Lithium–Iron (III) Fluoride Battery with Double Surface Protection

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Lithium–metal fluoride batteries promise significantly higher energy density than the state-of-the-art lithium-ion batteries and lithium–sulfur batteries. Unfortunately, commercialization of metal fluoride cathodes is prevented by their high resistance, irreversible structural change, and rapid degradation. In this study, a substantial boost in metal fluoride (MF) cathode stability by designing nanostructure with two layers of protective shells—one deposited ex situ and the other in situ is demonstrated. Such methodology achieves over 90% capacity retention after 300 charge–discharge cycles, producing the first report on FeF$_3$ as a cathode material, where a very high capacity utilization in combination with excellent stability is approaching the level needed for practical applications of FeF$_3$. The cathode solid electrolyte interphase (CEI) containing lithium oxalate and B–F bond containing anions is found to effectively protect the cathode material from direct contact with electrolytes, thus greatly suppressing the dissolution of Fe. Quantum chemistry and molecular dynamics calculations provide unique insights into the mechanisms of CEI layer formation. As a result, this work not only demonstrates unprecedented performance, but also provides the reader with a better fundamental understanding of electrochemical behavior of MF cathodes and the positive impact observed with the application of a lithium bis(oxalato)borate salt in the electrolyte.

1. Introduction

Electrochemical energy storage devices have been developing for more than a century, and are now broadly applied in our daily life, from portable electronics to energy-efficient industrial tools to electric ground, sea, and aerial transportation. As evolution of technology is rapidly being pushed forward, there is a consistently growing demand for next-generation energy storage devices that is cheaper, lighter, smaller, and safer. Unfortunately, lithium (Li)-ion batteries (LIBs) utilizing conventional intercalation-type electrodes approach to their theoretical limits and further improvements in their energy storage characteristics are limited.[1] With a relatively successful progress of advanced anode materials,[2] conventional cathode materials based on intercalation chemistries, such as lithium cobalt oxide, lithium nickel cobalt aluminum oxide, and lithium nickel manganese cobalt oxide, are becoming an energy-limiting...
factor typically only able to store less than one Li$^+$ per transition metal atom. In addition, the transition metal contents in such materials (particularly cobalt (Co) and to a less extent nickel (Ni)) are expensive, limited in world reserves, heavy, and toxic. Therefore, it is critical to explore other chemistries and achieve sufficient performance breakthroughs to meet the strong need for improved cathodes produced from cheap and abundant transition metals, such as iron (Fe).

Relatively new LIB cathode materials, such as metal chalcogenides and metal halides, based on conversion chemistry are now attracting renewed interest. They overcome the limits of intercalation materials by accommodating multiple Li$^+$ per compound, yielding transition metals (M) and Li$_{X}$ phases ($X = S$, F, Cl, etc.) during discharge and regenerating M$_{X}$$_{n}$ upon charge

$$M_{X_{n}} + nLi^+ + ne^- \leftrightarrow bLi_{n}X + aM \quad (1)$$

Among these candidates, intensive research efforts have been dedicated to Li–metal fluoride (MF) batteries owing to their high energy density, exceeding that of the Li–sulfur (S) cells. [3] FeF$_3$ is considered one of the most attractive due to the low cost and toxicity, abundance of Fe, the highest specific capacity of 712 mA h g$^{-1}$ and high average potential of $\approx$2.74 V. [4] Offering an exceptionally high cell-level theoretical energy density in excess of 1500 Wh kg$^{-1}$ and cell-level specific energy in excess of 800 Wh kg$^{-1}$ (both on a repeat unit basis). [5]

Unfortunately, commercialization of FeF$_3$ is still prevented by multiple challenges. One major barrier is its notoriously poor electronic conductivity, resulting from the large band gap induced by strong ionicity of Fe–F and Li–F bonds. [6] Thus, large voltage hysteresis during charge–discharge is typically observed. Another barrier is the rapid degradation typically observed during cycling, induced by the significant volume change during the conversion reaction and the consequent mechanical failures, as well as the dissolution of FeF$_3$ triggered by free protons produced from undesired electrolyte decomposition or oxidation. [7,8]

In order to address the two challenges above, recent endeavors have been devoted to intrinsic structure manipulation, such as open framework strategy, [9] and design of various nanostructures, through high-energy ball milling, [10] coating with polymers, [11] HF-based aqueous solution synthesis, [12,13] ionic liquid assisted synthesis, [14] prelithiation, [15] pulse laser deposition, [16] etc. But in spite of these efforts, the majority of previous works still showed limited capacity and fast decay in less than 50 cycles at room temperature. In some cases, although FeF$_3$ was only discharged to 2.0 V at the current rate of 100 mA g$^{-1}$, utilizing 1/3 of the total capacity and undergoing one $\epsilon$$^-$ reaction, it still failed to show stable cyclability after 30 cycles. [11,12] To conclude, the dissolution issue of FeF$_3$ has not been properly addressed. To inhibit such detrimental reactions occurred at the interface of cathodes and electrolytes, two strategies are commonly utilized. One involves the introduction of inert surface coatings to prevent direct contact, such as carbon and metal oxide coatings. [16] However, the associated highly reductive atmospheres commonly required for chemical vapor deposition or carbonization of hydrocarbon and organometallic precursors at elevated temperatures readily reduces FeF$_3$. Alternatively, effective design and selection of electrolyte additives become more attractive due to the in situ formation of the conformal Li$^+$ permeable cathode solid electrolyte interphase (CEI). [8,17] The presence of this passivation film inhibits capacity loss during long-term cycling upon initial cell charge–discharge. Lithium bis(oxalato)borate (LiBoB) as an electrolyte additive has been extensively studied for intercalation cathode materials such as lithium manganese oxide, lithium nickel manganese oxide, etc. with high cutoff voltages due to the generation of a borate-rich stable passivating CEI on the surface of cathode. [18,19] Dual salt difluoro(oxalato) borate and LiPF$_6$-based electrolytes also showed improved capacity retention compared to LiPF$_6$-based electrolytes for cells with the Li-excess layered oxide cathodes. However, the application of LiBoB for conversion materials still remains mostly unknown, which inspired us to explore the impact of LiBoB on the degradation of conversion cathode materials.

In this research, we report a holistic strategy to overcome the above limitations and improve the electrochemical performances of Li-FeF$_3$ cells by a novel design of the FeF$_3$ nanostructure (with a dimension of 20 nm), combined with a protective shell surrounding the composite particles and careful electrolyte optimization. The rational architecture of uniform FeF$_3$-multilawled carbon nanotube nanocomposites (FeF$_3$-CNTs) provides enhanced electronic conductivity and effectively accommodates the volume expansion during lithiation. This simple approach is applicable for the synthesis of a broad range of MFs and does not require the use of hazardous starting materials, such as hydrofluoric acid (HF). The use of uniform Al$_2$O$_3$ coatings produced by plasma-enhanced (PE) atomic layer deposition (ALD) at a low temperature in combination with the CEI induced by LiBoB prevent the active material from undesirable direct contact with electrolytes. As a result, Li-FeF$_3$ cells cycled between 2 and 4.2 V (one $\epsilon$$^-$ reaction) demonstrate remarkable performance characteristics, showing capacity of over 150 mA h g$^{-1}$ at the current rate of 100 mA g$^{-1}$ with a robust capacity retention of over 90% after 300 cycles. Postmortem analyses in combination with quantum chemistry (QC) modeling and molecular dynamics (MD) simulations provided insights on the mechanisms of the stability improvements by LiBoB additives to electrolyte. To our knowledge of published peer-reviewed publications, this is the first report on FeF$_3$ as a cathode material achieving 300 charge–discharge cycles. When compared with previously published work on FeF$_3$, our as-fabricated cells improve electrochemical stability for up to ten times.

2. Results and Discussion

The synthetic protocol for FeF$_3$-CNTs is schematically illustrated in Figure 1. As the first step, the low-cost and highly scalable solution-based synthesis of Fe-CNTs have been applied, as previously described by our group for alkaline batteries. [20] The as-prepared Fe-CNTs are then directly fluorinated under the flow of highly diluted nitrogen trifluoride (NF$_3$) gas at a mild temperature, yielding the FeF$_3$-CNTs, which retained the uniform morphology of the Fe-CNTs. [21] We would like to highlight the great flexibility and safety that our approach offers. The design and synthesis of nanostructured metals have been extensively
Once the FeF₃-CNTs electrode was fabricated, rapid PEALD of multiple metal oxides was performed in order to produce a protective shell surrounding the composites to suppress the dissolution of FeF₃ during charge–discharge cycling. Relevant parameters were controlled to be optimal, according to a previous ALD study.[22] Among the candidates of coating materials, titanium oxide (TiO₂), aluminum oxide (Al₂O₃), and zirconium oxide (ZrO₂) are selected and compared because of their excellent Li⁺ conductivity and good mechanical properties. The deposition procedures of all three coating materials were identical.

The morphologies and microstructures of as-prepared Fe-CNTs and FeF₃-CNTs have been characterized by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM) studies. Figure 2c exhibits the SEM images of Fe particles with an average diameter of 15 nm uniformly deposited on the surface of MWCNTs, which is further confirmed by TEM images in Figure 2d,e. After fluorination, as observed in Figure 2f,g, the particle size of FeF₃ (=20 nm) becomes approximately twice as large as the initial Fe nanoparticles, meanwhile, every single FeF₃ particle remained attached to the MWCNTs. Such a composite morphology enables one to effectively accommodate the volume expansion during both fluorination and electrochemical lithiation when discharging. The amount of the deposited metal oxides was below the detection limit of our analytical balance. Therefore, X-ray photoelectron spectroscopy (XPS) spectrum of Al₂p, was conducted and the strong peak at ≈74.5 eV implies the existence of Al₂O₃, as shown in Figure S2a of the Supporting Information. High-resolution TEM image of the composites (Figure S2b, Supporting Information) after ALD clearly indicates a uniform coating with the thickness of ≈2 nm.

In this work, we select a limited voltage range of 2–4.2 V and allow only one e⁻ reaction to occur, in order to best understand the impacts of protective shells from ALD coating and CEI formation by diminishing the pulverization of FeF₃. Such a voltage range is also adopted by other groups working on FeF₃.[11,12] First, the electrodes with different metal oxide coatings were compared in simple commercial electrolytes without additives (Figure S3, Supporting Information). After 300 cycles at the current rate of 100 mA g⁻¹, the electrode coated by Al₂O₃ thin film appears to be the most robust. TiO₂ coating does modestly improve the cycling stability, while no improvement was also observed by using ZrO₂ coating. Thus, all the electrodes used in the following endeavors were pre-treated by Al₂O₃ ALD coating.

In the next step, the carbonate-based electrolyte was modified to further improve cycling performance. After initial screening, LiBOB was identified a promising electrolyte additive, which has low solubility in a majority of common electrolyte solvents, but could be dissolved modestly in cyclic carbonates. In this work a commonly used EC/PC/DMC (1:1:3 wt%) cosolvent system was applied and the molarity of Li⁺ was fixed at a low level of 0.7 m to maintain the Li⁺ concentration constant in all electrolytes (limited by the solubility of pure LiBOB in this solvent system).[23] As shown in Figure 3, charge–discharge (C–D) cycling stabilities of the cells containing LiPF₆ (Figure 3a–d) or lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) (Figure 3e,f) with different LiBOB percentages are compared at the current density of 100 mA g⁻¹. While the specific capacity of cells using LiPF₆-LiBOB system tends to be

Figure 1. Schematic illustration of the synthesis of FeF₃-CNT nanocomposites: (1) iron nanoparticle deposition on MWCNT; (2) fluorination of Fe-CNT; (3) ALD coating of FeF₃-CNT.

Figure 2 presents the results of the selected characterizations. The X-ray diffraction (XRD) pattern of FeF₃-CNTs is shown in Figure 2a. The 2θ peak at 26° originates from the presence of CNTs. All the other Bragg peaks can be ascribed to the hexagonal FeF₃ phase (JCPDS card no. 33–0647, space group R3̅m) without any significant content of impurities. In order to determine the content of FeF₃ and CNTs in the composites, thermogravimetric analysis (TGA) was conducted in air, as shown in Figure 2b. The weight loss observed at 550–600 °C is corresponding to the burning of CNTs into CO and CO₂ gases and associated with the conversion of FeF₃ to iron oxide. According to the XRD patterns of the red-brown residue after TGA test (Figure S1, Supporting Information), pure phase Fe₂O₃ is detected. Therefore, the weight of FeF₃ in initial composites could be calculated based on the remained mass of Fe₂O₃. In a result, the weight fraction of FeF₃ turns out to be 80 wt% and may likely be further increased with further optimization.
similar after 300 cycles (Figure 3a), increasing LiBoB additive percentage from 0%, 5%, and 20% to 100% has a tremendous impact on capacity retention (Figure 3b) and coulombic efficiency (Figure S4, Supporting Information). The 100% LiBoB without LiPF₆ or LiTFSI exhibited noticeably improved stability, achieving over 90% capacity retention after 300 cycles with 99.3% average coulombic efficiency. To our knowledge, such a stable performance of FeF₃ as a cathode material is unprecedented, particularly considering low electrolyte molarity. In fact, very few previously reported works reached more than 20–50 cycles with comparable capacity degradation. After observing the dramatic degradation of the cathode without any ALD coatings in 100% LiBoB (Figure S5, Supporting Information), we conclude that such performance improvement is resulted from the synergy of Al₂O₃ coating and CEI layer formation.

C–D profiles of the cells with different LiBoB percentages are plotted every 50 cycles in Figure S6 of the Supporting Information. Regardless of the LiBoB concentration and the cycle number, all the cells showed a charge plateau at ≈3.3 V and a discharge plateau at ≈2.9 V, yielding a moderate hysteresis (the difference of discharge and charge voltages) of ≈0.4 V. It is clearly revealed that the 100% LiBoB cell demonstrates highest coulombic efficiency, close to 100%, while the cells with low and zero LiBoB contents have their lowest coulombic efficiencies in the first 50 cycles, which gradually increase during cycling, indicating that the Fe dissolution are more intensive at earlier stages. This is consistent with the degradation trend shown in Figure 3a,b and Figure S2 (Supporting Information). Capacity degradation is the most severe at the first 50 and 100 cycles and tends to be flattened afterward. Figure 3c and Figure 3d compare the C–D profiles of cells with different LiBoB concentrations after 150 and 300 cycles, respectively. Given a certain cycle index, the cell with 100% LiBoB appears to have the largest hysteresis, while the cell without LiBoB has the smallest hysteresis, implying growing impedance as the LiBoB ratio increases. To better understand the impact of LiBoB concentration on impedance, electrochemical impedance spectroscopies (EIS) of fresh (Figure S8, Supporting Information) and cycled cells (Figure S10, Supporting Information) of LiPF₆–LiBoB systems are contrasted as an example. Before cycling, higher LiBoB ratio consistently leads to higher charge transfer and electrode-electrolyte interface impedances, which matched with the fact that LiBoB has lower ionic conductivity than LiPF₆ and LiTFSI. However, the interface impedance significantly drops after 300 cycles and turned out to be lowest, suggesting a highly conductive layer of CEI has been formed during cycling.
Additional comparisons are studied to examine the flexibility that LiBoB offers. Figure 3e,f shows the charge–discharge cycling stabilities adopting LiTFSI–LiBoB system. We observed the same trend as in LiPF₆–LiBoB system. Meanwhile, the C-D profiles and EIS results of fresh cells are exhibited in Figures S7 and S9 of the Supporting Information, supporting the statement concluded above. It is worth mentioning that the cell without LiBoB fails after ≈70 cycles due to the electrode corrosion. This results manifests that the protection layer formed by LiBoB effectively prevents the corrosion and is instrumental for cell stability.

Postmortem studies of cycled Li foils reveal a dramatic impact of LiBoB on the morphologies. The fresh Li foil presents a smooth and flat surface as shown in Figure 4a, while cycled Li anode in the cell without LiBoB additive has uneven and rough surface with large cracks covered by deposited Fe particles, which is confirmed by EDX result (Figure 4e) and XRD patterns collected in Figure 4f. The formation of such a surface layer resulting from Fe dissolution diminishes the cell-level capacity due to irreversible reactions and associated lack of active material on the cathode side. In sharp contrast, the Li foil anode cycled with 5% LiBoB (Figure 4c) has a visually much smoother surface of an SEI layer, while 100% LiBoB (Figure 4d) yielded the smoothest morphology of the anode SEI. No Fe was detected in the XRD patterns of the anode cycled (300 cycles) with the presence of LiBoB in electrolyte (Figure 4f), indicating that Fe dissolution was dramatically reduced.

To clarify the impact of the LiBoB additive on the formation of the CEI on the cathode surfaces, SEM images of cycled cathodes are compared in Figure 5a and Figure S11 for LiBoB-LiPF₆ system, and Figure S12 of the Supporting Information for LiTFSI-LiBoB system. There are no major structural changes as the percentage of LiBoB increases, however, the morphologies become smoother due to the formation of CEI. To examine its chemical nature, X-ray photoelectron spectroscopies (XPS) of cycled cathodes were additionally studied. In LiPF₆–LiBoB system (Figure 6a), the major peak at 685–685.5 eV of the F 1s spectra in all samples is attributed to FeF₃ (fresh electrode) and/or LiF (cycled electrodes) as they have overlapped peak positions. The peak at 687.8–688.3 eV appears primarily due to the formed LiₓPO₄F₂ in the CEI, which is a common composition in LiPF₆-contained electrolytes as...
reported in previous publications. At the meantime, the rise of B–F peak at 685.9 eV is attributed to the generated Li$_x$BO$_y$F$_z$ species according to related LiBoB and lithium difluoro(oxalato)borate (LiDFOB) study conducted before. The B$_1$s spectra (Figure S13a, Supporting Information) confirm the existence of boron and could be contributed to B=F and/or B=O bonds. Switching to LiTFSI–LiBoB system, we observe similar results in Figure 6b for F$_1$s spectra and Figure S13b of the Supporting Information for B$_1$s spectra. Interestingly, the cell containing merely LiTFSI without LiBoB has very different CEI nature from the others. This is consistent with a reported research previously. Pure LiTFSI electrolyte could help to induce a CEI layer with heavy C–F content, as well as N and S rich decomposed salts (shown in Figure S14, Supporting Information). While cycled cathodes with LiBoB additive do not have traceable N or S contained CEIs, demonstrating that LiBoB could effectively tune the chemical nature of CEI in the LiTFSI system. Therefore, LiBoB performs as an impactful substance on the CEI formation at a high voltage in both common electrolyte system based on LiPF$_6$ and LiTFSI salts.

Two mechanisms of CEI formation are proposed—chemical decomposition and/or electrochemical decomposition. First, to test the decomposition possibility via fluorination, in situ NMR analysis of the reaction mixture was conducted after mixing 0.7 m LiBOB, 0.5 m LiF, and 0.5 m FeF$_3$ in EC/PC/DMC and stirring at 85 °C for 120 h. In $^{11}$B NMR (Figure S15, Supporting Information), LiBF$_4$ (−1.5 ppm), and LiDFOB (−2.7 ppm) showed up along with the initial LiBOB (−7.2 ppm). According to $^{19}$F NMR, we calculated the molar ratio of the LiBOB to LiBF$_4$/LiDFOB to be 5.74:1. These results are further corroborated by the $^{19}$F NMR spectrum (Figure S16, Supporting Information). Two sets of signals at around −153.4 and −154.1 ppm reveal, referring to the LiBOB decomposition products—LiBF$_4$ and LiDFOB, respectively. The coupling pattern of fluorine nuclei in $^{19}$F NMR has been complicated with coupling peaks on both $^{11}$B and $^{10}$B nuclei due to the boron isotopes natural
abundance. The integral intensity of the LiBF$_4$ as compared to the LiDFOB varies within the range 2.1–3.4 to 1 according to the $^{11}$B and $^{19}$F NMR. Remarkably, that the LiBOB also follows the decomposition route into LiBF$_4$ in the presence of FeF$_3$ with no LiF added, though no LiDFOB signal is seen (Figure S17, Supporting Information).

Therefore, the analyses of the spectra of the reaction mixture provide valuable insights about possible mechanism of the CEI
formation, which is likely to occur through the decomposition of the LiBOB to LiBF₄ and LiDFOB in the presence of the F⁻. The latter is likely to be given by LiF or FeF₃ because of their dissolution in the EC/PC/DMC mixture. F⁻ is a strong nucleophile, which attacks the BOB anion with the formation of the difluoro(oxalate)borate (DFOB) anion, which is then further fluorinated to the BF₄⁻ anion. Please note that we did not additionally use LiPF₆, which is a strong fluorination agent and can be readily decomposed with the formation of F⁻, therefore facilitating the fluorination of LiBOB and the CEI formation. Therefore, the rate of the fluorination reaction can likely be increased in the presence of the large excess of F⁻, which is probably the case of chemical reaction in the real battery tests conditions. In the absence of LiF, the rate of the fluorination reaction is considerably slower (Figure S17, Supporting Information). This can indicate the importance of the dissolved F⁻ presence to induce the LiBOB decomposition.

Moving forward, electrochemical decomposition has been studied next. A bare aluminum foil versus a Li counter electrode cell containing 0.7 M LiBOB and 0.5 M LiF (as a recourse of F) in EC/PC/DMC was tested for 300 C-D cycles. Areal current density and voltage window were identical to those used in regular cells. Due to the lack of active materials, this test was completed in 2 h, thus pure chemical decomposition was negligible. Post-mortem XPS analyses in Figure S18 of the Supporting Information demonstrated consistent chemical nature of the CEI (compare with Figure 7). The peak of B–F bonding rises at 685.9 eV in the F1s spectrum (Figure S18a, Supporting Information) along with the peak at 193.5 eV in the B1s spectrum (Figure S18b, Supporting Information). Please note that no aluminum signals are detected in Al2p spectrum (Figure S18c, Supporting Information), suggesting that the CEI layer formed on Al is sufficiently thick. Therefore, electrochemical decomposition was found to play a key role in the CEI formation.

QC calculations were performed in order to provide fundamental insights into the electrochemical stability of the LiBOB-containing electrolytes and potential pathways to form CEI on the FeF₃ cathode surface. Reduction and oxidation potentials were calculated using previously described methodology.[27] An accurate but computationally expensive G4MP2 was used for most calculations, while more computationally expedient density functional theory (DFT) calculations were used for the larger complexes where G4MP2 is prohibitively expensive. Oxidation of the BOB(EC) complexes without bond breaking is predicted to occur around 5.78 V versus Li/Li⁺, as shown in Figure 7a and corresponding to M₀ → M₁ reaction. The
oxidized BOB was found to readily undergo CO₂ detachment with a small barrier of 0.19 eV and reaction energy of ~0.56 eV, as shown in Figure S19 of the Supporting Information. These results are in accord with DFT calculations of Wang et al. If one assumes that oxidation of BOB is coupled with the CO₂ detachment due to low barrier, oxidation potential of BOB becomes 5.32 V for the isolated BOB anion (see Figure S19, Supporting Information) and 5.17 V to for the BOB (EC) complex shown as M₀ → M₂ reaction in Figure 7a. Another oxidation reaction M₀ → M₃ shown in Figure 7a involves the H-transfer from EC to BOB. It was predicted to occur at a similar potential to the M₀ → M₂ reaction. Predicted oxidation stability of the BOB (EC) complex of ≈5 V is in accord with the experimentally observed onset of CO₂ generation above 4.9 V in carbonate electrolyte when the LiBOB additive was added. Because calculated oxidation potentials of the BOB (EC) complexes are much higher than operating range 2 to 4 V of our cells, we conclude that the BOB anion direct oxidation in carbonate electrolytes is unlikely during C-FeF₃ cell cycling.

Reduction stability of the LiBOB and Li₂BOB clusters immersed in implicit solvent with dielectric constant ε = 20 was examined using QC, as shown in Figure 7b. Reduction potentials of LiBOB and Li₂BOB were predicted to be 1.85 and 2.20 V versus Li/Li⁺, respectively. Reduction potential of the isolated BOB anion was found to be much lower, 0.84 V versus Li/Li⁺ as shown in Figure S20 of the Supporting Information. Thus, QC calculations indicate that while the isolated BOB anion and LiBOB contract ion pair are not expected to be reduced during cell cycling above 2 V, ion aggregates where the BOB anion is bound to two Li⁺ cations are expected to be reduced during cell cycling. The propensity of the LiBOB to participate in aggregates was investigated in DFT calculations and MD simulations. DFT calculations predicted free energy of aggregate forming reaction (2LiBOB → Li-BOB-Li-BOB)) to be ~0.14 eV as shown in Figure S21 of the Supporting Information. MD simulations were performed in order to further investigate LiBOB aggregation. We find that, on average, 49% of the Li⁺ cations are solvent-separated from BOB anions, 43% of Li are bound to only one BOB anion and less than 8% of Li⁺ are coordinated by two BOB anions. A snapshot from MD simulations shown in Figure S22 of the Supporting Information illustrates that only a small fraction of BOB anions has two Li⁺ coordinating the same BOB. Thus, only a small fraction of BOB anions exist as Li₂BOB and have a reduction potential above 2 V versus Li/Li⁺ that is needed in order for the BOB anion to undergo reduction at the cathode surface. Decomposition reactions of the reduced BOB from QC calculations are shown in Figure S23 of the Supporting Information. While the C₂O₃⁻ detachment from the reduced BOB⁺⁺ anion in gas-phase is energetically favorable in agreement with previous calculations for the reduced DFOB, it becomes energetically unfavorable in implicit solvent due to solvent stabilization of the reduced BOB⁺⁺ anion. Similarly, B-O bond opening is energetically unfavorable for the reduced (LiBOB)⁻ complex in implicit solvent as shown in Figure S24 of the Supporting Information. Second reduction potential for Li₂BOB was predicted to be at 0.5 V in implicit solvent with ε = 20. Thus, we conclude that the singly reduced Li₂BOB radicals are likely to have long lifetime near cathode surface and could oxidize back to form LiBOB when cathode potential increases above 2.2 V that is Li₂BOB reduction potential. If LiBOB reductive decomposition occurs, dilithium oxalate and oligomeric borates are expected to form.

QC calculations were utilized to examine the reactions between LiBOB and F⁻ anions as a primary mechanism for forming CEI on the FeF₃ cathode. Figure 7c,d shows that such reactions are slightly exergonic and yield DFOB⁺⁺, BF₂⁻ anions and Li₂(oxalate). Reaction energies in presence of the dissociated F⁻ anion instead of (LiF)₂ during FeF₃ conversion reaction, however, would make the BOB anion reaction with F⁻ more energetically favorable. Note that XPS study of the CEI formed on the cathode surface has a strong signal attributed to the B–F bonds, which is corresponding with the exergonic energies obtained in QC calculations for the F⁻ anion reacting with LiBOB and forming Li₂(oxalate). Thus, QC calculations suggest the reaction between LiBOB and F⁻ as a most likely source of the cathode CEI formation.

Electrochemical stability of the Li₂(oxalate) clusters was estimated from QC calculations and is given in Figure 7e. Li₂(oxalate) and LiBF₄ are predicted to be stable within cathode operating potentials, thus are expected to be present in the CEI.LiDFOB is likely to be stable if located in the outer part of the CEI without direct contact with the dissolved F⁻ anions due to potential decomposition using reaction shown in Figure 7d. The Li₂(oxalate) salt has high propensity to aggregate with aggregation free energy of ~0.63 eV for dimerization of Li₂(oxalate) shown in Figure 7f. Fast aggregation of Li₂(oxalate) was confirmed in MD simulations shown in Figure 8, where the initial configuration with the uniformly distributed ox⁻² anions through the simulation box was generated after the initial pre-equilibration. After 2 ns, initial aggregates started forming, while after 19 ns most of Li₂(oxalate) assembled in two large aggregates. Fast aggregation and precipitation of Li₂(ox) in some way is similar to aggregation of a well-established anode SEI compound dilithium ethylene dicarbonate (Li₂EDC) that was previously observed. We conclude that a mixture dominated by the Li₂(oxalate) aggregates doped with LiBF₄ and LiDFOB is likely a dominant component of the cathode CEI that would be able to expand and contract during cathode cycling allowing Li⁺ to pass through, but preventing F⁻ diffusion.

Finally, for the sake of exploration, we extend the voltage window to 1.2–4.2 V to allow the occurrence of both intercalation and conversion reactions (3e⁻ reaction). Figure S26 of the Supporting Information shows the cycling performances of FeF₃-CNT cathode in 100% LiBOB. The initial specific capacity reached 620 mA h g⁻¹, however, it drops to ~100 mA h g⁻¹ in 60 cycles, implying diminished protection, which may due to the destroying of protective SEI when discharged to a lower voltage. Further study of cyclic stability of the 3e⁻ reaction of FeF₃ and its SEI protection are out of the scope of this work but will be covered in the future.

3. Conclusions

In summary, our efforts to develop a commercially viable cathode technology based on low-cost and extremely abundant Fe revealed multiple important observations. First, we have demonstrated an efficient approach to improving the
electrochemical performances of Li-FeF₃ cells by the introduction of a novel nanostructure of electrically connected FeF₃-CNT network, further comprising two layers of protective shells—one deposited ex situ and another one in situ. This proposed synthesis pathway is broadly applicable for a wide range of MFs, and is advantageous due to a minimal use of hazardous materials, such as HF. The first protection shell, uniform Al₂O₃ coating, produced by PEALD, significantly improved the capacity retention of FeF₃. The second level of surface protection, in situ formed CEI, induced both chemically and electrochemically by LiBoB additive in electrolytes, successfully elevated the capacity retention of Li-FeF₃ cells to over 90% after 300 cycles. The combination of these approaches allowed us produce the first report on FeF₃ as a cathode material, where a very high capacity utilization in combination with excellent stability is approaching to the level needed for practical applications of FeF₃. The CEI containing lithium oxalate and B–F bond contained anions was found to effectively protect the cathode material from direct contact with electrolytes, thus greatly suppressing the dissolution of Fe. QC and MD calculations provide unique insights into the mechanisms of CEI layer formation. Compared with open literature reports on FeF₃, our work not only demonstrated up to 10 time higher electrochemical stability, but also provided the readers with a better fundamental understanding of electrochemical behavior of MF cathodes above 2 V and the positive impact observed with the application of a LiBoB salt in the electrolyte.

4. Experimental Section

**Synthesis of Fe-CNTs:** First, 170 mg of MWCNTs (>90%, Research Nanomaterials, Inc., USA) and 150 mL of N-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%, Sigma-Aldrich, USA) were mixed together to form a slurry. After 1 h of sonication, the slurry was blended with 1.039 g of Fe(NO₃)₂·9H₂O (99.99%; Sigma-Aldrich, USA) and magnetically stirred for 1 h. Then the slurry was refluxed in a 300 mL three-necked round-bottomed flask with continuous magnetic stirring for another 1 h. Reflux temperature was maintained at 180 °C by an oil bath. Next, the suspension was cooled down at room temperature, filtered (pore size of 2.5 µm; Whatman, USA), and washed with ethanol for three times. After drying at 80 °C overnight in a vacuum oven, the filtered solid composites were annealed under 4% H₂ in argon at 600 °C for 2 h.

**Synthesis of FeF₃-CNTs:** The as-prepared Fe-CNTs was contained in a metal crucible made of Inconel (made in house), followed by placing the crucible in the middle of an Inconel tube (made in-house) and flowing helium (Airgas, USA). After elevating the temperature to 300 °C at the rate of 4 °C min⁻¹, the flowing gas was switched from helium to a mixture gas of 2% NF₃ balanced with helium (Linde Gas Electronics, USA). The Fe-CNTs was fluorinated completely into FeF₃-CNTs after 2 h at 300 °C.

**FeF₃-CNTs Electrode Fabrication:** The active material (FeF₃-CNTs) powders were mixed with carbon black (Superior Graphite, USA), and PVDF (Alfa Aesar, USA) in NMP with a ratio of 80:10:10 by weight, stirred for 8 h then casted on an Al foil and dried in vacuum at 60 °C for 12 h. PEALD was performed using the Cambridge Fiji Plasma ALD system (Ultratech, CA). Alumina film was coated on the FeF₃-CNTs electrode using trimethylaluminium (Al(CH₃)₃) as a precursor and oxygen plasma at 120 °C for 60 cycles. The precursor pulse time was set to 0.06 s.
Materials Characterization: XRD patterns were collected using Cu Kα radiation at a voltage of 40 kV and a current of 20 mA on an X’Pert PRO Alpha-1 (PANalytical, The Netherlands). SEM images and EDS elemental mapping were acquired using Hitachi SU8010 (Japan). HR-TEM images were collected on a Tecnai F30 (FEI, The Netherlands). Thermogravimetric analysis was performed on a Pyris 1 TGA. XPS was done using the Thermo K-Alpha system (Thermo Scientific, USA). NMR spectra were obtained using a Bruker AMX 400 (USA). Thermogravimetric analysis was performed on a Pyris 1 TGA. XPS was done using the Thermo K-Alpha system (Thermo Scientific, USA). NMR spectra were obtained using a Bruker AMX 400 (USA). Galvanostatic cycling was performed using type 2032 coin cells at room temperature. The cathode was FeF₃-CNTs electrode and the anode was pure lithium foil. Electrochemical characterization was carried out using a VMP3 potentiostat (Gamry Instruments, Inc., USA). Galvanostatic charge-discharge tests were performed with an Arbin BT-2043 (Arbin Instruments, USA). All the specific capacity calculations involved in this work are based on the mass of FeF₃ active material only.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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