The Case for Fluoride Ion Batteries

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Summary: Fluoride-ion batteries (FIBs) have recently emerged as a candidate for the next generation of electrochemical energy storage technologies. On paper, FIBs have the potential to match or even surpass lithium metal chemistries in terms of energy density, while further eliminating the dependence on strained resources such as lithium and cobalt. Research into FIBs has accelerated since its inception in 2011. In this perspective we examine the case for fluoride-ion batteries, considering electrode and electolytes from the literature and beyond, to outline the potential pathways to a competitive energy storage technology. We present the most promising, feasible conversion-type cathode and anode materials in terms of capacity, electrode potential, volume change, crystal structure, and cost/abundance. The capabilities of current and future fluoride intercalation electrodes are also examined. Using a subset of these materials, we conduct a techno-economic analysis comparing the energy density and cost of conversion and intercalation-type FIBs with state-of-the-art lithium-ion batteries and high energy density lithium-metal based chemistries. This investigation highlights the potential commercial value of conversion-type, liquid-cell FIB, with energy densities as high as 588 W h kg^{-1} (1393 W h L^{-1}) and costs as low as 20 US\$ kWh^{-1} at the stack level. This perspective highlights the major obstacles hindering the development of FIBs, drawing relevant lessons from the lithium ion literature. In order to practically advance FIBs into a viable technology, further research must be focused on safe liquid fluoride electrolytes and solid electrolyte interphase formation; mechanistic study and theoretical modelling of electrode materials; and stable non-active battery components and reference electrodes. We conclude by prescribing several critical research fronts in these areas.

Keywords: Fluoride-ion batteries, high energy density, techno-economics

Introduction

The maturation of energy dense (250 W h kg^{-1} to 300 W h kg^{-1}, 600 W h L^{-1} to 700 W h L^{-1}) lithium ion battery (LIB) technology has underpinned an electric vehicle (EV) revolution in the automobile industry, with the global market share of EVs projected to reach ~35% by 2030.[1] In the face of a climate crisis and increasing pressure to reduce greenhouse gas emissions, the aviation industry may soon follow suit. However, in order to get things off the ground (both figuratively and literally), batteries with significantly greater energy densities (closer to 800 W h kg^{-1}) are required[2]. A number of "post lithium-ion" battery technologies – such as lithium-sulfur and lithium-metal fluoride – are being explored to address this issue[2–4]. However, nearly all high-energy density battery chemistries rely on safe implementation of the lithium metal anode, which is proving difficult.[5–7] Furthermore, as the production of lithium-ion batteries increases, so too will the cost of its namesake element and other critical elements such as cobalt and nickel. Such increasing costs and issues with supply chain reliability have driven research into more-earth abundant, but less energy dense alkali-ion chemistries based on sodium and potassium.[8,9] Alternatively, multivalent charge carriers such as Mg^{2+}, Ca^{2+} have been explored to improve energy density and cost; however, the greater charge density associated with these ions introduces significant challenges for ion transport and reversible cycling.

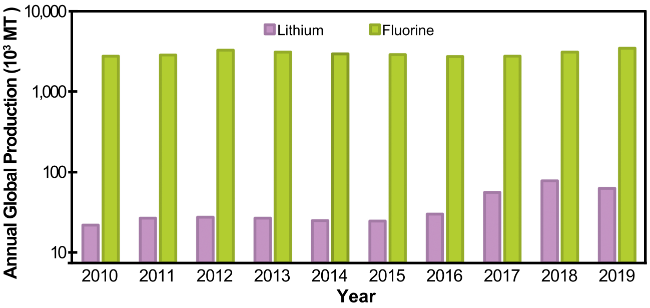


Figure 1: Global Production Fluorine and Lithium. Bar chart showing the global annual production of both lithium and fluorine from 2010 to 2019. Fluorine is mined as fluorspar (CaF$_2$); values shown are adjusted to reflect actual fluorine content. Production is displayed as a log scale. The annual production of fluorine is approximately two orders of magnitude greater than that of lithium.

In recent years, fluoride-ion batteries (FIBs) have emerged as a new field of research with the potential to address future electrochemical energy storage needs.[10] Importantly, FIBs are a distinct departure from the entrenched alkali-ion paradigm and are thus not dependent on the same strategies for technological success. As the name suggests, fluoride-ion batteries utilize fluoride anions (F$^-$) in place of lithium cations (Li$^+$) as the principal charge carrier. Despite this apparent antithesis, FIBs retain several of the fundamental properties that have made LIBs so successful. The large voltages possible with LIBs result in part from the high reductive stability of lithium cations. Analogously, fluorine is

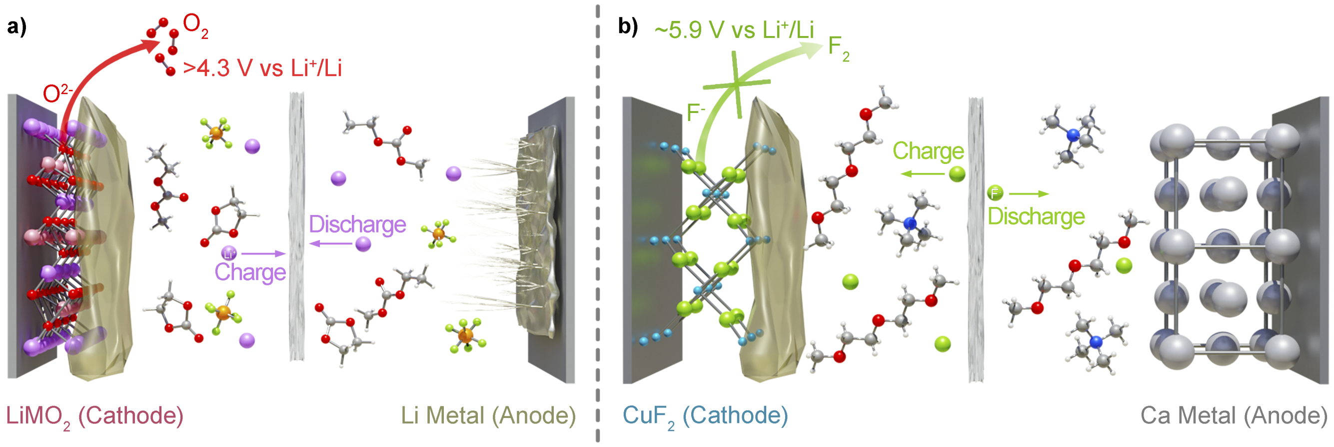


Figure 2: Lithium Ion Batteries vs. Fluoride Ion Batteries. (a) Schematic of a layered metal oxide–lithium metal cell with a conventional carbonate-based electrolyte. Dendrites can grow from the Li-metal anode, leading to capacity loss and potential short circuits. Oxygen evolution occurs from the oxide cathode in the charged state (>4.3 V vs. Li^+/Li) and can result in exothermic decomposition of the electrolyte.[11] **(b)** Schematic of a hypothetical conversion-type fluoride-ion battery with a CuF_2 cathode, a Ca anode, and a liquid fluoride electrolyte. The higher redox potential of $2F^- \rightarrow F_2 + 2e^-$ (5.9 V vs. Li^+/Li) results in greater oxidative stability for the cathode.[12] Dendrites are not expected at the anode, as no plating of metal occurs. Electrodes are shown in the fully charged state. In the following discussion, properties of electrodes are considered in the discharged state.

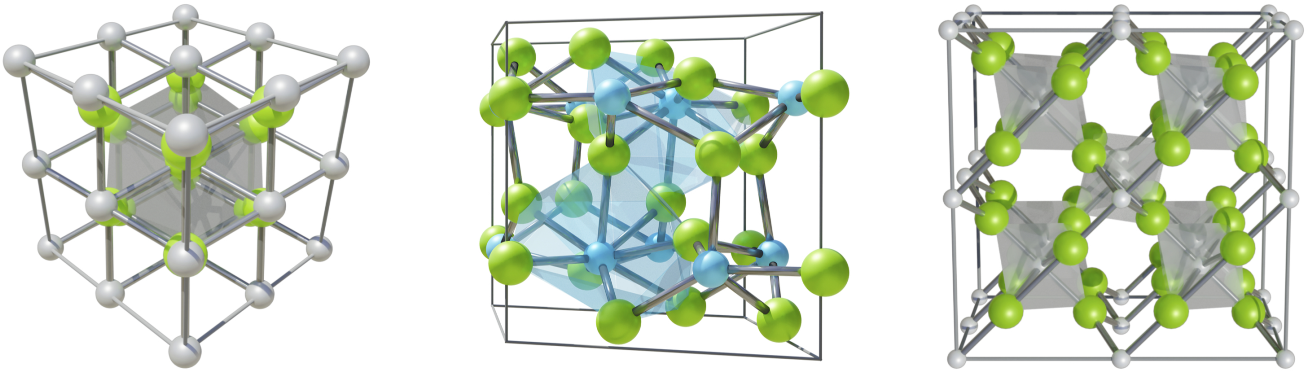
the most electronegative element, and fluoride anions exhibit a high oxidative stability, allowing for the use of higher voltage redox pairs. Much like lithium, fluorine is the smallest and lightest element in its group, allowing for faster ionic transport and higher energy densities than similar anionic chemistries (*e.g.* Cl^-)[13,14]. Fluorine is the 13th most abundant element in the earth's crust and exists primarily as fluorspar (CaF_2)[15]; it is widely distributed with major producers on four different continents.[12] The global production of fluorine, shown in Figure 1, is over 3.5 million tonnes per year, dwarfing the production of lithium by nearly two orders of magnitude.[16] The massive abundance of fluorine combined with this well established supply chain are beneficial for the development of FIBs as a low-cost alternative to LIB technologies. Other advantages may include higher volumetric and gravimetric energy densities resulting from multiple-electron redox reactions and improved safety in the absence of dendrite growth or exothermic oxygen decomposition.[17,18] The differences between lithium and fluoride ion batteries are summarised in Figure 2.

Research into fluoride-ion batteries is still at an incipient stage, and while they may avoid some pitfalls of LIBs, they also pose a new set of challenges. These are primarily related to the stability and conductivity of F-ion electrolytes as well as the usable capacity and reversibility of electrode redox reactions. This perspective is not intended to be a comprehensive review of the literature. Readers who are interested in a more detailed summary of developments in FIB research should refer to the recent reviews by Nowroozi *et al.* and Karkera *et al.*[19,20] In this perspective we begin by examining the projected utility of various cathode, anode, and electrolyte materials based on energy density, cost, and ease of implementation. We draw from recent developments in the literature to inform design considerations and strategies for improving FIB performance. To build a case for FIBs, we perform a basic techno-economic analysis comparing the realistic energy density and cost of various FIB constructions with those of state-of-the-art lithium-ion and lithium-metal chemistries. We then conclude by prescribing specific research topics to advance the development of high-performance fluoride-ion batteries. These fall into three critical research fronts: (i) electrolyte design and SEI formation, (ii) understanding of reaction mechanisms, and (iii) stable materials for cell construction.

Selection of Electrode Materials

While the use of fluoride-ions as charge carriers provides a suitable framework for a competitive battery technology, the salient properties of any such battery will be determined by the nature of the electrode materials. Batteries release energy as electrons move from a material with a high Fermi level (anode) to one with a low Fermi level (cathode). In a fluoride-ion battery, charge neutrality is maintained by the concurrent removal of fluoride ions from the cathode material and insertion of fluoride ions in the anode material (Figure 2b). In designing a viable fluoride ion battery, electrodes must be selected for energy density, reversibility of the (de)fluoridation reaction, and feasibility of production.

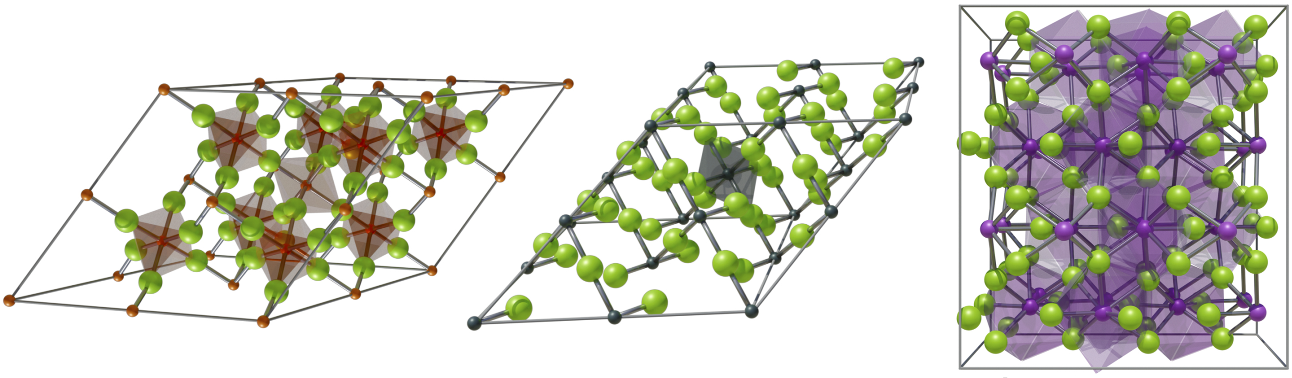
To a first approximation, selecting electrode pairs for high energy density involves combining low molecular weight materials that exhibit a large difference in redox potential. However, reversibility and feasibility



Cubic (*Fm*3*m*)
"Fluorite"
CaF_2, BaF_2, SrF_2

Rhombohedral (*P*3*c*1)
"Tysonite"
LaF_3, CeF_3

Tetragonal ($P4_2/mnm$)
"Rutile"
NiF_2, PbF_2, MgF_2



Trigonal (*R*3*c*)
FeF_3, CoF_3

Tetragonal (*I*4/*mmm*)
SnF_4, NbF_4

Orthorhombic (*Pnma*)
YF_3, BiF_3

Figure 3: Binary Fluoride Crystal Structures. "Ball and stick" models for the most common crystal structures adopted by binary metal fluorides. Structures are overlaid with cation-centered polyhedra. Fluoride anions are shown in light green. Cubic "Fluorite" and rhombohedral "tysonite" structures exhibit the highest ionic conductivities, and are considered superionic fluoride conductors at elevated temperatures. Many metal difluorides adopt the tetragonal "Rutile" structure. Some experimentally determined ionic conductivities are shown in the table below.

impose additional constraints on electrode materials. Materials that exhibit minimal volume change between fluoridation and defluoridation are preferred to mitigate internal stresses leading to pulverization, contact loss between the active material and the electrode, and degradation of the electrode/electrolyte interphase. Active materials should exhibit little to no solubility in the electrolyte to prevent self-discharge and continuous capacity loss. Electrode materials with significant electronic conductivity are preferred as this will lessen the need for small particle sizes and large proportions of conductive additives. Ultimately, materials that meet these conditions should also be of reasonable cost and reliable supply in order to produce a competitive technology.

Conversion Electrodes. The concept of the fluoride-ion battery was first demonstrated using conversion-type electrodes.[10] In the context of FIBs, the conversion reaction involves the electrochemical transformation between any metal and its corresponding metal fluoride $\mathrm{M} + \mathrm{xF}^- \leftrightarrow \mathrm{MF_x} + \mathrm{xe}^-$. A full cell in the discharged state consists of a metal fluoride as the anode and a metal as the cathode, with the two electrodes distinguished by the relative redox potentials of their constituent metals. While a vast number of compounds could potentially function as fluoride conversion electrodes, only those at the extremes of electrode potential would be technologically relevant.[21]

In addition to the criteria outlined above, potential conversion-type electrodes should also be considered based on the crystal structure of the relevant fluoride-phase, as this will impact the ionic conductivity and ultimately electrochemical performance of the active material. If the transformation between metal and metal fluoride relies on the movement of fluoride ions through a fluoride phase, it stands to reason that F^- ion conductive crystal structures would be beneficial for the kinetics of the conversion reaction. While these transformations similarly rely on the transport of electrons, electron conduction will likely depend more on the morphological evolution of the conversion reaction than the presumably limited electronic conduc-

Table 1: Fluoride-ion Conductivities. Experimentally measured ionic conductivities of some common binary metal fluorides as reported in the literature.

Material	Ionic Conductivity (S cm^{-1})	Crystal Structure
CaF_2	$5x10^{-5}$ (550 K)[22]	Cubic "Fluorite" ($Fm\bar{3}m$)
SrF_2	10^{-3} (900 K)[23]	
MgF_2	10^{-11} (578 K)[24]	Tetragonal "Rutile" ($P4_2/mnm$)
PbF_2	10^{-7} (303 K)[25]	
MnF_2	$2x10^{-9}$ (578 K)[24]	
LaF_3	$5.4x10^{-6}$ (633 K)[26]	Rhombohedral "Tysonite" ($P\bar{3}c1$)
CeF_3	$2x10^{-5}$ (454 K)[27]	
YF_3	10^{-11} (293 K)[28]	Orthorhombic ($Pnma$)
AlF_3	$2x10^{-11}$ (278 K)[29]	Rhombohedral ($R\bar{3}c$)
SnF_2	$2x10^{-6}$ (345 K)[25]	Monoclinic ($C2/c$)

Note: Measurement temperatures (K) vary between reports and are shown in parentheses. Materials are grouped by crystal structure to highlight trends in ionic conductivity.

tivity of the fluoride phase itself. Figure 3 shows the most common crystal structures for binary metal fluorides along with their typical ionic conductivities. Two of these crystal structures (Figure 3) are considered to be superionic conductors at elevated temperatures, namely the cubic Fluorite structure ($Fm\bar{3}m$) common to several alkaline earth fluorides (CaF_2, BaF_2, SrF_2) and the trigonal Tysonite structure ($P\bar{3}c1$) characteristic of many rare earth fluorides (LaF_3, CeF_3, NdF_3).[30,31] These materials have been studied extensively in the context of solid electrolytes, where high F-ion conductivity is necessary (Table 1). However, as they are typically composed of low work function metals, they also have inherent utility as conversion-type anode materials. In fluorite structures, F-ions diffuse through interstitial sites.[27] In tysonite structures, conduction occurs through a vacancy mediated mechanism as the interstitial sites are smaller than the radius of the F-ions (i.e. 0.84 Å versus 1.19 Å)[32–34]. The ionic conductivity of both Tysonite and Fluorite structures can be increased significantly (by one to three orders of magnitude) through aliovalent cation substitution.[25,30,35,36] The most commonly employed technique involves the introduction of divalent cations at the typically trivalent sites in the Tysonite lattice (*e.g.* $La_{1\text{-}x}Ba_xF_{3\text{-}x}$); this increases the ionic conductivity by introducing an additional fluoride anion vacancy.[34,37] The converse strategy of replacing divalent cations with trivalent cations in the Fluorite lattice (*e.g.* $Ba_{1\text{-}x}La_xF_{2+x}$) improves ionic conductivity by introducing additional fluoride anions at interstitial sites.[27,30,34] Such mixed cation species could readily be tested as anode materials, and may result in improved kinetics over the simple binary compounds. The development of a similar methodology for cathode materials is less straightforward, but particularly important as few cathode materials exhibit F-ion conductive crystal structures. It has been shown that the introduction of BiF_3 into PbF_2 results in a $Pb_{1\text{-}x}Bi_xF_{2+x}$ ($0 \leq x \leq 0.5$) solid solution with the Fluorite crystal structure. This system exhibited a high ionic conductivity (3×10^{-4} S cm^{-1} at 50 °C) but is especially interesting because both BiF_3 and PbF_2 are potential cathode materials with extremely similar redox potentials.[38]

The later 3 d transition metal fluorides are often considered among the most energy dense and economical conversion-type cathode materials.[3] The difluorides all exhibit a tetragonal rutile ($P4_2/mnm$) crystal structure, which is also shared by the frequently studied PbF_2. These rutile difluorides tend to exhibit the lowest F-ion conductivities (Table 1). In the context of LIBs, F^- diffusion in tetragonal transition metal difluorides was shown to be negligible.[39,40] In fact, the stationary nature of these F^- anions facilitates the reversibility of the lithium-ion conversion reaction by providing a stable sublattice through which cations can diffuse.[39] Other common fluoride crystal structures include the orthorhombic $R\bar{3}c$ (FeF_3, CoF_3, AlF_3) and the tetragonal $I4/mmm$ (SnF_4, NbF_4); the nature of F-ion conduction in these materials is less understood.

Table 2 lists the conversion-type FIB electrodes that are the most promising in terms of energy density and cost. None of the selected cathode materials exhibit crystal structures that are conducive to F^- ion conduction. However, this does not preclude their use as cathode materials, as nanostructuring can be employed to reduce the distance that ions are required to diffuse. Indeed, the reversible fluoridation of CuF_2 and BiF_3 has been demonstrated in numerous publications.[14,41–43] From a mechanistic standpoint, the F^- ion conductivity of a conversion electrode will affect the morphology evolution and reversibility of the fluoridation reaction. Logically, the fluoridation of a metallic particle should begin with the formation of a metal fluoride layer at the particle surface. The fluoride conversion reaction should then be governed by the differential diffusion rates of the metal cation and F^- anion through the fluoride layer. If the F^- ion diffuses faster, as in Fluorite compounds, one may see a simple particle expansion (and the resulting development of mechanical stresses) similar to the reaction of silicon and phosphorous with alkali ions.[44] If the metal cation diffuses faster, as may be the case in Rutile structures, one may see the formation of Kirkendall voids and resulting hollow structures. Such differences in morphology evolution appear to occur in thin film electrodes; further characterization of more practical active material particles is required.[45] Cases where anion and cation diffusion are comparable may also be possible.

As a cathode material, CuF_2 exhibits an ideal combination of high redox potential, low molecular weight, and relatively low cost. In the case of LIBs, it is often thought of as the ultimate conversion cathode.[3] However, after more than 16 years of research, the reversible cycling of CuF_2 in a Li-ion cell has never truly been demonstrated. Indeed, the irreversibility appears to be fundamentally tied to the lithium-ion conversion mechanism.[46] Fortunately, in the context of FIBs, the reversible (de)fluoridation of Cu/CuF_2 is experimentally achievable and has been demonstrated in a number of different formats.[14,42,45]

In a solid state construction, Nakano *et al.* demonstrated the reversible fluoridation of a 2.3 nm thick film of Cu at the theoretical capacity for a two electron transfer[45]. 76% of this capacity was retained after 30 cycles; this is surprising considering the mechanical degradation that accompanies large volume-change materials in solid-state cells. Importantly, the (de)fluoridation of much thicker (60 nm) Cu films was also demonstrated, suggesting fairly reasonable (less than ~120 nm) particle size requirements for utilizing the full capacity of Cu/CuF_2 in a practical cell. A high temperature (150 °C) and a very low current density ($0.188\,\mu A\,cm^{-2}$) was necessary to achieve this performance. However, the kinetics of this reaction can be improved considerably by replacing the monolithic Cu foil with a nanostructured carbon composite electrode and by using a liquid instead of a solid electrolyte. For example–using composite electrode with 100 nm to 200 nm CuF_2 particles in an ionic liquid electrolyte–Yamamoto et al. achieved a near-theoretical reversible capacity at room temperature with a slow but much more reasonable cycling rate (C/20)[42]. Although rapid capacity fading was observed over the first 10 cycles, these results suggest that the performance of CuF_2 and conversion-type FIB cathodes in general can be further improved by optimization of cathode structure and electrolyte composition. Several recent studies on all-solid-state FIBs have demonstrated improved performance in Cu cathodes by tailoring electrode chemistry (using a copper-gold alloy, Cu_3Au) and electrode composition (via formation of a Cu/PbF_2 composite).[47,48] In both cases improved capacity retention was demonstrated up to 20 cycles. The addition of ionically conductive PbF_2 further enabled cycling at the full theoretically capacity at room temperature.[48] Further development of such strategies should focus on employing lighter and less expensive additives.

NiF_2, FeF_3, and SnF_4 are also suitable cathodes materials for high energy applications. They exhibit significantly lower cathode potentials than CuF_2; however, this disadvantage is partially offset by their higher gravimetric capacities. In terms of energy density, FeF_3 is the closest to CuF_2 and is particularly interesting because of the low cost and extremely high crustal abundance of Fe.[12] The three-electron conversion reaction between Fe and FeF_3 presents an important case study as two redox steps ($Fe^{2+/0}$ and $Fe^{3+/2+}$) are expected at different potentials (2.63 V and 2.97 V vs. Li^+/Li respectively). Furthermore, interconversion between the thermodynamically stable crystal structures of FeF_2 ($P4_2/mnm$) and FeF_3 ($R\bar{3}c$) is kinetically limited.[49] The (de)fluoridation could occur as two distinct reactions ($Fe \rightleftharpoons FeF_2$ followed by $FeF_2 \rightleftharpoons FeF_3$) with separate plateaus, or as a single transition between Fe and defect-Rutile solid solution of FeF_2 and FeF_3, with a sloping potential profile. The nature of such reactions will determine the utility of FeF_3 and similar compounds with multiple accessible redox reactions. NiF_2 and SnF_4 are very similar in terms of redox potential, gravimetric capacity, density, and cost (Table 2, Supplementary Figure 1). While more costly than CuF_2 or FeF_3, these materials could still be viable if they exhibit superior rate-capability or cycle life. Recently, the electrochemical behaviour of Ni and Co was reported for the first time in all-solid-state FIBs. At high temperatures (150 °C) thin-film Ni and Co cathodes do appear to exhibit greater cycle life than Cu.[50]

The massive atomic weight of Bi makes BiF_3 the least energy dense cathode material among those listed in Table 2. BiF_3 does exhibit a relatively high redox potential and one of the lowest volume changes for cathodes on (de)fluoridation. However, BiF_3 is primarily interesting because the low cost of Bi presents

Table 2: Fluoride Conversion Electrodes. Salient properties of the five most attractive and practically viable conversion-type fluoride-ion battery cathodes and anodes, listed in order of theoretical energy density.

	Active Material	Redox Pot. (V vs. Li^+/Li)	Specific Cap.[a] ($mA\,h\,g^{-1}$)	Fluoride Crystal Structure	Density ($g\,cm^{-3}$)	Volume Change $M \rightarrow MF_x$	Metal Price (US$ kg^{-1})
Cathode	$Cu \leftrightarrow CuF_2$	3.54	843.5	Rutile-like $P2_1/c$	8.96	237%	\$7–\$9
	$Fe \leftrightarrow FeF_3$	2.74	1439.8	Rhombohedral $R\bar{3}c$	7.87	311%	~\$1
	$Ni \leftrightarrow NiF_2$	2.96	913.32	Rutile $P4_2/mnm$	8.91	211%	\$18–\$20
	$Sn \leftrightarrow SnF_4$	2.86	903.08	Tetragonal $I4/mmm$	7.27	150%	\$22–\$24
	$Bi \leftrightarrow BiF_3$	3.18	384.7	Orthorhombic $Pnma$	9.78	50%	\$5–\$6
Anode	$CaF_2 \leftrightarrow Ca$	0.00	686.5	Fluorite $Fm\bar{3}m$	3.18	-6%	~\$0.40[b]
	$MgF_2 \leftrightarrow Mg$	0.54	860.3	Rutile $P4_2/mnm$	3.15	42%	\$2–\$3
	$YF_3 \leftrightarrow Y$	0.41	551.1	Orthorhombic $Pnma$	4.01	168%	\$3–\$3.5[c]
	$SrF_2 \leftrightarrow Sr$	0.05	426.7	Fluorite $Fm\bar{3}m$	4.24	-11%	\$5–\$5.5
	$LaF_3 \leftrightarrow La$	0.66	410.4	Tysonite $P\bar{3}c1$	5.94	47%	\$1.5–\$3.5[c]

[a] Theoretical capacities calculated for the discharged state with a metal cathode and a metal fluoride anode.

[b] Price is shown for the metal fluoride.

[c] Price is shown for the metal oxide.

a potentially more cost-effective solution than either NiF_2 or SnF_4 (Supplementary Figure 1). The reversible (de)fluoridation of BiF_3 has already been demonstrated in a number of publications, albeit with limited capacity retention.[43,51,52] Considering its large ionic radius, propensity for alloying with other metals, and also its relative scarcity, Bi may be most useful as a redox-active substitutional component for tailoring the structure and F-ion conductivity of ternary metal fluorides.

Conversion-type anode materials are composed of electropositive (low work-function) metals, of which there are three major groups: alkali metals, alkaline earth metals, and rare earth metals. Alkali metal fluorides are not ideal candidates, as they are generally more soluble in liquid electrolytes.[53,54] Furthermore, they crystallize exclusively in the Rocksalt ($Fm\bar{3}m$) structure, which exhibits poor F^- ion conductivity and are limited to a one-electron transfer per metal atom. Divalent and trivalent metal fluorides exhibit lower solubilities because the greater charge density and smaller size of the cations results in higher lattice energies.[55] Unlike conversion cathodes, a number of conversion anodes do exhibit F^- ion conductive crystal structures (Table 2).

In many ways CaF_2 is the most ideal conversion-type F^- ion anode. With a reduction potential of ~0 V vs. Li^+/Li and a capacity of 686.5 $mA\,h\,g^{-1}$, CaF_2 is the most energy dense material of those considered here. While the energy density of MgF_2 is comparable, CaF_2 has an advantageous Fluorite crystal structure and undergoes practically no volume change on (de)fluoridation. While all the anode materials listed in Table 2 can be produced from relatively inexpensive metals or oxides, natural CaF_2 (>97%) can be purchased as "acid grade" Fluorspar for approximately 0.40 US$ kg^{-1}.[56] If this material can be purified to battery grade using an economical method such as melt processing, then CaF_2 would be truly incomparable as a cost-effective high-energy anode material.

After CaF_2 and MgF_2, YF_3 and SrF_2 have the next highest projected energy densities. While they are comparable in both energy density and cost, they present different practical challenges. Like CaF_2, SrF_2 exhibits a Fluorite crystal structure and low volume change, but has a markedly lower capacity. The low redox potential of these materials sits at the edge of the electrochemical stability window for many liquid electrolytes, making them difficult to utilize. For example, Davis *et al.* demonstrated limited cycling of CeF_3 and LaF_3 in an organic F^- electrolyte with reductive stability limit of ~1.0 V vs. Li^+/Li but were unable to cycle CaF_2 in the same electrolyte[14]. YF_3 has a more moderate and accessible anode potential, but does not have a F^- conductive crystal structure and exhibits a massive volume change.

A number of anode materials have already been studied in the literature, including MgF_2, CaF_2, LaF_3, CeF_3.[57,58] These reports appear to indicate that reversible (re)conversion of Tysonite structured materials (*i.e.* LaF_3, CeF_3) occurs more readily than other types of anodes. Indeed these anodes present fewer challenges as they exhibit higher F^- ion conductivities and more moderate electrode potentials. Other studies have also corroborated the idea that anodes with non-F^- ion conductive crystal structures (*e.g.* MgF_2) form a "passivation layer" which inhibits progress of the conversion reaction below the electrode surface[52,59,60]. However, the battery performance (capacity, cycle life, hysteresis) in all of these cases is less than optimal and appears to be more heavily influenced by electrode fabrication and electrolyte design than the intrinsic properties of the electrode material. In order to limit the deleterious effects of extraneous factors, closer attention must be paid to active material particle size, carbon-composite structure, binder & separator chemistry, and electrochemical stability of the electrolyte.

Intercalation Electrodes. While the concept of FIBs originated with conversion-type electrodes, recent literature has focused increasingly on electrodes that intercalate fluoride ions in a manner analogous to conventional LIB electrodes (*e.g.* $LiCoO_2$).[58,61–66] These fluoride intercalation electrodes have several established advantages over conversion-type electrodes such as higher cathode potentials and lower volume changes on (de)fluoridation. Intercalation reactions typically also exhibit superior rate capability and improved cycle life as they depend on the diffusion of only one species and do not require the formation and migration of metal/metal fluoride interfaces.

To date, electrochemical fluoride intercalation has only been experimentally demonstrated in all solid-state (ASS) cells, where high temperatures are typically required to improve the F^- ion conductivity of the solid electrolyte (140 °C to 200 °C). However, it's reasonable to assume that significant (de)intercalation would also occur at room-temperature; indeed several reports have demonstrated this using chemical reagents in lieu of electrochemical potentials.[63,67] Compared to conversion compounds, there is no clear indication that intercalation compounds would be less compatible with liquid electrolytes over a reasonable potential range. However, at high potentials (>> 4 V vs. Li^+/Li), the oxide lattice of fluoride intercalation cathodes may pose the same safety concerns as layered oxide cathodes for LIBs due to the risk of oxygen release and exothermic decomposition. In fact, oxygen redox has recently been reported in a preprint at ~4.7 V vs. Li^+/Li, in the case of a $La_{1.2}Sr_{1.8}Mn_2O_7$ FIB cathode.[64]

The fluoride intercalation electrodes explored thus far in the literature exhibit either the layer-structured Ruddlesden-Popper ($AO(AMO_3)_n$) or the tunnel-structured Schafarzikite (MSb_2O_4) crystal systems (where M is the redox active transition metal).[62,68] Fluoridation of the perovskite $BaFeO_{2.5}$ has also been reported.[69] In general, fluoride intercalation electrodes employ a 3d transition metal redox for charge storage; however, to accommodate fluoride insertion, the host lattice requires multiple high-molecular weight cations and oxygen anions per redox center. Inevitably this inactive structural bulk places severe limitations on the gravimetric capacity of such materials. The gravimetric capacities quoted by most authors reflect the hope that this drawback would be mitigated by intercalation of two fluoride ions per transition metal and an accompanying two-electron redox. Such reactions have been achieved using strong chemical fluorinating reagents.[61,70] Unfortunately, the electrochemical intercalation of much more than one fluoride has proven difficult. The high potentials (5 V vs. Li^+/Li) required to access the Mn^{5+}/Mn^{4+} and Co^{4+}/Co^{3+} redox compete with other oxidative processes such as carbon fluoridation and oxygen redox.[61,70] From this viewpoint, the La_2NiO_4 material may be the most likely to exhibit a reversible two-electron redox as the Ni^{4+}/Ni^{2+} redox generally occurs at lower potentials. Indeed electrochemical intercalation of nearly two fluoride ions with nickel valence increasing to 3.8+ was recently reported by Nowroozi *et al.*; however, reversible cycling was limited to less than one fluoride per formula unit.[62]

The realization of a reversible high-capacity fluoride intercalation cathode was reported in a recent preprint by Miki *et al.* by utilizing oxygen redox instead of a multi-electron transition metal redox.[64] In this case, a reversible intercalation of nearly two fluoride ions per transition metal was demonstrated in a $La_{1.2}Sr_{1.8}Mn_2O_7$ compound with a Ruddlesden-Popper (n = 2) structure ($AO(AMO_3)_2$). While F^- ions are typically intercalated into the rocksalt (AO) layers of Ruddlesden-Popper compounds, the extra fluoride in this case was reported to occupy an oxygen vacancy generated by the formation of O_2 in the Perovskite layer. The greater proportion of Perovskite layers in this compound may stabilize the structure against oxygen redox; however, it's uncertain if this stability can be maintained in a liquid electrolyte.

Unlike intercalation cathodes, very few intercalation anode materials have been identified. The only experimentally studied compound has been $Sr_2TiO_3F_2$, and in this case, (de)fluoridation was limited to only chemical methods.[67] Following chemical reduction by NaH, fully defluoridated Sr_2TiO_3 was observed at the surface; however, hydride substitution occurred in the bulk, limiting the reduction of titanium valence from 4+ to 3.5+. It is doubtful whether electrochemical defluoridation of this compound beyond one F^- would be reversible, as the introduction of 25% anion vacancies may destabilize the structure. While oxide-based intercalation compounds can function as high voltage cathodes, their use as anodes is limited as zero valence states are not accessible. Thus, even with the most electropositive transition metals (Ti, V, Cr), only moderately low potentials can be achieved.

Recently, Hartman and Mishra suggested the use of layered electrides as intercalation anodes with much lower electrode potentials.[71] Electrides are compounds in which a stoichiometric mismatch between anions and cations results in excess electrons occupying interstitial space in the crystal as delocalized "anionic" electrons (i.e. $[Ca_2N]^+e^-$).[72] Experimentally verified electrides take the form of nitrides, carbides, and silicides of electropositive metals (Ca, Sr, Y, Ce, La). The "nearly free" electrons in these compounds exhibit work functions close to that of the metal they originated from, resulting in very low redox potentials (the Ca_2N/Ca_2NF redox was estimated to be essentially 0 V vs. Li^+/Li). Hartman and Mishra described two electrides, $[Ca_2N]^+e^-$ and $[Y_2C]^{2+}e_2^-$, which are isostructural with $LiCoO_2$; however a number of other native electrides exist.[72] The much lower formula weight of these compounds yields much higher one-electron gravimetric capacities than oxide-based fluoride-intercalation electrodes (*e.g.* $Sr_2TiO_3F_2$,$LaSrMnO_4$, $FeSb_2O_4$). As with all low-potential compounds in their reduced state, native electrides are strong reducing agents, and this reactivity is only exacerbated by the high mobility of their free electrons.[73] Practical demonstration of their viability as anodes should first focus on the synthesis of these compounds in the discharged state (i.e. Ca_2NF and Y_2CF_2) and verification of electrochemical defluoridation therein. It should be noted that the synthesis of layered Y_2CF_2 has been established and that this compound can actually be classified as an MXene.[74]

While fluoride intercalation electrodes may offer improved rate capability and cycle life over conversion-type compounds, they may suffer from greater safety concerns.[62] Ultimately, the success of fluoride intercalation compounds hinges not on outperforming fluoride conversion chemistries, but rather showing some improvement over conventional lithium-ion technology. In our techno-economic analysis below, we will attempt to quantify whether such an advantage exists.

Fluoride Ion Electrolytes

Solid electrolytes have been heralded as a major breakthrough for the advancement of lithium-ion batteries. Their appeal boils down to several key advantages: first, the promise of prohibiting lithium dendrite growth, thereby enabling the use of high energy density lithium-metal anodes, and second, the potential to improve battery safety through the use of non-flammable materials. In the case of fluoride ion batteries, dendrite growth is a non-issue. While non-flammable solid electrolytes do still provide some safety benefits (*i.e.* in the event of battery puncture and short circuit), the likelihood of a spontaneous exothermic reaction with the electrolyte in a FIB would be significantly diminished if oxygen-free fluoride cathodes are used.[17,18] Solid electrolytes for FIBs are, in fact, problematic in a number of ways. In terms of performance, they typically require high temperatures (>~140 °C) in order to operate, and even at these temperatures they exhibit relatively low ionic conductivities. From a practical standpoint, they are not amenable to conventional cell fabrication techniques, and it is difficult to achieve good interfacial contact between the solid electrolyte and the electrode materials (Figure 4).[5] Furthermore, this interfacial contact is often lost if the active materials undergo significant volume change; this renders solid electrolytes essentially incompatible with most conversion-type materials. Perhaps most importantly, however, the high density of solid electrolytes significantly reduces the specific energy of solid cells compared to liquid cells. Simply replacing the liquid electrolyte with the exact same volume of solid electrolyte (equivalent to a ~50 µm-thick layer)—for example $La_{0.9}Ba_{0.1}F_{2.9}$ (~5.7 g mL^{-1})—would decrease the specific energy by approximately 42–46% depending on the cell chemistry (Supplementary Figure 2). Even if a functioning solid electrolyte layer could be fabricated with a thickness of 20 µm, the specific energy would still be nearly 35% lower than a comparable liquid cell (Supplementary Figure 2). Nevertheless, wide electrochemical stability windows are much easier to achieve with solid F^--ion electrolytes, and their much lower chemical reactivity makes them safer, easier to produce, and generally more stable (Figure 4). Further research should ultimately focus on improving these qualities for liquid electrolytes.

Interestingly, solid-electrolytes could be competitive with liquid electrolytes in terms of energy density if a kind of "anode-less" configuration is utilized.

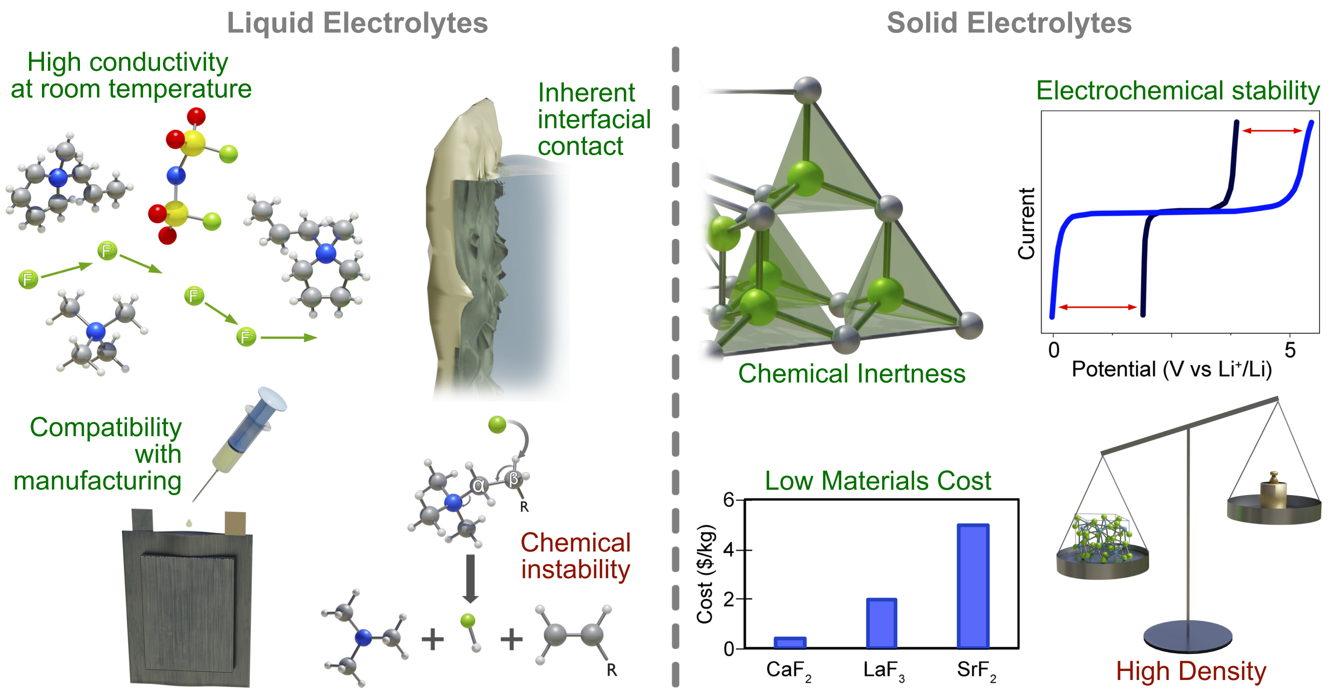


Figure 4: Fluoride Ion Electrolytes. Graphical representation of the pros (green) and cons (red) of liquid fluoride electrolytes relative to solid fluoride electrolytes. Liquid fluoride electrolytes exhibit ionic conductivities 2-3 orders of magnitude higher than solid fluoride electrolytes at room temperature. Liquid electrolytes naturally facilitates interfacial contact with the electrodes and are compatible with established manufacturing processes. Importantly the lower density of liquid electrolytes is crucial for achieving high energy densities. The main disadvantages of liquid fluoride electrolytes are their reduced chemical and electrochemical stability, safety concerns resulting from their corrosive nature, and the present high production costs that are primarily associated with the organic fluoride salt.

That is, the anode can be formed *in-situ* by reduction of the solid-electrolyte directly in contact with the negative current collector.[75] This concept has been demonstrated in thin-film cells, typically using LaF_3 and CeF_3 solid electrolytes; however, it is unclear if this strategy can be practically employed in a high capacity format. In the case of the Cu/LaF_3 system (Supplementary Figure 2), the energy density of an anode-less solid-state cell (415 $\mathrm{W\,h\,kg^{-1}}$) is marginally greater that of a liquid cell (380 $\mathrm{W\,h\,kg^{-1}}$). However, if a less dense solid-electrolyte is used—as in the case of Cu/CaF_2—the energy density of the anode-less configuration (693 $\mathrm{W\,h\,kg^{-1}}$) would be significantly higher than that of a liquid cell (588 $\mathrm{W\,h\,kg^{-1}}$).

The particular challenge of developing liquid fluoride electrolytes for higher voltage systems stems from the highly nucleophilic nature of the F-ion.[76] Due to electrostatic repulsion between the lone pairs contained within its small ionic radius, F^- is a much more willing electron donor than other halide ions.[55] This Lewis basicity is particularly exacerbated in most organic battery solvents (anhydrous, aprotic), wherein the F^- ion is unsolvated or "naked". Indeed the unsolvated F^- ion is iso-electronic with the hydroxide OH^- ion and similar in reactivity.[76] There are two main strategies for developing stable liquid electrolytes despite the reactive nature of the F^- ion. The first involves formulating electrolytes that are impervious toward nucleophilic F^- attack, while the second involves solvating the F^- ion to reduce it's basicity.

Davis *et al.* pioneered the development of a stable liquid fluoride electrolyte by identifying β-hydrogen elimination as the most prevalent decomposition pathway in otherwise unreactive organic compounds[14]. It was suggested that the lack of β-hydrogens was primarily important for preventing decomposition (*i.e.* Hofmann elimination) upon drying of organic fluoride salts at elevated temperatures. However, similar elimination reactions are known to happen in solution at room temperature, and would lead to the detrimental formation of HF.[77] The authors designed a β-hydrogen-free electrolyte composed of N,N,N-trimethyl-N-neopentylammonium fluoride dissolved in bis(trifluoroethyl)ether, which they claimed was stable for more than 3000 h. Unfortunately, even in this shelf-stable electrolyte, cycling behavior was dominated by electrolyte decomposition at the edge of the electrochemical stability window.[14] The reactive nature of the naked F^- ion limits the choice of both solvents and salts, making it difficult to produce electrolytes that are both chemically and electrochemically stable.[78] In addition to β-hydrogen eliminations, nucleophillic fluoride attack can occur at other kinds of atoms (α−H, C=O, C≡N, P, Si, etc.) if they are sufficiently acidic.[76]

However, such unwanted side reactions may be diminished or prevented if enhanced solvation of the F^- ion can be achieved.

The basicity and nucleophilicity of F^- ions is significantly decreased in protic solvents, where the F^- ion is strongly solvated by the acidic protons (forming hydrogen bonds). This hydrogen bonding is so strong that in most protic solvents, dissolved fluorides exist as bifluoride (HF_2^-) ions rather than naked F^- ions.[21] Protic solvents are seldom used in next-generation batteries, however, as the labile hydrogens are electrochemically reduced at relatively high potentials. A reasonable approach would be to employ organic compounds containing more electropositive elements (*e.g.* B, Si, P, etc·) as Lewis acidic solvating agents. This strategy has been explored in a number of reports from Takeshi Abe and Zempachi Ogumi, primarily using phenylboranes as fluoride complexing agents[79–81]. Solvation of F^- by the borane species (0.5 M) enabled the authors to dissolve CsF up to 0.51 M in tetraglyme as an electrolyte salt.[51] While the shelf-life of the resulting electrolyte was not examined, the electrochemical stability window appeared to extend from ~1.1 V to above ~3.6 V vs Li^+/Li. Interestingly, the authors noted that the borane additives could also facilitate dissolution of F^- from the active material.[51] Strongly solvating additives should be avoided for this reason, but also to minimize the free energy change associated with desolvation, which increases charge transfer resistance and the corresponding overpotentials. Ultimately, improving fluoride ion solvation will reduce F-ion reactivity but also F-ion conductivity; these two factors must be balanced in designing a F-ion electrolyte. As such, it is likely that weaker and softer Lewis acids would be more effective as F^- solvating additives. Ultimately, both Lewis base resistance as well as F^- ion solvation strategies should be incorporated along with SEI forming strategies to develop an optimized liquid fluoride electrolyte.

Battery safety is perhaps the greatest concern regarding liquid fluoride electrolytes. In addition to being potentially flammable, liquid fluoride electrolytes are generally both highly toxic and corrosive due to the chemical reactivity of the F^- ion. It is unclear if these properties can be addressed by tailoring electrolyte chemistry, and may necessitate additional engineered safety measures for the implementation of FIBs.

Lessons Learned from Lithium-Ion

While FIBs represent a new chemistry, distinct from that of LIBs, principles uncovered from decades of LIB research may still be highly relevant, particularly in the case of conversion-type electrodes. With any chemistry, achieving a long cycle life requires the mitigation of extrinsic failure mechanisms. In the case of conversion-type transition metal fluoride cathodes for LIBs, there are three major failure mechanisms: active material (transition metal) dissolution, electrolyte decomposition, and particle coarsening.[39] The first two failure mechanisms occur where bare metallic surfaces are in contact with the electrolyte, a morphological feature that has also been identified in FIB conversion cathodes. Transition metal dissolution can occur at these metal/electrolyte interfaces on oxidation and will compete with the (re)fluoridation of the metallic particles. This dissolution would be mitigated if the fluoride surface that forms on oxidation is an effective passivation layer. As with other aspects of the reaction mechanism, we expect this will depend heavily on the differential diffusion rates of metal and fluoride ions within the fluoride phase. The formation of an artificial passivation layer is the clear engineered solution; however the only way of achieving this without sacrificing energy density or increasing production cost is through the formation of a robust and dense solid electrolyte interphase (SEI) that prevents active material dissolution. In LIBs, fluorocarbon species (*e.g.* fluoroethylene carbonate) and bis(fluorosulfonyl)imide (FSI) salts are known to be effective in this regard.[3,82] The use of SEI forming additives in liquid fluoride electrolytes must be further explored.

The significant volume changes associated with the conversion reaction may lead to breaking and reforming of the SEI and consequent coulombic inefficiencies. However this will depend on the morphology evolution of active material particles how the volume change is accommodated within the material. In addition, this SEI degradation can be mitigated if the SEI exhibits some elasiticity, as in the case of polymeric SEI layers.[83]

Another failure mechanism arises from the fact that metallic surfaces can be highly catalytic for the decomposition of organic electrolytes. In the extreme, uncontrolled SEI growth can increase charge transfer resistance to the point of isolating the electrode from the electrolyte.[39] While this can again be forestalled by the formation of a robust SEI, carbon coating/encapsulation of active material particles has also proven useful.[3] Particle coarsening increases the length scales for ionic and electronic transport; this can be highly detrimental in a conversion-type electrode where conductivity is already limited. In LIBs, coarsening occurs as lithium diffuses across interparticle boundaries. It is uncertain whether fluoride diffusion would lead to the same effect. Strategies to prevent coarsening include carbon encapsulation, anchoring via the direct chemical growth of active materials on carbon, and electrostatic separation using ionic liquid electrolytes.

As with conversion-type fluorides for LIBs, the (de)fluoridation reaction must depend on the formation and migration of metal/metal fluoride interfaces.[39] Whether these interfaces are coherent, semicoherent, or incoherent will influence the rates of reaction, the reaction overpotential, and the optimum particle size for each active material. Structural and morphological characterization of these metal/metal fluoride interfaces with high spatial resolution, for example High Resolution Transmission Electron Microscopy (HRTEM), will be necessary for a complete mechanistic understanding of (de)fluoridation and should be supported by molecular dynamics (MD) simulations.

Techno-Economics

Fluoride ion batteries have been touted for their theoretically high volumetric and gravimetric energy densities, which far outpace those of conventional LIBs. However, the lofty numbers quoted by many authors completely ignore the constraints placed on energy density in a realistic cell design. Furthermore, the potential cost-efficiency—and economic viability—of FIB technology has not been considered. Logical arguments for various FIB chemistries were made in the sections above. Herein, we present the case for FIBs as an inaugural techno-economic analysis, comparing the potential of conversion and intercalation-type FIBs with current and future LIBs.

Our techno-economic model (Figure 5) extends only to the stack level, to highlight the effects of battery chemistry rather than cell/pack geometry and design. All stacks are modeled in the discharged state, reflecting the greater stability—and corresponding synthesizability/processability—of the discharged electrode active materials. The model is based on a conventional multilayer component stack, where current collector foils are coated on both sides with electrode material and interleaved with separator and electrolyte. The thickness of the electrode layers is set to 90 µm to achieve a high-energy design. A complete description of the parameters used and calculations/assumptions made is available in the supplementary information.

We model three different conversion-type chemistries, all utilizing metallic Cu as a cathode. The Cu/CaF_2 redox pair represents an ideal case where a reductively stable liquid fluoride electrolyte is available. Cu/MgF_2 and Cu/YF_3 redox pairs are modeled to explore possibilities in case the low-potential stability of electrolytes is limited. In order to judge the potential viability of these fluoride ion cells, we further model two high-energy lithium ion chemistries based on nickel-rich layered oxides. We select the NMC622-graphite system to represent the current state of the art and a hypothetical NMC811-lithium system to represent a next-generation lithium-metal technology.

With research on fluoride intercalation electrodes trending upward, it is now a highly pertinent time to evaluate and contextualize the projected capabilities of such materials. We first consider a realistic scenario based on the current literature using $LaSrMnO_4$ as the cathode and $Sr_2TiO_3F_2$ as the anode with a fully reversible one-electron transfer per formula unit.[67,70] The second system we model represents a hypothetical near-future, best-case scenario employing $La_{1.2}Sr_{1.8}Mn_2O_7$ as a reversible oxygen-redox cathode and the layered electride, Ca_2NF, as a low-potential, high-capacity anode.[64,71] In terms of energy density, every other potentially favorable case (*e.g.* La_2NiO_4 with a two-electron transfer) that is currently known would fall between these two systems. These compounds are also among the most cost-effective out of all the fluoride-intercalation electrodes that have been identified. Chemistries containing Co and Ni are understandably among the most expensive; however, as the redox-active metal represents only a minor fraction of the formula weight in many compounds, the inactive elements are also a major cost driver. For example, we predict that the price (US$) of $FeSb_2O_4$ would be higher than that of La_2NiO_4 as the higher cost of Sb compared to La overturns even the cost advantage imparted by the use of Fe.

The variable parameters (*i.e.* active material fraction, electrode porosity, excess electrolyte, negative:positive (N:P) ratio, etc.) used in this techno-economic model were set to reflect realistic requirements for the utilization of various chemistries; a number of these parameters were taken from the Battery Performance and Cost (BatPaC) modeling software developed by Argonne National Lab.[84] The construction of the NMC622-graphite stack was derived from the default BatPaC values, while that of the NMC811-lithium stack was similar to that suggested by Liu *et al.*.[6]

The parameters used to model conversion-type chemistries reflect the challenges imposed by generally slower reaction kinetics, larger volume changes on cycling, and increased electrolyte consumption in light of their high capacities. A lower active material mass fraction (85%), increased carbon and binder content, and higher electrode porosity (30%) were chosen to facilitate electron and ion conduction within the electrode, as well as to mitigate significant volume changes. A leaner stack design, closer to that of commercial LIBs, was used for the fluoride intercalation chemistries.[84] Electrodes were designed with a high active material mass fraction (95%) at 30% porosity. Similar considerations were made for the amount of excess

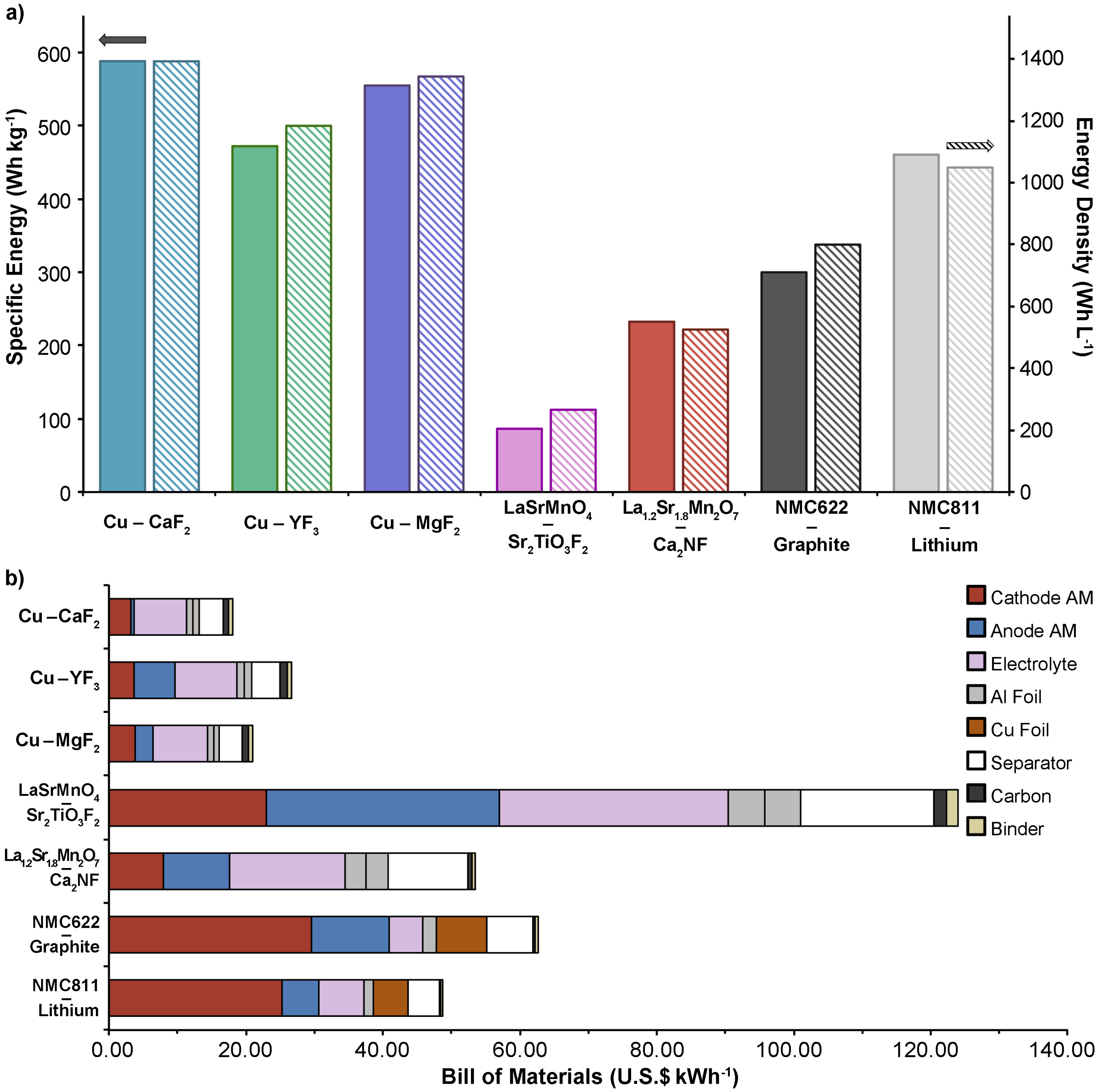


Figure 5: Techno-Economic Analysis. (a) A bar chart showing the projected stack-level energy densities various FIB and LIB chemistries. Solid bars correspond to specific energy values displayed on the left axis, while hollow bars correspond to volumetric energy density values shown on the right axis. The Cu–CaF_2 pair was chosen as the most ideal conversion cathode chemistry; YF_3 and MgF_2 are included as anodes that may be more compatible with liquid electrolytes due to their more moderate redox potentials. The intercalation-type $LaSrMnO_4$–$Sr_2TiO_3F_2$ FIB chemistry corresponds to an idealized case for current materials, while the $La_{1.2}Sr_{1.8}Mn_2O_7$–Ca_2NF represents a near-future best case scenario. Two LIB chemistries are modeled for comparison; the NMC622-graphite chemistry represents a commercially available technology, while the NMC811-lithium cell represents a hypothetical high-energy density case utilizing a lithium metal anode. Values reflect realistic limitations for each battery chemistry. **(b)** Chart showing the corresponding materials cost for the battery stacks shown in (a), normalized by their respective specific energies. Costs are itemized by battery component. It is assumed that Al current collectors are compatible with FIB anodes. Values for the LIB cells are taken from the BatPaC modelling software.[84] The costs of all other materials are calculated based on recent (2020) prices for commodity feedstock chemicals.[56] A detailed description of all the assumptions and calculations made in this techno-economic analysis are provided in the supporting information.

electrolyte and the negative to positive (N:P) excess capacity ratio (see supplementary information). In each FIB case, both anode and cathode were modelled using the same proportions of active material, conductive carbon (Super P), and binder (polyvinylidene fluoride). While a readily available fluoride-ion electrolyte does not yet exist, the electrolyte characteristics used for our model are based on a hypothetical 1 M solution of tetramethylammonium fluoride (TMAF) in tetraglyme (G4). TMAF is the most accessible organic fluoride salt and tetraglyme is a solvent of reasonable cost that has been used in a number of FIB publications.[51,78] We estimate that the price of such an electrolyte would be ~22 US\$ $\mathrm{kg^{-1}}$ if produced at scale, which is still significantly higher that the cost of a typical LIB electrolyte (12.5 US\$ $\mathrm{kg^{-1}}$).

The costs of fluoride ion electrode active materials were calculated using the most recent spot prices for the relevant commodity feedstock chemicals. In each case, the cost was estimated based on the series of physical and chemical processes required to convert the initial feedstock to the final active material. While this method is an oversimplification, the resulting prices faithfully reflect differences in the cost and earth-abundance of the elements without being unreasonably low. In addition, this method was able to accurately reproduce the market prices of commercial LIB cathodes, such as lithium cobalt oxide (LCO) and lithium nickel manganese cobalt oxide (NMC622). In any case, deviations in price of even 3 US\$ $\mathrm{kg^{-1}}$ to 4 US\$ $\mathrm{kg^{-1}}$ from our estimated values would not change the outcome of this analysis in any significant way.

Figure 5 quantifies the stack-level energy densities of the selected battery chemistries. Despite the significant penalties imposed on conversion-type systems, the energy densities of $\mathrm{Cu/CaF_2}$, $\mathrm{Cu/LaF_3}$, and $\mathrm{Cu/MgF_2}$ all exceed even that of a fictive NMC811-lithium stack. As expected, the $\mathrm{Cu/CaF_2}$ system exhibits the highest overall energy density at 588 $\mathrm{W\,h\,kg^{-1}}$ (1393 $\mathrm{W\,h\,L^{-1}}$). Furthermore, the low cost/capacity ratio of Cu and especially $\mathrm{CaF_2}$ yields an extremely low energy cost of less than 20 US\$ $\mathrm{kW^{-1}\,h}$ at the stack level. In the case of $\mathrm{Cu/MgF_2}$, the higher anode potential (0.54 V vs. $\mathrm{Li^+/Li}$) is compensated by the significant increase in anode capacity (860.3 $\mathrm{mA\,h\,g^{-1}}$), resulting in only a modest decrease (32 $\mathrm{W\,h\,kg^{-1}}$) in energy density. Compared to $\mathrm{CaF_2}$, $\mathrm{MgF_2}$ has a less ionically conductive rutile crystal structure and undergoes greater volume change on cycling. However, the energy density and cost of the two systems are so similar that choice of one over the other will be determined by ease of implementation. Changing the anode material to $\mathrm{YF_3}$ compounds a moderate anode potential (0.4 V vs. $\mathrm{Li^+/Li}$) with a lower capacity (551 $\mathrm{mA\,h\,g^{-1}}$) and results in a marked decrease in stack energy density to ~460 $\mathrm{W\,h\,kg^{-1}}$. Despite this lower energy density and the higher cost of $\mathrm{YF_3}$, the cost of energy stored is still less that 28 US\$ $\mathrm{kW^{-1}\,h}$.

These examples illustrate the main case for conversion-type FIBs: they could offer energy densities comparable to or even higher than a hypothetical NMC811-lithium cell at a greatly reduced cost. Importantly, their realization hinges on the development of an optimized liquid electrolyte, which may be a more tractable problem than enabling the use of lithium metal anodes with solid electrolytes. A suitable hypothetical liquid fluoride electrolyte may indeed be more expensive than the 22 US\$ $\mathrm{kg^{-1}}$ estimated herein. However, even doubling the electrolyte cost to 40 US\$ $\mathrm{kg^{-1}}$ would only increase the cost of conversion-type chemistries from ~27 US\$ $\mathrm{kW^{-1}\,h}$ to 38 US\$ $\mathrm{kW^{-1}\,h}$ at the stack level, which is still far lower than that of intercalation-type LIBs.

Unlike conversion-type fluorides, fluoride intercalation cells do not represent a high-energy chemistry. In fact, if the intercalation reaction is limited to one fluoride per redox center, as can be reasonably expected based on current experimental data, then the stack level energy density becomes exceedingly small (85 $\mathrm{W\,h\,kg^{-1}}$), and the corresponding cost of energy stored becomes untenable (125 US\$ $\mathrm{kW^{-1}\,h}$). In the near future best-case scenario (combining oxygen redox capacity in the cathode with a layered electride anode) the energy density (237 $\mathrm{W\,h\,kg^{-1}}$) edges closer to current NMC622-graphite chemistries (300 $\mathrm{W\,h\,kg^{-1}}$). However, under no circumstances—even if the electrode construction is optimized to limits of commercial Li-ion technology and the N:P ratio is set to unity with zero excess electrolyte—would the energy density exceed 292 $\mathrm{W\,h\,kg^{-1}}$ at the stack level.

A future intercalation-based fluoride cell could present a lower cost alternative to current LIBs; however, this margin of benefit would be jeopardized if the cost of the electrolyte exceeded 33 US\$ $\mathrm{kg^{-1}}$. Alternatively, an increase in the cost of LIBs could also present an opportunity for a future intercalation-type FIB to become competitive in terms of cost. Indeed, the main driver of materials cost for state-of-the-art LIBs is the cathode active material, the raw components of which (Li, Co, Ni) are subject to significant price fluctuations. However, even if cost parity can be met, these idealized fluoride-intercalation cells would have to be competitive in, and likely improve on, some aspect of performance (*e.g.* cycle life, rate capability, safety, environmental impact) in order to drive adoption. This is a tall task in an industry where the capabilities of even conventional lithium ion technologies are constantly being improved. However, this is a burgeoning field and more attractive electrode materials may yet be discovered.

Critical Research Fronts

Fluoride ion batteries have the potential to be a low-cost, energy-dense storage technology. However, their success will require vast improvements over the current state of the art. Herein, we draw from our preceding analysis to outline specific research tasks for

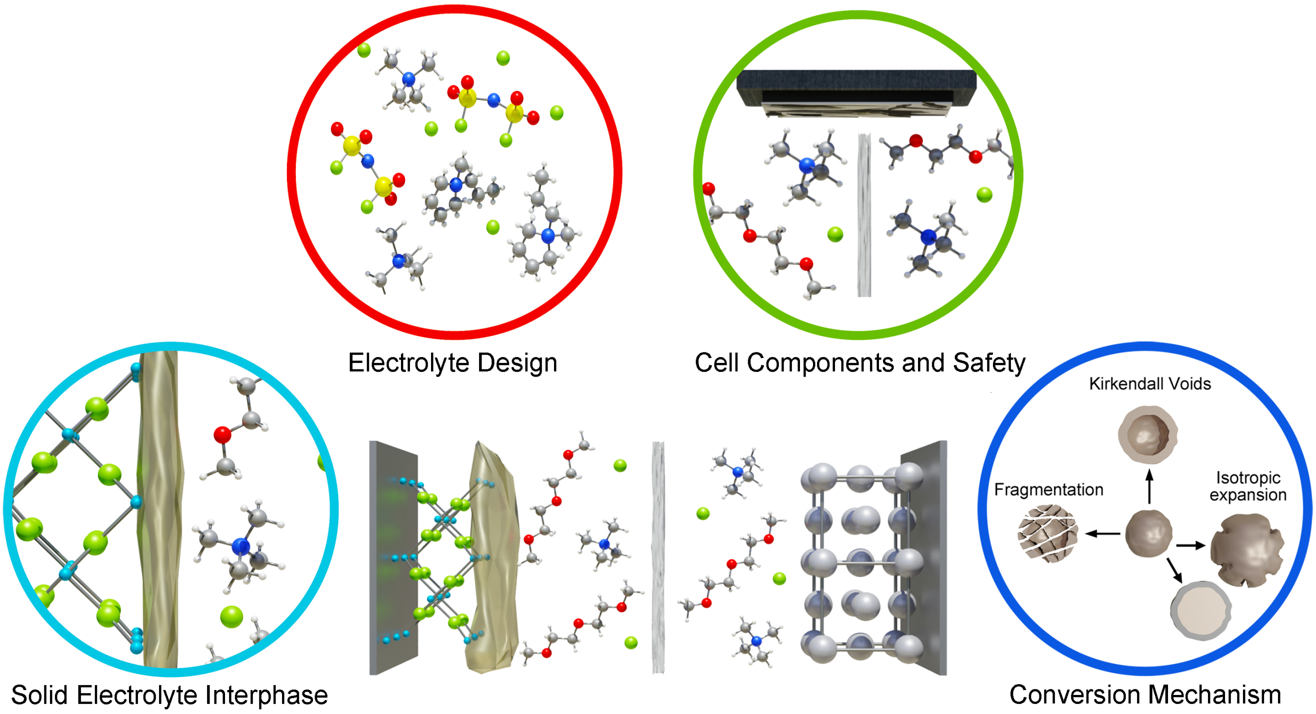


Figure 6: Critical Research Fronts. A graphical representation of the suggested avenues for future FIB research. The development of (electro)chemically stable liquid fluoride electrolytes with good SEI forming ability is paramount to the success of FIBs. Investigation of the fluoride conversion mechanism using both experimental and computational means is required to design electrodes with enhanced cycle life and rate capability. Stable components for cell construction and measurement should be utilized to preclude extraneous failure mechanisms.

accelerating the development and understanding of high-performance FIBs (Figure 6) . These are broadly grouped into the three categories below.

Mechanistic Understanding Uncovering the charge/discharge mechanisms of conversion-type fluoride electrodes is essential for understanding their capabilities and limitations.[39] Mechanistic studies of the fluoride conversion mechanism should proceed by experimentally evaluating morphology and phase equilibria at different states of charge using high-spatial resolution techniques such as HRTEM. Particular focus should be given to structural orientation relationships and lattice matching at the metal–metal fluoride interface. The formation and collapse of such interfaces can additionally be simulated using molecular dynamics. For the prominent fluoride crystal structures listed in Tables 1 and 2, the relative rates of anion and cation diffusion through the lattice should be modeled using Density Functional Theory (DFT). As mentioned above, this will inform the prediction of morphology evolution and reaction mechanisms.

From a practical standpoint, cation substitution should be explored as means of improving electrode performance and potentially even stabilizing energy dense active materials in more fluoride ion conductive crystal structures. In support of this effort, DFT can be used to predict the equilibrium crystals structures across the compositional space of various fluoride solid-solutions.

Electrolyte Design and Characterization The design of suitable liquid fluoride-electrolytes will be the linchpin for the development of FIBs as a competitive energy storage technology. Ultimately such an undertaking should begin with the experimental screening of F^- ion solvating solvents, cations, and additives for chemical and electrochemical stability. The design and synthesis of new electrochemically stable organic compounds containing soft Lewis acid centers (*i.e.* P, S^+, Si, etc·) should proceed in parallel.

In addition to (electro)chemical stability, the SEI forming ability of the electrolyte is of paramount importance to the stable cycling of FIB electrodes. Ultimately, the SEI will be formed from the species that migrate alongside the F^- ions.[3] To more effectively understand SEI formation, potential electrolyte components should be ranked according to their relative F^- solvating ability. Determination of such rankings can be achieved experimentally using Raman spectroscopy and NMR techniques or computationally by calculating solvation free energies using MD and DFT.[85] The resulting "solvating power series" would be an invaluable tool for predicting the primary SEI forming species in solution and tailoring the electrolyte composition to achieve more robust SEI layers. Experimental SEI characterization should focus on morphology and chemical composition.

Materials and Methods for Cell Fabrication and Construction Thus far, the practical comparison of different electrode materials has been impossible due to a multitude of extraneous contributions to cell failure and observed capacity. While inactive cell components (separators, binders, current collectors, etc.) are often taken for granted, their unforeseen decomposition represents a major obstacle to FIB operation at the lab scale and beyond. Materials entrenched in LIB research, such as polyvinylidene fluoride (PVDF), carboxymethylcellulose (CMC), polyacrylic acid, and glass fiber may not be compatible with FIBs. Research should focus on explaining how these inactive components can react with F^- ions as well as the identification of inert, economical alternatives and their systematic optimization.

Interpretation of FIB cycling data is further complicated by the lack of a standard counter/reference electrode. An effective counter electrode should exhibit minimal voltage hysteresis and a relatively constant potential over the majority of its capacity range and further provide a source of F^- in excess of the working electrode capacity. Composites of Pb/PbF_2 appear to meet these criteria[70]; however, detailed optimization of active material particle size and crystallinity as well as composite composition and structure should be performed with a thorough characterization of cycle life and hysteresis to improve consistency between studies. Similar composites with lower potential redox couples (*i.e.* Zn/ZnF_2) should also be explored in this way.

The use of liquid fluoride electrolytes raises major safety concerns regarding the potential formation of HF and the corrosivity/toxicity of the anhydrous F-ion itself. HF and HF_2^- contents in liquid electrolytes should be monitored over time. The long-term resistance of cell components to fluoride corrosion should be examined and the engineering solutions (*e.g.* nickel plating) should be considered. It is important to analyse the toxicity of gases and volatile compounds released on catastrophic battery failure and to develop physical and chemical methods to mitigate hazardous chemical formation and discharge.

Conclusions

There is a strong case for the development of fluoride ion batteries as a higher-energy density storage technology. The replacement of lithium with fluorine not only avoids obstacles (*i.e.* lithium metal) that hinder the development of next-generation LIBs, but also opens new avenues for drastically reducing the cost of energy storage through the use of earth abundant materials. From a techno-economic standpoint, a number of conversion-type FIB chemistries could easily exceed the energy density of an NMC811-lithium cell at a fraction of the cost. The $Cu–CaF_2$ cell is certainly the most attractive in terms of both energy density and cost; however, the higher voltage of this redox pair also presents a greater challenge for electrolyte development. Ultimately the success of FIBs hinges on the development of chemically and electrochemically stable liquid fluoride electrolytes with good SEI forming ability. While solid fluoride electrolytes currently facilitate many lab-scale cycling experiments, they are impractical to implement, and their high densities would decrease the specific energy of FIBs to a non-competitive level. The projected energy density of current intercalation-type FIBs is too low to be economically viable, even if state of the art materials are employed. Unless high capacity electrodes are discovered, intercalation-type FIBs would need to provide a major advantage (*e.g.* cost, cycle life) over conventional LIBs in order to be successful. Ultimately, the realization of high energy FIBs will depend on the result of future research. Such efforts should focus primarily on the development of safe liquid electrolytes, the understanding of the conversion mechanism, and the engineering of electrode and cell construction.

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