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Tailoring C–F configurations in O–CF_x cathodes via wet chemistry for 600 Wh kg^{−1} Li/O–CF_x pouch cells

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Li/CF_x primary batteries, featuring an ultra-high theoretical energy density (2180 Wh kg^{−1}), have been widely employed in critical military and commercial applications, *e.g.*, deep-space and deep-sea exploration. However, the underlying relationship between their specific C–F configurations and rate performance has not been fully understood. Herein, a scalable synthesis strategy for oxidized CF_x (O–CF_x) is reported. Notably, oxidation-time regulated C–F configurations, including the F/C ratio, type of C–F bonds and structure of carbon frameworks, can be synergistically achieved via defluorination followed by re-fluorination of pristine CF_x. Consequently, electrons from adjacent heteroatoms and functional groups occupy the antibonding orbitals of C–F bonds (σ_{C-F}^*), thereby increasing the proportion of electrochemically active semi-ionic C–F bonds by nearly twofold in O–CF_x. Benefiting from the optimized C–F configurations, Li/O–CF_x batteries deliver a power density of 8.44×10^4 W kg^{−1} at 50C and operate robustly across an all-climate temperature range (−40 °C to 60 °C). 21 Ah-level Li/O–CF_x pouch cells achieve impressive energy densities of 614.75 Wh kg^{−1} and 693.92 Wh L^{−1} at 0.5C. This work proposes a novel design strategy for all-climate Li/CF_x batteries featuring dual-high power and energy densities.

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Broader context

Li/CF_x primary batteries (LPBs) have been widely used in critical military and commercial applications, *e.g.* deep-space and deep-sea exploration. However, it is still difficult to simultaneously achieve the high-rate and all-climate capability of Li/CF_x batteries. Herein, a scalable synthesis strategy for oxidized CF_x (O–CF_x) with functional group and O atom doping is reported. An oxidation-time regulated C–F configuration, including the F/C ratio, type of C–F bonds and structure of carbon frameworks, can be synergistically achieved via defluorination followed by re-fluorination of pristine CF_x. Benefiting from the nearby heteroatoms (*e.g.* O) and functional groups (*e.g.* –COOH and –OH), electrons can be transferred to the antibonding orbitals of C–F (σ_{C-F}^*), thus facilitating the breaking of C–F bonds and endowing the system with high-rate and all-climate capabilities. Li/O–CF_x pouch cells can achieve outstanding energy densities of 614.75 Wh kg^{−1} and 693.92 Wh L^{−1} at 30 °C, as well as successfully operate at −40 °C (318.66 Wh kg^{−1}). This work highlights the important role of doping heteroatoms as electron donors in regulating C–F bond cleavage and provides a generalizable framework for designing all-climate Li/CF_x batteries with dual-high performance.

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1. Introduction

Primary lithium batteries (PLBs), which refer to non-rechargeable batteries, have been widely used in military, aerospace, and implantable medical devices.^{1,2} Among the different types of commercial PLBs, *e.g.* Li/SO₂, Li/MnO₂, Li/SOCl₂ and Li/CF_x batteries, Li/CF_x batteries have aroused great interest in the scientific community due to their ultra-high theoretical energy density (2180 Wh kg⁻¹), extremely low self-discharge rate (<0.5% per year), stable operating voltage (3.0–3.2 V), and excellent environmental stability (>10 years).³

In the research of CF_x cathodes, the “structure–performance” relationships governing their electrochemical behavior are pivotal. C–F patterns in CF_x, which typically refer to the (1) F/C molar ratio,⁴ (2) types of C–F bonds,⁵ and (3) carbon frameworks,⁶ represent the most critical aspects. For example, the non-stoichiometric F/C mole ratio (*x*, ranging from 0 to 1.3) is the key factor influencing the capacity, rate performance and low-temperature performance of batteries.⁷ Sub-fluorinated CF_x (*x* < 1) exhibits better performance at high discharge rates and low temperatures. Furthermore, the types of C–F bonds constitute another crucial factor affecting the electrochemical properties of Li/CF_x batteries.⁸ C–F bonds, which are generally categorized as covalent (~1.4 Å), semi-ionic (~1.7 Å), or ionic (~3.0 Å), are based on bond length and strength, with vastly distinct electrochemical activities.⁹ Specifically, a high proportion of covalent C–F bonds disrupts the conductive network of the conjugated graphite matrix, resulting in insulating properties. Unfortunately, ionic C–F bonds typically form only at low F/C ratios (*x* < 0.05) despite their ability to provide high conductivity. In contrast, semi-ionic C–F bonds (SI C–F) with a moderate binding energy (287.8 eV) are present in practical materials and supply electrons delocalized by conjugated C=C bonds,¹⁰ thereby enhancing the conductivity of CF_x.¹¹ Carbon frameworks, referring to the skeletal structures derived from carbon precursors, also regulate the conductivity and Li⁺ diffusion within the cathode, thus affecting the capacity and rate performance.^{12,13} Collectively, the above parameters provide a comprehensive framework for understanding and synergistically regulating the electrochemical performance of Li/CF_x batteries.

Based on the aforementioned concept, extensive efforts have been devoted to tailoring CF_x materials with optimal C–F configurations to boost the rate performance and adaptability under extreme conditions. The methods reported thus far for regulating C–F configurations fall into physical and chemical approaches.¹⁴ Physical approaches include ball milling¹⁵ and coating CF_x with active additives (*e.g.*, Ag,¹⁶ MnO₂¹⁷ and SiO₂¹⁸) to optimize the cathode conductivity. Unfortunately, these physical approaches exhibit obvious drawbacks, such as inhomogeneous modification, resulting in limited performance improvement. Chemical approaches, which typically aim at defluorination/fluorination of pristine CF_x,¹⁶ provide a versatile means of regulating the C–F configurations. Mainstream methods, including hydrothermal defluorination/fluorination,¹⁹ plasma treatment,²⁰ direct gas-phase defluorination/fluorination (*e.g.*, using F₂ or BF₃),²¹ and high-temperature

treatment have been reported recently.²² However, these approaches often require harsh reaction conditions and cumbersome procedures, while also involving environmentally hazardous side reactions. Therefore, developing an efficient and scalable method to precisely tailor C–F configurations *via* simple steps under mild conditions is crucial for fabricating dual high-performance Li/CF_x batteries that operate reliably across all-climate scenarios.

In this work, a kilogram-scale synthesis strategy for oxidized CF_x (O–CF_x) with functional groups (*e.g.*, –COOH and –OH) and heteroatom doping (*e.g.*, O, S, and N) is reported. Through a simple wet-chemistry treatment using HNO₃ and H₂SO₄ solutions, C–F configurations, including the F/C ratio (*x* = 0.62 to 0.52), types of C–F bonds, and interlayer spacings of the carbon framework, have been synergistically modified. More importantly, oxidation-time-dependent regulation of C–F configurations is verified *via* detailed characterization (*e.g.*, XPS, FT-IR, TEM and ToF-SIMS). Interestingly, defluorination and re-fluorination of pristine CF_x materials can be sequentially achieved by extending the oxidation time. Benefiting from this modification, electrons from adjacent O atoms occupy the antibonding orbitals of C–F bonds (σ_{C–F}^{*}), which weakens the C–F bonds and increases the proportion of SI C–F bonds in O–CF_x. Consequently, theoretical results and DRT analysis show that O atom doping significantly enhances the electrical conductivity and the reaction kinetics of O–CF_x, as well as the Li⁺ binding affinity. Meanwhile, the expanded interlayer spacing provides unobstructed pathways and storage sites for Li⁺ migration. Hence, Li/O–CF_x batteries exhibit excellent rate performance with an energy density of 8.44 × 10⁴ W kg⁻¹ at 50C, operate robustly in all-climate scenarios (–40 °C to 60 °C), and deliver a high specific capacity of 466 mAh g⁻¹ at 0.5C under –40 °C conditions. Additionally, 21 Ah pouch cells of Li/O–CF_x also provide outstanding energy densities of 614.75 Wh kg⁻¹ and 693.92 Wh L⁻¹ at room temperature and 318.66 Wh kg⁻¹ at –40 °C, which outperform values reported in previous literature. This work proposes a novel and cost-effective design strategy for high-performance all-climate Li/CF_x batteries with synergistically enhanced power and energy densities.

2. Results and discussion

The oxidation-time-dependent regulation of the C–F configuration process is conducted on CF_x through a mixed acid treatment (details in the Experimental Section, SI). Typically, a certain concentration of HNO₃/H₂SO₄ solution is used to functionalize pristine CF_x, yielding oxidized CF_x (O–CF_x). By adjusting the overall treatment time (up to 12 h), the proportion of semi-ionic C–F bonds (the C–F configuration with the highest electrochemical activity) can be precisely regulated through a sequential defluorination and re-fluorination process (Fig. 1a). To evaluate the effects of oxidation conditions (*e.g.* time and temperature) on the properties of O–CF_x, samples prepared with different oxidation times (O–CF_x-1, O–CF_x-2 and O–CF_x-5) and temperatures (O–CF_x-3 and O–CF_x-4) were tested

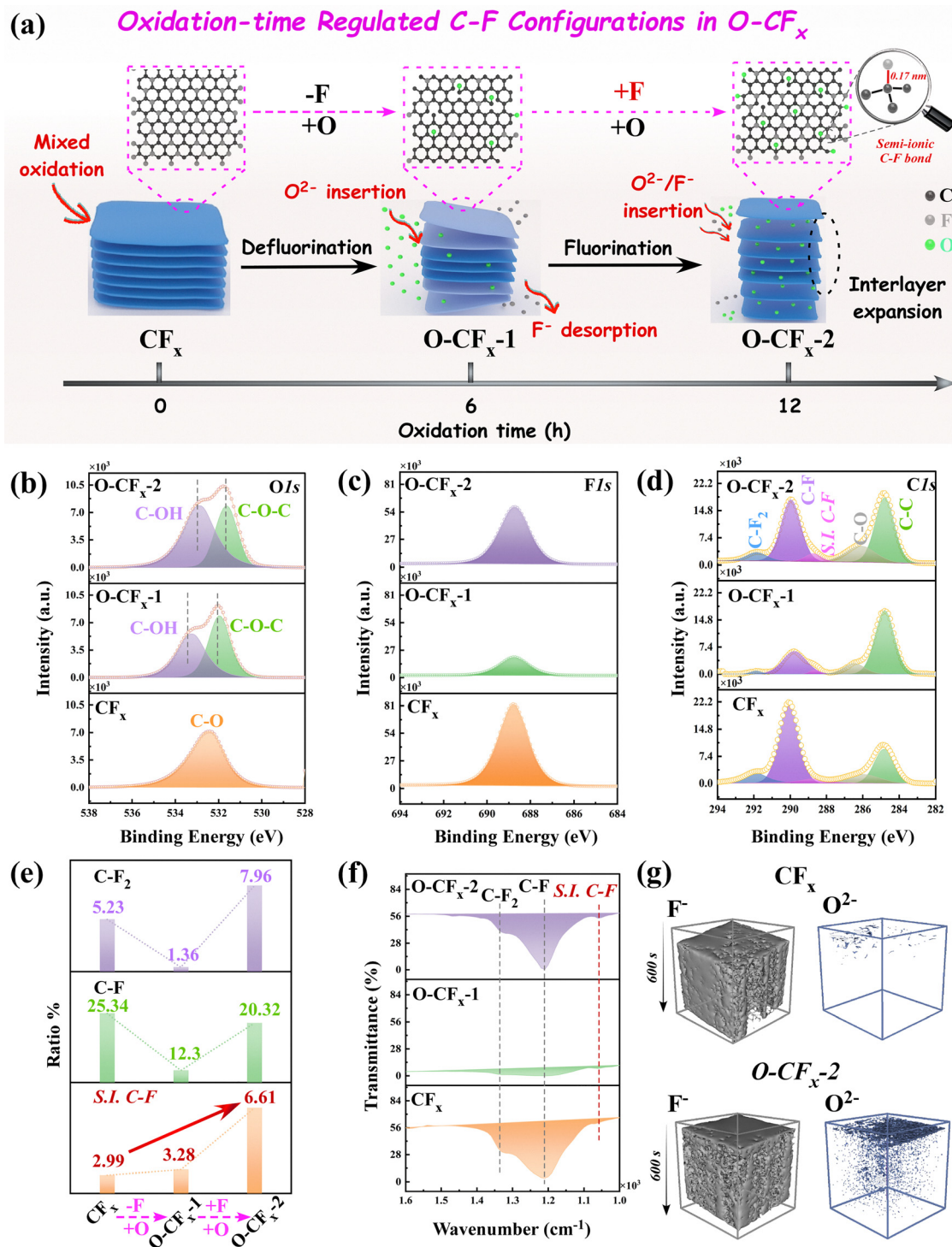


Fig. 1 Oxidation-time-dependent regulation of C-F configurations in O-CF_x. (a) Schematic of the oxidation-time-regulated preparation process for O-CF_x (CF_x for pristine materials, O-CF_{x-1} for 6 h and O-CF_{x-2} for 12 h oxidation). (b) O 1s XPS spectra. (c) F 1s XPS spectra. (d) C 1s XPS spectra. (e) Intensity ratio of semi-ionic C-F (SI C-F), C-F and C-F₂ bonds in the C 1s XPS spectra of different samples. (f) FT-IR spectra of SI C-F, C-F and C-F₂ bonds for different samples. (g) Depth-resolved ToF-SIMS results of F⁻ and O²⁻ ions of CF_x and O-CF_{x-2}.

to compare their chemical compositions and electrochemical performance (Table S1). It can be found that the proportion of semi-ionic C-F species in O-CF_x decreases at a lower oxidation temperature (80 °C) and prolonged oxidation time (16 h), leading to a poor high-rate performance limited to 20C (Fig.

S9 and S10). Therefore, 100 °C is set as the terminal oxidation temperature for further investigation. We specifically investigated the O-CF_{x-1} (6 h) and O-CF_{x-2} (12 h) samples at the same treatment temperature (100 °C) to understand how the C-F configurations varied with oxidation time. As shown in

Fig. 1b–d, X-ray photoelectron spectroscopy (XPS) analysis has been conducted on CF_x , O-CF_{x-1} and O-CF_{x-2} . Fig. 1b depicts the evolution of O 1s spectra. The pristine CF_x shows a single peak at 532.4 eV, which is attributed to the physically adsorbed oxygen species on the surface.²³ For O-CF_{x-1} , the O 1s spectrum can be deconvoluted into two characteristic peaks, corresponding to the C–O–C (532.0 eV) and C–OH (533.4 eV) groups, respectively. Similarly, the O 1s spectrum of O-CF_{x-2} shows two characteristic peaks, corresponding to C–O–C (531.7 eV) and C–OH (533.0 eV). In contrast to the pristine CF_x , the emergence of these new peaks in O-CF_x confirms the successful introduction of oxygen-containing functional groups *via* acid modification. Fig. 1c presents the F 1s spectra of CF_x , O-CF_{x-1} , and O-CF_{x-2} . Notably, at a fixed treatment temperature, the F content decreases initially and then increases with prolonged treatment time. This trend verifies the occurrence of a sequential defluorination and re-fluorination process during acid treatment. Unlike previous studies, where CF_x fluorination typically requires harsh conditions (*e.g.*, treatment with highly corrosive F_2 ²⁴ or HF ²⁵), this mild wet-chemistry fluorination route holds great promise for large-scale applications. In order to quantitatively evaluate the compositional variations among CF_x , O-CF_{x-1} , and O-CF_{x-2} , CHONS elemental analysis, inductively coupled plasma optical emission spectroscopy (ICP-OES), and high-performance liquid chromatography (HPLC) tests were conducted on different samples (Table S2, SI). After modification, the F/C ratio decreases to $x = 0.47$ in O-CF_{x-1} and then increases to $x = 0.52$ in O-CF_{x-2} , compared with $x = 0.62$ in pristine CF_x . This result further confirms that defluorination occurs in the early stage of oxidation, followed by re-fluorination as the treatment time is extended.

Fig. 1d shows the C 1s spectra of CF_x , O-CF_{x-1} , and O-CF_{x-2} . Here, the C 1s peaks of different samples all exhibit five different states, namely C–C, C–O, SI C–F, C–F, and C–F₂. However, the relative intensities of C–F and C–F₂ bonds in O-CF_x are significantly reduced when compared with CF_x , while the intensity of SI C–F bonds is increased. This implies that a large proportion of F^- ions can re-incorporate into CF_x in the form of SI C–F bonds during the subsequent fluorination process. Detailed quantitative studies of different C–F states of CF_x , O-CF_{x-1} , and O-CF_{x-2} are presented in Fig. 1e. The specific proportion of C–F, C–F₂ covalent bonds (electrochemically inert) and SI C–F bonds (electrochemically active) in all C–F bonds are calculated. Notably, with the extension of oxidation time, the proportion of SI C–F bonds increases from 2.99% to 6.61%, indicating the reintroduction of F^- ions in the form of SI C–F bonds. SI C–F bonds, which exhibit good Li^+ binding ability, can greatly improve the electrical conductivity, and further enhance the discharge capacity and rate performance of Li/CF_x batteries.²⁶ Additionally, Fourier transform infrared spectroscopy (FT-IR) results in Fig. 1f also indicate the increased proportion of SI C–F bonds after treatment. To intuitively characterize the elemental concentration and distribution of CF_x and O-CF_x , time-of-flight secondary ion mass spectrometry (ToF-SIMS) tests are conducted on different samples, as shown in Fig. 1g and Fig. S13. It can be seen that the

concentration of O^{2-} ions enhanced both on the surface and in the bulk of O-CF_{x-2} when compared with CF_x . Furthermore, F elements are distributed in both the surface and bulk phases of CF_x and O-CF_{x-2} , which indicates a real bulk F^- treatment of O-CF_{x-2} . XPS depth profiling of the F 1s, O 1s and C 1s spectra (Fig. S14), as well as the EELS analysis of F K-edge for a single O-CF_x particle shown in Fig. S15, further confirm the uniformity of oxidation and C–F configuration throughout the particle. Therefore, a combination of XPS, FT-IR, and ToF-SIMS characterization provides a comprehensive understanding of the oxidation-time-dependent regulation of C–F configurations in O-CF_x , demonstrating that the F/C ratio and type of C–F bonds can be synergistically optimized by this modification.

Fig. 2 explores the structural features and electrochemical property changes of O-CF_x . Fig. 2a shows the transmission electron microscopy (TEM) images of CF_x , O-CF_{x-1} , and O-CF_{x-2} , as well as the energy-dispersive X-ray spectroscopy (EDX) results of O elements. Here, with the extension of oxidation time, the content of O elements gradually increases in O-CF_x compared with pristine CF_x . Besides, the high-resolution transmission electron microscopy (HRTEM) images reveal an enlarged interlayer spacing with increasing oxidation time and temperature (Fig. 2b). It can be seen that the interlayer spacing of O-CF_x increases to 0.76 nm, which is almost twice as large as that of pristine CF_x ($d = 0.35$ nm). This enlarged interlayer spacing can further reduce the migration resistance of Li^+ , provide additional binding sites, and thereby improve the rate performance of Li/CF_x batteries.²⁷ Moreover, *in situ* electrochemical impedance spectroscopy (*in situ* EIS) tests were performed to verify the enhanced electrochemical properties of O-CF_x , and the relaxation time distribution (DRT) analysis is conducted to identify the kinetic changes during Li^+ intercalation. As shown in Fig. 2c and e, the impedance of O-CF_x decreases dramatically by a magnitude of $\Delta R = 110 \Omega$, while that of CF_x is only 70Ω . This indicates facilitated Li^+ intercalation in O-CF_x . Additionally, the DRT results in Fig. 2e and Fig. S18 show the in-depth analysis of kinetic differences between CF_x and O-CF_x during discharge. Generally, the impedance of Li/CF_x batteries continuously decreases with increasing depth of discharge (DOD), while O-CF_x cathodes exhibit lower impedance values when compared with that of CF_x cathodes, *e.g.*, bulk resistance, charge transfer resistance, and interfacial resistance. This implies the excellent electronic conductivity and rate performance of Li/O-CF_x batteries. Moreover, the galvanostatic intermittent titration technique (GITT) results also show a larger Li^+ diffusion coefficient (D_{Li^+}) for O-CF_x cathodes (Fig. S1). To further explore the effects of interlayer spacing on structural evolution during discharge, *in situ* Raman characterization was conducted on Li/CF_x and Li/O-CF_{x-2} batteries (Fig. 2d and f). The D band, which is typically regarded as an indicator of defects and disorders in carbon materials, can be used to evaluate the structural integrity of CF_x during discharge.²⁸ Here, the intensity ratio of D/G bands ($I_{\text{D}}/I_{\text{G}}$) differs between the cathodes before discharge: $I_{\text{D}}/I_{\text{G}}$ for O-CF_{x-2} is 1.22 and that for CF_x is 1.13 (Fig. S2). This indicates a higher proportion of defects and heteroatom doping in O-CF_{x-2} ,

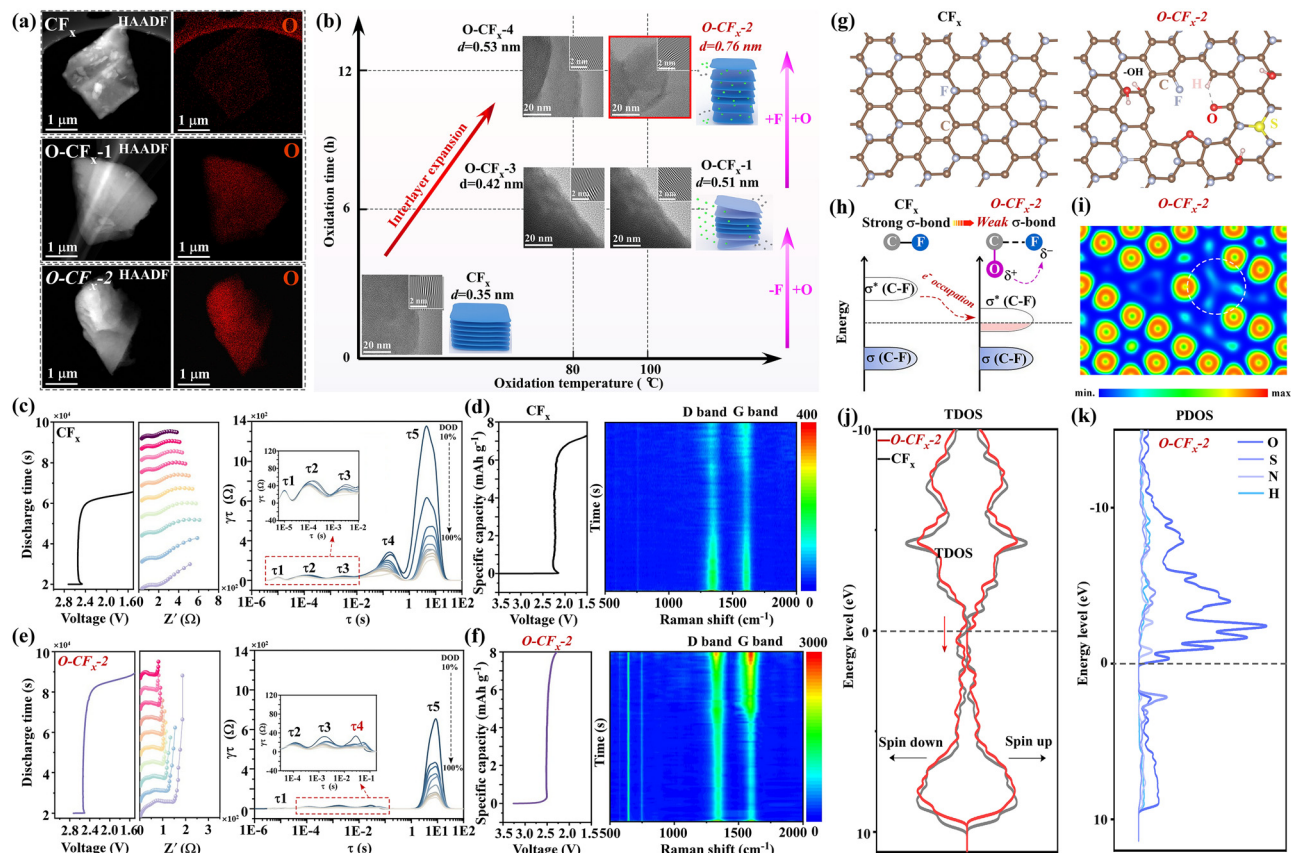


Fig. 2 Structural features, electrical and electrochemical properties of O-CFx. (a) HAADF-TEM images of CF_x, O-CFx-1 and O-CFx-2, corresponding to the EDX mappings of O elements. (b) Evolution of interlayer spacing (*d*) under different oxidation times and temperatures. (c) and (e) *In situ* EIS and DRT analysis of CF_x and O-CFx cathodes. (d) and (f) *In situ* Raman results of CF_x and O-CFx cathodes. (g) Structural models of CF_x and O-CFx. (h) Schematic diagram of the weakened C-F bonds in O-CFx. (i) Surface equipotential distribution of O-CFx-2. (j) DOS results. (k) PDOS results.

which is consistent with the XPS results in Fig. 1. During discharge, the intensities of the D band and G band are feeble at the initial stage and gradually diminish for CF_x, indicating an insufficient electrochemical reaction due to the narrow interlayer spacing. In contrast, O-CFx-2 cathodes exhibit the opposite trend, with a significant enhancement of both peaks, and the maximum intensity is nearly one order of magnitude higher than that of CF_x. These results clearly indicate that the enlarged interlayer spacing contributes to more adequate interfacial bonding between O-CFx and Li⁺.

Additionally, theoretical calculations based on density functional theory (DFT) verify the energetic advantages of O-CFx and elucidate the origins of C-F bond variations in O-CFx. Fig. 2g provides the computational models of CF_x and O-CFx-2, which are constructed based on the results of quantitative CHONS and HPLC measurements. Specifically, the pristine CF_x model has a fluorine content of *x* = 0.6, while the CF_x model corresponds to *x* = 0.5. Fig. 2i depicts the surface equipotential distribution of O-CFx-2 derived from the model shown in Fig. 2g. A pronounced accumulation of free electrons is observed at the defective carbon sites (marked by white dashed circles) and the C-F bonds adjacent to heteroatoms. This result indicates that the enhanced electrical conductivity

of O-CFx arises from atomic defects and surface modification effects. Moreover, free electrons are also detected around the undoped C atoms, demonstrating that the matrix C atoms still retain sp² hybridization, which further contributes to the electronic conductivity of O-CFx.²⁹ Fig. 2j and k show the total density of states (TDOS) and partial density of states (PDOS) of CF_x and O-CFx-2, respectively. In comparison with pristine CF_x, O-CFx-2 exhibits a significant increase in the density of states near the Fermi level, displaying distinctive quasi-metallic characteristics. In contrast, pristine CF_x has fewer occupied electronic states and behaves as a semiconductor. Detailed results of the PDOS reveal that O doping is the primary factor responsible for the modulation of electronic conductivity. The correlation between C-F bond evolution (from covalent to semi-ionic character) and conductivity enhancement in O-CFx is summarized in Fig. 2h. Given that oxygen has a lower electronegativity than fluorine, free electrons donated by O atoms can transfer to the unoccupied anti-bonding orbitals of C-F bonds (σ_{C-F}^{*}), thereby weakening the covalent C-F bonds.³⁰ This effect facilitates the cleavage of C-F bonds during the discharge process and endows O-CFx with excellent rate capability.

To evaluate the electrochemical behavior of O-CFx cathodes in PLBs, coin cells assembled with active materials of CF_x,

O-CF_x-1 and O-CF_x-2 were tested (details in the Experimental Section, SI). Fig. 3a shows the discharge curves of Li/CF_x batteries. The specific capacity of CF_x at 0.2C is 803.3 mAh g⁻¹, while the maximum discharge rate only reaches 10C with a specific capacity of 493 mAh g⁻¹. Moreover, a significant voltage hysteresis can be detected as the discharge rates increase, which is attributed to severe polarization in CF_x due to its poor electrical conductivity. Fig. 3b shows the behavior of O-CF_x-1 (with 6 h oxidation) at different rates from 0.2C to 10C, which is even worse than that of CF_x, e.g. 733.8 mAh g⁻¹ at 0.2C and 428.9 mAh g⁻¹ at 10C. This is because of insufficient active C-F bonds during the initial oxidation stage (*i.e.*, defluorination). In sharp contrast, O-CF_x-2 cathodes exhibit excellent rate performance with negligible voltage hysteresis even at 50C (Fig. 3c). The specific capacities of O-CF_x-2 cathodes at different discharge rates (0.2–50C) remain higher than those of CF_x and O-CF_x-1, along with enhanced discharge platforms. Even at the maximum discharge rate of 50C, O-CF_x-2 cathodes can deliver a specific discharge capacity of 244.4 mAh g⁻¹, confirming their outstanding rate capability. Fig. 3d shows the Ragone plot of Li/CF_x, Li/O-CF_x-1, and Li/O-CF_x-2 batteries, which is calculated from Fig. 3a–c. Here, O-CF_x-2 cathodes exhibit excellent dual-high performance with a power density of 84.4 kW kg⁻¹ and an energy density of 409 Wh kg⁻¹ at 50C, which is superior to CF_x, O-CF_x-1 and even the reported PLBs

based on CF_x (Fig. S3). To explore the adaptability of O-CF_x cathodes at all-climate environments, O-CF_x-2 cathodes with the DPM electrolyte (1 M LiClO₄ in 1,3-dioxolane (DOL):propylene carbonate (PC):methyl propionate (MP) = 1:1:12 vol%) were used for performance testing. Fig. 3e shows the discharge curves of CF_x and O-CF_x-2 cathodes at different discharge rates at –40 °C. It can be seen that the discharge capacities of the CF_x cathodes decrease rapidly, only maintaining 102 mAh g⁻¹ at 0.5C. In contrast, O-CF_x-2 cathodes can still exhibit a typical voltage plateau (1.8 ~ 2.0 V) and a capacity of 466.1 mAh g⁻¹ at –40 °C (0.5C). Specifically, the O-CF_x-2 cathode can reach 92.8% of the theoretical capacity at –40 °C (803 mAh g⁻¹ at 0.1C). These results comprehensively demonstrate the excellent low-temperature rate performance of Li/O-CF_x batteries. Fig. 3i provides the Ragone plot of O-CF_x and CF_x cathodes at –40 °C based on the results in Fig. 3e. Here, O-CF_x cathodes show excellent rate performance even at low temperatures. Besides, Fig. 3f and g show the discharge behavior of Li/O-CF_x batteries with the DPM electrolyte in a wide temperature range from 60 °C to –40 °C at 0.2C and 0.5C, respectively. It can be seen that Li/O-CF_x batteries deliver high capacities at all testing temperatures. Meanwhile, when compared to Li/O-CF_x batteries with commercial electrolyte (COE) (Fig. 3h), both electrolytes can provide a high specific capacity at 0.2C from 25 °C to –40 °C, which further verifies the

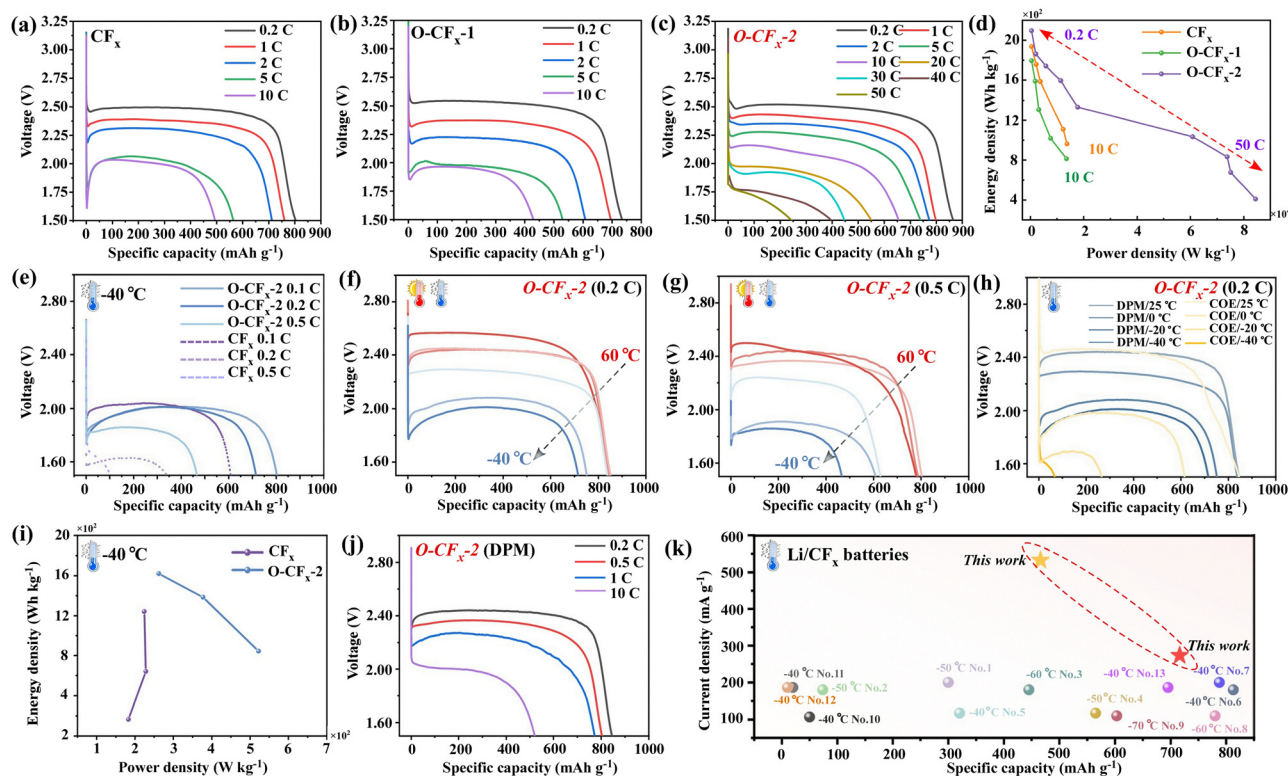


Fig. 3 Electrochemical behavior of Li/O-CF_x batteries. (a) Rate performance of Li/CF_x batteries (25 °C). (b) Rate performance of Li/O-CF_x-1 (6 h) batteries (25 °C). (c) Rate performance of Li/O-CF_x-2 (12 h) batteries (25 °C). (d) Ragone plots of Li/CF_x, Li/O-CF_x-1 and Li/O-CF_x-2 batteries (25 °C). (e) Discharge curves of Li/CF_x and Li/O-CF_x-2 batteries at different rates (–40 °C). (f) All-climate (60 °C to –40 °C) performance of Li/O-CF_x-2 batteries at 0.2C. (g) All-climate (60 °C to –40 °C) performance of Li/O-CF_x-2 batteries at 0.5C. (h) Low-temperature behavior (25 °C to –40 °C) of Li/O-CF_x-2 batteries with COE and DPM electrolytes. (i) Ragone plots of Li/CF_x and Li/O-CF_x-2 batteries at –40 °C. (j) Rate performance of Li/O-CF_x-2 (12 h) batteries with the DPM electrolyte (25 °C). (k) Comparison of low-temperature behaviors of recently reported Li/CF_x batteries (see Table S3).

temperature adaptability of O-CF_x-2 cathodes. Besides, the discharge plateau of batteries with the DPM electrolyte is longer and more stable. Furthermore, N₂ adsorption-desorption characterization of CF_x and O-CF_x-2 in Fig. S22 indicates that mix-acid oxidation does not markedly increase the surface area or porosity of materials, supporting that the enhanced performance is primarily associated with the intrinsic regulation of C-F configurations. Detailed effects of electrode-electrolyte relationships on discharge behavior will be discussed in Fig. 4 and 5. Even with the DPM electrolyte, O-CF_x-2 cathodes can reach a discharge rate of 10C (Fig. 3j). Thus, O-CF_x-2 cathodes in this work show outstanding rate performance when compared with recently reported studies on low-temperature Li/CF_x batteries (Fig. 3k), further highlighting their application prospects in extreme environments. Besides, in order to confirm the consistent effects of semi-ionic C-F bonds in O-CF_x during discharge, XPS analysis of the C 1s and F 1s spectra has been conducted on O-CF_x-2 cathodes with the DPM electrolyte under different discharge rates (10, 20 and 50C) and temperatures (0, -20 and -40 °C) at 50% depth of discharge (DoD) (Fig. S16). It shows that the proportion of SI C-F bonds in

O-CF_x-2 exhibits small variation with different discharge rates and temperatures, which suggests that the semi-ionic feature still persists of O-CF_x-2 during discharge at low temperature and high current (Fig. S17).

To comprehensively investigate the underlying mechanism for the outstanding rate performance of O-CF_x cathodes, theoretical calculations on the properties of C-F bonds in O-CF_x have been conducted. Fig. 4a shows the adsorption energy of Li⁺ on CF_x and O-CF_x models. It indicates that O-CF_x has a lower adsorption energy (-5.03 eV) with Li⁺ (O and F atoms as the binding sites) compared with that of CF_x (-4.35 eV), implying that O-CF_x cathodes have a stronger binding affinity toward Li⁺ during discharge. Fig. 4b shows the binding energy of C-F bonds in CF_x and O-CF_x. It can be found that F atoms have a lower binding energy with C atoms in O-CF_x (3.22 eV) when compared with that in CF_x (4.82 eV). This should be the result of the weakened C-F bonds due to the charge transfer from O to F atoms in O-CF_x. Also, the radial distribution function (RDF) analysis of C-F bonds in CF_x and O-CF_x models indicates that the average length of C-F bonds in O-CF_x

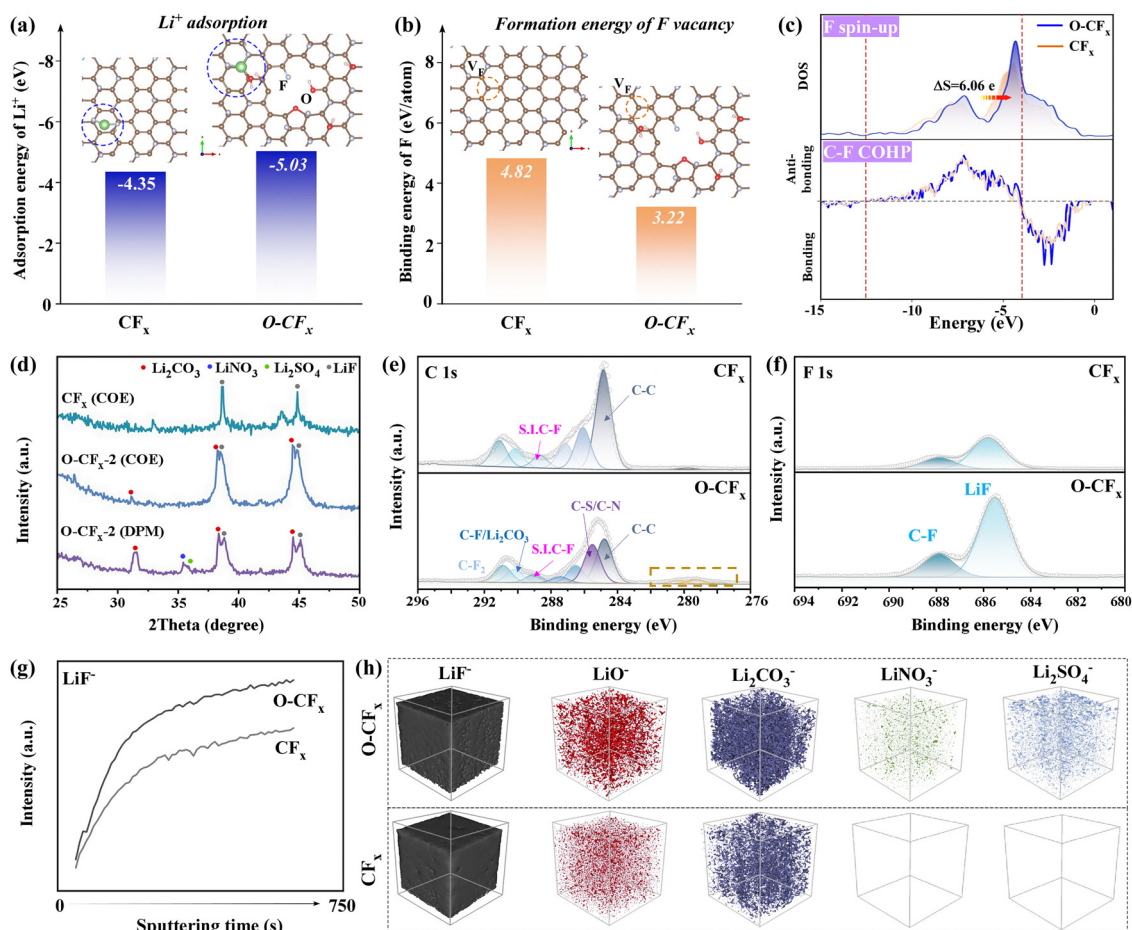


Fig. 4 Discharge products of CF_x and O-CF_x cathodes. (a) Adsorption energy of Li⁺ on CF_x and O-CF_x. (b) Binding energy of C-F bonds in CF_x and O-CF_x. (c) DOS of F spin-up orbitals and C-F COHP of CF_x and O-CF_x. (d) XRD results of CF_x and O-CF_x-2 cathodes after being discharged with different electrolytes. (e) C 1s and (f) F 1s XPS spectra of CF_x and O-CF_x-2 cathodes after being discharged with DPM. (g) ToF-SIMS depth profiles of LiF⁻ in discharged CF_x and O-CF_x-2 cathodes. (h) 3D plots of the ToF-SIMS depth profiles of various secondary ion species in discharged CF_x and O-CF_x-2 cathodes.

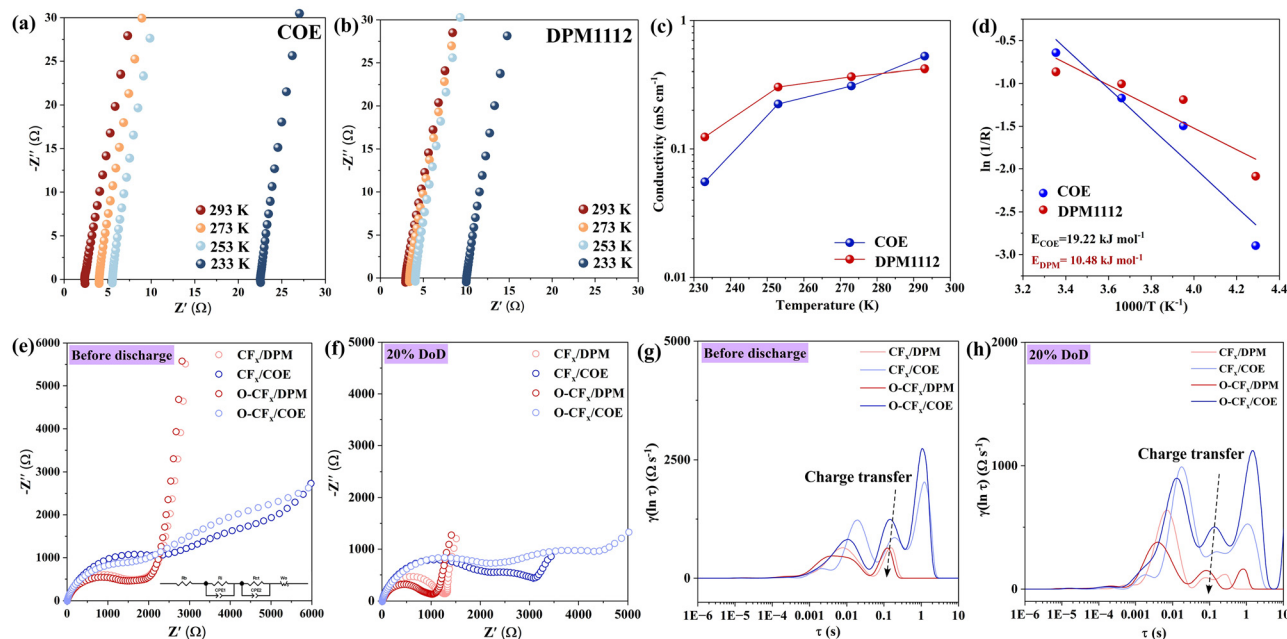


Fig. 5 Analyses of the kinetics of different cathodes and electrolytes at low temperatures. EIS results for SS||SS (stainless steel) symmetric cells with (a) COE and (b) DPM electrolytes measured at different temperatures. (c) Calculated ionic conductivities of (a) and (b). (d) Activation energy of different electrolytes fitted with the Arrhenius function. EIS results of Li/CF_x and Li/O-CF_x batteries with COE and DPM1112 electrolytes at -40°C (e) before discharge and (f) at 20% DoD. (g) and (h) Corresponding DRT of (e) and (f).

($d = 1.343 \text{ \AA}$) is larger than that in CF_x ($d = 1.338 \text{ \AA}$) (Fig. S21). Furthermore, to qualitatively analyze the electron-donor to $\sigma^*(\text{C-F})$ occupancy, the crystal orbital Hamilton population (COHP) analysis of C-F bonds in CF_x and O-CF_x models has been conducted to observe the energy levels of antibonding C-F (Fig. 4c). It can be seen that $\sigma^*(\text{C-F})$ bonds occupy the energy level from $\sim -12.06 \text{ eV}$ to $\sim -4.42 \text{ eV}$. By integrating the area of F spin-up orbitals from $\sim -12.06 \text{ eV}$ to $\sim -4.42 \text{ eV}$ in CF_x and O-CF_x models, it shows that more electrons have been filled into the $\sigma^*(\text{C-F})$ bonds in O-CF_x. Thus, the stronger binding affinity toward Li⁺ and the weakened C-F bonds in O-CF_x contribute together to the excellent rate performance of Li/O-CF_x batteries.

In addition, the discharge products of CF_x and O-CF_x cathodes have been studied to verify the aforementioned conclusions. Fig. 4d shows the XRD patterns of CF_x and O-CF_x-2 cathodes after discharging in COE and DPM electrolytes. For CF_x cathodes with the COE electrolyte, only peaks of LiF are observed. However, peaks of LiF and Li₂CO₃ (at 31° , 38° , and 44°) can be clearly seen in O-CF_x-2 cathodes with the COE electrolyte. The formation of additional Li₂CO₃ is possibly due to the decomposition of the electrolyte, which has been verified by the discharge products of Li||Li symmetric cells and Li||Graphite cells with the DPM electrolyte (Fig. S19). Besides, O-CF_x-2 electrodes with the DPM electrolyte exhibit a diverse range of discharge products. Specifically, characteristic peaks of Li₂CO₃, LiNO₃ and Li₂SO₄ can be clearly found, which is properly due to the residual NO₃[−] and SO₄^{2−} groups in O-CF_x-2 due to the acid treatment (Fig. S20). Furthermore, Fig. 4e and f exhibit the C 1s and F 1s XPS spectra of CF_x and O-CF_x-2 cathodes after

discharging in the DPM electrolyte, respectively. Specifically, the C 1s spectra show the Li₂CO₃ peak at 289.8 eV, which is consistent with the XRD results. Also, three peaks (shown in red dashed rectangles) at lower binding energies for O-CF_x-2 cathodes after discharging can be found in Fig. 4b, which are related to intercalated Li⁺ and their adjacent but non-equivalent C atoms.³¹ Fig. 4f shows the F 1s XPS spectra of CF_x and O-CF_x-2 cathodes, in which the intensity of the C-F states (688.5 eV) and Li-F states (685.5 eV) is significantly higher in O-CF_x-2 compared with that in CF_x. This also verifies a more comprehensive electrochemical reaction due to the larger interlayer spacing of O-CF_x-2 cathodes, thus affecting battery performance. Moreover, a larger proportion of amorphous C layers can be seen in O-CF_x-2 (Fig. S5) due to the comprehensive reaction, which is consistent with the *in situ* Raman results. Fig. 4g and h present the ToF-SIMS depth profiles of LiF[−] and various secondary ion species and the corresponding 3D reconstruction images of CF_x and O-CF_x-2 electrodes discharged with the DPM electrolyte (details in the Experimental Section, SI). Here, the signals of LiF[−] ions gradually increase with sputtering time, and the overall intensity in O-CF_x-2 is significantly higher than that in CF_x, indicating a higher proportion of LiF in O-CF_x-2 after discharge. Additionally, Fig. 4h clearly shows stronger intensities of LiO[−] in O-CF_x-2 electrodes, verifying the stronger binding affinity toward Li⁺. Combining the aforementioned results, it can be inferred that O atoms doping in O-CF_x-2 contribute to abundant binding sites, leading to the formation of enriched discharge products (LiF), thereby enhancing the rate performance and specific capacity of Li/O-CF_x batteries.

To further investigate the key factor of the excellent performance of Li/O- CF_x batteries at low temperatures with the DPM electrolyte, EIS measurements of different cells at different temperatures are conducted as shown in Fig. 5. Symmetric stainless steel cells (SS||SS) with DPM and COE electrolytes are assembled and tested under different temperatures. As illustrated in Fig. 5a, the high-frequency intercept on the real axis (R_b) of the two cells are comparable in the range of 253 K and 293 K, while the R_b of the COE increases significantly when the temperature is at 253 K, indicating the sluggish kinetics. The extracted ionic conductivities are plotted in Fig. 5c. It can be found that the DPM electrolyte has much higher ionic conductivity at low temperatures when compared to the COE electrolyte. Besides, by fitting with the Arrhenius function, it shows that the DPM1112 electrolyte has a lower activation energy ($10.48 \text{ kJ mol}^{-1}$) when compared to the COE electrolyte ($19.22 \text{ kJ mol}^{-1}$), which implies a lower desolvation energy barrier of Li^+ in the DPM electrolyte (Fig. 5d). Furthermore, Li/ CF_x and Li/O- CF_x cells with COE and DPM electrolytes are assembled to test the contribution of different cathodes (CF_x and O- CF_x) and different electrolytes (COE and DPM) on the reduction of charge transfer impedance (R_{ct}) at low

temperatures.^{32,33} Fig. 5e and f show the EIS and the corresponding DRT curves of the four batteries. It can be seen that the batteries with the DPM electrolyte always have a smaller R_{ct} at -40°C . It should be mentioned that cells with O- CF_x cathodes still offer smaller impedance, whether using COE or DPM electrolytes. Therefore, O- CF_x cathodes dominantly contribute to the fast kinetics at room temperature, which is due to their high conductivity and lower binding energy with Li^+ (Fig. S18). However, the electrolyte dominates performance at low temperatures (-40°C), which is due to the high ionic conductivity and lower activation energy barriers.

In addition to the experimental observation on the electrode/electrolyte interfacial interactions of O- CF_x -2 cathodes at low temperature, theoretical simulations have been conducted on different electrodes (CF_x and O- CF_x -2) with the same electrolyte (DPM) to clarify the advantages of oxidized cathodes. Fig. 6a shows the electrostatic potential (ESP) distributions of DOL, MP, and PC molecules and their binding energies with Li^+ (details of the calculations in the SI). It can be seen that negative potentials (red regions) are distributed around the O atoms in all molecules, among which PC and MP (C=O) exhibit more negative potentials at the C=O sites. Moreover, the

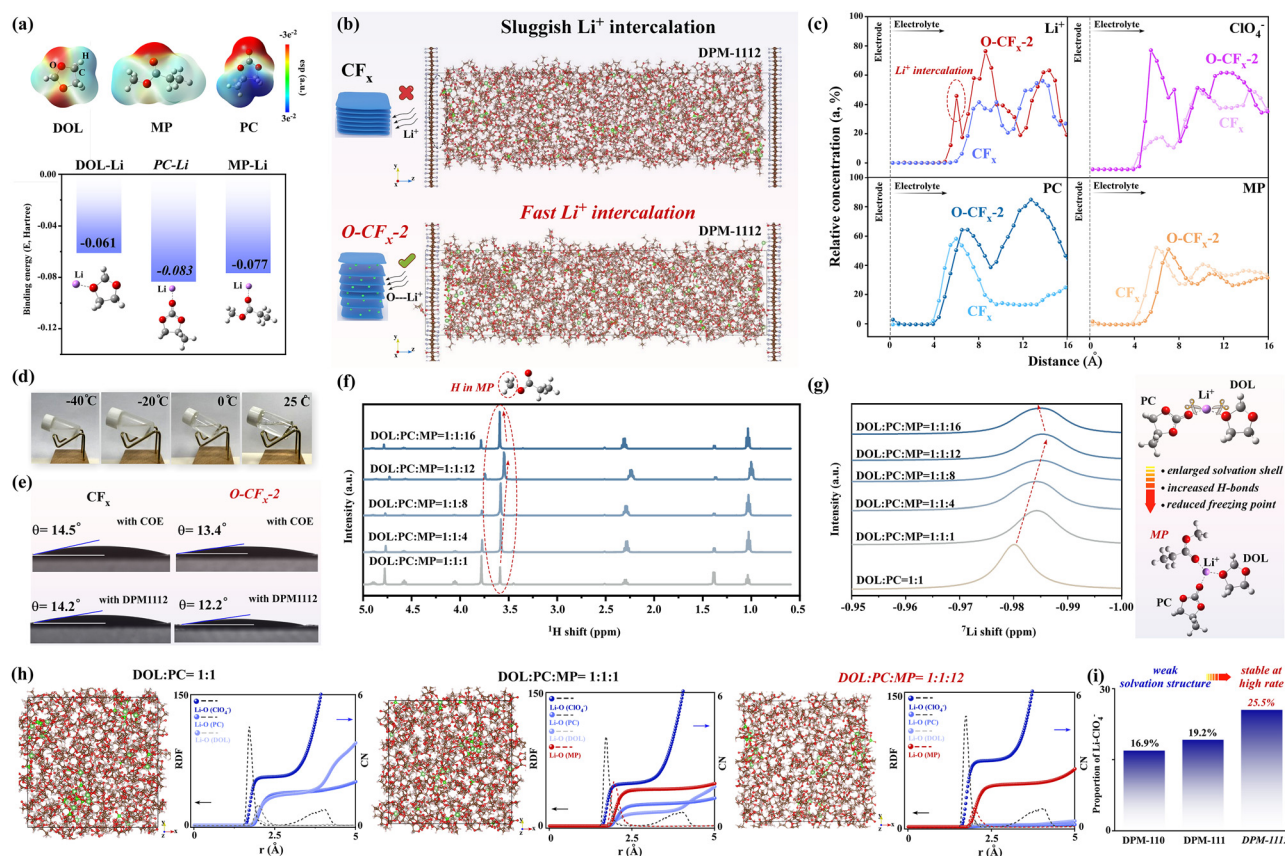


Fig. 6 Theoretical illustrations of the interfacial interactions on O- CF_x /DPM. (a) ESP distributions of DOL, MP, and PC and the corresponding binding energies with Li^+ . (b) MD simulations of the DPM electrolyte on CF_x and O- CF_x -2 electrodes. (c) Concentration distributions of different ions and components on the surface of CF_x and O- CF_x -2 electrodes. (d) Digital images of the DPM electrolyte at low temperature. (e) Contact angles of CF_x and O- CF_x -2 electrodes with COE and DPM. (f) and (g) NMR ^1H and ^7Li spectra of DPM with different concentrations of MP. (h) MD snapshots of DPM-110, DPM-111 and DPM-112, as well as the corresponding RDFs and Li-O coordination environments in different electrolytes. (i) Proportion of $\text{Li}^+-\text{ClO}_4^-$ coordination in DPM-110, DPM-111 and DPM-112 electrolytes.

binding energies (ΔE) of PC-Li⁺, MP-Li⁺, and DOL-Li⁺ show consistent results that PC has the strongest interaction with Li⁺. This indicates that Li⁺ preferentially coordinates with PC and MP in DPM first, as DOL has the weakest binding energy. Notably, Fig. 6b and c present the molecular dynamics (MD) simulations of DPM with CF_x and O-CF_x-2 electrodes. According to the statistical analysis of Li⁺, ClO₄⁻, PC and MP concentrations on the O-CF_x-2 electrode surface (along the z-axis in Fig. 5b), Li⁺ and ClO₄⁻ ions display significantly higher concentrations in the near-surface region. This implies that the functional groups and heteroatom doping in O-CF_x-2 are beneficial to the adsorption of lithium salts (LiClO₄ in both COE and DPM electrolytes). In contrast, PC and MP show relatively lower concentrations in the near-surface region, which clearly indicates that O-CF_x-2 can promote the dissociation of lithium salts. These conclusions are well consistent with the discharge behavior of O-CF_x-2, which shows less voltage hysteresis at the initial stage. Fig. 6d shows the digital images of the DPM electrolyte at different temperatures (−40 °C to 25 °C). It can be seen that DPM remains in a transparent and homogeneous liquid state from −40 °C to 25 °C, providing a basic guarantee for the efficient transport of Li⁺ at low temperatures. Besides, O-CF_x-2 electrodes exhibit smaller contact angles with both COE and DPM (Fig. 6e), indicating that the wettability and polarity of the electrodes have been enhanced after oxidation. Thus, reduced interfacial contact impedance and improved Li⁺ intercalation kinetics can be achieved, which is consistent with the DRT results and the electrochemical behavior of O-CF_x-2 cathodes.

To reveal the concentration-dependent effects of MP in the DPM electrolyte on Li⁺ intercalation into the O-CF_x-2 electrode, nuclear magnetic resonance (NMR) spectroscopy was employed to characterize the solvation structure of Li⁺ in DPM electrolytes with varying MP concentrations (DOL:PC:MP = 1:1:0, 1:1:1, 1:1:4, 1:1:8, 1:1:12 and 1:1:16, v/v/v). Fig. 6f and g display the ¹H and ⁷Li NMR spectra, respectively. Notably, the resonance peak intensities of both ¹H (assigned to the −CH₃ groups in MP) and ⁷Li first increased with increasing MP content (from 1 to 12 vol%), followed by a gradual upfield shift at 16 vol%. This phenomenon indicates that the increase in MP content enables MP molecules to participate in the formation of Li⁺ solvation shells,³⁴ thereby enriching the hydrogen-bonding environment and enhancing the electronic shielding effect on nuclear spins.³⁵ When the MP content was further increased to 16 vol%, the excessive MP molecules led to a reduction in the overall dielectric constant of the electrolyte, as well as a decrease in the dissociation degree of the Li salt.³⁶ Furthermore, Raman, FT-IR characterization and electrochemical performance tests (LSV) of DPM electrolytes with different MP concentrations yield consistent results, as presented in Fig. S5 and S11. Therefore, DPM-1112 (1 M LiClO₄ in DOL:PC:MP = 1:1:12, v/v/v) was selected for all the aforementioned electrochemical tests for Li/O-CF_x batteries. Additionally, Fig. 6h further elucidates the effects of MP on the Li⁺ solvation structure *via* MD simulations. For the DOL:PC = 1:1 (v/v) electrolyte (DPM-110), the Li⁺ solvation shell was primarily

composed of DOL, PC and ClO₄⁻ anions. In contrast, for the DOL:PC:MP = 1:1:1 (v/v/v) electrolyte (DPM-111), a considerable amount of MP molecules began to participate in Li⁺ coordination. Moreover, MP accounted for a larger proportion of the Li⁺ solvation sheath in DPM-1112. These results are consistent with the ⁷Li NMR findings, confirming that MP can engage in Li⁺ coordination, expand the overall solvation shell, and stabilize the electrolyte *via* a loose solvation structure.³⁷ Furthermore, the specific proportion of ClO₄⁻ anions coordinated with Li⁺ in the different electrolytes was quantitatively studied in Fig. 6I, based on the snapshots from MD simulations. Notably, the percentage of Li⁺-ClO₄⁻ coordination was the highest in the DPM-1112 electrolyte (25.5%), which is indicative of the weakest solvation interaction; this feature is conducive to maintaining electrolyte stability under high discharge rates. Thus, by leveraging the functional groups and heteroatom doping of the O-CF_x cathode, as well as the expanded solvation structure of the DPM electrolyte, Li⁺ intercalation into the electrode is facilitated in an electrochemically stable electrolyte system, thereby improving the rate performance of Li/O-CF_x batteries under all-climate conditions.

To further validate the practical potential of the O-CF_x cathode materials, we designed 21 Ah Li/O-CF_x pouch cells under aggressive conditions (24 mg cm⁻² O-CF_x-2 loading and the DPM-1112 electrolyte at 1.2 g Ah⁻¹). Fig. 7a presents the large-scale production of O-CF_x materials, which enables the fabrication of pouch cells. Furthermore, energy densities are calculated based on the total weight of the pouch cells (Fig. S8). Notably, Fig. 7c shows that the 21 Ah Li/O-CF_x pouch cell delivers a discharge capacity of 24.4 Ah and an energy density of 614.75 Wh kg⁻¹ (693.92 Wh L⁻¹) at 30 °C and a discharge rate of 0.5C, which also provides the discharge capacity of 23.3 Ah (energy density of 575.64 Wh kg⁻¹ and 649.78 Wh L⁻¹) at 1C, respectively. These results indicate the excellent rate performance of Li/O-CF_x pouch cells. Moreover, at an ultra-low temperature of −40 °C (Fig. 7c), the 21 Ah Li/O-CF_x pouch cells can provide 15.09 Ah (energy density of 318.66 Wh kg⁻¹ and 359.70 Wh L⁻¹) at 0.5C, along with a smaller volume expansion (inset in Fig. 7c). Furthermore, the specific volume expansion for a single cathode in the 21 Ah Li/O-CF_x pouch cells has been observed by SEM in Fig. S24. The cross-sectional morphology of O-CF_x exhibits an expansion equal to 29.4 μm. Furthermore, the thermal behavior of Li/CF_x and Li/O-CF_x pouch cells at the same discharge rate (0.5C) and temperature (25 °C) is evaluated (Fig. S25). It shows that the maximum temperature rise of the Li/O-CF_x pouch cells is lower than that of the Li/CF_x pouch cell, indicating an alleviated discharge thermal effect of Li/O-CF_x pouch cells. These results demonstrate the feasibility of all-climate Li/O-CF_x pouch cells in scaled-up formats. Fig. 7d statistically plots the energy densities of 21 Ah Li/O-CF_x pouch cells at different discharge rates and temperatures. Besides, to meet the actual performance demands in the low-altitude economy, the inset in Fig. 6d shows an unmanned aerial vehicle powered by a single 21 Ah Li/O-CF_x pouch cell (Fig. S9). Besides, the calendar aging of the

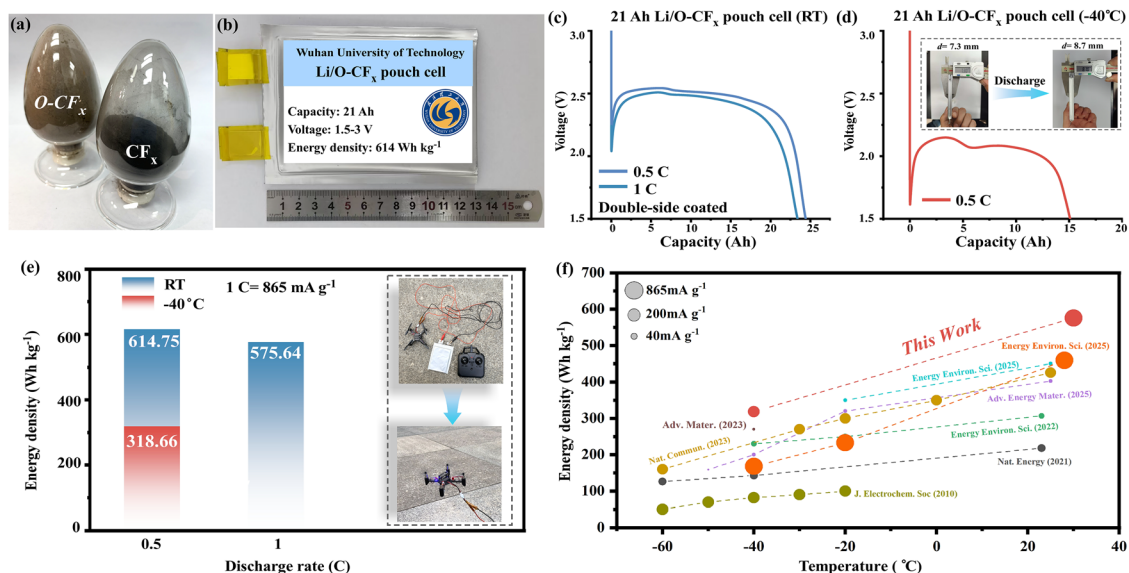


Fig. 7 Electrochemical behavior of Li/O-CFx pouch cells. (a) Digital image of the kilogram-scale production of O-CFx materials. (b) 21 Ah Li/O-CFx pouch cell with the DPM-1112 electrolyte. (c) Discharge curves of the Li/O-CFx pouch cell at room temperature (30 °C). (d) Discharge curves of the Li/O-CFx pouch cell at -40 °C. Inset: volume expansion of the pouch cell before and after discharge. (e) Energy densities of 21 Ah Li/O-CFx pouch cells at different discharge rates and temperatures. Inset: applications of a single Li/O-CFx pouch cell in an unmanned aerial vehicle. (f) Comparison of the reported energy densities of lithium-based pouch cells at different temperatures with those of this work. The circle size corresponds to the discharge current density. Detailed parameters are listed in Table S4.

21 Ah Li/O-CFx pouch cell has been evaluated and shows good capacity retention over 40 days (Fig. S13). Finally, Fig. 7f compares the low-temperature energy densities of various state-of-the-art systems, including Li/CFx, lithium-metal batteries (LMBs), and lithium-ion batteries (LIBs). Notably, the electrochemical performance of Li/O-CFx pouch cells in this work successfully exceeds most of the reported studies, exhibiting superior high-rate capability and exceptional low-temperature performance. These results demonstrate the rational design of O-CFx cathodes *via* an efficient wet-chemistry strategy and imply their promising applications in deep-space and deep-sea exploration.

3. Conclusions

In summary, this work demonstrates a scale-up synthesis of oxidized CFx (O-CFx) cathodes with dual-high performance and all-climate adaptability for primary lithium batteries (PLBs). *Via* a simple mixed-acid treatment based on wet chemistry, the C-F configurations, including the F/C ratio, types of C-F bonds and structure of carbon frameworks, can be accurately and synergistically regulated by the oxidation time. Detailed characterization and control experiments show that this oxidation-time-dependent regulation process involves defluorination and subsequent re-fluorination steps in pristine CFx, leading to a nearly twofold increase in the proportion of semi-ionic C-F bonds. Additionally, the electronic conductivity and interlayer spacing of the graphite matrix are significantly enhanced. Benefiting from the optimized C-F configurations, the O-CFx cathodes exhibit outstanding rate performance and

temperature adaptability. Li/O-CFx batteries achieve a power density of 84.4 kW kg⁻¹ at 50C, operate stably across all-climate scenarios (-40 °C to 60 °C), and deliver an impressive specific capacity of 466 mAh g⁻¹ at 0.5C (-40 °C). Moreover, the 21 Ah Li/O-CFx pouch cells achieve an energy density of 614.75 Wh kg⁻¹ and have been successfully applied in unmanned aerial vehicles. This work paves the way for large-scale application of Li/CFx batteries and provides insights into the design of CFx cathodes with dual-high performance in pivotal battery systems.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

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

The supplementary information file includes details of the synthesis experiments of the O-CFx cathode, various characterization data (XPS spectra and in-depth analysis, ToF-SIMS, Raman, TEM-EELS, BET), electrochemical performance tests under different conditions, electrolyte characterization (GITT, spectroscopy, LSV, impedance, XRD), assembly specifications and performance curves for 21 Ah pouch cells, theoretical calculation details (DFT, molecular dynamics), and performance comparison tables with literature. See DOI: <https://doi.org/10.1039/d6ee00658b>.

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References

- 1 M. Gao, D. Cai, S. Luo, Y. Yang, Y. Xie, L. Zhu and Z. Yuan, *J. Mater. Chem. A*, 2023, **11**, 16519–16538.
- 2 S. Su, J. Ma, L. Zhao, K. Lin, Q. Li, S. Lv, F. Kang and Y.-B. He, *Carbon Energy*, 2021, **3**, 866–894.
- 3 R. Yazami, A. Hamwi, K. Guérin, Y. Ozawa, M. Dubois, J. Giraudet and F. Masin, *Electrochem. Commun.*, 2007, **9**, 1850–1855.
- 4 J. Meng, Z. Xiao, L. Zhu, X. Zhang, X. Hong, Y. Jia, F. Liu and Q. Pang, *Matter*, 2023, **6**, 1685–1716.
- 5 M. Adamska and U. Narkiewicz, *J. Fluorine Chem.*, 2017, **200**, 179–189.
- 6 C. Peng, Y. Li, F. Yao, H. Fu, R. Zhou, Y. Feng and W. Feng, *Carbon*, 2019, **153**, 783–791.
- 7 L. Kong, Y. Li, C. Peng, L. Sun, K. Wang, Y. Liu and W. Feng, *Nano Energy*, 2022, **104**, 107905.
- 8 S. Zhang, L. Kong, Y. Li, C. Peng and W. Feng, *Energy Environ. Sci.*, 2023, **16**, 1907–1942.
- 9 W. Feng, P. Long, Y. Feng and Y. Li, *Adv. Sci.*, 2016, **3**, 1500413.
- 10 Y. Sato, H. Watano, R. Hagiwara and Y. Ito, *Carbon*, 2006, **44**, 664–670.
- 11 Y. Sato, K. Itoh, R. Hagiwara, T. Fukunaga and Y. Ito, *Carbon*, 2004, **42**, 3243–3249.
- 12 K. Fan, J. Fu, X. Liu, Y. Liu, W. Lai, X. Liu and X. Wang, *Chem. Sci.*, 2019, **10**, 5546–5555.
- 13 Y. Ahmad, M. Dubois, K. Guerin, A. Hamwi and E. Flahaut, *J. Alloys Compd.*, 2017, **726**, 852–859.
- 14 Z. Sun, S. Fang and Y. H. Hu, *Chem. Rev.*, 2020, **120**, 10336–10453.
- 15 R. Zhang, L. Zhang, C. Xu, L. Bao, G. Zhang, B. Wang, X. Wang and H. Yue, *J. Power Sources*, 2024, **614**, 235026.
- 16 H. Zhang, P. Xiao, J. Shi, C. Wang, J. Wang, Q. Wang, X. Chen and B. Shi, *J. Electron. Mater.*, 2021, **50**, 4075–4082.
- 17 L. Li, R. Wu, H. Ma, B. Cheng, S. Rao, S. Lin, C. Xu, L. Li, Y. Ding and L. Mai, *Small*, 2023, **19**, 2300762.
- 18 Y. Zhu, L. Zhang, H. Zhao and Y. Fu, *J. Mater. Chem. A*, 2017, **5**.
- 19 Y. Dai, S. Cai, L. Wu, W. Yang, J. Xie, W. Wen, J.-C. Zheng and Y. Zhu, *J. Mater. Chem. A*, 2014, **2**, 20896–20901.
- 20 G. Chen, H. Zhou, S. Zhang, Z. Zhang, T. Feng, Z. Xu and M. Wu, *ACS Appl. Energy Mater.*, 2021, **4**, 8615–8620.
- 21 S. Rehman, M. Pope, S. Tao and E. McCalla, *Energy Environ. Sci.*, 2022, **15**, 1423–1460.
- 22 J. Liang, Y. Sun, Y. Zhao, Q. Sun, J. Luo, F. Zhao, X. Lin, X. Li, R. Li, L. Zhang, S. Lu, H. Huang and X. Sun, *J. Mater. Chem. A*, 2020, **8**, 2769–2776.
- 23 Z. Wang, M. Wang, X. Li, H. Huang, X. Sun, J. Feng, S. Liu, H. Luo, L. Li, X. Zou and X. Zhao, *Nano Lett.*, 2025, **25**, 13267–13275.
- 24 R. Jayasinghe, A. K. Thapa, R. R. Dharmasena, T. Q. Nguyen, B. K. Pradhan, H. S. Paudel, J. B. Jasinski, A. Sherehiy, M. Yoshio and G. U. Sumanasekera, *J. Power Sources*, 2014, **253**, 404–411.
- 25 S. K. Padamata, A. Yasinskiy, S. Stopic and B. Friedrich, *J. Fluorine Chem.*, 2022, **255–256**, 109964.
- 26 C. Peng, S. Zhang, L. Kong, H. Xu, Y. Li and W. Feng, *Small Methods*, 2024, **8**, e2301090.
- 27 M. Wu, Y. Zhao, H. Zhang, J. Zhu, Y. Ma, C. Li, Y. Zhang and Y. Chen, *Nano Res.*, 2022, **15**, 9779–9784.
- 28 B. Sayahpour, H. Hirsh, S. Bai, N. B. Schorr, T. N. Lambert, M. Mayer, W. Bao, D. Cheng, M. Zhang, K. Leung, K. L. Harrison, W. Li and Y. S. Meng, *Adv. Energy Mater.*, 2022, **12**, 2103196.
- 29 D. Zhan, Z. Ni, W. Chen, L. Sun, Z. Luo, L. Lai, T. Yu, A. T. S. Wee and Z. Shen, *Carbon*, 2011, **49**, 1362–1366.
- 30 J. Huang, S. Zhang, B. Wan, W. Liu, R. Li, Z. Yang, L. Li, J. Hua, F. Chu, M. Li, T. Zhou, J. Wang, Y. Wu, Z. Li, L. Fan, L. Chen, T. Deng and X. Fan, *Energy Environ. Sci.*, 2025, **18**, 10328–10337.
- 31 K. Ji, J. Han, A. Hirata, T. Fujita, Y. Shen, S. Ning, P. Liu, H. Kashani, Y. Tian, Y. Ito, J.-i. Fujita and Y. Oyama, *Nat. Commun.*, 2019, **10**, 275.
- 32 Y. Yin, J. Holoubek, A. Liu, B. Sayahpour, G. Raghavendran, G. Cai, B. Han, M. Mayer, N. B. Schorr, T. N. Lambert, K. L. Harrison, W. Li, Z. Chen and Y. S. Meng, *Adv. Mater.*, 2023, **35**, 2207932.
- 33 J. Chen, E. Quattrocchi, F. Ciucci and Y. Chen, *Chem*, 2023, **9**, 2267–2281.
- 34 S. R. Galle Kankanamge and D. G. Kuroda, *J. Phys. Chem. B*, 2020, **124**, 1965–1977.
- 35 P. Xiao, X. Yun, Y. Chen, X. Guo, P. Gao, G. Zhou and C. Zheng, *Chem. Soc. Rev.*, 2023, **52**, 5255–5316.
- 36 K. Xu, *Chem. Rev.*, 2014, **114**, 11503–11618.
- 37 Y. Huang, J. Geng, Z. Jiang, M. Ren, B. Wen, J. Chen and F. Li, *Angew. Chem., Int. Ed.*, 2023, **62**, e202306236.