Transition metal fluorides (MF$_x$) offer remarkably high theoretical energy density. However, the low cycling stability, low electrical and ionic conductivity of metal fluorides have severely limited their applications as conversion-type cathode materials for lithium ion batteries. Here, a scalable and low-cost strategy is reported on the fabrication of multifunctional cobalt fluoride/carbon nanotube nonwoven fabric nanocomposite, which demonstrates a combination of high capacity (near-theoretical, 550 mAh g$^{-1}$ CoF$_2$) and excellent mechanical properties. Its strength and modulus of toughness exceed that of many aluminum alloys, cast iron, and other structural materials, fulfilling the use of MF$_x$-based materials in batteries with load-bearing capabilities. In the course of this study, cathode dissolution in conventional electrolytes has been discovered as the main reason that leads to the rapid growth of the solid electrolyte interphase layer and attributes to rapid cell degradation. And such largely overlooked degradation mechanism is overcome by utilizing electrolyte comprising a fluorinated solvent, which forms a protective ionically conductive layer on the cathode and anode surfaces. With this approach, 93% capacity retention is achieved after 200 cycles at the current density of 100 mA g$^{-1}$ and over 50% after 10 000 cycles at the current density of 1000 mA g$^{-1}$.

1. Introduction

Due to their large energy density, lithium ion batteries (LIBs) have been extensively studied to satisfy the ever increasing need of power sources.[1–5] In order to further increase functionality or operational time of LIB-powered devices, two general strategies could be considered: (i) development of multifunctional LIBs (such as structural LIBs, which may carry mechanical load and be a part of the structure) with the potential to minimize the device weight and volume on
a system level, even when such batteries offer energy density comparable or slightly lower than state-of-the-art and (ii) development of new materials that increase energy density in LIBs.

Currently, only a very few studies reported on the development of high strength electrodes for LIBs and other energy storage devices, generally focusing on the structural anode or supercapacitor development. Some of the most promising performance characteristics were recently achieved in electrodes utilizing carbon nanotubes (CNTs); these demonstrated high strength, flexibility, high thermal and electrical conductivities.

Significant effort has been placed on the development of alloying-type anode materials with extremely high capacity, including Si and Sn. At the same time, the state-of-the-art cathode materials, namely, LiCoO$_2$ (LCO), LiNi$_x$Mn$_{1-x}$O$_2$ (NMC), and LiNi$_x$Co$_{1-x}$Al$_{0.3}$O$_2$ (NCA), cannot match both the gravimetric and, more importantly, volumetric capacity of Si anodes. Such imbalance of capacity constituted the major challenge for fabricating advanced LIBs that target larger energy density. In order to overcome this issue, the number of studies of various high capacity conversion-type cathode materials has been rapidly increasing in the last few years.

Chalcogen-based cathodes (mostly sulfur, S) have received the most attention due to their high theoretical potentials of up to $\approx 2.2$ V vs Li/Li$^+$. Their low average potential (theoretical $\approx 2.2$ V vs Li/Li$^+$), however, limits the cell energy density. More recently, metal fluorides (MF), a subclass of conversion-type transition metal halides cathodes, have showed potential on achieving high capacity and high energy density. The full utilization of the oxidation state in the corresponding metal (M) becomes possible in MF, resulting in higher theoretical volumetric capacity (up to $\approx 2.2$ Ah cm$^{-3}$) and higher theoretical potential (up to $\approx 3.5$ V vs Li/Li$^+$) than that in S cathodes. Nevertheless, among MFs, cobalt (II) fluoride (CoF$_2$), with the theoretical specific capacity of 553 mAh g$^{-1}$, is rarely studied because of its extremely poor cycling stability. Somewhat stable cycling performance of thin film CoF$_2$ was achieved through a deposition of a protective coating by a pulsed laser deposition (PLD) process, which made the CoF$_2$ hard to be utilized for rechargeable LIBs. The reason for the extremely low stability of CoF$_2$ was proposed to be the result of its poor conductivity and slow kinetics. Therefore, the research focus shifted to size reduction because nanostructures would reduce the Li ion diffusion paths and hence, improve the ion insertion rate. One of the highest capacities were demonstrated in hierarchical CoF$_2$ spheres synthesized using a supercritical fluid method. Unfortunately, while this unique structure delivered high initial capacity, it rapidly dropped to $\approx 50$ mAh g$^{-1}$ after ten cycles. More recently, fast capacity degradation was also reported with nano-sized CoF$_2$ by Teng et al. All these reports indicated that there might be other unrevealed reason for the fast capacity degradation of CoF$_2$.

Herein, it was revealed for the first time that the dissolution of CoF$_2$ cathode during cycling in conventional electrolytes is a major contributor to its poor cycling stability. We further identified and provided insights on CoF$_2$ performance enhancements that greatly enhanced stability of CoF$_2$ cathodes could be achieved with the electrolytes comprising fluorinated carbonates. In order to synergistically enhance electrical conductivity and load-bearing properties of CoF$_2$ cathodes, a novel electrode preparation method was employed, where we incorporate CoF$_2$ nanoparticles within a porous, high strength CNTs fabric. As a result of the innovative combination of the proposed electrode and electrolyte, a theoretical capacity under 10 mA g$^{-1}$ current density was achieved with an unprecedentedly stable (for this system) capacity of $\approx 360$ mAh g$^{-1}$ under a relatively high (for this system) current density of 100 mA g$^{-1}$. Under a very high current density of 1000 mA g$^{-1}$, over 50% of the initial capacity was retained after 10 000 cycles. Furthermore, a high strength demonstrated in the fabricated CoF$_2$/CNT nonwoven fabrics suggests the promise of MF$_x$-based materials for their application in multifunctional batteries with load-bearing capabilities.

2. Results and Discussion

The overall process flow utilized for the CoF$_2$/CNTs composite fabrication is shown in Figure 1. As a starting material for this project, we introduced binder-free CNT-based nonwoven fabric (Figure 1a) produced on a commercial scale[10]. The CNT fabric was produced by continuous chemical vapor deposition (CVD) for a high-throughput, low-cost manufacturing of a uniform high-strength CNT material. The next step involved the infiltration of the CNTs with an aqueous precursor solution of CoSiF$_6$. Surfactant of Triton X-100 was utilized to improve the wetting property of highly hydrophobic CNTs surface. A uniform coating of the CNTs with the CoSiF$_6$ layer was achieved after drying (Figure 1b). Subsequently, post-annealing step was conducted at 400 °C for 6 h in argon (Ar) atmosphere to chemically transform CoSiF$_6$ into CoF$_2$ (Figure 1c), according to \[ \text{CoSiF}_6 \xrightarrow{\Delta} \text{CoF}_2 + \text{SiF}_4 \uparrow \] (1)

Figure 2 shows the selected morphological characterization of the produced CoF$_2$/CNTs composite. With high flexibility, the produced composite fabric can be rolled
up, cut, and directly used as binder-free electrodes in LIBs (Figure 2a, inset). Scanning electron microscopy (SEM) studies showed that the produced samples exhibited uniform distribution of well-dispersed CoF$_2$ nanoparticles without any large agglomerates visible (Figure 2a). Note that without surfactant, however, such a result could not be achieved and high aggregation of CoF$_2$ was observed. High-resolution SEM showed CoF$_2$ nanoparticles on the top surface of the electrode to be spherical in shape and have a diameter in the range from $\approx30$ to $50$ nm (Figure 2b). Transmission electron microscopy (TEM) studies further verified the size and shape of CoF$_2$ nanoparticles coated on the top layer of the CNT fabric (Figure 2c).

In order to confirm the composition of the nanoparticles, X-ray diffraction (XRD) (Figure 2d), energy dispersive spectroscopy (EDS) (Figure S1a, Supporting Information), and X-ray photoelectron spectroscopy (XPS) (Figures S1b and S3, Supporting Information) tests were additionally conducted. XRD spectra revealed typical CoF$_2$ diffraction peaks indexed to the (110), (101), (111), (211), (202), and (301) crystal planes associated with the tetragonal-phase CoF$_2$, according to the database JCPDS No. 33-0417. Additional peaks at $\approx26^\circ$, $41^\circ$, and $43^\circ$ are associated with the nanostructured carbon of the CNTs substrates (Figure 2d).$^{[50]}$ By conducting Scherrer analysis on the strongest (110) peak we estimated the average crystal size to be $\approx45$ nm. We propose that the bulk of the electrode (not easily accessible by SEM and TEM due to high strength of the fabric) comprise particles larger than what we observe on the surface. Indeed, these larger particles located between the CNTs thin layers could be observed by the cross-section SEM images (Figure S2, Supporting Information). EDS studies showed the presence of cobalt (Co), fluorine (F) (with the atomic ratio of Co to F being $\approx1.2$) (Figure S3a, Supporting Information), further confirming the formation of CoF$_2$. EDS also revealed the presence of small amount of Si and O impurities. The likely origin of Si is the incomplete conversion of the precursor, while O may originate from the CNTs and the moisture adsorbed during sample handling. EDS studies (Figures S1b and S3, Supporting Information) further confirmed the oxidation state of Co (II), which was expected for CoF$_2$. Specific surface area (SSA) of the composite was measured by the Brunauer–Emmett–Teller (BET) analysis of N$_2$ sorption isotherm collected at 77 K. It revealed a BET SSA of $\approx230$ m$^2$ g$^{-1}$ compared with the pure CNTs of 220 m$^2$ g$^{-1}$. The results of tensile tests (Figure S4, Supporting Information) demonstrated modulus of toughness of the composite (which is a measure of the energy of mechanical deformation per unit volume prior to fracture) of 97.5 MJ m$^{-3}$, which was higher than that for the initial CNT fabric (75.5 MJ m$^{-3}$) and showed clear advantages compared to various commonly used structural materials, including lightweight metals and metal matrix composites. The result of the thermal gravimetric analysis (TGA) is illustrated in Figure S5 (Supporting Information).

The most common electrolyte utilized in CoF$_2$ and in most other cathode studies has been 1 M LiPF$_6$ salt solution in a ternary mixture of carbonate solvents, such as ethylene carbonate, dimethyl carbonate, and diethyl carbonate.

![Figure 2. The morphology and structural characteristics of CoF$_2$/CNTs composite fabric: a) SEM image of the composite surface (inset photograph of the composite, scale bar of 5 cm); b) high-resolution SEM image of the interface of CoF$_2$-decorated CNTs with a close-up of a single CoF$_2$ nanoparticle on a CNT (inset, scale bar of 50 nm); c) TEM image of the CoF$_2$-decorated CNTs; and d) XRD spectrum of the composite.](https://www.small-journal.com)
(EC/DMC/DEC). In such electrolytes, EC forms a favorable solid electrolyte interphase (SEI) on a graphite anode and provides high salt solubility due to its high dielectric constant while that adding DEC to electrolyte mixture greatly improves the electrolyte performance at low temperature due to its low melting point (−43 °C,[51]) but at the expense of reducing SEI stability. And other solvents (such as DMC) are commonly required as additives to improve miscibility of DEC with EC, particularly at low temperatures. In the case of CoF₂ cathode, we speculated that the formation and stability of SEI played an important role on the conversion-type lithiation and delithiation process as following

$$\text{CoF}_2 + 2\text{Li}^+ + 2e^- \rightarrow \text{Co} + 2\text{LiF} \quad (2)$$

Unfortunately, the commonly used electrolyte (EC/DMC/DEC) leads to unsatisfactory performance for metal fluoride cathodes. Such poor performance triggered our investigation of alternative electrolytes comprising fluoroethylene carbonate (FEC), which was recently demonstrated the capability of inducing a more stable SEI on the anode surface than EC.[52–58] Furthermore, while prior studies made great effort on reducing the characteristic dimensions of CoF₂, little improvement of cycling stability was achieved. This inspired us to find other issues attributed to the cell instability, such as transition metal (Co in the case of CoF₂) dissolution during cycling of high energy CoF₂/Li cells, which may negatively affect the SEI on both CoF₂ cathode and the Li anode.[59] As a low melting point cosolvent we selected ethyl methyl carbonate (EMC) due to its excellent miscibility with FEC without any additional cosolvents needed. Keeping two solvents in the electrolyte simplifies analysis of the obtained results. As an additional bonus, EMC is known to form a superior SEI than DMC.

As will be later demonstrated, we indeed observed a significant improvement in the capacity retention when an FEC/EMC electrolyte replaced an EC/DMC/DEC one. The optimization of FEC fraction in a binary FEC/EMC electrolyte further confirmed the important role of FEC for the capacity, rate performance, and stability of the CoF₂/CNTs composite (Figure 3a). In all three FEC/EMC electrolytes (with 10%, 20%, and 30% FEC, respectively), a near theoretical capacity utilization was achieved when cycled at 10 mA g⁻¹ current density (note that small deviations may be related to known variations in the built properties of the coin cells, the small errors in the estimation of the CoF₂ content in the samples

![Figure 3. Rate performance and cycle stability of CoF₂/CNT composite: a) effect of 1 M LiPF₆ electrolyte solvent composition on the cell rate performance and capacity retention; b) the charge/discharge profiles at different current density in 3:7 FEC/EMC electrolyte; c) capacity retention and columbic efficiency in 3:7 FEC/EMC electrolyte at 100 and 500 mA g⁻¹ of current density; and d) capacity retention and coulombic efficiency in 3:7 FEC/EMC electrolyte during ultra-long test (10 000 cycles) conducted at a current density of 1000 mA g⁻¹. Capacity is shown for the CoF₂ contribution only.](5167)
and to side reactions). The high capacity achieved in all cells suggests excellent electrical connectivity of CoF₂ in the composite, as expected by the employment of CNTs. Similar rate performance was observed by continuously varying current density from 100 mA g⁻¹ to 2 A g⁻¹. However, suggested by the consequent 100-cycle performance of the electrodes charged and discharged at 100 mA g⁻¹, that increasing FEC content from 10% to 30% gave rise to a significant improvement in the stability of the CoF₂/CNT composite (Figure 3a). And the high-level (30%) FEC-containing electrolyte revealed nearly no fading of capacity. Thereafter, the high-level FEC/EMC ratio electrolyte was applied in the following experiments.

It should be pointed out that even though the electrode capacity retention at increasing current density was clearly not as fast as that of most conventional intercalation-type electrodes, it was still a significant upgrade for an MF system. In Figure 3b, typical charge/discharge profiles showed a high (over 1.3 V) voltage hysteresis. While the origin(s) of the hysteresis is under investigation, it is commonly observed in MFs and is certainly undesirable because it reduces the energy efficiency of the cell. On a positive note, since some of our studies (to be reported separately) demonstrated the opportunity to dramatically reduce the hysteresis in MFs, we are optimistic that this negative factor could be greatly diminished. Furthermore, in some applications, such as for using structural batteries in drones or sensors powered by solar cells, rapid charging is not needed and slow charging capability (e.g., within 4 h or more) is sufficient.

As previously discussed, prior studies on CoF₂ [46,48] reported very poor cycle stability. In contrast, here we demonstrate excellent electrochemical stability in constant-current galvanostatic tests conducted at 100, 500, and 1000 mA g⁻¹ (Figure 3c,d). When tested at moderately high current densities of 100 and 500 mA g⁻¹, the composite electrodes showed initial capacity of 260–360 mAh g⁻¹ of CoF₂, and showed a good stability with a remarkable capacity retention (93% for 100 mA g⁻¹) in 200 cycles (Figure 3c). In order to reveal the contribution of CNTs to the electrode capacitance, we tested CoF₂-free CNT electrodes in the same potential range and at the same current densities observed only ~3 mAh g⁻¹, which could almost be neglected (Figure S6, Supporting Information). When tested the CoF₂/CNT electrode at a high current density of 1000 mA g⁻¹, the cell showed initial capacity of 130 mAh g⁻¹, and moderately slow capacity decrease to 70 mAh g⁻¹ within the first 4000 cycles (Figure 3d). Meanwhile, as we discussed in our recent review paper, some of the capacity fading could be related to the growing resistance of the Li counter electrode, which is known to be suffered from the growth of Li dendrites and increase in the Li SEI resistance with cycling at real current densities above 0.5 mA cm⁻².

Figure 4 emphasizes the important roles of both the nanofibrous electrode structure and the presence of FEC in electrolyte on CoF₂ cycling stability. The comparison of the CoF₂/CNT nanocomposite fabric composite with the electrode comprising CoF₂/CNTs mixture (both with optimized FEC/EMC electrolyte), noticeably superior capacity utilization and cycle stability of the composite were observed (Figure 4a). The conventionally prepared electrode showed a maximum capacity of ~200 mAh g⁻¹ during charge-discharge tests at a moderate current density of 100 mA g⁻¹, followed by a relatively fast capacity fading to 100 mAh g⁻¹ after 50 cycles, presumably due to the formation of SEI that breaks electrical contact between CoF₂ particles and the CNTs. In contrast, the CoF₂/CNTs composite, where each CoF₂ particle was bonded to a CNT, exhibited capacity of ~360 mAh g⁻¹ for the same current density, which remained unchanged during the next cycles (Figure 4a). Similarly, when we utilized a more “stable” nanofibrous composite electrode, but conducted tests in conventional FEC-free electrolyte and FEC/EMC electrolyte, rapid degradation was observed after only ten cycles (Figure 4b) with FEC-free electrolyte. Since both the electrical conductivity within the electrode and the ionic conductivity of the electrolyte should be nearly identical in both cells, the lack of electrochemical stability in conventional electrolyte was proposed to be linked to irreversible cathode corrosion. The corresponding charge-discharge curves were presented in Figure S7 (Supporting Information).

In order to gain further insights of how the proposed electrode microstructure and electrolyte composition improved the electrochemical properties of CoF₂ electrodes, we have conducted electrochemical impedance spectroscopy (EIS) tests. Figure 5 compares the electrochemical charge transfer resistance (Rct) of the cells with different electrolytes and...
which correlate well with the results of cycling performance (Figure 4).

Postmortem SEM and EDS analysis of surface characteristics of both cathode (CoF₂) and anode (Li foil) electrodes provided insights on the origin of the improved cycle stability of FEC-comprising electrolytes. First, we compared the morphology and chemical composition of cycled Li metal anodes (Figure 6). The SEM image of the Li anode cycled in FEC/EMC-based electrolyte showed smooth (at a low magnification) Li surface with only a few salt residues visible (Figure 6a). The corresponding EDS spectrum showed the presence of C from the SEI, F from the LiPF₆ and FEC, O from the EMC, FEC, and unintentional oxidation during the sample transfer to the SEM chamber, and P from the LiPF₆ (Figure 6b). No traces of Co could be observed, suggesting that no significant CoF₂ dissolution took place during lithiation/delithiation processes. In a sharp contrast, SEM of the Li cycled in EC/DEC/DMC-based electrolyte showed extremely rough surface morphology. EDS studies further revealed significant content of both Co and Fe (Figure 6c,d). These results indicated that the dissolution of both Co from the CoF₂ cathodes and corrosion of the coin cell took place. Furthermore, because the rough surface morphology correlated well with the metal coprecipitation it could be suggested that both the reduction of Fe and Co ions destroyed the uniformity of SEI on an Li foil and contribute to the surface roughening. Similar conclusion has been previously made during the studies of the SEI on graphite during the metal dissolution in NCM, LMO, and other intercalation-type cathodes,[63–67] but the extent of the metal dissolution is dramatically higher in MF electrodes. Cycled electrolytes and the separators additionally revealed significant differences in
appearance. In case of the FEC/EMC electrolyte cells, both the separator and electrolyte looked nearly identical to the original ones—the separator was clean and the electrolyte clear and transparent. However, the cycled EC/DEC/DMC-based electrolyte became brown and opaque and the separator becoming brown-colored as well, which is consistent with the expected contamination by Fe. The EDS tests on such a separator in EC/DEC/DMC similarly revealed the presence of Co and Fe, as expected (Figures S8 and S9, Supporting Information). The postmortem XRD test also indicated that CoF$_2$ was partially dissolved in the EC/DMC/DEC containing cells (Figure S10, Supporting Information).

Clearly, the FEC/EMC efficiently prevented the dissolving of CoF$_2$, which was an important advantage for the cycling stability. We propose that FEC induced formation of the protective surface (SEI) layer not only on the anode, but also on the cathode. Such a layer evidently does not induce any significant reduction in an Li ion transport (Figure 3a), but protect the cathode from corrosion effectively. Prior studies on conventional cells also showed that FEC additives in the electrolyte not only produced a thinner and a more stable SEI layer on the anode but suppressed the dissolution of metallic elements from the cathode material and their re-deposition on the anode.$^{[57,68]}$

In order to provide more evidence for the formation of the protective (FEC-induced) layer on the CoF$_2$ cathode surface, we have conducted XPS analyses on cycled CoF$_2$ cathode surfaces in the discharged state (Figure 7). The Cls spectrum (Figure 7a,c) shows a difference in the SEI layers for EC-based and FEC-based electrolytes. The Cls C—C peak was much stronger on the CoF$_2$ electrode cycled in FEC-based electrolyte (17 at%) than in EC based electrolyte (7 at%). Given that XPS can only detect the top 20–30 nm of a material, this suggests that the FEC-based electrolyte maintains a thinner SEI than the EC-based electrolyte after cycling, explaining the lower impedance observed via EIS.$^{[69]}$ Prior studies on FEC-induced SEI on the anodes observed similar phenomena.$^{[52,53,70,71]}$ Meanwhile, the presence of the C1s spectrum (Figure 7a,c) indicates the formation of a passivation layer on the cathode surface for both cells cycled with EC-based and FEC-based electrolytes. And the detailed comparison of Cls spectrum enabled us to estimate the relative components of carbonates and other decomposition products in the SEIs. The peak located at 290 eV corresponds to the signals of carbon atom in inorganic carbonates (such as Li$_2$CO$_3$), ROCO$_2$Li, ROCO$_2$R (dialkylcarbonates), or polycarbonates. Li$_2$CO$_3$ and ROCO$_2$Li are typical decomposition products of EC.
The peak located at 286–288 eV is related to the ethereal and alkoxy carbons as well as the poly(ethylene oxide) (PEO)-like polymers. It appeared that in FEC-based electrolyte, the SEI mainly consisted of ethereal and alkoxy carbons, suggested by the high intensity of the peak around 286–288 eV along with the relatively low peak intensity at 288–292 eV. However, in the EC-based electrolyte, the decomposition of EC, DMC, and DEC continued more extensively (due to lower passivation ability) and formed an SEI with relatively large amount of inorganic Li$_2$CO$_3$, ROCO$_2$Li, and ROCO$_2$R. Compared to the organic PEO-like components of the SEI, such inorganic compounds should be more permeable to solvent molecules and various corrosive products and their high concentration is undesirable. Not surprisingly, the SEI induced by the decomposition of EC/DEC/DMC electrolyte evidently failed to prevent CoF$_2$ cathode dissolution.

The high-resolution XPS of F1s showed similar features in both electrolytes, the main being the formation of nonconductive LiF, which is both a discharge product of CoF$_2$ and also a possible decomposition product from EC and LiPF$_6$ in the SEI. Possible reactions involved in the electrolyte decomposition are listed below:

\[
\begin{align*}
\text{Li}_2\text{CO}_3 + \text{HF} &\rightarrow \text{LiF} + \text{H}_2\text{CO}_3 \\
\text{LiPF}_6 &\rightarrow \text{LiF} + \text{PF}_5 \\
\text{LiPF}_6 + \text{H}_2\text{O} &\rightarrow \text{LiF} + \text{POF}_3 + \text{HF} \\
\text{POF}_3 + \text{H}_2\text{O} &\rightarrow \text{PO}_2\text{F}^- + \text{HF} + \text{H}^+ \\
\text{PO}_2\text{F}^- + \text{H}_2\text{O} &\rightarrow \text{PO}_3\text{F}^- + \text{HF} + \text{H}^+
\end{align*}
\]

The relative fraction of LiF in the SEI of the FEC-based electrolyte is also smaller (25%–21%, Figure 7). Combined with EDS results showing less Co dissolution and deposition and less metal corrosion, the C1s and F1s XPS spectra indicated that the SEI layer formed on the cathode surface in FEC-comprising electrolyte offered dramatically better protection against the cobalt dissolution than that of the EC-based electrolyte.

### 3. Conclusion

The CoF$_2$/CNTs nanocomposite was successfully produced via continuous CVD synthesis of CNT nonwoven fabric followed by a surfactant-assisted aqueous infiltration of Co precursor and its transformation to 30–50 nm CoF$_2$ nanoparticles uniformly distributed on the CNT surface. The flexible CoF$_2$/CNTs nanocomposite exhibited an improvement on composite strength and a remarkable modulus of toughness, an important feature as a binder-free multifunctional electrode for LIBs. The uniform and small size of CNT-linked CoF$_2$ allowed the produced composite to demonstrate near theoretical capacity of ≈ 550 mAh g$^{-1}$ at a small current density, ≈ 360 mAh g$^{-1}$ at a medium current density of 100 mAh g$^{-1}$ and ≈ 130 mAh g$^{-1}$ at a high current density of 1000 mAh g$^{-1}$. Electrolyte solvent composition was found to have a major impact on electrochemical stability of the composite. In FEC-comprising electrolytes, hundreds of stable cycles with little degradation were achieved. When tested at the highest current density of 1000 mAh g$^{-1}$, only 50% degradation occurred after 10,000 cycles. EDS measurements revealed that the FEC induced a very stable “protective” SEI on the CoF$_2$ cathode surface that prevented the cathode corrosion and dissolution. In contrast, conventional electrolyte comprising EC/DMC/DEC solvents leads to severe CoF$_2$ dissolution, corrosion of the coin cell, and severe roughening of the Li anode. XPS on the cathode surface revealed a significantly higher degree of the polymeric (PEO-like) components in the SEI induced by the reduction of the FEC-comprising electrolyte, which proved more effective on protecting the cathode surface against undesirable side reactions. Attractive mechanical properties of the composite in combination with its high specific capacity demonstrate promise for the formation of high strength flexible fluoride-comprising cathodes for multifunctional battery applications.

### 4. Experimental Section

**Materials:** Cobalt hexafluorosilicate (CoSiF$_6$) solution was prepared from cobaltous carbonate (CoCO$_3$, 99.9%, Sigma Aldrich) and fluosilicic acid (99.9%, aqueous solution, Sigma Aldrich). The surfactant of Triton X-100 was purchased from Alfa Aesar and also a possible decomposition product from EC and LiPF$_6$ in the SEI. Possible reactions involved in the electrolyte decomposition are listed below:

\[

\text{Li}_2\text{CO}_3 + \text{HF} \rightarrow \text{LiF} + \text{H}_2\text{CO}_3 \\
\text{LiPF}_6 \rightarrow \text{LiF} + \text{PF}_5 \\
\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{LiF} + \text{POF}_3 + \text{HF} \\
\text{POF}_3 + \text{H}_2\text{O} \rightarrow \text{PO}_2\text{F}^- + \text{HF} + \text{H}^+ \\
\text{PO}_2\text{F}^- + \text{H}_2\text{O} \rightarrow \text{PO}_3\text{F}^- + \text{HF} + \text{H}^+
\]

The surfactant of Triton X-100 was purchased from Alfa Aesar and fluosilicic acid (99.9%, aqueous solution, Sigma Aldrich). The surfactant of Triton X-100 was purchased from Alfa Aesar and the carbon nanotubes fabric was from Nanocomp Technologies. The CNTs fabric was prewashed with ethanol and acetone, and annealed in argon for 12 h to remove the possible polymer.

**Preparation of CoF$_2$-Infiltrated CNTs:** The in situ construction of CoF$_2$/CNT nanofibrous cathode was carried out through a surfactant-assistant aqueous deposition process. In a typical synthesis, a CNT’s membrane (1.2 × 1.2 cm) was immersed into CoSiF$_6$ solution (0.05 M). Because the surface of CNTs is highly hydrophobic, Triton X-100 (0.1 (V/V)%), was added into the precursor solution in order to increase the precursor wetting. After infiltration and 12 h drying in a 70 °C oven, the samples underwent 400 °C postannealing treatment in argon for 6 h. By varying the concentration of CoSiF$_6$ solution (from 0.05 to 0.5 M), the mass fraction of CoF$_2$ in the CoF$_2$/CNT composites (demonstrated from ≈ 30 to ≈ 70 wt% in our experiments) could be controlled and quantitatively measured by mass difference before/after loading. In order to compare the battery performance of pure CoF$_2$, CoF$_2$/CNTs mixture and CoF$_2$/CNTs nanofibrous composite, the pure CoF$_2$ nanopowder was synthesized using the same procedure (without addition of CNTs). And the CoF$_2$/CNTs mixture was fabricated by simply blending the CNTs and CoF$_2$ powder together with the same amount of CoF$_2$ as that in CoF$_2$/CNTs composite.
Characterizations: The morphology of samples was characterized by using field-emission scanning electron microscope (FESEM; Hitachi, SU8010, Japan) and TEM (FEI, Tecnai 30, Holland). The crystallinity of these samples was analyzed by XRD (Panalytical, XPert PRO α-1 diffractometer, Netherland). The surface area of CoF₂/CNTs composite was determined by the isotherms of N₂ gas adsorption, collected at 77 K using an ASAP 2020 Surface Area and Porosimetry Analyzer (Micromeritics Inc., USA). The content of CoF₂ in the composite was analyzed by TGA (TA Q600). The cell was disassembled for ex situ EDS and XPS tests. The cycled anode (lithium metal) was directly used for the EDS (Zeiss, Ultra 60, Germany) as the counter and reference electrodes. The prepared CoF₂/CNTs orride (PVDF) binder was used for benchmark comparison. The rest of the preparation procedure of CoF₂/CNTs composite was directly cut into electrode disks (10 mm diameter) with a strain rate of 10% min⁻¹ and then washed with EMC or DMC to remove any lithium hexafluorophosphate (LiPF₆) and dried in argon atmosphere naturally. After cleaning, this cathode was tested by XPS (Kratos Analytical Ltd., Japan) and Ar-filled sample transfer chamber was used to prevent air exposure of the electrodes. The CoF₂ electrode fabric comprising with ~60 wt% CNT (no other conductive additives and no binder) was selected for both electrochemical and mechanical tests. An electrode comprising CoF₂ nanopowder milled with CNT (similar CoF₂:C ratio) and additionally containing 5 wt% polyvinylidene fluoride (PVDF) binder was used for benchmark comparison.

Mechanical Properties Measurement: Mechanical properties were measured using a tensile test frame (MTS Insight 2, USA) with a strain rate of 10% min⁻¹ and a 100 N load cell. Strain was measured without a strain gauge or extensometer due to the large displacements achieved in accordance with ASTM D882-12. Five sample specimens from each were cut into a length of ~10 cm and width of 5 mm. Actual sample width and thickness were measured via micrometer and were found to be ~5.5 mm and ~33 μm.

Electrochemical Measurements: The electrochemical properties were evaluated by using 2016 coin cells with Li metal disks as the counter and reference electrodes. The prepared CoF₂/CNTs composite was directly cut into electrode disks (10 mm diameter) and assembled using a polypropylene membrane (Celgard, 2500) as a separator. The electrolytes used were 1 M LiPF₆ dissolved in 1:1:1 (V/V/V%) EC/DMC/DEC solvents and FEC/EMC solvents with variable volume fraction, as indicated in the figures. As for the CoF₂/CNTs mixture, 5 wt% of PVDF was added as the binder to the 1-methyl-2-pyrrolidinone (NMP) solution to make the slurry on an aluminum (Al) foil. The rest of the preparation procedure of CoF₂/CNTs mixture electrode was the same with that of CoF₂/CNTs composite electrode. The electrode mass loading was ~1 mg cm⁻² in all tests. The cyclic voltammetry (CV) of CoF₂/CNTs composite was tested using a Solartron potentiostat (AMATEK Inc., USA) within the potential window of 1–4 V (vs Li⁺/Li) and the galvanostatic charge–discharge properties were evaluated on an Arbin battery system (Arbin Instrument, USA) with the same potential window as in CV tests. The EIS was conducted by using a Gamry EIS system (Gammy Instruments, USA) from 10⁵ to 0.01 Hz with an amplitude of 10 mV.

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