

RESEARCH ARTICLE

A High-Energy Aluminum-Fluorinated Carbon Battery Enabled by Chemical Bond Activation in Molten Salt Electrolytes

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Received: 23 December 2025 | **Revised:** 5 March 2026 | **Accepted:** 11 March 2026

Keywords: aluminum-fluorinated carbon battery | chemical bond activation | high energy density | kinetics enhancement | molten salt electrolyte

ABSTRACT

Aluminum-fluorinated carbon (Al–CF_x) primary batteries show potential in aerospace, military, and related fields, due to the inherent safety and abundance of aluminum, long-term reliability, and high theoretical energy density. However, the practical performance of these batteries is impeded by high energy barriers for Al³⁺ desolvation and C–F bond cleavage, which leads to slow kinetics and thereby restricts the achievable energy density. Here, we report a high-energy Al–CF_x primary battery via a chemical bond activation strategy in molten salt electrolytes. The designed quaternary molten salt contains electrochemically active high-order Al–Cl clusters to accelerate Al³⁺ desolvation; crucially, abundant alkali metal ions activate CF_x's C–F bonds via strong electrostatic attraction, promoting stable AlF₃ formation. Operated at 85°C and 10 mA g^{−1}, this battery achieves a discharge plateau of 1.75 V and a specific capacity of 897.7 mAh g^{−1}, outperforming the ionic liquid system (0.21 V, 464.4 mAh g^{−1}). A high-rate Al–MnO₂@CF_x battery is developed via engineering a MnO₂–CF_x heterointerface, offering a low-cost route for high-energy-density energy storage.

1 | Introduction

The rapid advancement of sustainable energy technologies has significantly increased the demand for high-performance, environmentally benign electrochemical energy storage systems. Among these, charge-constrained fields such as deep-sea exploration, medical implant devices, aerospace, and military equipment exhibit particularly urgent requirements, necessitating primary battery technologies with high energy density, exceptional safety, and reliable performance [1, 2]. Lithium-fluorinated carbon (Li–CF_x) primary batteries have historically

held a prominent position in primary battery research due to their high theoretical energy density (2180 Wh kg^{−1}), theoretical specific capacity (865 mAh g^{−1}), low self-discharge rate, and excellent long-term storage performance [3–6]. However, challenges such as the high cost of organic electrolytes, scarcity and high price of metallic lithium, and insufficient thermal stability have confined Li–CF_x batteries predominantly to niche, high-end specialized applications [7–10]. These limitations hinder their widespread industrial adoption despite their promising performance metrics [11, 12]. Alternative systems, including sodium-fluorinated carbon (Na–CF_x) and potassium-fluorinated carbon (K–CF_x) batteries,

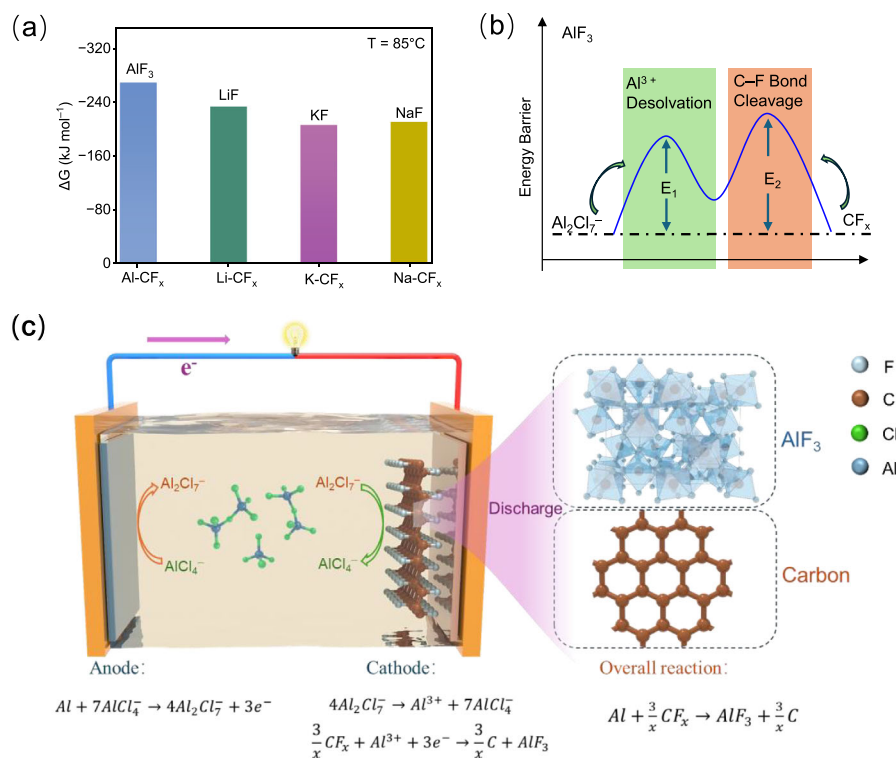


FIGURE 1 | Schematic of the design rationale, critical discharge energy barriers, and discharge mechanism of the Al-CF_x primary battery. (a) Gibbs free energy comparison of Al-, Li-, Na-, and K-based metal fluorinated carbon primary batteries at 85°C. (b) Two major energy barriers during AlF₃ formation in the Al-CF_x battery system. (c) Discharge mechanism of the Al-CF_x primary battery.

have recently been explored [13]; however, they currently face significant obstacles, such as electrolyte-electrode incompatibility, pronounced polarization effects that impede discharge kinetics, and potential thermal runaway risks at elevated temperatures [14–16].

As the most abundant metallic element, aluminum exhibits multiple advantages, including low cost, environmental benignity, high safety, and ultrahigh theoretical capacity (8040 mAh cm⁻³, 2980 mAh g⁻¹), positioning it as a highly promising candidate for high-energy electrochemical systems [17]. Thermodynamic analysis based on Gibbs free energy change (ΔG) confirms that the formation of AlF₃ is significantly more spontaneous than that of LiF, NaF, and KF ($\Delta G(\text{AlF}_3) < \Delta G(\text{LiF}) < \Delta G(\text{NaF}) < \Delta G(\text{KF}) < 0$) (Figures 1a and S1). This trend indicates a stronger reaction driving force in the conversion reaction $\text{Al}(\text{s}) + 3/x \text{CF}_x(\text{s}) \rightarrow \text{AlF}_3(\text{s}) + 3/x \text{C}(\text{s})$, primarily attributed to the superior thermodynamic stability of AlF₃ relative to LiF, NaF, and KF [18]. Accordingly, aluminum-fluorinated carbon (Al-CF_x) batteries combine the intrinsic high capacity, chemical safety, and resource abundance of aluminum with the electrochemical attributes of CF_x, exhibiting great potential for enhanced electrochemical performance and safe cell assembly [19, 20]. However, early Al-CF_x batteries suffer from actual capacities significantly below their theoretical limits, predominantly due to sluggish electrochemical kinetics. Although approaches such as optimized ionic liquid electrolytes and cathode additives have been employed to improve electron transport and cathode reactivity, these batteries remain limited in performance, generally exhibiting discharge voltages below 1.6 V and specific capacities under 500 mAh g⁻¹ [21, 22]. The kinetic bottlenecks of Al-CF_x batteries arise

from multiple synergistic factors: high charge density of Al³⁺ ions, intricate multielectron transfer processes, and the inherent rigidity and strong C–F bonding within the CF_x matrix [23–26]. Together, these factors introduce substantial energy barriers for Al³⁺ desolvation and C–F bond cleavage, resulting in pronounced electrochemical overpotentials and hindered reaction kinetics (Figure 1b).

Herein, we harness the distinctive ionic regulation properties of the AlCl₃–NaCl–LiCl–KCl quaternary molten salt electrolyte to achieve kinetic breakthroughs and successfully construct a high-energy molten salt-based Al-CF_x primary battery (Figure 1c). The molten salt electrolyte, enriched with Al₂Cl₇⁻ and Al₃Cl₁₀⁻ clusters featuring abundant electrochemically active Al–Cl–Al linkages, effectively reduces the Al³⁺ desolvation energy barrier, thereby enhancing electrochemical kinetics. Furthermore, alkali metal ions (Li⁺, Na⁺, K⁺) with small ionic radii and low steric hindrance form strong electrostatic interactions with F atoms in CF_x, activating C–F bonds and promoting AlF₃ formation—enabling fast reaction kinetics and superior electrochemical performance. Under testing conditions of 85°C and 10 mA g⁻¹, this molten salt-based battery achieves, for the first time, a discharge voltage of 1.75 V and a specific capacity of 897.7 mAh g⁻¹, corresponding to a theoretical energy density of 1571 Wh kg⁻¹. This performance significantly outperforms the conventional ionic liquid-based system (0.21 V discharge voltage, 464.4 mAh g⁻¹ specific capacity, and ~97.5 Wh kg⁻¹ theoretical energy density). We further developed a MnO₂@CF_x composite cathode that substantially improves charge transfer and ion diffusion kinetics: this cathode retains a specific capacity of 426.4 mAh g⁻¹ at a high rate of 400 mA g⁻¹ and achieves 743.6 mAh g⁻¹ at a high

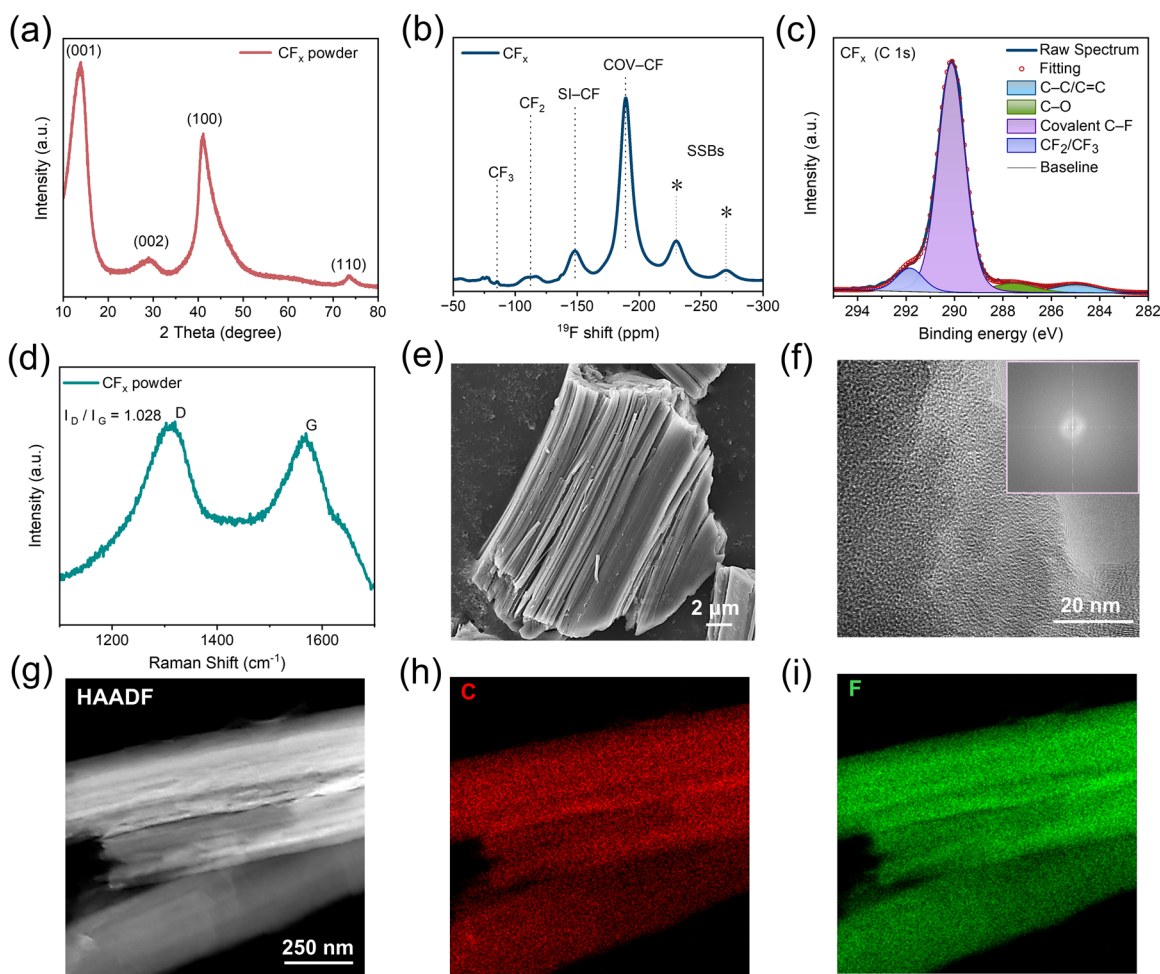


FIGURE 2 | Structural and morphological characterizations of CF_x . (a) XRD patterns. (b) ^{19}F MAS NMR spectra (15 kHz spinning rate). The peaks marked with asterisks (*) denote spinning sidebands associated with the isotropic peak at -190 ppm. (c) C 1s XPS spectrum. (d) Raman spectra. (e) SEM image. (f) TEM image; inset: SAED pattern. (g–i) HAADF-STEM image and elemental mapping images.

mass loading of 6 mg cm^{-2} . This study pioneers' new avenues for the practical implementation of intrinsically safe, cost-effective Al– CF_x primary batteries in chemical energy storage and furnishes critical theoretical and experimental insights to advance high-performance Al-based energy storage technologies.

2 | Results and Discussion

2.1 | Characterizations of Fluorinated Carbon Fibers

Commercial fluorinated carbon fibers (CF_x , $x = 0.89$) were used as cathode materials for Al– CF_x batteries [27]. X-ray diffraction (XRD) analysis shows that the CF_x structure has four characteristic peaks (Figure 2a). The prominent peak at $2\theta = 13.8^\circ$ corresponds to the (001) crystal plane, highlighting fluorination characteristics. The weak, broad peak at $2\theta = 28.9^\circ$ corresponds to the (002) crystal plane of graphite, indicating reduced order in the graphitic carbon structure. The two peaks at $2\theta = 41.1^\circ$ and 73.6° correspond to the (100) and (110) crystal planes of carbon, respectively [28–30]. Nuclear magnetic resonance (NMR) analysis was used to explore the structural characteristics of CF_x (Figure 2b). The ^{19}F NMR spectrum showed a weak CF_3

signal at -85 ppm and a broad peak at -112 ppm, indicating that CF_2 groups were formed during the fluorination process. The peaks at -149 ppm and -190 ppm correspond to semi-ionic and covalent fluorocarbon bonds, respectively [31–33]. X-ray photoelectron spectroscopy (XPS) was used to analyze the elemental bonding in CF_x (Figures 2c and S2a). The C1s spectrum shows four characteristic peaks at 284.8, 287.5, 290.07, and 291.8 eV, corresponding to C–C/C=C, C–O, covalent C–F, and C– F_2 /C– F_3 bonds, respectively [16, 28]. Raman spectroscopy shows that the I_D/I_G ratio is 1.028 (Figure 2d), indicating that there are some defects in the carbon structure [30]. Scanning electron microscopy (SEM, Figures 2e and S2b) reveals that CF_x exhibits a uniformly dispersed rod-like morphology with a layered surface structure composed of stacked fibrous filaments [34]. High-resolution transmission electron microscopy (HR-TEM) analysis indicates an amorphous structure without distinct lattice fringes, further confirmed by selected area electron diffraction (SAED, Figure 2f). Elemental distribution analysis verifies the uniform distribution of carbon and fluorine (Figure 2g–i). These characterization results collectively confirm the microstructure and chemical composition of CF_x . Consequently, CF_x formation primarily involves fluorine incorporation into the carbon skeleton via fluorination, forming C–F bonds and increasing disorder in the graphitic carbon structure [27, 35].

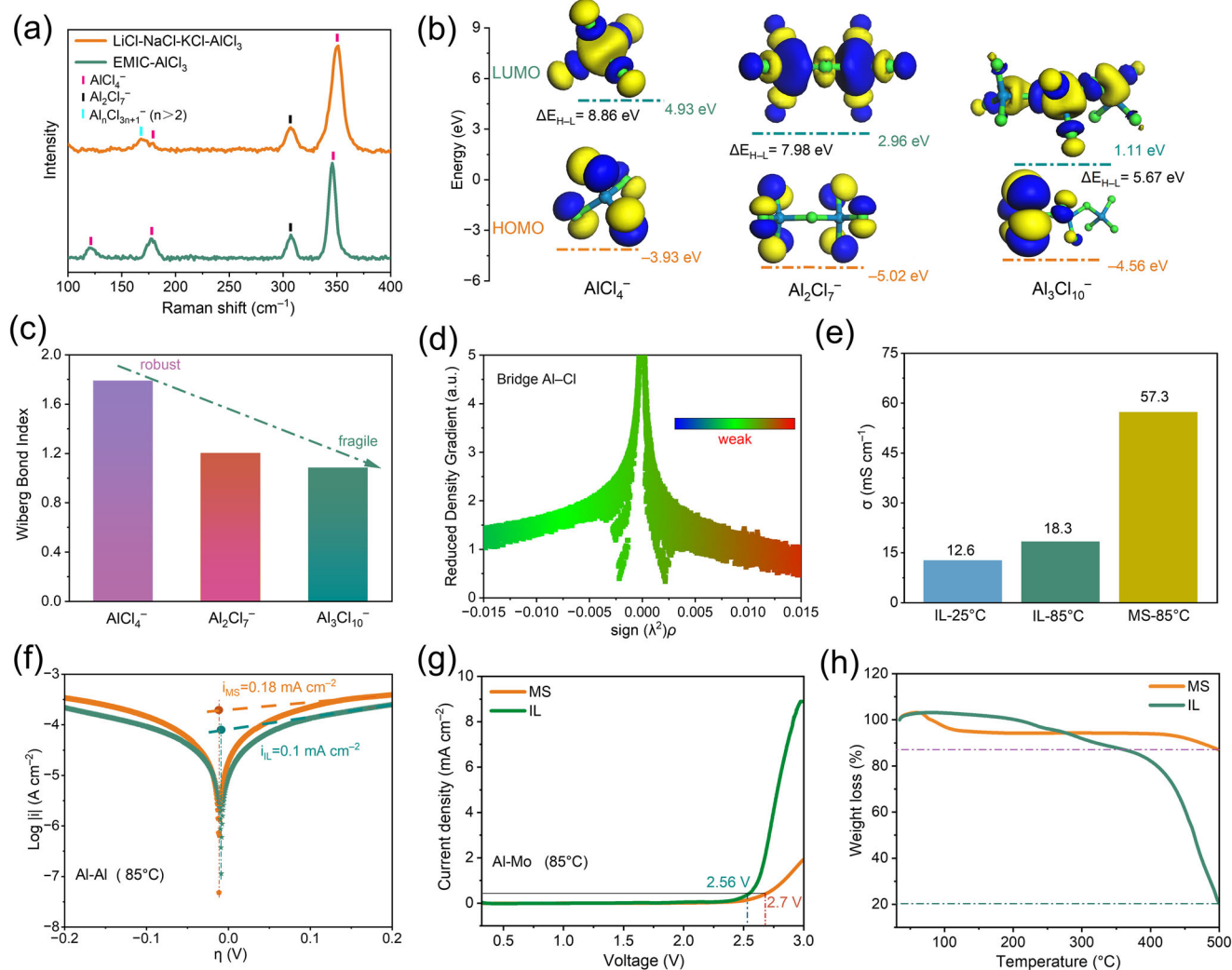


FIGURE 3 | Comparative investigation on structural characteristics, kinetic behaviors, and thermal stability of molten salt versus ionic liquid electrolytes. (a) Raman spectra. (b) Evolution of HOMO-LUMO gaps for Al-based clusters ($\text{AlCl}_4^- \rightarrow \text{Al}_3\text{Cl}_{10}^-$) in electrolyte systems. (c) Wiberg Bond Index characterization of Al-based clusters ($\text{AlCl}_4^- \rightarrow \text{Al}_3\text{Cl}_{10}^-$). (d) NCI analysis of noncovalent interactions in large Al-based clusters. (e) Ionic conductivity of various electrolytes calculated via EIS tests of the Mo–Mo cell. (f) Tafel polarization plots of Al symmetric cells. (g) LSV curves of Al–Mo half-cells. (h) TGA thermograms of the two electrolytes as a function of temperature.

2.2 | Electrolyte Characterizations

We first investigate the structures and physicochemical properties of the molten salt (MS) and ionic liquid (IL) electrolytes. The quaternary molten salt electrolyte consisted of AlCl₃, NaCl, LiCl, and KCl in a molar ratio of 1.3:0.43:0.42:0.15. For comparison, the conventional ionic liquid electrolyte was the AlCl₃–EMIC (1-ethyl-3-methylimidazolium chloride) system with a molar ratio of 1.3:1. Raman spectra exhibit characteristic peaks of Al₂Cl₇⁻ and AlCl₄⁻ at 311 and 349.1 cm⁻¹ [23, 36], respectively, with a higher Al₂Cl₇⁻/AlCl₄⁻ intensity ratio in the molten salt electrolyte compared to the ionic liquid electrolyte (Figure 3a). Furthermore, a shoulder peak at 175 cm⁻¹ is observed in the molten salt electrolytes, assigned to multi-ion clusters ($\text{Al}_n\text{Cl}_{3n+1}^-$, $n > 2$). [37]

Quantum chemical simulations reveal that the structural evolution of Al-based clusters (from AlCl₄⁻ to Al₃Cl₁₀⁻) in electrolytes is accompanied by a continuous decrease in the

highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap, indicating enhanced reactivity of the clusters (Figure 3b). Concurrently, Wiberg Bond Index analysis establishes a quantitative correlation: as the cluster size increases, the Al–Cl bond order systematically decreases, reflecting a reduction in bond stability and strength (Figure 3c). Subsequently, noncovalent interaction (NCI) analysis confirms that negative $\text{sign}(\lambda_2)\rho$ regions correspond to attractive interactions. In Figure 3d, as this parameter approaches zero within the negative regime, the reduced density gradient (RDG) on the ordinate exhibits a continuous increasing trend, indicative of weakened attractive interactions. This evidence confirms that Al–Cl bridge bonds in large clusters feature typical characteristics of weak noncovalent interactions, with low stability and a pronounced dissociation tendency. Notably, these theoretical results establish a clear correlation between the Al–Cl–Al linkages in larger clusters and enhanced electron transfer kinetics and chemical reactivity, thereby

providing pivotal thermodynamic insights into the dissociation mechanism of Al^{3+} .

Electrochemical impedance spectroscopy (EIS) was used to characterize the ionic conductivity of the electrolyte in Mo–Mo cells. Fitting analysis shows that the molten salt electrolyte exhibits an ionic conductivity of $\sim 57.3 \text{ mS cm}^{-1}$ at 85°C , significantly higher than that of the ionic liquid electrolyte at 25°C and 85°C (Figure 3e). Tafel analysis of Al–Al symmetric cells shows that the exchange current density for the molten salt electrolyte (0.18 mA cm^{-2}) is higher than that for the ionic liquid electrolyte (0.10 mA cm^{-2}) (Figure 3f). Cyclic voltammetry (CV) characterization reveals that the redox peak area of the molten salt electrolyte in Al–Mo cells exhibits a continuous increase with increasing scan rate, which is notably larger than the corresponding value for the ionic liquid electrolyte (Figure S3). These results indicate that the lower activation energy in the molten salt system accelerates charge transfer and enhances the desolvation rate of Al^{3+} , leading to superior electrochemical reactivity. The high voltage stability of the electrolytes was assessed using linear sweep voltammetry (LSV) in an Al–Mo cell (Figure 3g). The molten salt electrolyte demonstrated superior voltage tolerance of 2.7 V, compared to 2.56 V for the ionic liquid electrolyte, indicating better high-voltage stability in the molten salt electrolytes. The thermal stability of the electrolytes was assessed using thermogravimetric analysis (TGA) (Figure 3h). The ionic liquid begins to decompose at 300°C . In contrast, the molten salt system maintains thermal stability up to 420°C , demonstrating remarkable high-temperature resistance.

2.3 | Electrochemical Performance

The electrochemical performance of Al– CF_x batteries is systematically compared for molten salt and ionic liquid electrolytes. At 85°C and a current density of 10 mA g^{-1} , the Al– CF_x battery in the molten salt electrolytes achieved a discharge capacity of 897.7 mAh g^{-1} with a discharge plateau at 1.75 V. In contrast, the battery in the ionic liquid electrolytes showed a discharge capacity of only 464.4 mAh g^{-1} , with a discharge voltage of around 0.21 V. At 25°C and 10 mA g^{-1} , the ionic liquid electrolytes exhibited a much lower discharge capacity of 9.2 mAh g^{-1} (Figure 4a). The Al– CF_x battery performs significantly better in molten salt electrolytes than in ionic liquid electrolytes. Galvanostatic intermittent titration technique (GITT) was employed at 85°C and 20 mA g^{-1} to evaluate the kinetic performance of Al– CF_x batteries in two electrolytes, and the Al^{3+} diffusion coefficient was calculated. The results show that the molten salt system has a discharge capacity of 854.5 mAh g^{-1} , significantly higher than the ionic liquid system at 611.4 mAh g^{-1} , with the molten salt electrolytes exhibiting a higher kinetic voltage plateau (Figure 4b). The higher Al^{3+} diffusion coefficient in the molten salt electrolytes significantly enhances electrochemical reaction kinetics (Figure 4c). Tafel analysis reveals that the molten salt electrolytes exhibit a significantly higher exchange current density (0.039 mA cm^{-2}) than the ionic liquid electrolytes (0.006 mA cm^{-2}) (Figure 4d), further confirming the superior electrochemical kinetics of the molten salt electrolytes [38].

To elucidate the impedance evolution of Al– CF_x batteries during discharge, in situ EIS was performed in two types of electrolytes,

coupled with distribution of relaxation times (DRT) analysis (Figures 4e,f, S4, and S5). In the molten salt electrolytes, the in situ EIS data show a relatively high charge-transfer resistance (R_{ct}) in the mid-to-high frequency region at the beginning of discharge (Depth of Discharge, DOD = 0). As DOD increases, R_{ct} gradually decreases and eventually plateaus, indicating accelerated electrochemical kinetics and a stabilized charge-transfer process. DRT analysis of the molten salt electrolytes further elucidates the physical origin of impedance variations across the full EIS frequency range through relaxation time distribution deconvolution, allowing clear assignment of individual electrochemical processes [39]. In contrast, the ionic liquid electrolytes initially exhibit an R_{ct} value similar to that of the molten salt electrolytes. Although R_{ct} also decreases and stabilizes with increasing DOD, a key difference is observed: the ionic liquid electrolytes display significantly higher diffusion impedance, which rises progressively throughout discharge. This distinct and irregular trend directly confirms the inferior ion transport capability of the ionic liquid electrolytes compared to the molten salt electrolytes. To validate the practical potential of the molten salt Al– CF_x primary batteries, we connected four cells in series, achieving a total voltage of 8.01 V, which successfully powered a purple LED (Figure S6). Discharge tests were performed on molten salt electrolyte batteries at various current densities (10, 20, 50, and 100 mA g^{-1}), as shown in Figure 4g. The results indicate that the discharge capacity at lower current densities closely aligns with the theoretical capacity of CF_x . As current density increases, a decline in discharge capacity is observed, suggesting that the molten salt electrolyte performs optimally at lower discharge currents. The capacity loss at higher currents is likely due to the limited conductivity of the CF_x cathode material [40].

To unravel the superior performance of Al– CF_x batteries in molten salt electrolytes, we systematically investigated the effects of Na^+ , K^+ , and Li^+ by substituting 20 mol% of EMIC in the AlCl_3 –EMIC electrolyte with NaCl, KCl, or LiCl. Electrochemical measurements revealed that LiCl substitution afforded the optimal performance, elevating the discharge voltage plateau to $\approx 0.4 \text{ V}$ and delivering a specific capacity of 850 mAh g^{-1} . Substitution with NaCl increased the voltage plateau to $\approx 0.28 \text{ V}$ with a specific capacity of 750 mAh g^{-1} , while KCl substitution resulted in only a modest improvement, yielding a specific capacity of 560 mAh g^{-1} with voltage enhancement confined to the early discharge stage. Compared to the AlCl_3 –EMIC baseline, the introduction of these alkali metal salts markedly enhanced the discharge performance of Al– CF_x batteries (Figure 4h). To further verify this cation-dependent enhancement and extend its generality, we evaluated Al– CF_x batteries at room temperature using ionic liquid electrolytes modified with single or multiple alkali cations (Figure S7). The results demonstrate that incorporating any single alkali cation (Li^+ , Na^+ , or K^+) at room temperature markedly elevates both the discharge plateau and capacity, following the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ —consistent with the trend observed at 85°C . More importantly, the coexistence of multiple alkali cations leads to further enhanced discharge performance, outperforming all single-cation systems. These findings confirm that the benefits of multi-cation incorporation are operative across both room and elevated temperatures, underscoring the critical role of cation identity and interionic interactions in governing discharge kinetics. Consequently, the novel quaternary molten salt

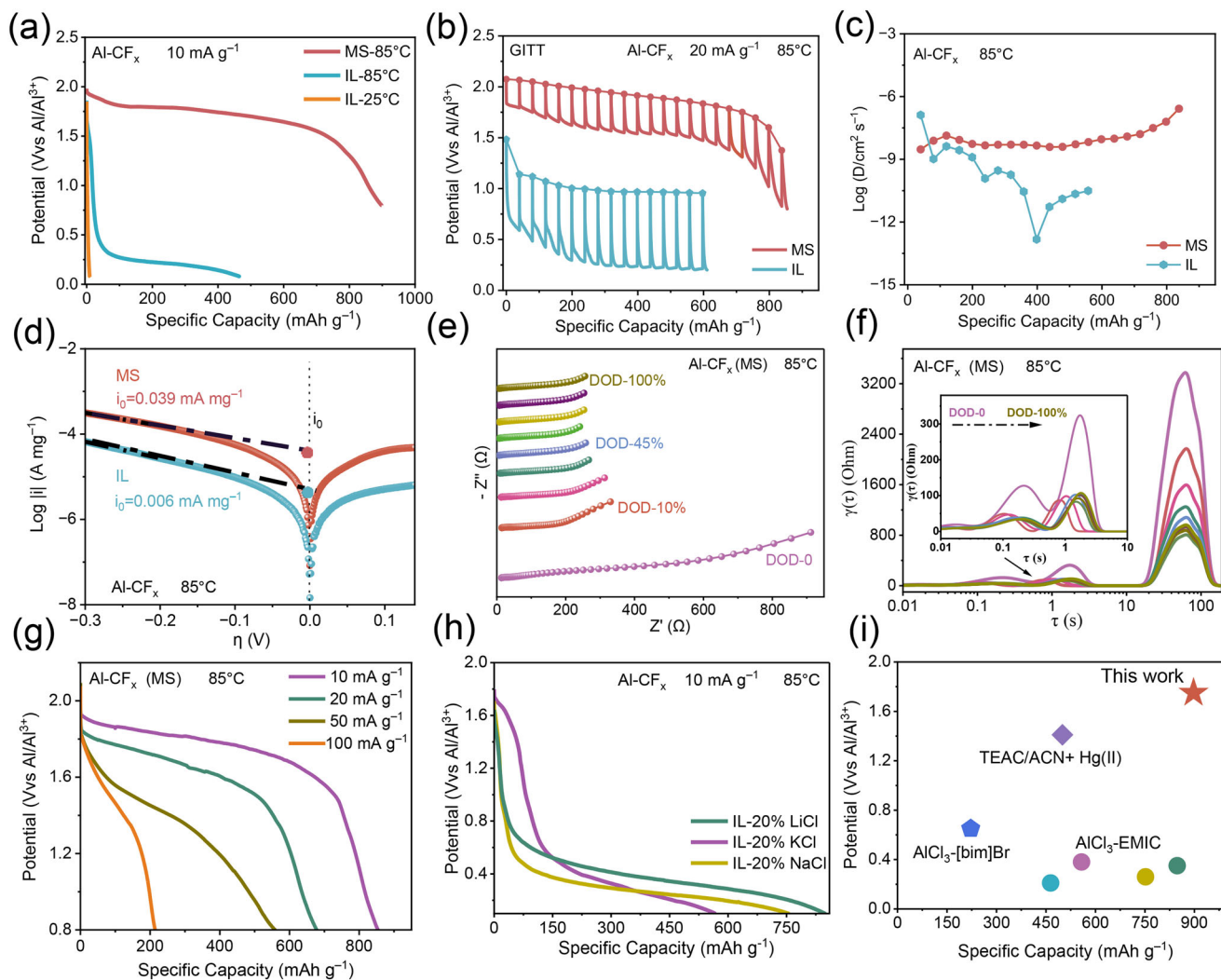


FIGURE 4 | Electrochemical performance of Al-CF_x primary batteries in molten salt and ionic liquid electrolytes. (a) Galvanostatic discharge curves at a current density of 10 mA g⁻¹. (b) GITT curves at a current density of 20 mA g⁻¹. (c) Comparison of Al³⁺ diffusion coefficient curves in the two electrolytes. (d) Tafel polarization plots. (e) In situ EIS in molten salt electrolytes. (f) DRT analysis of in situ EIS data from the molten salt system. (g) Rate performance at varied discharge rates in molten salt electrolytes. (h) Discharge curves of ionic liquid electrolytes doped with 20 mol% LiCl/NaCl/KCl. (i) Comparison of electrochemical performance between this work, previous reports, and control samples in this study (based on discharge specific capacity and discharge voltage data).

electrolyte—integrating Li⁺, Na⁺, and K⁺—exhibits superior electrochemical performance over conventional ionic liquid electrolytes. Notably, compared with previously reported Al-CF_x batteries and the control samples in this work, our molten salt Al-CF_x battery exhibits a significantly higher discharge capacity and a superior discharge voltage (Figure 4i).

2.4 | Reaction Mechanism Identifications

XRD analysis revealed that as the discharge capacity increased, the fluorine-rich peak at $2\theta = 13.8^\circ$ in the CF_x electrode of the molten salt system gradually weakened and eventually disappeared. Meanwhile, enhanced peaks at $2\theta = 25.1^\circ$ as well as weak peaks at $2\theta = 42^\circ$ and 51.8° matched the standard JCPDS No.01-080-1007 for AlF₃ [41], indicating that the reaction is a conversion process, resulting in AlF₃ (Figure 5a). In the ionic liquid system, although the fluorine-rich peak weakened, it did

not completely vanish, suggesting that the conversion reaction was not fully completed, but AlF₃ was still produced (Figure S8a). Raman spectroscopy was performed on CF_x electrodes at different discharge depths in the molten salt system (Figure 5b). The I_D/I_G ratio increased with discharge depth, indicating an increase in structural defects within the carbon matrix [42]. This suggests that the formation of AlF₃ during the discharge reaction deposits onto the CF_x structure, exacerbating these defects [33, 43]. XPS analysis revealed significant changes in the C 1s spectra of CF_x as the discharge depth increased in the molten salt system (Figure 5c). Specifically, the C-F bond weakened significantly with increasing discharge capacity, while other bond types remained stable [44]. The modest surface signal change after 50% depth of discharge (DOD) is due to XPS probing only the surface, while the continued capacity stems from bulk C-F bond reduction. In the Al 2p spectra, Al-Cl bonds were gradually replaced by Al-F bonds (Figure S9), indicating that the reaction primarily involves the consumption of C-F bonds and the

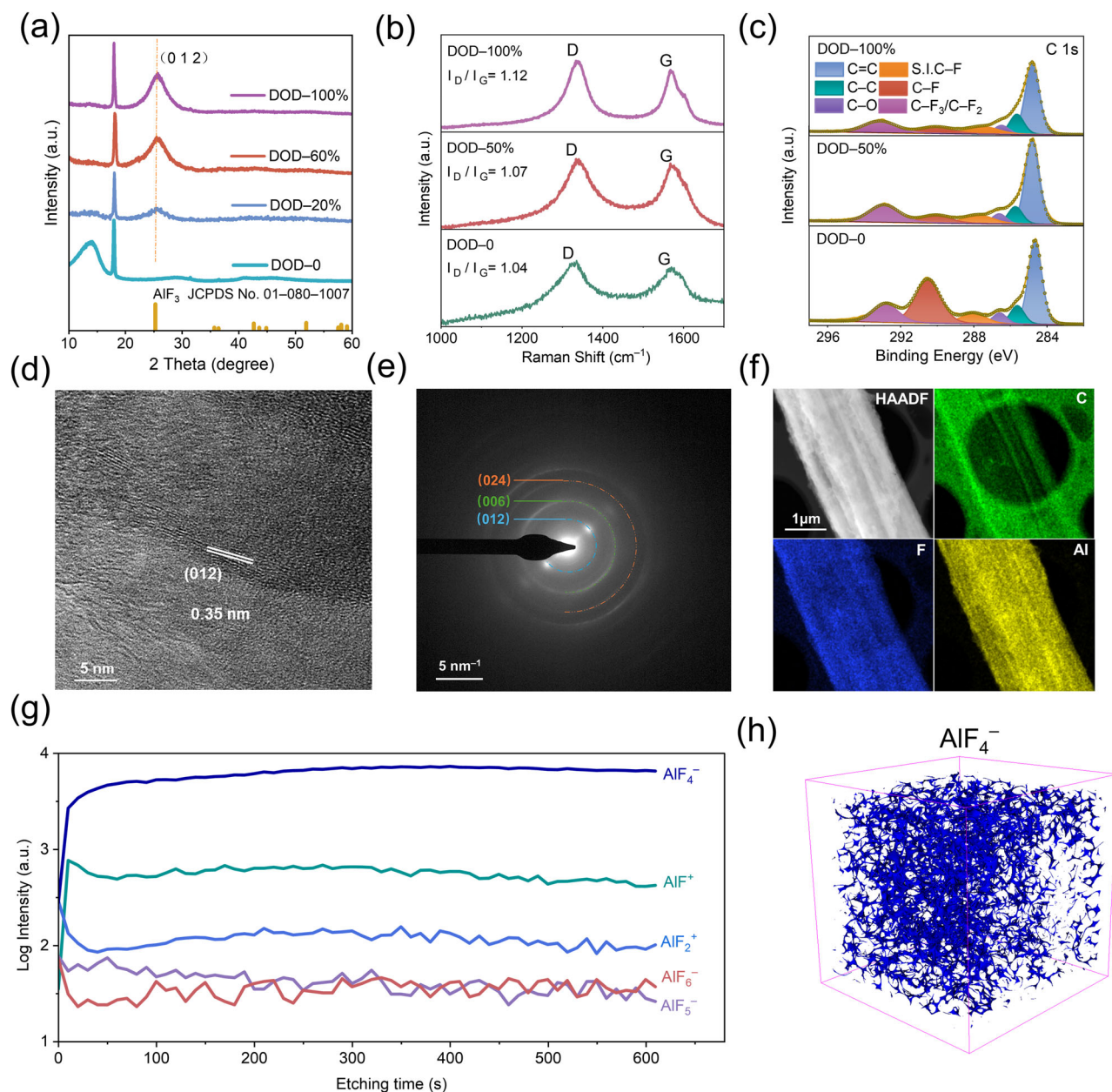


FIGURE 5 | Characterizations of the CF_x cathodes in molten salt Al-CF_x batteries during discharging. (a) XRD patterns of CF_x cathodes at different discharge depths. (b) Raman spectroscopy measurements of CF_x cathodes at different discharge depths. (c) XPS analysis of CF_x cathodes at different discharge depths. (d) HRTEM images of CF_x cathodes post-discharge. (e) SAED pattern of the CF_x cathode after full discharge. (f) HAADF-STEM images and elemental distribution maps of CF_x cathodes after full discharge. (g, h) TOF-SIMS depth profiling and 3D analysis of different secondary ions on CF_x cathode surfaces after full discharge.

formation of Al-F bonds, leading to the formation of AlF_3 . In the ionic liquid system, similar trends were observed. As the discharge depth increased, C-F bonds were significantly consumed, and Al-F bonds increased, while Al-Cl bonds remained dominant, suggesting that the conversion reaction was incomplete (Figure S8b,c).

To further investigate the microstructural properties of the discharge products on the CF_x surface, HRTEM and SAED analyses were conducted. In the molten salt system, lattice fringes with a spacing of 0.35 nm, corresponding to the (012) plane of AlF_3 , were observed (Figure 5d). The diffraction points and rings in the SAED pattern matched the (012), (006), and (024) planes

of AlF_3 , confirming its polycrystalline nature and small grain size (Figure 5e). Elemental analysis shows that after complete discharge, C, F, and Al elements are uniformly distributed on the CF_x cathode in the molten salt system (Figure 5f). In contrast, the elemental distribution in the ionic liquid system is uneven, as shown in Figure S8d. The SAED pattern analysis reveals a single diffraction ring with no distinct symmetric diffraction points corresponding to the (012) plane, indicating difficulty in product formation and the absence of well-defined crystallinity (Figure S8e). To assess AlF_3 distribution uniformity, post-discharge CF_x samples underwent 600 s time-of-flight secondary ion mass spectrometry (TOF-SIMS) depth etching. In the molten salt system, $\text{AlF}_4^+/\text{AlF}_2^+$ (positive mode) and $\text{AlF}_4^-/\text{AlF}_5^-/\text{AlF}_6^-$ (neg-

ative mode) were detected; AlF_4^- showed the highest signal intensity and homogeneous distribution (Figures 5 g,h and S10), confirming uniform AlF_3 formation. In contrast, the ionic liquid system exhibited stronger AlF_2^+ signals relative to AlF_4^- , with only weak AlF_4^- detected (Figures S8f–h and S11), indicating incomplete AlF_3 generation. These results demonstrate that in the molten salt system, the CF_x electrode undergoes a complete reaction, forming uniformly distributed AlF_3 , whereas in the ionic liquid system, AlF_3 forms, but the reaction is incomplete and the distribution is uneven, indicating reaction limitations.

The molten salt system comprises alkali metal cations (Li^+ , Na^+ , K^+), with its ionic clusters dominated by Al_2Cl_7^- and AlCl_4^- , along with minor amounts of $\text{Al}_n\text{Cl}_{3n+1}^-$ ($n > 2$) clusters. In contrast, the ionic liquid system contains large-sized EMI^+ cations, and its ionic clusters are primarily AlCl_4^- with trace Al_2Cl_7^- . Notably, the molten salt system exhibits a substantially higher $\text{Al}_2\text{Cl}_7^-/\text{AlCl}_4^-$ ratio than the ionic liquid system. To elucidate the role of intrinsic electrolyte properties in Al^{3+} desolvation and C–F bond cleavage in CF_x during the discharge of Al– CF_x batteries, we conducted in-depth investigations via theoretical computational chemistry. Density functional theory (DFT) calculations reveal that in the molten salt system, the high concentration of Al_2Cl_7^- is more broadly distributed on the CF_x surface, where Al^{3+} in Al_2Cl_7^- bears an average charge of 1.22 |e| and the CF_x surface carries a negative charge of –0.33 |e|, indicating high reactivity toward the discharge reaction. In contrast, the ionic liquid system is dominated by AlCl_4^- , where Al^{3+} bears a higher average charge of 1.51 |e| and the CF_x surface exhibits a lower negative charge of –0.21 |e|, suggesting reduced reactivity (Figure 6a). Integrated Crystal Orbital Hamilton Population (ICOHP) analysis further shows that the Al–Cl–Al linkages in Al_2Cl_7^- are weaker than Al–Cl single bonds, facilitating the dissociation of Al_2Cl_7^- and Al^{3+} desolvation (Figure S12). DFT structural optimization indicates that alkali metal cations (Li^+ , Na^+ , K^+) in the molten salt system significantly enhance C–F bond cleavage through electrostatic interactions (Figures 6b and S13). Smaller cations like Li^+ exhibit stronger attraction to F^- , activating the C–F bond, elevating the negative charge density of F^- , and facilitating its dissociation from the CF_x carbon framework. In contrast, the larger EMI^+ cation in the ionic liquid system exerts weaker attraction to F^- due to steric hindrance, resulting in lower C–F bond cleavage efficiency. Bond energy calculations demonstrate that the bond energies of AlCl_4^- and Al_2Cl_7^- are significantly lower than those of AlF_4^- and Al_2F_7^- , indicating a thermodynamic driving force for the conversion of Al–Cl to Al–F bonds during the discharge reaction, which releases energy and forms stable Al–F bonds (Figure 6c). Additionally, density of states (DOS) analysis reveals that fluorination induces a transition in CF_x from sp^3 (σ bonds) to sp^2 ($\sigma+\pi$ bonds) hybridization in FC–FC bonds, enhancing the bond strength, mechanical stability, and conductivity of the carbon framework (Figures S14 and S15).

Molecular dynamics (MD) simulations further elucidate the discharge behavior of Al– CF_x batteries in the molten salt system (Figure 6d). Radial distribution function (RDF) and coordination structure analyses reveal that in the F^- -dominated inner coordination shell (ICS), the average Al–F bond length is 2.37 Å with a coordination number of 4.2, forming a compact tetrahedral coordination (Figure 6e). In contrast, the Al–Cl bond exhibits

a longer length (2.89 Å) and lower coordination number (3.1) (Figure S16a), indicating that Al^{3+} preferentially forms stable coordination with F^- in the early stage of the discharge reaction. For the Cl^- -dominated outer coordination shell (OCS), the Al–F and Al–Cl bond lengths are 5.15 and 5.54 Å, respectively, confirming a dual-layer solvation structure (ICS: F^- ; OCS: Cl^-). The high stability of the Al–F coordination layer in the ICS provides a critical structural foundation for AlF_3 formation. Further MD simulations demonstrate that Li^+ and Na^+ preferentially coordinate with F^- to accelerate F^- transfer toward Al^{3+} , while K^+ primarily interacts with Cl^- to stabilize the molten salt electrolyte (Figure S16b–g). Ab initio molecular dynamics (AIMD) simulations validate the dynamic transition from Al–Cl to Al–F bonds, with six Al–F bonds formed within 30 ps (Figure 6f). This transition concurrently induces localized graphitization and conjugated structure formation in the CF_x carbon framework, which may further modulate the electrochemical performance (Figures S17–S19).

Comprehensive analyses demonstrate that the molten salt system, via the synergy between higher-order $\text{Al}_n\text{Cl}_{3n+1}^-$ clusters and alkali metal cations (Li^+ , Na^+ , K^+), facilitates facile Al^{3+} desolvation and C–F bond cleavage. Specifically, the small-sized and low-steric-hindrance alkali metal ions activate and cleave C–F bonds through strong electrostatic attraction to F atoms; the desorbed F^- subsequently undergoes substitution with desolvated Al^{3+} to form more stable AlF_3 (Figure 6g). Notably, different alkali metal cations exhibit differentiated functional roles during the discharge process: K^+ acts as an efficient “surface initiator” via its mild adsorption, ensuring rapid C–F bond activation in the initial stage; whereas Li^+/Na^+ serve as superior “bulk converters” by virtue of their stronger interactions and smaller ionic radii, driving sustained reaction during deep discharge. This trade-off and synergy between surface compatibility and bulk mobility underpins the exceptional overall performance of the multi-cation molten salt system. (Figure S20). In contrast, the ionic liquid system—characterized by a low content of higher-order clusters and significant steric hindrance from EMI^+ —exhibits restricted Al^{3+} desolvation and inefficient C–F bond cleavage, resulting in compromised AlF_3 formation efficiency (Figure 6h). The molten salt system’s superiority stems from efficient Al^{3+} desolvation, facile C–F bond scission, and thermodynamically favorable Al–F bond formation, which collectively enhance discharge capacity and reaction kinetics. Integrating advanced characterization and theoretical simulations, this study systematically elucidates the discharge mechanism of molten salt-based Al– CF_x batteries. It delineates the pivotal mediating role of higher-order $\text{Al}_n\text{Cl}_{3n+1}^-$ clusters and alkali metal cations in C–F bond activation. Relative to ionic liquid counterparts, the molten salt electrolyte exhibits substantially enhanced charge transfer kinetics and reactivity, furnishing robust support for developing high-capacity, high-stability Al– CF_x batteries.

2.5 | Electrochemical Performance of the Al– MnO_2 @ CF_x Battery

The low conductivity of CF_x and the stable deposition of its discharge product, AlF_3 , on carbon structures, limit the rate performance of Al– CF_x batteries [4]. To address this, we employed an interface engineering strategy to enhance the electrochemical

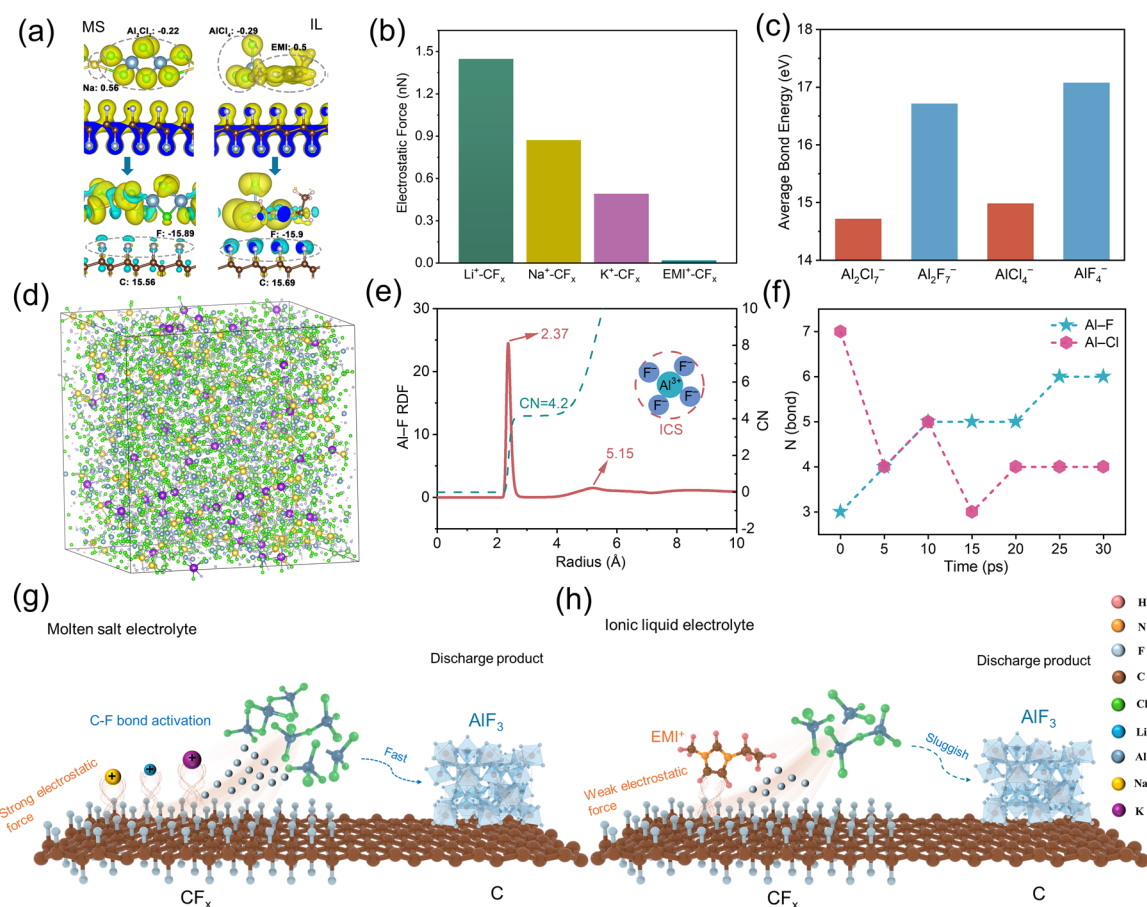


FIGURE 6 | Investigations on the discharge mechanisms of Al- CF_x batteries in molten salt and ionic liquid electrolytes. (a) Differential charge calculations for molten salt and ionic liquid reaction systems based on DFT. (b) Magnitudes of electrostatic attraction between cations and fluorine atoms in CF_x across different electrolyte systems. (c) Simulated calculations of Al-Cl and Al-F bond energies in AlCl_4^- , Al_2Cl_7^- , AlF_4^- and Al_2F_7^- ionic clusters. (d) MD simulations of reaction behaviors in the molten salt electrolyte. (e) RDF and inner coordination sphere of Al^{3+} during the reaction in molten salt electrolytes. (f) AIMD simulations uncover the dynamic transformation of Al-Cl bonds to Al-F bonds during the reaction process in the molten salt electrolyte. (g) Schematic illustration of the discharge reaction mechanism for primary Al- CF_x batteries in the molten salt electrolyte. (h) Schematic illustration of the discharge reaction mechanism for primary Al- CF_x batteries in the ionic liquid electrolyte.

performance. Specifically, we synthesized $\text{MnO}_2@\text{CF}_x$ composites containing 10 wt% MnO_2 via a hydrothermal method to construct an engineered $\text{MnO}_2\text{-CF}_x$ heterointerface. XRD confirmed the stable phase structure of CF_x , with weak MnO_2 peaks due to its low content (Figure S21a). XPS detected characteristic peaks of C, F, Mn, and O, with C 1s and Mn 2p spectra verifying chemical bonding between MnO_2 and CF_x (Figure S21b-d) [30], confirming that the contact is not merely physical but a chemically integrated interface. SEM revealed the MnO_2 coating on the CF_x surface, preserving its original structure, while EDS confirmed the uniform distribution of C, F, Mn, and O in $\text{MnO}_2@\text{CF}_x$ (Figures 7a and S21e, f). Electrochemical measurements in molten salt electrolyte at $20\text{ mA}\cdot\text{g}^{-1}$ show the Al- $\text{MnO}_2@\text{CF}_x$ battery exhibits a high discharge capacity of $791\text{ mAh}\cdot\text{g}^{-1}$ and a discharge voltage of $\approx 1.8\text{ V}$, versus a mere $22.4\text{ mAh}\cdot\text{g}^{-1}$ for the Al- MnO_2 battery (Figure 7b). These results confirm MnO_2 's negligible capacity contribution and highlight the advantage of the $\text{MnO}_2@\text{CF}_x$ composite cathode with an engineered heterointerface in synergistically enhancing battery capacity and voltage [40, 45, 46].

Subsequently, we probed the enhanced electrochemical performance of Al- $\text{MnO}_2@\text{CF}_x$ batteries via GITT at $20\text{ mA}\cdot\text{g}^{-1}$ (Figure 7c). Notably, relative to the CF_x -based counterpart, the Al- $\text{MnO}_2@\text{CF}_x$ battery delivers a substantially elevated kinetic voltage and a high discharge specific capacity of $830\text{ mAh}\cdot\text{g}^{-1}$. Concomitantly, the Al^{3+} diffusion coefficient in $\text{MnO}_2@\text{CF}_x$ is two orders of magnitude higher than that in CF_x (Figure 7d), demonstrating that the engineered $\text{MnO}_2\text{-CF}_x$ heterointerface remarkably accelerates Al^{3+} diffusion kinetics. Tafel analysis further confirms the kinetic superiority of the Al- $\text{MnO}_2@\text{CF}_x$ system: it delivers an exchange current density (i_0) of $0.12\text{ mA}\cdot\text{mg}^{-1}$, which is substantially higher than the $0.039\text{ mA}\cdot\text{mg}^{-1}$ of the Al- CF_x battery (Figure 7e), indicative of superior electrochemical reaction kinetics. Electrochemical performance tests under varied current densities reveal that the $\text{MnO}_2@\text{CF}_x$ electrode retains a discharge capacity of $426\text{ mAh}\cdot\text{g}^{-1}$ even at a high current density of $400\text{ mA}\cdot\text{g}^{-1}$, significantly improving the rate capability of the Al- CF_x battery (Figure 7f). Notably, under a high areal loading of $6\text{ mg}\cdot\text{cm}^{-2}$, the electrode still achieves an impressive specific capacity of $743.6\text{ mAh}\cdot\text{g}^{-1}$ at $20\text{ mA}\cdot\text{g}^{-1}$ (Figure 7g).

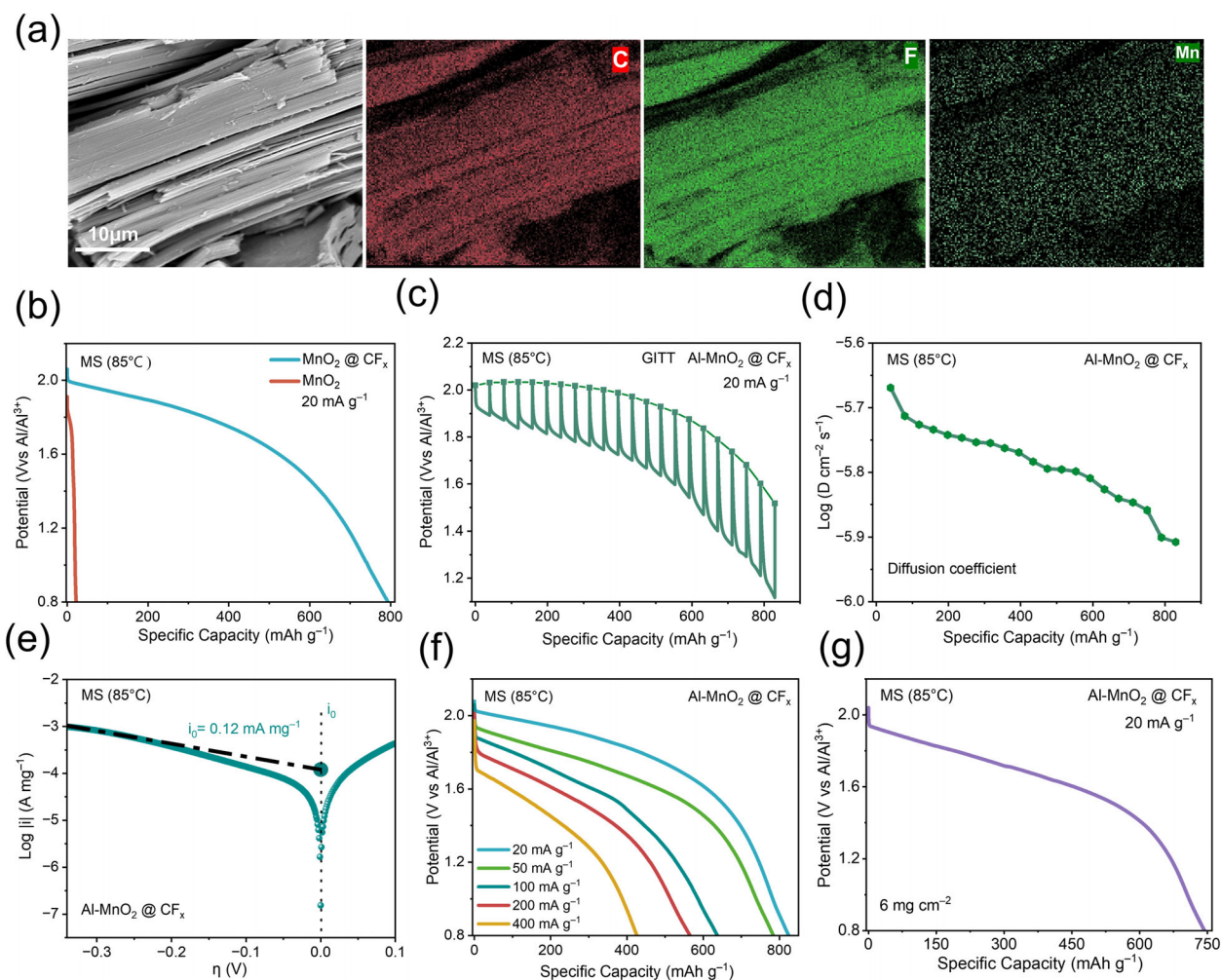


FIGURE 7 | Characterizations of the MnO₂@CF_x cathode and its electrochemical performance in molten salt electrolytes. (a) SEM morphologies and elemental analyses. (b) Electrochemical performances of Al-MnO₂@CF_x and Al-MnO₂ primary batteries. (c) GITT test of the Al-MnO₂@CF_x primary battery at 20 mA g⁻¹. (d) Diffusion coefficients of Al³⁺ during the reaction of the Al-MnO₂@CF_x primary battery. (e) Tafel tests of the Al-MnO₂@CF_x primary battery. (f) Rate performances of the Al-MnO₂@CF_x Battery. (g) Electrochemical performances of the Al-MnO₂@CF_x primary battery with a high-loading cathode.

Collectively, these results verify that the Al-MnO₂@CF_x battery, constructed with MnO₂@CF_x electrodes featuring an engineered heterointerface, exhibits excellent electronic conductivity and remarkable electrochemical activity in molten salt electrolytes.

3 | Conclusion

We have developed a high-energy Al-CF_x primary battery employing a molten salt electrolyte, demonstrating the crucial role of chemical bond activation in governing electrochemical performance. The molten salt electrolyte features abundant higher-order clusters (e.g., Al₂Cl₇⁻, Al₃Cl₁₀⁻) containing electrochemically active Al-Cl-Al linkages that markedly lower the desolvation energy barrier of Al³⁺ ions, thereby accelerating the overall electrochemical reaction kinetics. Meanwhile, alkali metal ions (Li⁺, Na⁺, K⁺), characterized by small ionic radii and minimal steric hindrance, interact strongly with F⁻ ions within CF_x, effectively activating C-F bonds. This interaction facilitates the migration of F⁻ toward Al³⁺ ions and promotes the thermodynamically favorable formation of AlF₃. As a result,

the molten salt-based Al-CF_x battery achieves an exceptional discharge plateau of 1.75 V and a specific capacity of 897.7 mAh g⁻¹ at 85°C and 10 mA g⁻¹. Moreover, the MnO₂@CF_x composite cathode significantly enhances charge transfer and ion diffusion kinetics, retaining 426.4 mAh g⁻¹ at 400 mA g⁻¹ and 743.6 mAh g⁻¹ under a high mass loading of 6 mg cm⁻², demonstrating excellent rate and load performance. This study elucidates the C-F bond activation mechanism induced by alkali metal ions in molten salt electrolytes and provides an in-depth understanding of its critical role in enhancing reaction kinetics within the Al-CF_x system. These insights offer essential theoretical support for achieving high electrochemical performance and establish a solid foundation for future developments in related energy storage technologies.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (2024YFA1211800), the National Natural Science

Foundation of China (52127816), the Science and Technology Special Fund of Hainan Province (ZDYF2025GXJS008), the Hubei Provincial Science and Technology Innovation Talent Scheme Project (2024DJA006), Hubei Provincial Key Research and Development Program (2023BAB140) and the Natural Science Foundation of Hubei Province (2025AFA105, 2022CFD007, 2024BAA013).

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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