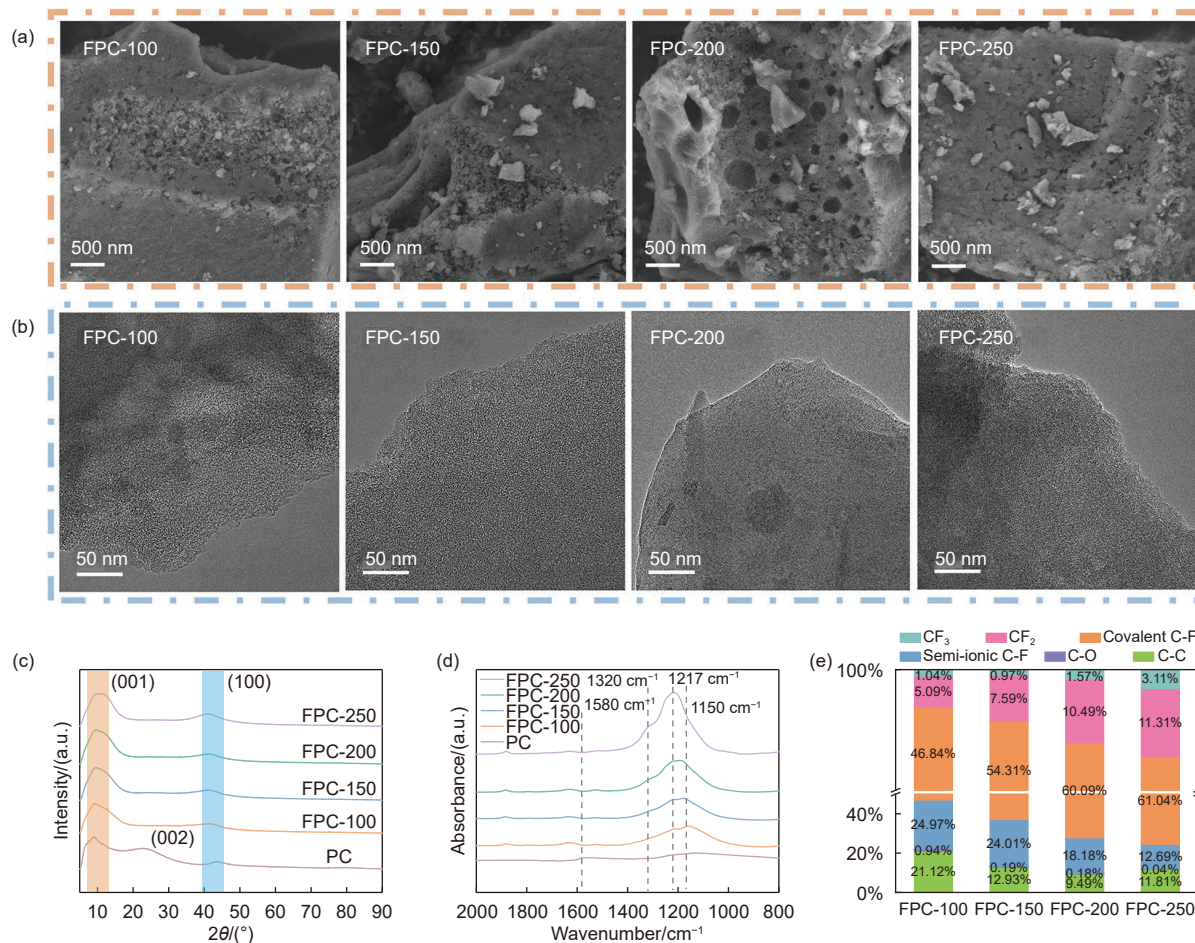


Fig. 1 Structural and chemical characterization of PC and FPC-x samples. (a) SEM images of FPC-x. (b) TEM images of FPC-x. (c) XRD patterns and (d) FTIR spectra of PC and FPC-x. (e) Relative fractions of C–C, semi-ionic C–F, covalent C–F, CF_2 and CF_3 species on an atomic basis

C 1s spectra (Fig. S7 and Table S3), the peak at 284.8 eV is assigned to C—C, whereas those at 287–294 eV correspond to semi-ionic C—F, covalent C—F, and highly fluorinated $-\text{CF}_2/-\text{CF}_3$ species. As shown in Fig. 1e, with increasing fluorination temperature, the relative fractions of covalent C—F and $-\text{CF}_2/-\text{CF}_3$ species increase, while that of semi-ionic C—F decreases^[19,22]. These results confirm that the fluorine content and bonding state of FPC can be effectively tuned by controlling fluorination temperature^[19,21,24].

Fig. S10(a, b) show that PC and FPC samples exhibit type-IV N_2 adsorption-desorption isotherms^[25]. Relative to PC, the fluorinated samples display slightly more pronounced hysteresis loops, suggesting that fluorination reconstructs the original porous framework^[18–19]. Pore-size distribution analysis (Fig. S10c and Table S5) reveals that PC contains a considerable fraction of subnanometer pores (< 1 nm), whereas this contribution is sharply reduced after fluorination and becomes nearly negligible in FPC-150, FPC-200 and FPC-250. At higher fluorination temperatures, the proportion of pores below 2 nm shows an overall decreasing trend, while that of 2–50 nm pores correspondingly increases, especially for FPC-250. Combined with the parameters summarized in Tables S5 and S6, these results indicate that fluorination first consumes the subnanometer pore structure of PC and then tends to broaden the pore system at higher temperature, while all fluorinated samples exhibit substantially lower specific surface area and pore volume than pristine PC^[26]. Conductivity measurements (Fig. S11) further reveal that all FPC samples exhibit significantly lower conductivity than PC. A progressive decrease is also observed from FPC-100 to FPC-250. This result suggests that increasing fluorination temperature gradually suppresses electron transport in FPC, because fluorination progressively disrupts the conjugated carbon framework and increases charge-transport resistance^[27–28].

3.2 Validation of electrochemical consistency between low-mass-loading coin cells and high-mass-loading pouch cells

Before discussing the heat-generation behavior

of Li/FPC pouch cells, it is necessary to verify whether the electrochemical trends observed in low-mass-loading coin cells are preserved in high-mass-loading pouch cells. As shown in Fig. 2a–d, the FPC-100, FPC-150, FPC-200 and FPC-250 cathodes exhibit distinct discharge characteristics in low-mass-loading coin cells ($1.95\text{--}3.71$ mg/cm²), including differences in specific capacity and discharge plateau. These results show that increasing fluorination temperature increases discharge capacity and alters the discharge plateau, consistent with the higher fluorination degree of the cathode. Low-current discharge tests were then conducted on pouch cells with different FPC cathodes at higher mass loading (Fig. 2e). The results show the same relative trend as in coin cells, confirming that the electrochemical differences are preserved in the pouch-cell configuration^[29–30]. As shown in Fig. 2f, low-current discharge tests yielded practical specific capacities of 350, 445, 534, and 743 mAh/g for FPC-100, FPC-150, FPC-200 and FPC-250, respectively. These values were used to define the corresponding 1 C discharge current densities for the subsequent heat-generation tests.

3.3 Heat-generation behavior of Li/FPC pouch cells regulated by fluorination temperature

The photographs of the pouch cells and the schematic illustration of the heat-generation test (Fig. 3a, b), together with the electrode dissection schematic shown in Fig. S12, demonstrate that Ah-level practical cells were used in this study, providing a reliable basis for establishing the relationship among fluorination temperature, cathode structure, and heat-generation behavior. As shown in Fig. S13, the discharge voltage-temperature profiles of pouch cells using FPC-100, FPC-150, FPC-200 and FPC-250 cathodes at 1 A/g show clear differences in temperature evolution during discharge. The maximum surface temperatures of the FPC-100, FPC-150, FPC-200 and FPC-250 cells are 66.81, 75.72, 78.57 and 84.42 °C, respectively, corresponding to total temperature rises of 42.07, 51.43, 54.54 and 59.23 °C. For FPC-100, the voltage curve exhibits a distinct dip followed by recovery in the initial discharge stage and reaches a

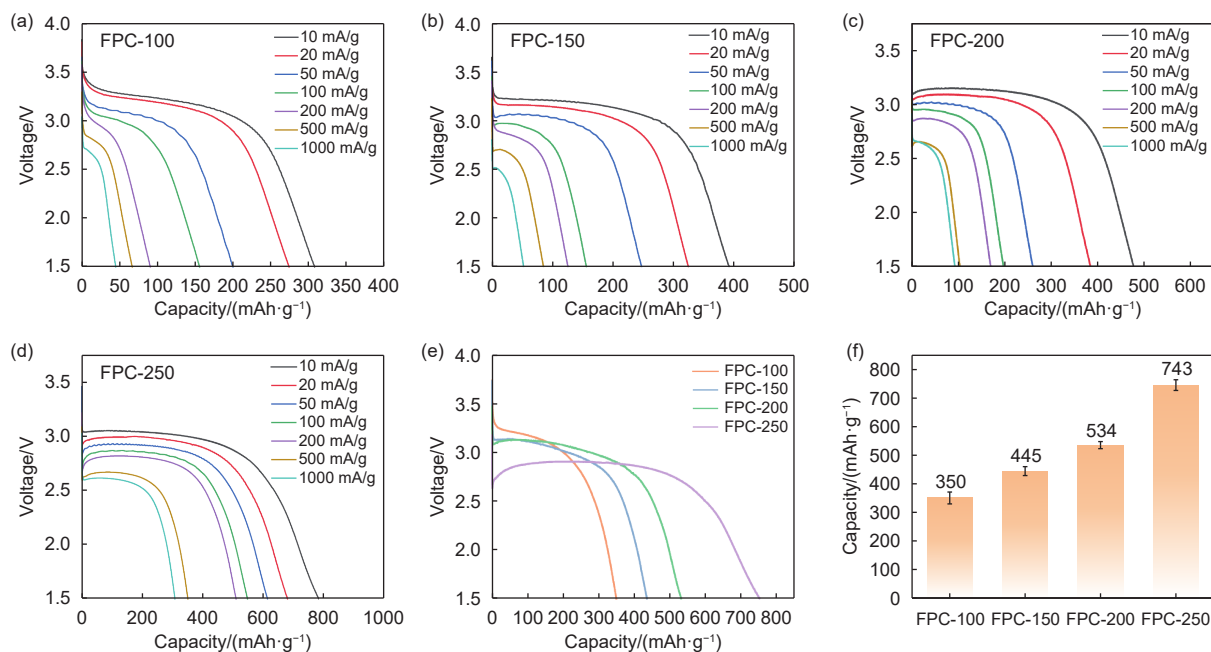


Fig. 2 Electrochemical consistency between low-mass-loading coin cells and high-mass-loading pouch cells. (a–d) Discharge curves of FPC-100, FPC-150, FPC-200 and FPC-250 coin cells at different current densities. (e) Low-current discharge curves of pouch cells assembled with the four FPC cathodes. (f) Specific capacities of the pouch cells at 10 mA/g

plateau after approximately 93 s. As shown in Fig. S14, the corresponding nucleation overpotential, defined as the difference between the minimum potential during nucleation and the maximum potential during the subsequent recovery, is approximately 275 mV, indicating that the system must overcome an initial nucleation barrier before entering a stable reaction stage^[13,31].

The dT/dt curves were obtained by differentiating the temperature profiles recorded at 1 A/g (Fig. 3c), and the 4 types of pouch cells show clear differences in temperature-rise rate. The peak dT/dt values of Li/FPC-100, Li/FPC-150, Li/FPC-200 and Li/FPC-250 are 0.19, 0.20, 0.25 and 0.28 °C/s, respectively. The peak dT/dt of Li/FPC-250 is about 49.4% higher than that of Li/FPC-100, indicating a much stronger heat-generation response within the same discharge window. Fig. 3d further shows the temperature evolution of the 4 types of pouch cells as a function of depth of discharge (DOD) at 1 A/g. Based on the Kelvin-based normalized temperature increase defined in Eq. S1, the stage-wise normalized temperature increases of FPC-100 are 5.90% and 4.91% in the 0–20% DOD and 20%–80% DOD

ranges, respectively, while those of FPC-250 are 14.24% and 2.94%. The ratio of the temperature rise in the early stage (0–20% DOD) to that in the subsequent discharge stage is 4.8 for the Li/FPC-250 pouch cell, compared with only 1.2 for the Li/FPC-100 pouch cell. Consequently, pouch cells with different FPC cathodes differ in total temperature rise as well as in the temporal characteristics of heat generation during discharge.

Given the large difference in heat-generation behavior observed between Li/FPC-100 and Li/FPC-250 at 1 A/g, these 2 types of pouch cells were selected for further comparison at 1 C. As shown in Fig. S15, at 1 C, the Li/FPC-100 pouch cell exhibits a maximum temperature of 52.68 °C with a total temperature rise of 27.09 °C, whereas the corresponding values for the Li/FPC-250 pouch cell are 76.29 and 48.77 °C, respectively. The peak temperature rise rates (dT/dt) of Li/FPC-100 and Li/FPC-250 are 0.09 and 0.21 °C/s (Fig. 3e), respectively, and the peak dT/dt of Li/FPC-250 is approximately 2.41 times that of Li/FPC-100. As shown in Fig. 3f, the temperature rise of FPC-100 is 5.61% in the 0–20% DOD range and 1.73% in the 20%–80% DOD range, whereas the corresponding

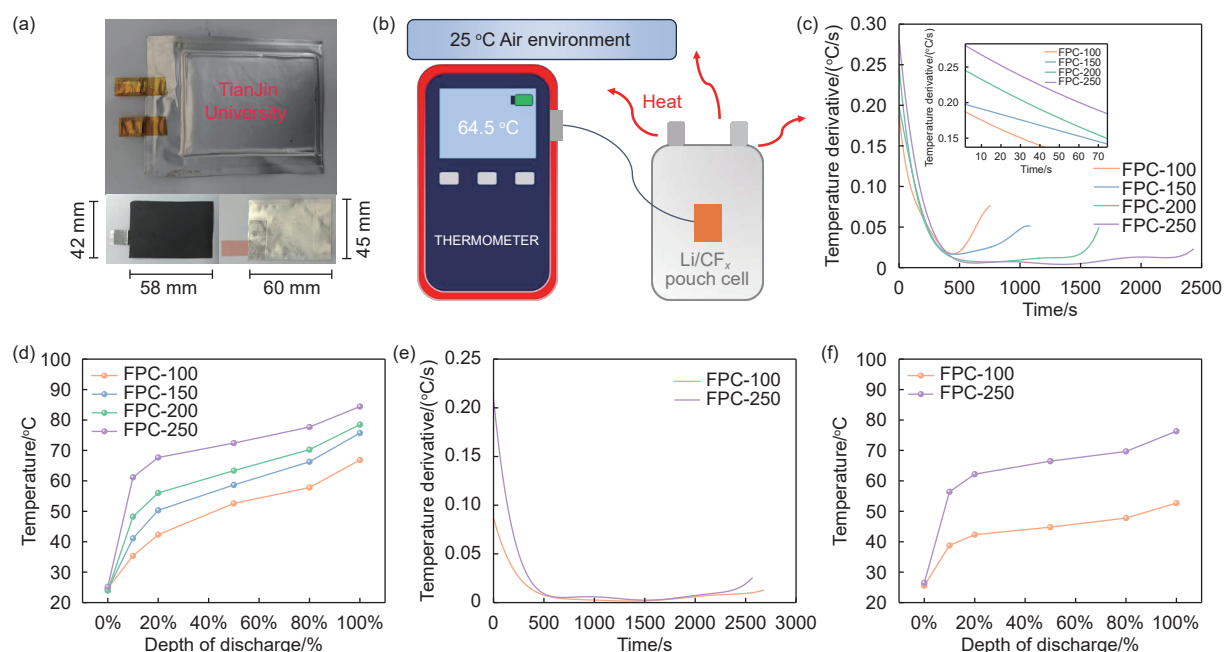


Fig. 3 Heat-generation behavior of Li/FPC pouch cells regulated by fluorination temperature. (a) Photograph and dimensions of a representative Li/FPC pouch cell based on the FPC cathode. (b) Schematic diagram of the heat-generation measurement for the Li/FPC pouch cell. (c) dT/dt curves of Li/FPC pouch cells at 1 A/g. (d) Temperature versus DOD of Li/FPC pouch cells at 1 A/g. (e) dT/dt curves of FPC-100 and FPC-250 pouch cells at 1 C. (f) Temperature versus DOD of FPC-100 and FPC-250 pouch cells at 1 C

values for FPC-250 are 11.91% and 2.23%, respectively. A similar trend is also observed at 1 C, with heat generation being much more concentrated in the early discharge stage for FPC-250 than for FPC-100. These results confirm that higher fluorination degree intensifies early-stage heat generation in Li/FPC pouch cells.

3.4 Structural evolution of FPC cathodes at different depths of discharge

Li/FPC-100 and Li/FPC-250 pouch cells exhibit clear differences in heat-generation behavior. We conducted a systematic investigation of the 2 representative FPC cathodes to further clarify the structural evolution associated with their different heat-generation characteristics, and performed comparative characterizations at 20% DOD and 80% DOD, corresponding to the early and deep discharge stages, respectively. As can be seen from the SEM images of FPC-100 at 20% DOD (Fig. 4a and b), only a small amount of LiF granular deposits is present on the surface, covering only local regions. This indicates that although fine LiF particles are formed in the early discharge stage, a dense and continuous coating layer is not established. At 80% DOD, a large number of fine LiF particles are

present on the surface, almost fully covering the FPC substrate, yet the surface still exhibits a loose and porous morphology. In contrast, the Li/FPC-250 pouch cell exhibits obvious LiF particle agglomeration and extensive surface coverage at 20% DOD (Fig. 4d and e), with very little exposed substrate surface. At 80% DOD, a denser agglomerated structure further forms on its surface, with plenty of pores filled by LiF, showing more significant surface coverage and accumulation of LiF. These observations indicate that LiF accumulation on FPC-250 is much more concentrated in the early discharge stage than on FPC-100.

The XRD results further support this conclusion (Fig. 4c and f). In the Li/FPC-100 pouch cell, the diffraction peaks corresponding to the (111), (200) and (220) planes of LiF can already be detected at 20% DOD, but the peaks remain broad and weak, indicating the initial formation of LiF as the discharge product^[31–32]. Upon discharging to 80% DOD, these characteristic peaks are significantly enhanced, demonstrating the continuous formation and progressive accumulation of LiF during discharge. By comparison, the Li/FPC-250 pouch cell already shows strong LiF characteristic peaks at the early discharge stage

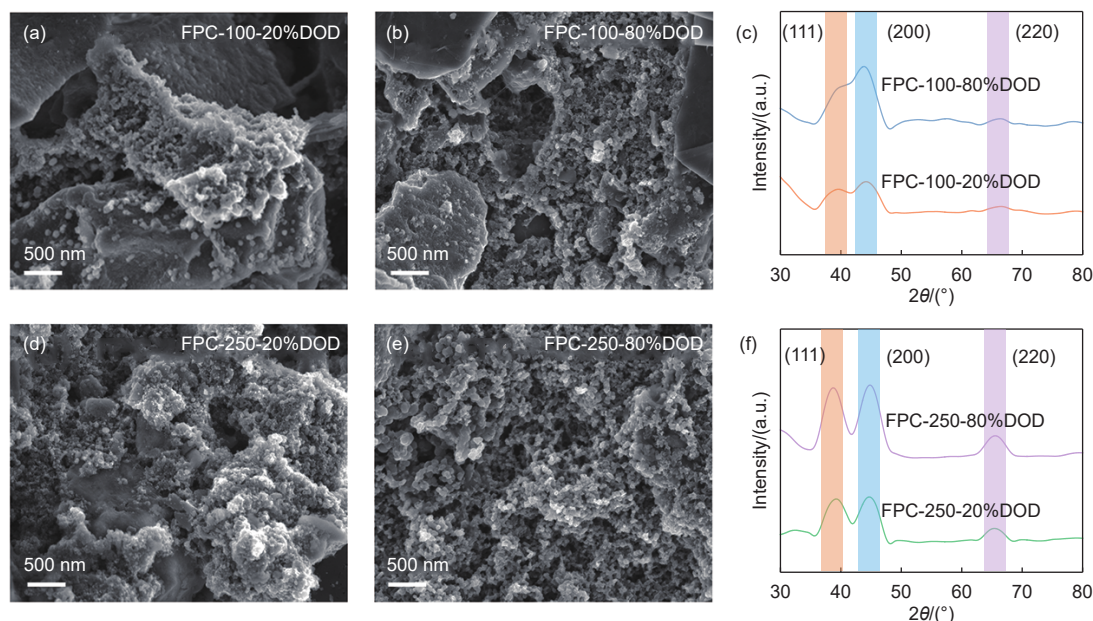


Fig. 4 Structural evolution of representative FPC-100 and FPC-250 cathodes at different DOD. (a, b) Post-discharge SEM images of FPC-100 at 20% and 80% DOD. (c) XRD patterns of FPC-100 at 20% and 80% DOD. (d, e) Post-discharge SEM images of FPC-250 at 20% and 80% DOD. (f) XRD patterns of FPC-250 at 20% and 80% DOD

(20% DOD), and the peak intensities further increase at 80% DOD. This result indicates that the highly fluorinated cathode exhibits more concentrated LiF accumulation in the early discharge stage^[15,32].

The post-discharge Raman spectra of FPC-100 and FPC-250 at different DOD (Fig. S16) further support the above structural evolution. Both cathodes still display the characteristic *D* and *G* peaks after discharge, indicating that the residual carbon framework is retained during discharge^[14,32]. For FPC-100, the I_D/I_G ratio increases from 1.03 at 20% DOD to 1.09 at 80% DOD, whereas for FPC-250 it increases from 1.14 to 1.21. Compared with the corresponding pristine cathodes, the increase in I_D/I_G indicates that electrochemical defluorination and the accompanying deposition of discharge products continuously disturb the local carbon structure during discharge^[32]. Meanwhile, FPC-250 maintains a higher I_D/I_G than FPC-100 at both discharge states, indicating that the highly fluorinated cathode evolves on a more defective residual carbon framework throughout discharge. Combined with the SEM and XRD results, the Raman results further suggest a relatively gradual structural evolution for FPC-100, whereas FPC-250 shows more concentrated product accumulation during discharge.

The distinct heat-generation behaviors of pouch cells employing FPC cathodes fluorinated at different temperatures are closely associated with differences in LiF evolution during discharge. Compared with FPC-100, FPC-250 exhibits more concentrated LiF accumulation in the initial discharge stage and more severe surface coverage at high DOD, which can be attributed to its higher fluorination degree and poorer electronic transport capability, leading to a less homogeneous discharge process. In addition, the more strongly disrupted carbon framework and the stronger polarization of FPC-250 are consistent with a less homogeneous discharge process and a relatively more concentrated formation and accumulation of LiF during discharge. However, the stronger heat generation of the FPC-250 pouch cell cannot be simply attributed to the presence of more LiF. To further clarify the origin of the stage-dependent heat-generation behavior, kinetic characterization is required to compare the reaction resistance and ion-transport properties of the 2 FPC cathodes during discharge.

3.5 The kinetic origins of heat-generation behavior of Li/FPC pouch cells

As shown in Fig. 5a–c, the evolution of internal resistance during discharge was evaluated by electro-

chemical impedance measurements at different DOD values (0%, 20% and 80%). The results show that the charge-transfer resistances (R_{ct}) of FPC cathodes prepared at different fluorination temperatures are 49.06, 57.53, 62.00, and 71.19 Ω at 0% DOD; 59.45, 94.78, 134.38, and 162.99 Ω at 20% DOD; and 85.49, 115.15, 169.72, and 223.31 Ω at 80% DOD for FPC-100, FPC-150, FPC-200, and FPC-250, respectively. The electrolyte resistance (R_s) remains within a narrow range of 1.79–2.72 Ω , indicating that the main differences among the cells originate from R_{ct} rather than R_s . These results show that higher fluorination temperature increases charge-transfer limitation during discharge^[23,33].

The GITT results (Fig. 5d) further reveal differences in polarization among the 4 types of FPC cathodes during discharge. Among the four FPC cathodes, FPC-100 shows the weakest polarization, whereas FPC-250 shows the strongest polarization. The calculated Li^+ diffusion coefficients (Fig. 5e), obtained according to Eq. S2, show that FPC-100 maintains relatively fast Li^+ transport over a wide potential range, with values of approximately $10^{-12.5}$ to $10^{-9.5}$ cm^2/s . In contrast, the diffusion coefficient of FPC-250 is gen-

erally lower, ranging from about $10^{-15.5}$ to 10^{-11} cm^2/s , indicating that FPC-250 is more susceptible to ion-transport limitations during discharge. To quantify the early-stage kinetic barrier more directly, Fig. 5f summarizes the nucleation overpotentials of the different FPC cathodes. At 1 A/g, the nucleation overpotentials of FPC-100, FPC-150, FPC-200 and FPC-250 are 275, 301, 368 and 404 mV, respectively, showing a gradual increase with fluorination temperature. At 1 C, the corresponding values for FPC-100 and FPC-250 are 248 and 341 mV, respectively. The larger nucleation overpotential of FPC-250 indicates a higher early-stage kinetic barrier, which is associated with increased polarization loss and heat generation, particularly at the beginning of discharge where the largest thermal difference is observed^[13].

These kinetic results are consistent with the structural evolution discussed in Section 3.4. A schematic summary of the relationship between fluorination degree, discharge kinetics, and heat generation is provided in Fig. S17. Higher fluorination degrees impair electronic transport and make the discharge process less uniform, promoting more localized LiF accumulation and greater kinetic losses. The accompanying increase in interfacial resistance and

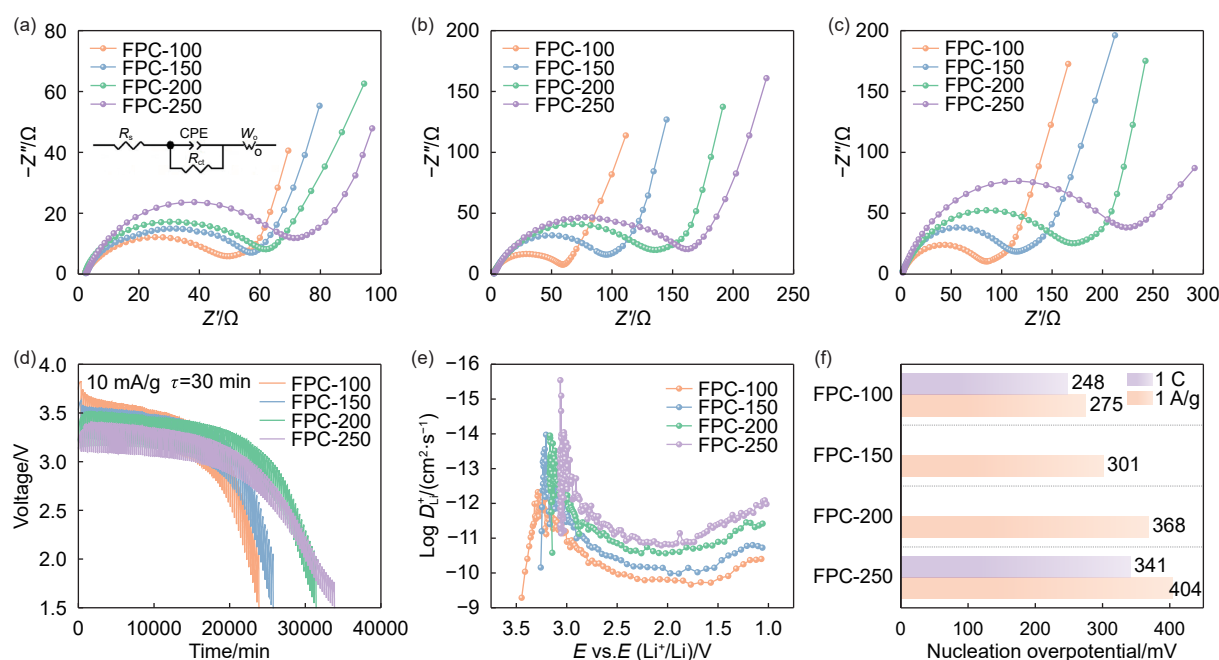


Fig. 5 Kinetic origin of the different heat-generation behaviors of Li/FPC pouch cells. (a–c) EIS Nyquist plots of FPC-100, FPC-150, FPC-200 and FPC-250 measured at 0%, 20% and 80% DOD. The fitted R_s and R_{ct} values are summarized in Table S7. (d) GITT profiles of the 4 FPC cathodes. (e) Li^+ diffusion coefficients calculated from the GITT results according to Eq. S2. (f) Nucleation overpotentials at 1 A/g and 1 C

polarization enhances heat generation, leading to a larger temperature rise in Li/FPC pouch cells^[13,34].

4 Conclusions

In summary, this study systematically investigates the effects of fluorination engineering on the structure and kinetics of FPC cathodes and on heat generation in the corresponding pouch cells. With increasing fluorination temperature, the F/C ratio of FPC increases, accompanied by changes in the C–F bonding configuration, pore structure, and electronic transport capability, while the heat generation of the corresponding pouch cells becomes progressively stronger. This heat generation exhibits obvious stage dependence and is mainly concentrated in the early discharge stage (0–20% DOD). Post-discharge structural characterization reveals that FPC-100 and FPC-250 exhibit distinctly different structural evolution at 20% DOD, and this difference remains pronounced at 80% DOD, indicating that the highly fluorinated cathode undergoes more concentrated LiF accumulation during discharge. Kinetic analysis further shows that FPC-250 has a higher charge-transfer resistance, poorer Li⁺ diffusion capability, and a larger nucleation overpotential during discharge, which together lead to stronger polarization and more severe heat generation. This study establishes the correlation of fluorination temperature not only with the structure and bonding state, but also the discharge-product evolution, discharge kinetics, and heat generation. This work demonstrates that regulating the fluorination temperature for tuning the structure and chemical environment of CF_x cathodes is an effective strategy for improving the thermal safety of Li/CF_x batteries.

References

- [1] Zhang S, Kong L, Li Y, et al. Fundamentals of Li/CF_x battery design and application[J]. *Energy & Environmental Science*, 2023, 16(5): 1907-1942.
- [2] Fang Z, Peng Y, Zhou X, et al. Fluorinated carbon materials and the applications in energy storage systems[J]. *ACS Applied Energy Materials*, 2022, 5(4): 3966-3978.
- [3] Feng W. Status and development trends for fluorinated carbon in China[J]. *New Carbon Materials*, 2023, 38(1): 130-142.
- [4] Wang D, Wang G, Zhang M, et al. Composite cathode materials for next-generation lithium fluorinated carbon primary batteries[J]. *Journal of Power Sources*, 2022, 541: 231716.
- [5] Sayahpour B, Hirsh H, Bai S, et al. Revisiting discharge mechanism of CF_x as a high energy density cathode material for lithium primary battery[J]. *Advanced Energy Materials*, 2022, 12(5): 2103196.
- [6] Chen X, Fan K, Liu Y, et al. Recent advances in fluorinated graphene from synthesis to applications: Critical review on functional chemistry and structure engineering[J]. *Advanced Materials*, 2022, 34(1): 2101665.
- [7] Li Y, Feng Y, Feng W. Deeply fluorinated multi-wall carbon nanotubes for high energy and power densities lithium/carbon fluorides battery[J]. *Electrochimica Acta*, 2013, 107: 343-349.
- [8] Peng C, Li Y, Yao F, et al. Ultrahigh-energy-density fluorinated calcinated macadamia nut shell cathodes for lithium/fluorinated carbon batteries[J]. *Carbon*, 2019, 153: 783-791.
- [9] Li W, Kong L, Hu Y, et al. Electroplated silver-modified CF_x cathode for lithium primary batteries with high rate capability[J]. *ACS Applied Energy Materials*, 2023, 6(11): 6132-6140.
- [10] Sun L, Peng C, Kong L, et al. Interface-structure-modulated CuF₂/CF_x composites for high-performance lithium primary batteries[J]. *Energy & Environmental Materials*, 2023, 6(2): e12323.
- [11] Chen J, Wu C, Liu W, et al. Li/CF_x battery thermal analysis: Experiment and simulation[J]. *Journal of Energy Storage*, 2024, 84: 110994.
- [12] Wan B, Liu W, Ma S, et al. Embedded sensors for in situ measuring and safety warning in lithium carbon fluorides batteries[J]. *Applied Physics Letters*, 2024, 124(21): 213902.
- [13] Du J, Xi Y, Ma D, et al. LiF pre-nucleation strategy for mitigating heat generation at the kinetic bottleneck in Li/CF_x batteries[J]. *Small*, 2025, 21(34): 2502941.
- [14] Leung K, Schorr N B, Mayer M, et al. Edge-propagation discharge mechanism in CF_x batteries: A first-principles and experimental study[J]. *Chemistry of Materials*, 2021, 33(5): 1760-1770.
- [15] Zhang F, Gao M, Lan Y, et al. Operando optical imaging of cathode swelling process inside lithium primary batteries: Comparative studies between different structured CF_x[J]. *ACS Applied Materials & Interfaces*, 2024, 16(47): 64898-64906.
- [16] Hu Y, Kong L, Li W, et al. Fluorinated microporous carbon spheres for Li/CF_x batteries with high volumetric energy density[J]. *Composites Communications*, 2023, 40: 101607.
- [17] Zhao Z, Kong L, Sun J, et al. Fluorinated polymer-derived microporous carbon spheres for CF_x cathodes with high energy density[J]. *Giant*, 2024, 18: 100273.
- [18] Wang X, Wang W, Xu D, et al. Activation effect of porous structure on fluorination of graphene based materials with large specific surface area at mild condition[J]. *Carbon*, 2017, 124: 288-295.

- [19] Zhang S, Li Y, Xu H, et al. Elucidating the effects of the carbon source on fluorination kinetics and the CF_x structure to tailor the energy density of Li/CF_x [J]. *Journal of Materials Chemistry A*, 2025, 13(3): 1820-1829.
- [20] Peng C, Kong L, Li Y, et al. Fluorinated graphene nanoribbons from unzipped single-walled carbon nanotubes for ultrahigh energy density lithium-fluorinated carbon batteries[J]. *Science China Materials*, 2021, 64(6): 1367-1377.
- [21] Ha S, Lim C, Lee Y. Fluorination methods and the properties of fluorinated carbon materials for use as lithium primary battery cathode materials[J]. *Journal of Industrial and Engineering Chemistry*, 2022, 111: 1-17.
- [22] Wang K, Feng Y, Kong L, et al. The fluorination of boron-doped graphene for CF_x cathode with ultrahigh energy density[J]. *Energy & Environmental Materials*, 2023, 6(4): e12437.
- [23] Kong L, Li Y, Peng C, et al. Defective nano-structure regulating C-F bond for lithium/fluorinated carbon batteries with dual high-performance[J]. *Nano Energy*, 2022, 104: 107905.
- [24] Zhou H, Chen G, Yao L, et al. Plasma-enhanced fluorination of layered carbon precursors for high-performance CF_x cathode materials[J]. *Journal of Alloys and Compounds*, 2023, 941: 168998.
- [25] Thommes M, Kaneko K, Neimark A, et al. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)[J]. *Pure and Applied Chemistry*, 2015, 87(9-10): 1051-1069.
- [26] Zou Y, Yan K, Bao L, et al. Fluorinated hollow porous carbon spheres as high-performance cathode material for primary battery[J]. *Batteries*, 2024, 10(9): 310.
- [27] Chen N, Zhang G, Chen H, et al. Conductive carbon-wrapped fluorinated hard carbon composite as high-performance cathode for primary lithium batteries[J]. *Coatings*, 2023, 13(5): 812.
- [28] Wang J, Liu Y, Qin G, et al. Rational design of Ag nanowires growth engineered conductivity chain toward Li/CF_x primary batteries with high-energy and high-power density[J]. *Materials Today Energy*, 2023, 37: 101403.
- [29] Qiu H, Zhang H, Song L, et al. Ammonium bicarbonate template-assisted thick cathode for $\text{Li}-\text{CF}_x$ primary batteries with enhanced surface loading and energy density[J]. *Energy & Fuels*, 2023, 37(6): 4650-4657.
- [30] Huo H, Radhakrishnan S, Shaw L, et al. High-energy and high-power primary $\text{Li}-\text{CF}_x$ batteries enabled by the combined effects of the binder and the electrolyte[J]. *Batteries*, 2023, 9(5): 268.
- [31] Zhang S, Foster D, Wolfenstine J, et al. Electrochemical characteristic and discharge mechanism of a primary Li/CF_x cell[J]. *Journal of Power Sources*, 2009, 187(1): 233-237.
- [32] Zhong G, Chen H, Cheng Y, et al. Insights into the lithiation mechanism of CF_x by a joint high-resolution ^{19}F NMR, in situ TEM and ^7Li NMR approach[J]. *Journal of Materials Chemistry A*, 2019, 7(34): 19793-19799.
- [33] Liu W, Ma S, Li Y, et al. Electrochemical impedance spectroscopy analysis for lithium carbon fluorides primary battery[J]. *Journal of Energy Storage*, 2023, 68: 107699.
- [34] Schoetz T, Robinson L, Gordon L, et al. Elucidating the role of electrochemically formed LiF in discharge and aging of $\text{Li}-\text{CF}_x$ batteries[J]. *ACS Applied Materials & Interfaces*, 2024, 16(15): 18722-18733.