Liquid phase exfoliation of nonlayered non-van der Waals iron trifluoride (FeF$_3$) into 2D-platelets for high-capacity lithium storing cathodes

Tingting Chen$^{a,b,1}$, Harneet Kaur$^{b,1}$, Mark McCrystall$^b$, Ruiyuan Tian$^b$, Ahin Roy$^c$, Ross Smith$^b$, Dominik Valter Horvath$^b$, Jack Maughan$^b$, Bharathi Konkena$^b$, Munuswamy Venkatesan$^b$, Kevin Synnatschke$^b$, Tian Carey$^b$, Ji Liu$^b$, Joshua Pepper$^b$, Rui Zhang$^b$, Claudia Backes$^d$, Valeria Nicolosi$^c$, Hui Xia$^{b,2}$, Jonathan N. Coleman$^{b,3,*}$, Harneet Kaur$^b$, Ji Liu$^b$, Joshua Pepper$^b$, Rui Zhang$^b$, Claudia Backes$^d$, Valeria Nicolosi$^c$, Hui Xia$^{b,2}$, Jonathan N. Coleman$^{b,3,*}$

$^a$ Herbert Gleiter Institute of Nanoscience, School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094 China
$^b$ School of Physics, CRANN & AMBER Research Centres, Trinity College Dublin, Dublin 2, Ireland
$^c$ School of Chemistry, CRANN & AMBER Research Centres, Trinity College Dublin, Dublin 2, Ireland
$^d$ Physical Chemistry of Nanomaterials, University of Kassel, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

A R T I C L E   I N F O

Keywords:
Iron trifluoride
Liquid phase exfoliation
Nanosheets
cathodes
Li-ion batteries

A B S T R A C T

Developing high-performance cathode materials for lithium-ion batteries is necessary to maximise both energy and power density. One promising cathode material is iron trifluoride (FeF$_3$) having a high theoretical capacity of 712 mAh/g, although achieving this value experimentally is challenging. Our previous works has shown that achievable capacity can be maximised when active materials are in a two-dimensional (2D) form. Liquid-phase exfoliation (LPE) method seems intuitively inappropriate to produce 2D-platelets from non-layered non-Van der Waals (non-VdW) bulk materials. However, in this manuscript, we show that bulk non-layered non-VdW material, FeF$_3$ can be converted from its 3D form to quasi-2D platelets. The XRD, TEM and elemental analysis showed the structure and stoichiometry of these platelets to be similar to that of bulk material. Interestingly, although AFM showed majority of platelets to be quasi-2D, it revealed the platelet aspect-ratio to be thickness dependent, falling from ~12 for the thinnest platelets to ~1 for the thickest ones. Lithium storage experiments showed that, once coated in carbon and mixed with single walled nanotubes, FeF$_3$ platelets display good Li storage capability coupled with reasonable stability. At very low currents, this material displays an active-mass normalised capacity of ~700 mAh/g, very close to the theoretical value. However, the capacity fell off at higher currents with detailed analysis implying FeF$_3$ cathodes in general to display poor rate performance due to low ionic diffusivity.

Introduction

Lithium-ion batteries (LiIBs) are widely used as energy storage devices in areas such as electronics, the automotive industry and aerospace [1]. The ultimate energy storage performance of LiIBs is generally limited by the cathode due to the relatively low specific capacity of cathode materials compared to anode materials. For example, a commonly used anode material, graphite has a theoretical capacity of 379 mAh/g while the state-of-the-art anode material, silicon, has a capacity of approximately 3500 mAh/g. By contrast, the most common commercial cathode material, LiCoO$_2$ has a theoretical capacity of 274 mAh/g [2], but can only achieve a capacity of approximately 200 mAh/g under normal circumstances [3]. In contrast to anodes, relatively high-performance cathode materials such as LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (NMC, 278 mAh/g) [4], LiNi$_{0.2}$Co$_{0.2}$Al$_{0.6}$O$_2$ (NCA, 279 mAh/g) [5], LiFePO$_4$ (170 mAh/g) [6], and LiMn$_2$O$_4$ (148 mAh/g) [7], all possess theoretical capacities below 300 mAh/g. There would be significant advantages if high-specific-capacity cathode materials were available to complement the many existing high-specific-capacity anode materials [8].

More specifically, it is easy to show theoretically that increasing the cathode specific capacity results in increased energy densities [9]. In addition, when the specific capacity of the cathode is much less than that
One particularly promising, high-capacity cathode material is FeF$_3$ which has a maximum theoretical capacity of 712 mA h g$^{-1}$ [11], much higher than almost all other cathode materials. In addition to a very high capacity, FeF$_3$ exhibits superior thermal stability at elevated temperatures [12], and shows relatively high working potential and reasonable reversibility [13]. This has driven many researchers to study this material, usually as a composite with nano-carbon in order to enhance the conductivity, with varying degrees of success, as shown by our literature review which is summarised in Table 1.

The high theoretical capacity of FeF$_3$ is based on two lithium-storing reactions which occur in different potential ranges [14]: a 1-electron for insertion reaction and a 2-electron conversion reaction (although this insertion reaction is not significantly less reversible than the insertion one (at least in this data set, see SI Fig. S1)). This makes the trade-off described above less attractive and encourages the focus on lower cut-off potentials of 1.5 V or lower, with the aim of achieving capacities approaching 712 mA h g$^{-1}$ as well as reasonable stability.

It is also worth noting that of the 13 studies shown in Table 1 that used lower cut-off potentials of 1.5 V or lower, only 4 achieved capacities higher than 600 mA h g$^{-1}$. This implies that there are additional factors beyond active material choice that are important for achieving near-theoretical capacities in metal fluoride-based electrodes. To this end, many strategies have been attempted to maximise capacity, for example coating the FeF$_3$ with carbon to improve electrode conductivity [14, 20–22] and controlling particle size [21, 23]. Indeed some of the highest combinations of capacity and stability have come from combining small FeF$_3$ particles with carbon coatings or frameworks [24, 25].

Our goal is to build on previous insights which have been used to maximise the achieved capacity of a range of active materials. As mentioned previously, nano-sizing of active materials can significantly improve battery performance [26]. More specifically, it has been shown that for electrodes based on layered materials, exfoliation of the layered crystal to yield 2D nanosheets can dramatically improve electrode capacity. For example, nanosheet-based electrodes tend to have higher capacity than those fabricated from the equivalent bulk layered crystal [27–30]. In addition, although poor cycling stability is often observed in lithium ion battery electrodes incorporating layered materials such as bulk MoS$_2$, this problem is often significantly reduced by using nanosheets rather than particles of bulk layered crystal [28]. These observations have been extended to 2D forms of non-layered, lithium storing materials such as LiMn$_2$O$_4$ and LiFePO$_4$ [31] or FeS$_2$ [32, 33], where electrodes based on 2D platelets display significantly better capacity and stability than those based in the bulk form. Indeed, because 2D materials are extremely thin, solid state diffusion lengths can be relatively small, leading to enhanced rate performance [27].

Furthermore, we and others have shown that incorporating carbon nanotubes in electrodes based on both 2D [34–36] and 3D materials allows them to approach their theoretical capacity. This is because the high conductivity of the nanotubes allows effective charge distribution increasing both initial capacity and rate performance [9, 37, 38].

Thus, we propose that high-performance electrodes based on FeF$_3$ could be achieved using 2D platelets of FeF$_3$ mixed with carbon nanotubes. LPE is widely used method to exfoliate layered VdW materials in liquid media and it seems inappropriate to produce 2D-platelets from non-layered non-VdW bulk materials, but recent literature has shown that non-layered non-VdW compounds including FeS$_2$ [32, 33], Fe$_3$O$_4$ [39], WO$_3$ [40], LiMn$_2$O$_4$ and LiFePO$_4$ [31], as well as elemental materials such as germanium [41] and silicon [42], can be directly converted into quasi-2D platelets using LPE [43–45]. This process produces large quantities of platelets in a liquid environmental which will facilitate mixing with carbon nanotubes and casting into battery electrodes.

Here, we demonstrate the production of FeF$_3$ 2D-platelets by LPE. We characterise the resultant nano-platelets in detail, reporting their morphology, structure, and stoichiometry. The as-produced platelets

---

**Table 1**

Comparison of this work to FeF$_3$-based cathodes reported in the literature.

| Author       | Material | Max Q/M (A/g) | I/M (ma/\(g\)) | V-range (V) | Stability (Capacity retention after 50 cycles) |
|--------------|----------|---------------|----------------|-------------|-----------------------------------------------|
| This work    | FeF$_3$/C-SWT | 685           | 20             | 4.0–1.0    | 0.73                                          |
| Fu, W [24]   | FeF$_3$/CNSF | 560           | 100            | 4.0–1.0    | 1                                             |
| Zhao, X [88] | FeF$_3$/Gra | 690           | 20             | 4.5–1.0    | 0.3                                           |
| Li, T [25]   | FeF$_3$/C | 712           | 500            | 4.5–1.0    | 0.84                                          |
| Tang, M. [73] | FeF$_3$/C | 350           | 50             | 4.0–1.0    | 0.46                                          |
| Tawa, S. [74] | FeF$_3$/AB | 700           | 71             | 4.5–1.0    | 0.29                                          |
| Fan, X. [85] | FeF$_3$/C | 400           | 25             | 4.5–1.2    | 0.75                                          |
| Ma, R. [75]  | FeF$_3$/Gra | 400           | 10             | 4.5–1.5    | 0.67                                          |
| Li, Linpo [89] | FeF$_3$/C | 320           | 100            | 4.5–1.5    | 0.85                                          |
| Bao, T [76]  | FeF$_3$/Gra | 200           | 60             | 4.2–1.5    | 0.5                                           |
| Badway, F [90] | FeF$_3$/C | 700           | 7.6            | 4.5–1.5    | 0.7                                           |
| Jung, H [91] | FeF$_3$/G | 420           | 71             | 4.5–1.5    | 0.67                                          |
| Martha, SK [92] | FeF$_3$/C | 500           | 9              | 4.5–1.5    | 0.9                                           |
| Shen, Y [14] | FeF$_3$/G | 500           | 14             | 4.5–1.5    | 0.4                                           |
| Li, CL [93]  | FeF$_3$.0.33H$_2$O | 134 | 14 | 4.5–1.6 | 0.85 |
| Li, CL [94]  | SWNT-FeF$_3$.0.33H$_2$O | 170 | 23.7 | 4.5–1.7 | 0.66 |
| Kim, S-W [20] | FeF$_3$/CNT | 230 | 20 | 4.5–2.0 | 0.87 |
| Wu, F [95]   | FeF$_3$/C-framework | 230 | 120 | 4.5–2.0 | 1 |
| Lee, J [78]  | FeF$_3$/C | 100           | 500            | 4.5–2.0    | 0.8                                           |
| Li, J [68]   | FeF$_3$/N-doped C | 180 | 24 | 4.5–2.0 | 0.66 |
| Li, J [68]   | FeF$_3$/C | 150           | 24             | 4.5–2.0    | 0.45                                          |
| Kim, T [21]  | FeF$_3$/C | 182           | 24             | 4.5–2.0    | 0.9                                           |
| Liu, J [96]  | FeF$_3$/Gra | 225           | 71             | 4.5–2.0    | 0.88                                          |
| Liu, L [19]  | FeF$_3$/C | 180           | 20             | 4.5–2.0    | 0.9                                           |
| Nishijima [97] | FeF$_3$/C | 213           | 0.2            | 4.5–2.0    | 0.76                                          |
| Yabuuchi [98] | FeF$_3$/C | 200           | 20             | 4.5–2.0    | 0.84                                          |

FeF$_3$ + Li$^+$ + e$^-$ $\rightarrow$ LiFeF$_3$ Insertion. 4.5–1.7 V, 237 mA h g$^{-1}$ LiFeF$_3$ + 2Li$^+$ + 2e$^-$ $\rightarrow$ 3LiF + Fe Conversion. 1.7–1.5 V, 475 mA h g$^{-1}$
were size-selected, and their dimensions carefully measured by AFM. Finally, we have demonstrated that these FeF₃ nano-platelets can be coated with carbon and mixed with carbon nanotubes to form lithium storing electrodes. These electrodes have high capacity, approaching the theoretical value and reasonable cycling stability.

Results and discussion

Exfoliation of bulk FeF₃ into 2D-platelets

Prior to exfoliation, commercial sourced FeF₃ bulk powder was analysed using scanning electron microscopy (SEM). As shown in Fig. 1a, it consists of particles with size ranging from a few hundred nanometres to a few microns. The crystal structure was analysed by X-ray diffraction (XRD) as shown in the supplementary information (Fig. S2). The diffraction spectra were indexed to the rhombohedral crystal system (reference JCPDS card number-33-0647, space group R₃̅₃) with no impurity peaks. This is the expected structure for FeF₃ which, we emphasise, is a non-layered material.

To convert the FeF₃ powder to quasi-2D nanosheets, we applied the liquid-phase exfoliation protocol, probe-sonicating the powder in NMP solvent (details are described in the methods section). This process is expected to break up the starting power with previous papers indicating significant quantities of 2D platelets can be produced [31,32,39,40,42,46,47]. The resultant liquid was subjected to two-step centrifugation process [2,33] , designed to remove both the smallest nanoparticles, and any large pieces of unexfoliated material. This results in a dark green dispersion as shown in Fig. 1b.

These dispersions were characterized with UV–vis absorption spectroscopy. Here the measured transmittance was converted to extinction, Ext, \((T = 10^{-\text{Ext}}})\ which was then converted to extinction coefficient \((\varepsilon)\) using the Beer-Lambert law \((\text{Ext} = c\varepsilon L)\) where \(c\) is the concentration of the dispersion, and \(L\) is the path length of the cuvette. The concentration was measured by filtering the dispersion onto a membrane and carefully weighing the mass increase. As shown in Fig. 1c, the extinction coefficient spectrum (black line) was featureless in the visible regime but increases rapidly in the UV range. In dispersions of 2D materials, extinction coefficient spectra contain contributions, not only from absorbance, but also from scattering such that \(\varepsilon = \alpha + \sigma\) where \(\alpha\) and \(\sigma\) are the absorption and scattering coefficients respectively [48,49]. Here we used an integrating sphere to separate out the contributions of \(\alpha\) and \(\sigma\) which are plotted in Fig. 1c alongside the extinction coefficient spectrum. This graph shows the absorption to be very small for energy below about 3.5 eV but to increase sharply above 3.5 eV. Metal fluorides have been known for their wide energy bandgaps > 5 eV [50,51], particularly for FeF₃, which displays an optical gap of 6 eV [52]. Shrinking the grain size often results in the change of absorption edge due to quantum confinement effects [32,53–55]. For example, nanoparticulate FeF₃ has shown optical gaps as low as 2 eV [56]. In our case, the absorption spectrum indicates that the optical band edge is reduced from a bulk value of bulk ~6 eV [53] to ~3.5 eV in 2D-platelets of FeF₃ (refer SI, Fig. S3).

Transmission electron microscopy (TEM) was performed to further investigate the morphology and composition of the exfoliated material. As shown in Fig. 1d, TEM image confirmed the presence of platelets varying in length from tens to hundreds of nanometres. Fig. 1e displays Fig. 1. Exfoliation of bulk FeF₃ into quasi-2D flakes by LPE process. (a) SEM image of the bulk FeF₃ powder shows presence of large micron sized three-dimensional nonlayered particles. (b) Photo of standard dispersion obtained after the LPE process. (c) Extinction, absorption, and scattering coefficient spectra of the dispersion. The concentration \((c)\) of the dispersion was measured by filtering the dispersion through a membrane. The coefficients were calculated using Beer-Lambert law, \(\varepsilon = \frac{A}{cL}\), where \(A\) is the measured extinction in arbitrary units, \(c\) is the concentration of dispersion and \(L\) is the path length of the cuvette. (d) TEM image of the FeF₃ flakes showing several thick and thin platelets as depicted by the contrast with the electron beam. (e) Statistical distribution on the length of the exfoliated platelets showed a mean length of 300 nm as depicted by the TEM images. (f) shows an EDX spectrum on the platelet (inset) confirmed the elemental composition is Fe, F and O elements. The C, and Cu signal is from the TEM grid. (g) A statistical distribution of the atomic percentage ratio of F/Fe for 32 individual randomly selected isolated flakes. The mean atomic ratio was found to be 3/1.
the statistical distribution of the length of the exfoliated platelets showed mean length of 300 nm. In order to determine the elemental composition on individual platelets, we performed energy-dispersive X-ray spectroscopy (EDX) in-situ with TEM on a platelet-by-platelet basis [58]. The EDX spectrum captured from one individual platelet is shown in Fig. 1f. This spectrum confirmed the presence of oxygen, iron, and fluorine, with the carbon and copper signals coming from the TEM grid. The individual platelet stoichiometries were extracted from each spectrum with the resultant ratio of fluorine to iron plotted as a histogram in Fig. 1g. This data shows the average platelet stoichiometry to be \(<\text{Fe}/\text{F}> = 3\), in line with expectations. While the presence of oxygen may indicate the existence of oxides passivating the surface of the nanoplatelets [58], it may also be due to adsorbed water as FeF<sub>3</sub> is known to be a hygroscopic material [59,60]. This means that unlike previous reports [57], we cannot use statistical EDX to quantify surface passivation of the platelets.

**Structural studies**

To get insight into the crystal structure of exfoliated platelets, high-resolution transmission electron microscopy (HR-TEM), diffraction, scanning transmission electron microscopy (STEM), and X-ray diffraction (XRD) were used. Fig. 2a shows the TEM image of an individual platelet of FeF<sub>3</sub> which is 250 nm in length and 200 nm in width. Selected area electron-diffraction pattern (Fig. 2b) was acquired from a region of this platelet as shown in Fig. 2b. Such patterns map the reciprocal lattice of the crystal structure with each spot representing a plane in the reciprocal space. The sharpness of the spots is indicative of the highly crystalline nature of the platelets. The planes were indexed to the miller indices (hkl) as 012 and 104 (marked in the Fig. 2b) in the [20T] zone axis of the rhombohedral crystal structure of FeF<sub>3</sub>. The high resolution HAADF-STEM image (Fig. 2c) shows the atomic-structure. The lattice spacing 0.38 nm and 0.27 nm were assigned to the Miller indices of 012 and 104 of bulk FeF<sub>3</sub>, respectively.

Furthermore, XRD pattern from a film of exfoliated platelets (prepared and measured immediately after exfoliation) was also acquired and was compared with the XRD of the bulk FeF<sub>3</sub> powder as shown in Fig. 2d. The pattern matches well with the rhombohedral crystal lattice structure of FeF<sub>3</sub> according to the JCPDS card number 33–0647, space group R 3 c. The strongest line in both bulk and exfoliated FeF<sub>3</sub> corresponds to the 012 plane. The peak centre (2θ) was increased by 1.2 mrad for 012 atomic plane after exfoliation as compared to the bulk, possibly due to the generation of residual strain. More importantly, we observed significant broadening in the full width and half maximum (β) of 2.1 mrad for 012 atomic plane after exfoliation as compared to the bulk, possibly due to the generation of residual strain. More importantly, we observed significant broadening in the full width and half maximum (β) of 2.1 mrad (refer to SI, Fig. S4). This increase in β is due to the decrease of crystallite size (l) according to the Scherrer formula [61], l = Kλ/(β × cos(θ)); where l is the crystallite domain size, K is the shape factor (K = 0.9), λ is X-ray wavelength, β is the full width at half maximum intensity and, θ is the Bragg angle. The crystallite domain size for the high intensity plane 012, for bulk was calculated to be 75 nm which is decreased to 35 nm after exfoliation. This domain size may not necessarily be the particle size as particles can be polycrystalline and may contain multiple crystalline domains. However, it does signify towards the decrease in grain size after exfoliation.

**Stability in ambient**

The stability was studied by taking the extinction spectra of the dispersion with respect to time as shown in Fig. 3a. The dispersions were agitated before each measurement to remove the effects of any
sedimentation, such that we only investigate chemical degradation of platelets in ambient conditions. A clear overlap in the line shape of extinction spectra over time indicate high stability of the platelets in ambient conditions over 19 days with relatively little change occurring over 4 months (see SI Fig. S5).

In order to further probe the stability of the exfoliated nanoplatelets we used EDX spectroscopy to measure the F/Fe ratios of individual platelets on both the first day after exfoliation and four days later. As shown in Fig. 3b-c, over this timeframe, the overall stoichiometry remains unchanged with mean values $<\text{F/Fe}>$ close to 3. This shows that the platelet stoichiometry remains largely intact, implying that the bulk structure of the platelets is preserved. Although oxygen is detected in the EDX spectrum of each individual nanoplatelet as shown in the SI Fig. S6, quantitative analysis has not been performed because $\text{FeF}_3$ is known to be a hygroscopic material. Thus, we cannot quantify how much oxygen is related to oxidation versus hydration. However, it is likely that bulk oxidation of the nanoplatelets would result in changes in the relative stoichiometry of Fe and F. Thus, since the Fe/F atomic ratio remains constant, we believe that the oxidation is only limited to the surface of the nanoplatelets.

**Size-selection of platelets**

The main dispersion described above consists of polydisperse platelets with a wide range of sizes. The best way to quantitatively characterise nanosheet dimensions is using statistical AFM. However, it is extremely difficult to perform such measurements on samples with very broad size distributions. Thus, in order to accurately measure size distributions, it is common practice to use size-selection techniques such as liquid-cascade centrifugation (LCC) to separate the platelets into fractions with relatively narrow size distributions which are more easily characterized [62]. In this way, we separated the main dispersion into 5 different size-selected fractions which were characterised individually by AFM.

Fig. 4ab shows representative AFM images captured for the largest and smallest fraction of flakes respectively (for all other fraction, refer SI Fig. S7). For each individual flake, the length, $L$, width, $W$, and thickness, $t$, were measured with approximately 80 platelets studied per fraction. The length is defined as the longest platelet dimension and the width the platelet size in the direction perpendicular to the length. The nanosheet thickness is defined as the out of plane direction. This data was plotted as histograms in Fig. 4c-d and Fig. S7 (SI). The largest fraction showed a wide distribution in length ranging from 100 nm to 500 nm with average length $<L>$ of 279 ± 10 nm, whereas the smallest fraction showed a narrow distribution in length ranging from 50 nm to 150 nm, with an average value of 93 ± 2 nm (Fig. 4c). The values reported here are with standard errors. Similarly, the thickness of the flakes for the largest and smallest fraction showed a similar distribution with an average value $<t>$ of 127 ± 6 nm, and 23 ± 1 nm respectively.

For each fraction, we calculated the mean platelet length and thickness which we have plotted as a function of the central relative centrifugal force used in the size selection process. As is usually observed, $<L>$, $<W>$ and $<t>$ decrease with increasing centrifugal force (Fig. 4e). This behaviour allows some control of mean platelet size by control of centrifugation parameters. In addition, while the mean platelet length and width are similar, the mean thickness is somewhat smaller, as expected for a quasi 2D material.

To investigate the nanosheet dimensions in more detail, in Fig. 4f, we plot the individual platelet length versus thickness with the data colour coded by size-selection fraction. The most obvious feature of this graph is that the nanosheet length scales with thickness. Such scaling is a general feature of liquid exfoliated materials and is associated with the energetics of the exfoliation process [62]. Secondly, for virtually all nanosheets, the length is greater, usually considerably so, than the thickness. We also plot length versus width on a platelet-by-platelet basis in Fig. 4g. While some of the largest nanosheets have $L/W$ values...
of up to 3, most of the nanosheets have similar length and width (typical $L/W$ values are $\sim 1.5$). Taken together, the data in Fig. 4f and 4g shows the FeF$_3$ platelets produced by LPE to be quasi-2-dimensional because of their similar length and width and the fact that the length can be significantly larger than the thickness.

However, to quantitatively assess how 2-dimensional these platelets really are, we must consider the platelet aspect ratio, which we define as $L/t$. Plotted in Fig. 4h is a platelet-by-platelet graph of the aspect ratio of individual platelets plotted versus platelet thickness. This graph is extremely interesting as it shows the thickest objects (e.g., $t > 100$ nm) to have aspect ratios close to 1 and so be more like cubes than platelets. However, as the thickness decreases, the aspect ratio increases, signifying that the platelets become more 2-dimensional as they become thinner. The thinnest platelets, those with $t < 10$ nm, have aspect ratios $\sim 10$. This value is somewhat larger than the (thickness independent) aspect ratios of $\sim 5$ reported for non-layered FeS$_2$ produced by LPE [32,33]. However, it is of course lower than aspect ratios for many layered nanosheets produced by LPE which be as high as $\sim 100$ for graphene [62]. However, it is worth noting that some layered nanosheets produced by LPE have very small aspect ratios with $L/t$ values as low as $\sim 3$ observed for layered hydroxides [63].

While it is not clear why the platelet aspect ratios decrease with increasing thickness, it is almost certainly associated with the details of the exfoliation process. We have shown previously that a range of layered nanosheets produced by LPE have dimensions consistent with $L^2 \propto t^\beta$ where $\beta$ is a parameter which depends on both material and details of the exfoliation method and has been observed to lie roughly in the range 1.75 to 3.25 [62]. This relationship can be rearranged to give $L \propto t^{\beta+1}$. The trend observed in Fig. 4h is consistent with the exponent relating $L/t$ to $t$ being negative ($\beta/2 < 1$) which means this behaviour occurs when $\beta < 2$. This implies the increase in aspect ratio with decreasing thickness to be quite uncommon as the condition of $\beta < 2$ only holds at the edge of the observed $\beta$-distribution. Indeed, to our knowledge, the increase in aspect ratio with decreasing thickness has not been previously reported.

The data presented above clearly shows that, at least for the thinnest platelets, liquid exfoliated FeF$_3$ is quasi-2D. However, it must be pointed out that, when applied to non-layered materials, LPE is only expected to yield quasi-2D platelets when the starting material has an anisotropic bonding scheme [32]. As such, one would expect isotropic materials such as FeF$_3$ to be converted to 3D nano/micro particles on exfoliation making it quite surprising that quasi-2D FeF$_3$ particles were produced. However, recently there have been several reports of isotropic, non-layered materials being converted to 2D platelets using LPE such as boron carbide [64], silicon [42], α-germanium [41], magnesium [65], lanthanum hexaboride [66], and silicon carbide [67]. It is still not understood what causes the 2D nature of the exfoliated materials in such cases.

**Application as a cathode in battery**

Fluorides of iron, such as anhydrous iron trifluoride (FeF$_3$) [24,68], iron difluoride (FeF$_2$) [69,70], and hydrous iron (III) fluoride trihydrate (FeF$_3$·3H$_2$O) [71] have all generated a lot of interest as potential lithium-storing cathodes. In particular, anhydrous FeF$_3$ is well studied as a cathode material in lithium batteries due to its attractive redox properties and better reversibility compared to other metal fluorides. Although FeF$_3$ displays a high theoretical capacity of 712 mAh/g, in practice it has proven difficult to achieve this value while also achieving cycling stability. As summarised in Table 1, most papers show capacities well below the theoretical value and often display capacity degradation with cycling [14,22,72-77]. Such behaviour has been attributed to a number of factors including the low electronic conductivity [13,76] of FeF$_3$ as well as unwanted interactions between the FeF$_3$ and the electrolyte [24] and is often addressed via the production of composites by mixing FeF$_3$ with a carbon-based conductive additive (see Table 1). In addition, FeF$_3$ has quite a low solid-state lithium ion diffusion coefficient, $D_{AM}$, with some papers reporting values as low as $10^{-12}$-$10^{-19}$ cm$^2$ s$^{-1}$ [79]. This leads to increased solid-state diffusion time, $t_{SSD}$, and so reduced rate performance [10,80]. This can be somewhat mitigated by...
reducing the diffusion length, $L_{\text{diff}}$, which can be achieved by reducing the particle size ($r_{50} = L_{\text{diff}}/D_{\text{am}}$) [10,80]. This can have additional advantages as it has been reported that a smaller crystal size controlled by the milling time leads to a higher specific capacity [81].

We believe the requirements of identifying an effective conductive additive and reducing diffusion length discussed above can be achieved by fabricating battery electrodes from mixtures of liquid exfoliated FeF$_3$ nanoplatelets with carbon nanotubes. As mentioned above, electrodes based on 2D materials demonstrate dramatically enhance electrode performance compared to non-2D analogs [27–32]. In addition, it is known that adding carbon nanotubes to electrodes based on both 2D [30,35–37] and 3D$^9$ materials allows them to attain capacities approaching their theoretical values due to the high conductivity of the nanotube network [9,38,39].

To test this hypothesis, we used vacuum filtration to fabricate electrodes from FeF$_3$ nanosheets mixed with approximately 30 wt% single walled carbon nanotubes. We then used galvanostatic charge/discharge measurements to measure the capacity (normalised to FeF$_3$ mass) over different cycles (applying a current of 0.03 A/g for 5 cycles followed by 0.3 A/g in subsequent cycles). However, as shown in Fig. 5a (blue curve, marked FeF$_3$), these electrodes showed considerable capacity fade, reaching ~60 mAh/g after 100 cycles, a 70% reduction compared to the first 0.3 A/g cycle. As mentioned above, such poor capacity stability has been observed for FeF$_3$ by several authors (Table 1).

To address this instability, we took inspiration from work showing that using solid polymer electrolytes effectively supressed leaching of Fe$^+$ or Fe and achieved improved cycling stability [16]. However, here we aimed to use a combination of polymer adsorption and annealing to coat the FeF$_3$ platelets with carbon (in addition to the nanotube network). We expect this coating to provide added conductivity and stability to the electrodes as well as acting as an interfacial layer between FeF$_3$ and electrolyte, and thus inhibit side reactions and the dissolution of reaction products in the electrolyte. In parallel, the SWCNT act as both conductive additive and mechanical binder.

In practice, we exfoliated FeF$_3$ nano-platelets which were then mixed with a diluted dispersion of the conductive polymer PEDOT: PSS. After stirring for 2 days and washing with IPA followed by centrifugation, excess PEDOT: PSS was removed and PEDOT:PSS coated FeF$_3$ platelets were extracted. We name this sample as FeF$_3$-P. FeF$_3$-P was then annealed at 350 °C for 1 h in vacuum tube furnace leading to a product which we label as FeF$_3$-P-350. XRD of the FeF$_3$-P and FeF$_3$-P-350 were acquired to test for any structural changes (Fig. S8, SI). Diffraction peaks of FeF$_3$-P were indexed based on the JCPDS-33-0647 (FeF$_3$). No other peaks positions were observed except that of FeF$_3$, implied the conservation of the crystal structure of FeF$_3$ after coating with PEDOT: PSS. However, while the diffractogram of FeF$_3$-P-350, showed peaks which were indexed to the rhombohedral crystal system of FeF$_3$ (JCPDS-33-0647), it also showed two additional weak peaks at 2θ = 26.8° and 51.6°. Although, PEDOT:PSS films display a characteristic diffraction peak at 25.9° [82], this peak is not consistent with our data. In FeF$_3$-P we do not observe this peak, and in FeF$_3$-P-350 sample, the peak at 26.8° is not broad enough to be assigned to PEDOT: PSS polymer [83]. In addition, we cannot attribute it to the effect of annealing. While the decomposition of PSS via rupture of sulfonate group from styrene occurs at 320 °C [84,85], a complete decomposition of PEDOT: PSS via polymer backbone rupturing occurs above 500 °C [84,85]. Since FeF$_3$-P was annealed at 350 °C, we believe PEDOT: PSS should not have fully decomposed into carbon meaning these peaks cannot be associated with carbonization. In fact, these two new diffraction peaks in the XRD spectra of FeF$_3$-P-350 could be assigned to the presence of the tetragonal crystal system of FeF$_3$ (JCPDS-45-1062). This implies that annealing converts a small portion of the FeF$_3$ to FeF$_2$.

This is consistent with UV–Visible absorption studies and Tauc analysis of the dispersion of FeF$_3$-P-350 which showed an optical band-edge of 2.6 eV somewhat lower than the value of 3.5 eV found for FeF$_3$ platelets (refer to SI, Fig. S9 for more details). This reduction in band-edge energy in FeF$_3$-P-350 sample is consistent with the presence of FeF$_2$ because its band gap is known to be lower than that of FeF$_3$ [69,70]. The analysis described above suggests FeF$_3$-P-350 to consist of carbon coated particles of FeF$_2$ with a small component of FeF$_2$. We note that because the theoretical capacity of FeF$_2$ is reasonably large (571 mAh/g) [16], we don’t expect the presence of a small amount of FeF$_2$ to significantly degrade the capacity of our material.

The FeF$_3$-P-350 was dispersed in IPA, mixed with approximately 30 wt% single walled carbon nanotubes and fabricated into electrodes. We then measured the cycling stability in the same way as for the FeF$_3$ data. This data is plotted in Fig. 5a as the red curve (labelled FeF$_3$-P-350) with the capacity normalised to the total FeF$_3$-P-350 mass (not including nanotubes). This data set shows a considerably higher initial capacity compared to the FeF$_3$-only sample. In addition, while the capacity is still not perfectly stable, it only shows a 73% and 60% capacity retention after 50 and 100 cycles respectively (compared to the first 0.3 A/g cycle). This capacity retention is considerably better than the FeF$_3$ only sample and is competitive with the literature data described in Table 1.

To compare the electrochemical properties of the FeF$_3$-SWNT and FeF$_3$-P-350/SWNT electrodes, we performed cyclic voltammetry (CV) in the potential range of 1.1–3.8 V as shown in Fig. 5b (scan rate = 0.1 mV s$^{-1}$). The two curves exhibit similar shapes with two pairs of reduction/oxidation peaks corresponding to the insertion and conversion reaction reactions. For FeF$_3$/SWNT, the cathodic peaks are at 2.9 and 1.7 V and the anodic peaks are at 3.5 and 2.9 V while for FeF$_3$-P-350/SWNT, the equivalent positions are 2.9 V and 1.8 V (cathodic) and 3.0 V and 2.4 V (anodic). The peaks observed for FeF$_3$ are very similar to those previously reported [11,25,86]. The cathodic peak at 2.9 V and the corresponding anodic peak at 3.5 V are associated with the de-intercalation/intercalation of FeF$_3$ while the cathodic/anodic peaks at 1.7 V/2.9 V are due to the conversion reaction. The potential difference between the pairs of cathodic and anodic peaks associated with intercalation and conversion are 0.6 V and 1.2 respectively, with the larger difference in the case of the conversion reaction due to the large energy barrier for the formation/dissociation of the LiF [86]. For FeF$_3$-P-350/SWNT the cathodic peaks are at almost at the same position comparing to FeF$_3$/SWNT while the anodic peaks of FeF$_3$-P-350/SWNT are shifted to a lower potential. This means FeF$_3$-P-350/SWNT has smaller potential difference between cathodic and anodic peaks (0.1 V and 0.6 V) compared to FeF$_3$/SWNT (0.6 V and 1.2 V). This could imply a smaller energy barrier for the formation/dissociation of the LiF in the case of FeF$_3$-P-350/SWNT. In addition, FeF$_3$-P-350/SWNT shows a larger area in the CV curve, which implying a higher effective capacitance.

Given the improved stability of the FeF$_3$-P-350/SWNT electrodes, we will focus on them for the rest of this work. The morphology of an FeF$_3$-P-350/SWNT electrode (~30 wt% SWNT, thickness = 8 µm) is shown in Fig. 5c. This electrode clearly consists of small platelets embedded in a conductive network of SWNT. The platelet size is close to that measured for the FeF$_3$ nanoplatelets suggesting that the PEDOT: PSS-coating and annealing process doesn’t significantly change the nanoplatelet morphology (refer to SI, Fig. S8 for the TEM image comparison).

The performance of FeF$_3$-P-350/SWNT films as Li storing cathodes was characterised using coin cells employing lithium foil as counter/reference electrode and FeF$_3$-P-350/SWNT as the working electrodes (mass loading of FeF$_3$-P-350 ~0.44 mg cm$^{-2}$, nanotube loading ~0.21 mg cm$^{-2}$, thickness ~8 µm). In this way, we measured the capacity as a function of both charge and discharge currents to reveal the intercalation in Fig. 5d. As is generally observed, the capacity tends to fall off with increasing current, both due to the capacity instability observed in Fig. 5a but also due to the ubiquitous degradation of capacity with rate (see below) [110]. For example, as the current was changed from 0.03 to 0.11 to 0.57 A g$^{-1}$, capacities of 480, 330, and 140 mAh/g were found. Returning the current to 0.11 A/g gave a capacity of 275 mAh/g. While this does not represent full recovery expected for a stable material, the final capacity reaches 83% of its previous value at 0.11 mA/g, showing
Fig. 5. Performance of composites of FeF$_3$ nanosheet-based lithium-ion battery cathodes. (a) Cycling capacity versus cycle number for both FeF$_3$/SWCNT and FeF$_3$-P-350/SWCNT composite cathodes cycled at 0.03 A g$^{-1}$ and 0.3 A g$^{-1}$. (b) Cyclic voltammograms, recorded at a scan rate of 0.1 mV s$^{-1}$, for FeF$_3$/SWCNT and FeF$_3$-P-350/SWCNT composite cathodes. (c) SEM image of the surface of a composite electrode fabricated from FeF$_3$-P-350 loaded with SWCNT (30 wt%). (d) Galvanostatic charge discharge curves for FeF$_3$-P-350/SWCNT composite cathodes measured at different currents. (e) Capacity as a function of both discharge and charge current for various currents for a FeF$_3$-P-350/SWCNT composite cathode. (f) Specific capacity as a function of charging rate (defined as R=$(I/M_T)/(Q/M_T)$) for a FeF$_3$-P-350/SWCNT composite cathode. The lines are fits to equation (2) and fit parameters are given in the inset. All specific capacities and currents are normalized to the mass of the FeF$_3$-P-350 mixture. Total electrode mass loadings were approximately 0.52 mg/cm$^2$ with a nanotube content close to 30 wt% and approximate electrode thicknesses were 10 μm.
that the instability, while present, is a minor source of capacity fall off with increasing rate.

Quantitative analysis of rate performance

Although this is not often performed, it is possible to quantitatively analyse the capacity versus current density shown in Fig. 5e [10,81]. To do this, we plot the measured specific capacity (normalised to FeF$_3$-P-350 mass, i.e., not including the SWNT mass) versus a parameter, R, representing rate in Fig. 5f. This parameter is defined as $R = I/Q$ where $Q$ is the charge actually stored at a current $I$ (put another way R is the specific current divided by the measured specific capacity). In this way, $1/R$ is a measure of the actual charging time at constant current. This data shows the measured capacity to fall off with rate as is generally observed [10,81].

Although a number of equations have been proposed to analyse capacity versus rate data [87], we use a semiempirical equation proposed recently by us [10]:

$$Q/M \approx Q_e \left[1 - \left(\frac{R}{\tau}\right)^n \left(1 - e^{-\left(\frac{R}{\tau}\right)^n}\right)\right]$$

(2)

which can be used to fit data for measured capacity (Q/M) versus rate (R). Such fitting outputs three fit parameters: $Q_e$, the capacity at very low rate which can be compared to the theoretical capacity; $\tau$, the characteristic time associated with charge/discharge and $n$, a parameter whose value indicates the dominance of diffusive ($n = 0.5$) or electrical ($n = 1$) limitations on rate performance [10]. As shown in Fig. 5f, this equation fits the data extremely well using fit values of $Q_e = 698$ mAh/g, $\tau = 4100$ s and $n = 0.44$ (here $Q_e$ is normalised to the FeF$_3$-P-350 mass). While we will discuss $\tau$ and $n$ in more detail below we note that the value of $Q_e = 698$ mAh/g is very close to the theoretical capacity of FeF$_3$. The means that the carbon coating achieved via annealing in the presence of PEDOT: PSS, coupled with the nanotube network allows the value of $Q_e$ ($\sim 700$ mAh/g) to be realised once rate limitations are removed. Combined with the CNT mass loading of 32% means this low-rate capacity is equivalent to 475 mAh/h when normalised to total mass. Even with $>30$ wt% nanotubes present, this value is considerably higher than typical lithium storing cathode materials.

To compare our results with the literature, we plot our capacity versus current density data (Fig. 6) on the same graph as a number of published data sets (these data are collected from a subset of the papers listed in Table 1). It is clear from this data that our performance is superior to those data sets measured in the potential window of 4.5–2.0 V (i.e., those curves whose low-current values tend to $\sim 200$ mAh/g). In addition, it is competitive with most of the data collected in the wider potential window although, it is clear that our material displays lower capacity than that of Fu et al (open squares) [24].

However, while our low-rate capacities are clearly approaching the state-of-the-art and our rate performance as a whole appears fairly standard for FeF$_3$, it is worth considering how these results compare to lithium-storing electrodes in general. To do this, we consider the fit parameters obtained in Fig. 5f ($\tau = 4100$ s and $n = 0.44$). Recently, we analysed a large quantity of published data reporting a well-defined correlation between $\tau$ and electrode thickness [24], $L_e$ (here $L_e = 8 \mu m$). Typically, for such an electrode thickness, we would expect a value of $\tau$ of $\sim 1$ s [10]. This means our measured $\tau$-value is much larger than expected indicating extremely slow charge/discharge times. This indicates that our rate-performance (and indeed by comparison most of the other data sets shown in Fig. 5) is relatively poor compared to the broad spectrum of battery materials.

To analyse this more deeply, we note that, because of the dependence of $\tau$ on $L_e$, a better parameter to consider is $\tau/L_e^2$ [10,81]. For our FeF$_3$-P-350 data, $\tau/L_e^2 = 6 \times 10^{-13}$ s/m$^2$, a value which is among the highest in the literature that we have found [10,81] (high values of this parameter represent poor rate performance, a detailed review of $\tau/L_e^2$ values is given in ref [81]). Although such a high value is partly due to our low electrode thickness [80], it is a strong indicator that the rate performance of FeF$_3$ is very poor. Given the similarity between our rate data and other published rate data we suspect this is a general property of FeF$_3$.

We can understand the causes of this by noting that the value of $n = 0.44$ indicates that our electrodes are diffusion limited [10]. A detailed analysis of rate limited process in battery electrodes shows the relevant ion diffusive process to be diffusion in the separator, diffusion in the porous interior of the electrode and solid state diffusion within the active particles [10]. Using the equations given in ref [10], we can estimate the timescales associated with the first two processes in our case to be $\tau_1 = 21$ s and $\tau_2 = 6$ s respectively (assuming a bulk electrolyte diffusivity of $3 \times 10^{-6}$ cm$^2$/s and electrode and separator porosities of 0.5 and 0.4 respectively). These timescales are negligible compared to $\tau = 4100$ s, implying that $\tau$ is predominantly controlled by solid state diffusion and so $\tau \approx \tau_{SDD}$ = LAM2/DAM We note that $\tau_{SDD} \sim 4100$ s is an extremely high value, close to the highest values of $\sim 10^4$ s which can be extracted from the literature [81]. Given the relatively short diffusion lengths at work here, this implies very slow diffusion in our materials. Taking $L_{ss} \sim 20$ nm (half the thickness of a typical platelet) then allows us to estimate the solid-state diffusion coefficient of FeF$_3$-P-350 to be $D_{ss} = 10^{-16}$ cm$^2$/s. Although not as low as values of $10^{-17}$-$10^{-18}$ cm$^2$/s reported by Ko et al [80], these values are quite low ($\sim 10^4$ times slower than ion diffusion in bulk electrolyte). For comparison, solid state lithium-ion diffusion coefficients in other 2D materials are within the range of $10^{-5}$-$10^{-15}$ cm$^2$/s [81]. This, combined with the data in Fig. 6, implies FeF$_3$ to display extremely slow lithium diffusion compared to other materials. This raises questions as to whether FeF$_3$-based cathodes can provide rate performance good enough for use in practical devices at room temperature [88].

Conclusion

In summary, we have used liquid phase exfoliation to convert bulk FeF$_3$ to FeF$_3$ nano-platelets. The structure and stoichiometry of these platelets is consistent with that of bulk FeF$_3$ as confirmed by XRD, HRTEM and elemental analysis. Size selection combined with detailed AFM analysis shows the platelets to be quasi 2D with aspect ratios of $<13$. Interestingly, while the thinnest platelets have the highest aspect ratios, thicker flakes have aspect ratios approaching 1, consistent with a 3D geometry. Finally, we have characterised these FeF$_3$ platelets as
lithium storing cathodes. We found that mixing with a polymer and annealing to coat the platelets with carbon, combined with the presence of a carbon nanotube network, yielded composite electrodes with good initial capacity coupled with reasonably cycling stability. Rate performance measurements showed a low-rate capacity (normalised to FeF$_3$-P-350 mass) of $\sim 700$ mAh/g, very close to the theoretical value for FeF$_3$. However, the capacity falls off quite rapidly with rate. More detailed analysis shows such behaviour to be typical of FeF$_3$ and to be due to the very low solid state diffusion coefficient of this material.

Methods

Materials

Iron (III) fluoride powder was purchased from Sigma-Aldrich. P3-SWNT was purchased from Carbon Solutions with a carbonaceous purity $> 90\%$. Solvents, N-methyl-2-pyrrolidone, and 2-propanol were purchased from Sigma-Aldrich, HPLC grade $> 99\%$. Aqueous poly(3,4-ethylenedioxythiophene)/poly(styrene-4-sulfonate) (PEDOT: PSS) dispersion (10.5 mg/ml, Heraeus, Clevox PH1000) was purchased from Heraeus Electronic Materials.

Exfoliation of FeF$_3$

The commercial powder, FeF$_3$ was mixed in the solvent N-methyl-2-pyrrolidone (NMP) with initial concentration of 20 mg/ml ($\sim 1400$ mg of FeF$_3$, in 70 ml NMP) in a metallic beaker of 100 ml capacity. The mixture was subjected to sonication using a horn probe tip (VibraCell VCX, 750 W) for a time-period of 10 h at 55% amplitude with pulse 6 s on,2s off, under ice cooling. After sonication, the dispersion was centrifuged at 3663 g for 10 h for 2 h in 35 ml aliquots using 50 ml centrifuge tubes in a Hettich Mikro 220R centrifuge equipped with a fixed-angle rotor of radius 91 mm. The sediment obtained after this step, was re-dispersed in 70 ml fresh NMP and bath sonicated for another 10 h at the same conditions. Two steps of centrifugations were then employed to obtain standard dispersion. Step 1 involves removal of unexfoliated as well as non-platelet material from the as-obtained dispersion. This was achieved by centrifugation of dispersion at 102 g force for 2 h at 10 $^\circ$C. The sediment containing the (large) unexfoliated material is discarded, while the supernatant consisting of exfoliated material is subjected to a second centrifugation at 3663g for 2 h at 10 $^\circ$C. This high-speed centrifuge step results in a supernatant consists of very small nanoparticles and degraded solvent impurities, thus is discarded. The sediment obtained after this step is redispersed in fresh NMP or in 2-propanol. This dispersion is named as the standard dispersion and consists of polydisperse nanosheets.

Size selection

For the size selection, liquid-cascade centrifugation is used. This process involves a continuous increase in the relative centrifugal force (RCF) on the nanosheets to size separate them. The centrifugal force is calculated using the rotation speed and is expressed in units of g-force. All centrifugation steps were performed using a Hettich Mikro 220R centrifuge, for a time-period of 2 h at 10 $^\circ$C. After sonication, the unexfoliated material was removed by centrifuging the dispersion at 102 g force for 2 h at 10 $^\circ$C. The sediment containing the (large) unexfoliated material is discarded, while the supernatant consisting of exfoliated material is subjected to a second centrifugation at 3663g for 2 h at 10 $^\circ$C. This high-speed centrifuge step results in a supernatant consists of very small nanoparticles and degraded solvent impurities, thus is discarded. The sediment obtained after this step is redispersed in fresh NMP or in 2-propanol. This dispersion is named as the standard dispersion and consists of polydisperse nanosheets.

Synthesis of composites

FeF$_3$ platelets of smaller size fractions were used to make composites for battery electrodes. To obtain the dispersion of smaller-size fractions, the standard dispersion of FeF$_3$ is centrifuged for 2 h at g-force of 916g. The sediment is discarded, and the supernatant obtained after this step is further centrifuged for 2 h at 3663g-force. The supernatant at this step consists of degraded NMP which is discarded, while the sediment consists of smaller size of platelets is extracted. This sediment is then mixed with IPA, to obtain a dispersion of smaller fraction. Following this step, the concentration of the dispersion is measured by weighing method. For this, 1 ml of this dispersion is filtered through the membrane (Celgard 2320) and the mass difference in the membrane is measured. This gives us the concentration of the dispersion ($\sim$1 mg/ml). These small platelets were then coated uniformly with PEDOT: PSS. For the coating process, commercial PEDOT: PSS solution ($\sim$11 mg/ml) was diluted by adding IPA solvent to achieve a concentration of 0.1 mg/ml. This diluted PEDOT: PSS solution ($\sim$0.1 mg/ml, 4 ml) is then mixed with the dispersion of smaller platelets ($\sim$1 mg/ml, 2 ml) such that the mass ratio of FeF$_3$ platelets to the PEDOT: PSS is 5:1. The mixed dispersion was then bath-sonicated for 1 h, and subsequently stirred at 2000 rpm for two days in ambient at room temperature. To remove the excess the PEDOT: PSS, the resultant dispersion was then centrifuged at 3663g for 2 h. The supernatant consists of free PEDOT: PSS is discarded, and the sediment is collected. The sediment obtained after this step was further washed with IPA a few times. The washing step ensures to remove any free PEDOT: PSS. This sample is named FeF$_3$-P. FeF$_3$-P was then dried in vacuum oven at 80$^\circ$C and further annealed for 1 h at 350$^\circ$C in vacuum. After, annealing the colour of the sample changes to orange (refer SI, Fig. S8). This orange sample is named FeF$_3$-P-350, which is used for making electrodes.

Characterisation

The UV–vis extinction and absorption measurements were carried on the Perkin Elmer Lambda 1050 spectrometer. Wavelengths range of 220 nm to 900 nm were used in acquiring the extinction spectra with steps of 1 nm at room temperature. Quartz cuvettes with a pathlength of 4 mm were filled with the dispersion of known concentration and the spectra was acquired. The concentration of the dispersions was determined by filtration onto membranes (Celgard 2320) and weighing the mass difference. This concentration was used for calculating the extinction coefficient by using Beer-Lambert law. For the absorbance measurements, an integration sphere of radius 150 mm was used in the setup and spectra was acquired at the same conditions as used for extinction measurements.

Transmission electron microscopy was performed using JEOL 2100 instrument. TEM grids were prepared by drop-casting the dispersion on holey carbon grids (400 mesh), followed by vacuum drying in the oven overnight at 80 $^\circ$C. The measurements were performed at an accelerating voltage of 200 KV. The EDX spectrum was acquired using 80 mm$^2$ X-Max detector from Oxford instruments attached to JEOL 2100. Selected area electron diffraction (SAED) and scanning transmission electron microscopy (STEM) was performed on FEI TITAN microscope. The high-angle annular dark field (HAADF) imaging was carried out at
The spectra was scanned in the 2300 KV.-55% amplitude with pulse 6 s on/2 s off, under ice cooling. Normally, the concentration should be lower than 0.1 mg mL on the Celgard 2320 membrane and an additional Celgard 2320 membrane to remove the excess solvent and dried using argon gas.

Electrochemical studies

The electrodes were made by a filtration process. First, the FeF₃ dispersion and SWCNTs dispersion in IPA were mixed by bath sonication. The SWCNT dispersion was made by horn-tip sonic probe for 2 h at 55% amplitude with pulse 6 s on/2 s off, under ice cooling. Normally, the concentration should be lower than 0.1 mg mL. For example, 7 mg P3-SWCNTs were added to 70 ml IPA. Second, the mixed dispersion was sonicated for 20 min and filtered by Celgard 2320 (thickness 20 μm) membrane. The resulting films with membrane (A = 2 cm²) were cut to the required dimensions for electrochemical testing (A = 0.178 cm²). The mass loading of FeF₃ in electrodes were 0.4 mg cm⁻², with 32 wt% SWCNT (0.1 mg cm⁻²) and approximate thicknesses 8 μm. The coin cells were assembled in a glovebox filled with highly pure argon gas (O₂ and H₂O levels < 0.1 ppm). Li-metal discs (diameter, 14 mm; MTI Corp.) were used as the counter/reference electrode. The electrodes were left on the Celgard 2320 membrane and an additional Celgard 2320 membrane used as a separator, giving a total separator thickness of 40 μm. We assume a separator porosity of 40%. An Al foil disc (D = 12 mm) was used as a current collector. Lithium hexafluorophosphate (LiPF₆, 1.2 M) in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 in vol/vol, BASF) with 10 wt% fluoroethylene carbonates (FEC, Sigma-Aldrich) was used as the electrolyte.

Cyclic voltammetry of the cells was conducted using a galvanostat-potentiotstat (VMP-3, Biologic) between 1.1 and 3.8 V vs Li/Li⁺ used as the electrolyte. BASF) with 10 wt% fluoroethylene carbonates (FEC, Sigma-Aldrich) was used as the electrolyte.

The rate capacity measurements were carried out by 10 cycles at 0.3 A g⁻¹ and approximate thicknesses 8 μm. The coin cells were assembled in a glovebox filled with highly pure argon gas (O₂ and H₂O levels < 0.1 ppm). Li-metal discs (diameter, 14 mm; MTI Corp.) were used as the counter/reference electrode. The electrodes were left on the Celgard 2320 membrane and an additional Celgard 2320 membrane used as a separator, giving a total separator thickness of 40 μm. We assume a separator porosity of 40%. An Al foil disc (D = 12 mm) was used as a current collector. Lithium hexafluorophosphate (LiPF₆, 1.2 M) in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 in vol/vol, BASF) with 10 wt% fluoroethylene carbonates (FEC, Sigma-Aldrich) was used as the electrolyte.

Cyclic voltammetry of the cells was conducted using a galvanostat-potentiotstat (VMP-3, Biologic) between 1.1 and 3.8 V vs Li/Li⁺ at a scanning rate of 0.1 mV s⁻¹ for 10 cycles. The electrochemical properties of the FeF₃ cathodes were measured within a voltage range of 1.1–3.8 V by a potentiostat, using the symmetric galvanostatic charge/discharge mode (Arbin). The cyclabilities of the electrodes were evaluated at 0.3 A g⁻¹ (normalized to total mass) after 3 initial formation cycle at 0.03 A g⁻¹. The rate capacity measurements were carried out by 10 cycles at various higher current rates and went back to 0.1 A g⁻¹ for 10 cycles. And the Coulomb efficiency was calculated from the ratio of charge capacity to discharge capacity. All specific capacities and currents are normalized to total electrode mass (MT).

CRedit authorship contribution statement

Tingting Chen: Methodology, Validation, Formal analysis,Investigation, Visualisation, Writing - original draft. Harneet Kaur: Methodology, Validation, Formal analysis, Investigation, Visualisation, Writing - original draft, Writing - review & editing, Supervision. Mark McCrystall: Investigation. Ruiyuan Tian: Investigation. Ahin Roy: Investigation, Formal analysis. Ross Smith: Investigation. Dominik Valter Horvath: Investigation, Formal analysis. Jack Maughan: Investigation. Bharathi Konkana: Investigation. Munuswamy Venkatesan: Investigation. Kevin Synatschke: Formal analysis. Tian Carey: Formal analysis. Ji Liu: Investigation. Joshua Pepper: Investigation. Rui Zhang: Investigation. Claudia Backes: Formal analysis. Valeria Nicolosi: Project administration. Hui Xia: Project administration, Funding acquisition. Jonathan N. Coleman: Conceptualization, Validation, Formal Analysis, Writing-Review & Editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We acknowledge the European Research Council Advanced Grant (FUTURE-PRINT), the European Union under Graphene Flagship cores 2 & 3 (grant agreements 785219 and 881603) and the Irish Research Council (GOIPG/2018/2000). We have also received support from the Science Foundation Ireland (SFI) funded centre AMBER (SFI/12/RC/2278) and availed of the facilities of the SFI-funded AML and ARM labs. Tingting Chen was supported by the China Scholarship Council for 1 year’s study at the Trinity College Dublin. Tian Carey acknowledges funding by a Marie Skłodowska-Curie Action “MOVE” (Grant Number 101030735).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.flatc.2022.100360.

References

[1] S.-H. Yu, X. Feng, N. Zhang, J. Seok, H.D. Abruna, Understanding conversion-type electrodes for lithium rechargeable batteries, Acc. Chem. Res. 51 (2) (2018) 273–281.
[2] Z. Chen, J. Dahn, Methods to obtain excellent capacity retention in LiCoO₂ cycled to 4.5 V, Electrochim. Acta 49 (7) (2004) 1079–1090.
[3] Y. Liu, X. Wang, Z. Feng, Y. Cheng, Y. Liu, M. Wang, R. Chen, L. Xu, J. Zhou, Y. Lu, B. Guo, An overview on the advances of LiCoO₂ cathodes for lithium-ion batteries, Adv. Energy Mater. 11 (2) (2021) 2000982.
[4] J. Kasnatscheew, M. Evertz, B. Streipert, R. Wagner, R. Klöptsch, B. Vortmann, H. Hahn, S. Nowak, M. Amezquita, A.-C. Gentsch, P. Lamp, M. Winter, The about the cycle Coulombic efficiency of LiNi₁/₃Co₁/₃Mn₁/₃O₂ (NMC) cathodes, PCCP 18 (5) (2016) 3956–3965.
[5] A.W. Golobuk, S. Scheikl, R. Planteu, G. Voitic, H. Wilsche, C. Stangl, G. Fauler, A. Theiler, V. Hacker, Thermal runway of commercial 18650 Li-ion batteries with LFP and NCA cathodes-impact of state of charge and overcharge, RSC Adv. 5 (70) (2015) 57171–57186.
[6] K. Dokko, S. Koizumi, K. Sharashi, K. Kasamura, Electrochemical properties of LiFePO₄ prepared via hydrothermal route, J. Power Sources 165 (2) (2007) 656–659.
[7] C. Jiang, Z. Tang, S. Wang, Z. Zhang, A truncated octahedral spinel LiMn₂O₄ as high-performance cathode material for ultralast and long-life lithium-ion batteries, J. Power Sources 357 (2017) 144–148.
[8] H. Cheng, J.G. Shapfer, Y. Li, G. Gao, Recent progress of advanced anode materials of lithium-ion batteries, Journal of Energy Chemistry 57 (2021) 451–468.
[9] S.-H. Park, P.J. King, R. Tian, C.S. Boland, J. Coelho, C. Zhang, P. Mclean, N. McEvoy, M.P. Kremer, D. Daly, J.N. Coleman, V. Nicoli, High areal capacity battery electrodes enabled by segregated nanotube networks, Nat. Energy 4 (7) (2019) 560–567.
[10] R. Tian, S.-N. Park, P.J. King, G. Cunningham, J. Coelho, V. Nicoli, J.N. Coleman, Quantifying the factors limiting rate performance in battery electrodes, Nature Commun. 10 (2019).
[11] L. Li, F. Meng, S. Jin, High-capacity lithium-ion battery conversion cathodes based on iron fluoride nanowires and insights into the conversion mechanism, Nano Lett. 12 (11) (2012) 6030–6037.
[12] M. Zhou, L. Zhao, S. Okada, J.-I. Yamaki, Quantitative studies on thermal stability of a FeF₃ cathode in methyl difluoroacetate-based electrolyte for Li-ion batteries, J. Power Sources 357 (2017) 144–148.
[13] L. Wang, Z. Wu, J. Zou, P. Gao, X. Niu, H. Li, L. Chen, Li-free cathode materials for high energy density lithium batteries, Joule 3 (9) (2019) 2086–2102.
[14] Y. Shen, X. Wang, H. Hu, M. Jiang, X. Yang, H. Shu, A graphene loading heterogeneous hydrated forms iron based fluoride nanocomposite as novel and high-capacity cathode material for lithium/sodium ion batteries, J. Power Sources 283 (2015) 204–210.
[15] X. Hua, A.S. Eggeman, E. Castillo-Martínez, R. Rober, H.S. Geddes, Z. Lu, C. J. Pickard, W. Meng, K.M. Widder, N. Peretza, G.G. Amatucci, P.A. Midgley, K. W. Chapman, U. Steiner, A.L. Goodwin, C.P. Grey, Revisiting metal fluorides as lithium-ion battery cathodes, Nat. Mater. 20 (6) (2021) 841–850.
[16] Q. Huang, K. Turchinziuk, X. Ren, A. Magdanski, A.T. Song, Y. Xiao, D. Kim, G. Yushin, Cycle stability of conversion-type iron fluoride lithium battery cathode
at elevated temperatures in polymer electrolyte composites, Nat Mater 18 (2019) 1343-1349.

[17] B. Li, X. Zhou, C. Zhan, L. Ma, Y. Yuan, C. Wu, M. Chen, G. Chen, Q. Ni, F. Wu, R. Shahbazian-Yassar, T. Wu, J. Lu, K. Amine, 3D Hierarchical nano-Bake/micro-flower iron fluoride with hydration water induced tunnels for secondary lithium battery cathodes, Nano Energy 32 (2017) 10-18.

[18] W. Wu, X. Wang, X. Yang, Y. Li, K. Yuan, Y. Khan, K. Young, A. Gaucher, S. De, R.J. Smith, I.V. Shvetks, S.K. Arora, G. Stanton, H-Y. Kim, K. Lee, G.T.K. Kim, G.S. Duesberg, T. Hallam, J.J. Boland, J.J. Wang, J.F. Donegan, J. C. Grunlan, G. Mortuary, A. Shmeliov, R. Nicholls, J.M. Perkins, E.M. Grieveson, K. Thevendran, D.W. McComb, P.D. Nellist, V. Nicolosi, Two-dimensional nanosheets produced by liquid exfoliation of layered materials, Science 331 (2011) 568-571.

[19] Hernandez, V. Nicolosi, M. Lotya, F.M. Blighne, Z. Sun, S. De, L.T. McGovern, B. Holland, M. Byrne, Y.K. Gunjo, J.J. Boland, P. Nairaj, G. Duesberg, S. Krishnamury, R. Goodhue, J. Hutchinson, V. Scardaci, A.C. Ferrari, J. N. Coleman, High-yield production of graphite by phase-liquid exfoliation of graphite, Nat. Nanotechnol. 3 (9) (2008) 563-568.

[20] V. Nicolosi, M. Chhowalla, M.G. Kanatzidis, M.S. Strano, J.N. Coleman, Liquid Exfoliation of Layered Materials, Science 340 (6139) (2013) 1420–.

[21] C. Xing, Z. Xie, Z. Liang, W. Liang, T. Fan, J.S. Penry, S.C. Dhanabalan, D. Fan, H. Zhang, 2D layered selenium nanosheets: facile synthesis, photoluminescence, and ultrafast photonics, Adv. Mater. 5 (24) (2017) 1700884.

[22] Z. Xie, C. Xing, W. Huang, T. Fan, Z. Li, Z. Zhao, Y. Xiang, Z. Guo, J. Li, Y. Zhang, Ultrathin 2D nanolayered tellurium nanosheets: facile liquid-phase exfoliation, characterization, and photoresponse with high performance and enhanced stability, Adv. Funct. Mater. 28 (16) (2018) 1705833.

[23] C. Backes, R.J. Smith, N. McEvoy, N.C. Berner, D. McCreesh, H.C. Nel, A.-O. Pell, J. King, T. Higgins, H. Li, J. Matz, J. Wang, J. Ahn, J. Liu, J. Wang, G. Mecerreyes, J. Zhang, L. Liu, M. Zhou, L. Yi, H. Guo, J. Tan, H. Shu, X. Yang, Z. Yang, X. Wang, Excellent performance of Co-doped FeF3/C nanocomposite cathode material for lithium-ion batteries, Adv. Funct. Mater. 28 (32) (2018) 1801711.

[24] J. Kim, W.J. Lee, H. Kim, M.P. Han, J. Kim, A cathode material for lithium-ion batteries based on graphitized carbon-wrapped FeF3 nanoparticles prepared by facile polymerization, J. Mater. Chem. A 4 (38) (2016) 14857-14864.

[25] Y. Li, M.-F. Shen, S.-D. Xu, Q.-C. Zhan, L. Jiang, Y.-H. Qiang, Electrochemical impedance spectroscopy investigation of the FeF3/C cathode for lithium-ion batteries, Solid State Ionics 212 (2012) 13-20.

[26] W. Fu, E. Zhao, Z. Sun, X. Ren, A. Magasinski, G. Yushin, Iron fluoride-carbon nanocomposite nanofibers as free-standing cathodes for high-energy lithium battery anodes, Nat. Commun. 7 (1) (2016) 12606-2627.

[27] M. Wang, F. Zhang, Z. Wang, X. Xu, Liquid-phase exfoliated silicon nanosheets: tunable absorber for solid-state lasers, Materials 12 (2) (2019).

[28] J.N. Coleman, M. Lotya, L.T. McGovern, J. Wang, J.F. Donegan, J. C. Grunlan, G. Mortuary, A. Shmeliov, R. Nicholls, J.M. Perkins, E.M. Grieveson, K. Thevendran, D.W. McComb, P.D. Nellist, V. Nicolosi, Two-dimensional nanosheets produced by liquid exfoliation of layered materials, Science 331 (2011) 568-571.

[29] S.W. Kim, D.H. Seo, H. Gwon, J. Tan, H. Shu, X. Yang, Z. Yang, X. Wang, Excellent cycle performance of Co-doped FeF3/C nanocomposite cathode material for lithium-ion batteries, J. Mater. Chem. 22 (34) (2012) 17539.

[30] M. Wang, F. Zhang, Z. Wang, X. Xu, Liquid-phase exfoliated silicon nanosheets: tunable absorber for solid-state lasers, Materials 12 (2) (2019).
T. Chen et al.

[81] N. Yamakawa, M. Jiang, B. Key, C.P. Grey, Identifying the local structures formed during lithiation of the conversion material, iron fluoride, in a Li-ion battery: a solid-state NMR, X-ray diffraction, and pair distribution function analysis study, J. Am. Chem. Soc. 131 (30) (2009) 10525–10536.

[82] Z. Li, H. Sun, C.L. Hsiao, Y. Yao, X. Xiao, M. Shahi, Y. Jin, A. Cruise, X. Liu, Y. Jiang, A free-standing high-output power density thermoelectric device based on structure-ordered PEDOT: PSS. Adv. Electron. Mater. 2018, 4 (2), 1700496 @-2199-160X.

[83] D. Antichos, G. Folkes, P. Sherrell, S. Ashraf, G.G. Wallace, P. Atchinson, A. T. Harris, J. Chen, A.I. Minett, Composition effects of PEDOT:PSS/single walled carbon nanotube films on supercapacitor device performance, J. Mater. Chem. 21 (40) (2011) 15907–15994.

[84] B. Friedel, P.E. Keivanidis, T.J.K. Brenner, A. Abruci, C.R. McNell, R.H. Friend, N. C. Greenham, Effects of layer thickness and annealing of PEDOT: PSS layers in organic photodetectors. Macromolecules 2009, 42 (17), 6741-6747 @-0024-9297.

[85] F. Fan, Y. Zhu, C. Luo, T. Gao, L. Suo, S.-C. Liu, K. Xu, C. Wang, In situ lithiated FeF3/C nanocomposite as high energy conversion-reaction cathode for lithium-ion batteries, J. Power Sources 307 (2016) 435–442.

[86] J.N. Coleman, R. Tian, Developing models to fit capacity-rate data in battery systems, Curr. Opin. Electrochem. 21 (2020) 1–6.

[87] F.L. Olbrich, W.A. Xiao, M. Pasta, Conversion-type fluoride cathodes: current state of the art. Current Opinion, Electrochemistry 30 (2021).

[88] X. Zhao, C.M. Hayner, M.C. Kung, H.H. Kung, Photo-thermal-assisted fabrication of iron fluoride-graphene composite paper cathodes for high-energy lithium-ion batteries, Chem. Commun. 48 (79) (2012) 9909-9911.

[89] L. Li, J. Zhu, M. Xu, J. Jiang, C.M. Li, In situ engineering toward core regions: a smart way to make applicable FeF3/carbon nanorod cathodes for Li-ion batteries, ACS Appl. Mater. Interfaces 9 (21) (2017) 17992–18000.

[90] F. Badway, F. Cosandey, N. Pereira, G.G. Amatucci, Carbon metal fluoride nanocomposites – high capacity reversible metal fluoride conversion materials as rechargeable positive electrodes for Li batteries, J. Electrochem. Soc. 150 (10) (2003) A1318-A1327.

[91] H. Jung, H. Song, T.K. Kim, J.K. Lee, J. Kim, FeF3 microspheres anchored on reduced graphene oxide as a high performance cathode material for lithium ion batteries, J. Alloy. Compd. 647 (2015) 750–755.

[92] S.K. Mathra, J. Nanda, H. Zhou, J.C. Idrobo, N.J. Dudney, S. Pannala, S. Dai, J. Wang, P.V. Braun, Electrode architectures for high capacity multivalent conversion compounds: iron (II and III) fluoride, RSC Adv. 6 (2013) 6730–6737.

[93] C. Li, L. Gu, S. Tsukimoto, P.A. van Aken, J. Maier, Low-temperature ionic-liquid-based synthesis of nanostructured iron-based fluoride cathodes for lithium batteries, Adv. Mater. 22 (33) (2010) 3650–3654.

[94] C. Li, L. Gu, J. Tong, J. Maier, Carbon nanotube wiring of electrodes for high-rate lithium batteries using an imidazolium-based ionic liquid precursor as dispersant and binder: a case study on iron fluoride nanoparticles, ACS Nano 5 (4) (2011) 2930–2938.

[95] F. Wu, V. Srot, S. Chen, L. Lorger, P.A. van Aken, J. Maier, Y. Yu, 3D honeycomb architecture enables a high-rate and long-life iron (III) fluoride-lithium battery, Adv. Mater. 31 (43) (2019).

[96] J. Liu, Y. Wan, W. Liu, Z. Ma, S. Ji, J. Wang, Y. Zhou, P. Hodgson, Y. Li, Mild and cost-effective synthesis of iron fluoride-graphene nanocomposites for high-rate Li-ion battery cathodes, J. Mater. Chem. A 1 (6) (2013) 1969–1975.

[97] M. Nishijima, I.D. Gocheva, S. Okada, T. Doi, J.-I. Yamaki, T. Nishida, Cathode material for lithium secondary batteries, J. Alloys Compounds 2020, 840, 155719 @-0925-8388.

[98] F. Badway, F. Cosandey, N. Pereira, G.G. Amatucci, Carbon metal fluoride nanocomposites – high capacity reversible metal fluoride conversion materials as rechargeable positive electrodes for Li batteries, J. Electrochem. Soc. 150 (10) (2003) A1318-A1327.

[99] H. Jung, H. Song, T.K. Kim, J.K. Lee, J. Kim, FeF3 microspheres anchored on reduced graphene oxide as a high performance cathode material for lithium ion batteries, J. Alloy. Compd. 647 (2015) 750–755.

[100] S.K. Mathra, J. Nanda, H. Zhou, J.C. Idrobo, N.J. Dudney, S. Pannala, S. Dai, J. Wang, P.V. Braun, Electrode architectures for high capacity multivalent conversion compounds: iron (II and III) fluoride, RSC Adv. 6 (2013) 6730–6737.

[101] C. Li, L. Gu, S. Tsukimoto, P.A. van Aken, J. Maier, Low-temperature ionic-liquid-based synthesis of nanostructured iron-based fluoride cathodes for lithium batteries, Adv. Mater. 22 (33) (2010) 3650–3654.

[102] C. Li, L. Gu, J. Tong, J. Maier, Carbon nanotube wiring of electrodes for high-rate lithium batteries using an imidazolium-based ionic liquid precursor as dispersant and binder: a case study on iron fluoride nanoparticles, ACS Nano 5 (4) (2011) 2930–2938.

[103] F. Wu, V. Srot, S. Chen, L. Lorger, P.A. van Aken, J. Maier, Y. Yu, 3D honeycomb architecture enables a high-rate and long-life iron (III) fluoride-lithium battery, Adv. Mater. 31 (43) (2019).

[104] J. Liu, Y. Wan, W. Liu, Z. Ma, S. Ji, J. Wang, Y. Zhou, P. Hodgson, Y. Li, Mild and cost-effective synthesis of iron fluoride-graphene nanocomposites for high-rate Li-ion battery cathodes, J. Mater. Chem. A 1 (6) (2013) 1969–1975.

[105] M. Nishijima, I.D. Gocheva, S. Okada, T. Doi, J.-I. Yamaki, T. Nishida, Cathode material for lithium secondary batteries, J. Alloys Compounds 2020, 840, 155719 @-0925-8388.