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## **Fluoride Ion Batteries – Past, Present, and Future**

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## **Abstract**

Fluoride-Ion Batteries (FIBs) have been recently proposed as a post-lithium-ion battery system. This review article presents recent progress of the synthesis and application aspects of the cathode, electrolytes, and anode materials for fluoride-ion batteries. In this respect, improvements in solid-state electrolytes for FIBs as well as liquid electrolytes will be discussed. Furthermore, the achievements regarding the development of cathode and anode materials will be considered. With the improvements made, the field is currently attracting a steady increase of interest, and we will discuss the potentials of this technology together with necessary future milestones to be achieved in order to develop FIBs for future energy storage.

**Keywords:** fluoride ion batteries, liquid electrolytes, solid-state electrolytes, ionic conductivity, intercalation-based cathode materials, conversion-based cathode materials, intercalation-based anode materials, conversion-based anode materials

## 1 Introduction

Modern life is highly dependent on energy storage devices. From portable electronics to electric vehicles (EVs), electric trains and airplanes, which may or may not become the future of mobility, all benefit from modern rechargeable energy storage technologies. Moreover, energy storage devices are required to store the energy generated from solar, wind, and tidal sources. Therefore, the demand for efficient and sustainable systems is increasing drastically.

Lithium-ion batteries (LIBs) turned out to be the best choice for portable electronics and are the main contenders for emerging EVs due to their high energy density, specific power, and cycling stability.<sup>1</sup> However, the large adoption of LIBs for these applications led to the depletion of lithium resources, which are low in abundance and geometrically constrained. Not only the abundance of lithium, but also the abundance of other key elements (e. g., Co) used in LIBs is critical. Even if Cobalt-free and high energy nickel-rich materials have been developed recently, the safety and thermal stability of such Ni-rich materials is a concern. Though this might not necessarily impact small scale technologies, these aspects will become of tremendous importance for large scale storage. In this context, it is important to consider alternative energy storage systems, which work based on shuttling ions other than  $\text{Li}^+$ .

In response, several alternative battery technologies were proposed and investigated. Alternative rechargeable battery systems, which perform based on shuttling of ions other than  $\text{Li}^+$ , have been investigated so far, including sodium-ion batteries (NIBs)<sup>2,3</sup>, magnesium-ion batteries<sup>3,4</sup>, calcium-ion batteries<sup>5</sup> and aluminum-ion batteries.<sup>6</sup> For these systems, the shuttling ions possess low standard reduction potentials (i. e., the ionic species can be reduced, but not oxidized), which are similar to lithium. In contrast, chloride-ion batteries<sup>7</sup> and fluoride-ion batteries (FIBs)<sup>8</sup> rely on shuttling ions with potentials at the other side of electromotive force (EMF) series (i. e., those species can be oxidized, but not be reduced). Figure 1 compares the gravimetric and volumetric energy densities (these energy densities are theoretical and on the material basis), from which it can be seen that FIBs would be in principle favourable to LIBs in this respect. The volumetric energy density of FIBs is particularly high which is of interest for EV and large scale storage applications. Besides the high energy density, batteries based on a fluoride shuttle offer some further unique features. Fluorine is the most electronegative element in the periodic table and consequently, the fluoride ion is a very redox-stable anion, which enables a wide electrochemical potential window. Further, FIBs can be made in an all-solid-state modification. Therefore, safety issues as found in the Li-ion battery technology due to metal dendrite growth become irrelevant for FIBs. Additionally, fluoride containing materials are globally more abundant as compared to lithium reserves.<sup>9</sup>

In this review, the advancement of FIBs and their components, including solid and liquid electrolytes and electrode materials from the early stages to the most recent studies are presented. Further, recent advances in FIB chemistry and systems, fluoride-ion-transport mechanisms, and fundamental properties of solid-state/liquid fluoride electrolytes for FIBs will be discussed. Given the importance of next-generation energy storage applications and perspectives, challenges, opportunities, and potentials for future research directions will be highlighted.

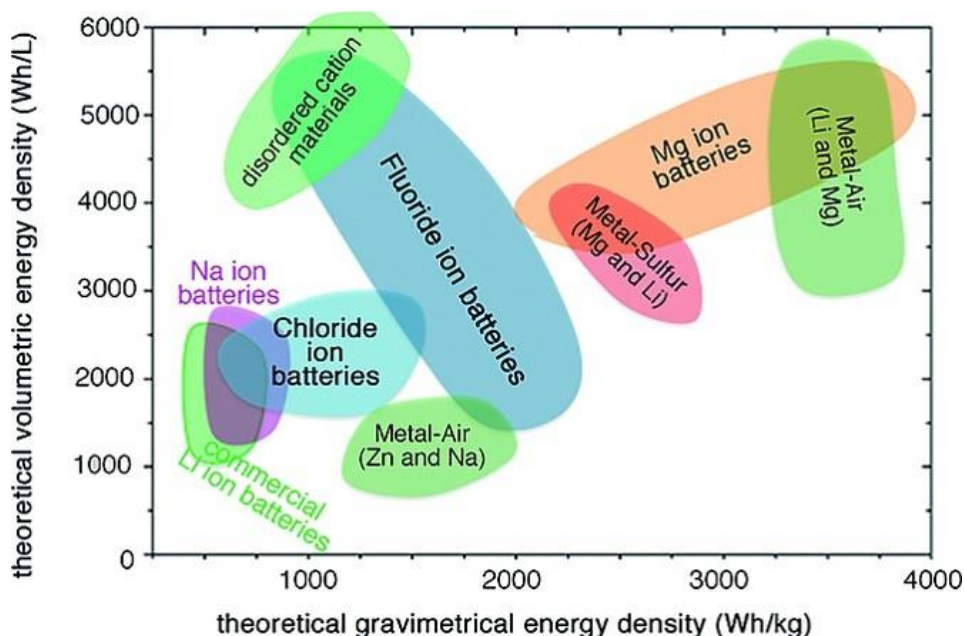


Figure 1. Overview of secondary ion batteries for future battery technologies.<sup>10</sup> The charge transfer ions can be distinguished into cationic shuttles (such as  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{Mg}^{2+}$ ), and anionic shuttles (such as  $\text{Cl}^-$  and  $\text{F}^-$ ), providing a wide variety of different battery types. From bottom left to upper right: commercial Li-ion batteries (LIBs), sodium-ion batteries (SIBs), chloride-ion batteries (CIBs), Zn-air batteries, Na-air batteries, fluoride-ion batteries (FIBs), metal-sulphur batteries (with Mg and Li as the anode), magnesium-ion batteries, and top right for lithium-air and magnesium-air batteries. Reproduced from ref.<sup>10</sup> with permission<sup>i</sup>.

## 2 Early Work on Fluoride-ion Batteries

FIBs have been first proposed in the 1970s, and at the time they were mostly referred to as fluoride galvanic cells. Baukal<sup>11</sup> claimed that  $\text{CaF}_2$  could serve as a solid electrolyte in an all-solid-state FIB in a high temperature range of 400 – 500 °C. However, no experimental results on the operation of a full cell were reported. Kennedy and Miles<sup>12</sup> showed the first experimental observation of an electrochemical cell based on shuttling of fluoride ions, using KF-doped  $\beta\text{-PbF}_2$  as a solid electrolyte in  $\text{CuF}_2|\beta\text{-PbF}_2|\text{Pb}$  and  $\text{AgF}|\beta\text{-PbF}_2|\text{Pb}$  electrochemical cells. Although the observed starting potentials (0.70 V and 1.3 V for  $\text{CuF}_2|\text{Pb}$  and  $\text{AgF}|\text{Pb}$  cells, respectively) were close to the open cell voltage (OCV) ( $\text{Pb} + \text{CuF}_2 \rightarrow \text{PbF}_2 + \text{Cu}$ ;  $\Delta E^\circ = 0.72$  V;  $\text{Pb} + 2 \text{AgF} \rightarrow \text{PbF}_2 + 2 \text{Ag}$ ;  $\Delta E^\circ = 1.32$  V), poor capacities were observed. This has been related to strong polarizations which have been suggested to be a result of the formation of the  $\alpha\text{-PbO}_2$  phase in the anode material leading to a poor ionic conductivity of the cell. They also reported on discharging of a thin-film cell made up of  $\text{CuF}_2$ , Pb, and  $\text{PbF}_2$  cathode, anode, and electrolyte materials, respectively.<sup>13</sup> Results revealed that discharge capacities as large as ~ 40% of the theoretical capacity of  $\text{CuF}_2$  (528  $\text{mAh g}^{-1}$ ) could be obtained, though further charging of the cell could not be achieved.

In 1976 Schoonman<sup>14</sup> reported on building a  $\text{Pb}|\beta\text{-PbF}_2:\text{AgF}|\text{BiO}_{0.09}\text{F}_{2.82}|\text{Bi}$  cell, which was fabricated by spring-loading the disks of Pb and Bi, which were painted with powders of  $\beta\text{-PbF}_2$ , AgF or  $\text{BiO}_{0.09}\text{F}_{2.82}$ , respectively, from dispersions in ethyl acetate. The observed discharge potential (0.330 – 0.335 V) was close to the OCV (0.37 V), showing that oxyfluorides can

<sup>i</sup> 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

principally be candidates for the electrolyte materials in FIBs. However, no further information about the reversibility of the cell was reported. Following Schoonman's work, in 1978 Danto et al. reported on the reversible cycling of thin-film solid-state galvanic cells with a mean thickness of 0.55  $\mu\text{m}$  made up of Pb as the anode, Bi/BiF<sub>3</sub> as the cathode, and PbF<sub>2</sub> (cubic  $\beta$ -PbF<sub>2</sub>) as the electrolyte.<sup>15</sup> The measurements were performed at room temperature. They reported on a starting discharge potential as high as 353 mV, followed by a flat discharge plateau at around 280 mV for a current density of 40  $\mu\text{A}/\text{cm}^2$ .

Investigations on the electrolytes for fluoride-ion galvanic cells were followed up by Schoonman. In 1979 he reported<sup>16</sup> on the solid solution based electrolyte  $\text{M}_{1-x-y}\text{U}_x\text{Ce}_y\text{F}_{2+2x+y}$  (M = Ca, Sr, Ba) for thin-film galvanic cells with BiF<sub>3</sub> and Ca as cathode and anode materials, respectively.

In 1981, the term of solid-state fluoride-ion battery had been used for the first time by Schoonman and Wolfert.<sup>17, 18</sup> In these publications, they reported on improvements in ionic conductivity of CaF<sub>2</sub> anodes by doping with La or Yb (for instance Ca<sub>1-x</sub>La<sub>x</sub> to form the corresponding fluoride of Ca<sub>1-x</sub>La<sub>x</sub>F<sub>2+x</sub>).

### 3 Re-introduction of Rechargeable Fluoride-Ion Batteries: A Proof of Principle

Between 1981 and 2011, not much has been done in the field of FIBs. However, in 2011 FIBs attracted some attention again, when Reddy and Fichtner reported on reversible all-solid-state conversion-based FIBs using metal/metal fluoride electrode materials along with Ba doped LaF<sub>3</sub> (La<sub>1-x</sub>Ba<sub>x</sub>F<sub>3-x</sub>) as a solid-state electrolyte. They were able to operate FIBs at elevated temperatures (~ 150 – 200 °C) with comparatively short life cycling performances. This study opened new horizons for battery technologies by introducing new battery chemistry. The cathodic and anodic reactions during discharging of a cell can be written as follows (also see Figure 2):

At cathode side:  $x\text{e}^- + \text{MF}_x \rightarrow \text{M} + x\text{F}^-$ ;

At anode side:  $x\text{F}^- + \text{M}' \rightarrow \text{M}'\text{F}_x + x\text{e}^-$ .

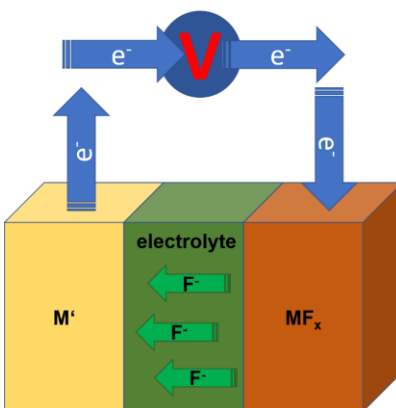


Figure 2. A schematic illustration of the metal/metal fluoride conversion based FIB proposed by Reddy and Fichtner<sup>8</sup>.

In that study, it was shown that doping of Ba into tysonite-type LaF<sub>3</sub> results in a significant increase (roughly two orders of magnitude) of the ionic conductivity compared to the undoped state, and

that this increase is necessary to obtain current densities reasonable high to achieve C-rates of  $\sim C/25$  to  $C/50$  to make testing at lab scale feasible. Results suggest that  $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$ , which was produced by mechanochemical milling of  $\text{BaF}_2$  and  $\text{LaF}_3$ , has the highest ionic conductivity among all other  $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$  ( $0 \leq x \leq 0.15$ ) compounds (about  $2.8 \times 10^{-4}$  S/cm at  $160^\circ\text{C}$ )<sup>8</sup> with a good electrochemical stability due to the low electrochemical potentials of  $\text{Ba}^{2+}$  and  $\text{La}^{3+}$ . Various metal fluorides including  $\text{CuF}_2$ ,  $\text{BiF}_3$ ,  $\text{SnF}_2$ , and  $\text{KBiF}_4$  were tested as cathode materials against Ce metal to make all-solid-state FIBs in their charged states. Since most of the electrode materials (e.g.,  $\text{BiF}_3$  and  $\text{CuF}_2$ ) suffered from low ionic and electronic conductivity, they were mixed with the solid electrolyte and carbon for better electrochemical performance, and their conversion between the metal and metal fluoride state could be well confirmed with diffraction studies.

After this proof-of-concept paper, research on FIBs has gained increased attention over the last years, with studies appearing in the field of electrolyte (solid and liquid), electrode (conversion and intercalation), and cell design development. In the following, we will summarize the attempts that have been made together with the key findings.

#### 4 Solid Electrolytes for FIBs

Solid-state batteries have certain advantages compared to corresponding liquid electrolytes batteries, particularly concerning safety. To operate solid-state batteries, solid electrolytes (SEs) are required. Interestingly, fluoride ions show a high mobility in the solid-state. Though the ionic size of  $\text{F}^-$  is large ( $\sim 1.33 \text{ \AA}$ )<sup>19</sup> it shows significant high mobility in solids, due to its monovalency and high charge density. Indeed, there are several solid fluoride conducting electrolytes that show significantly high conductivities at RT. For example,  $\text{PbSnF}_4$  has an ionic conductivity of  $1 \times 10^{-3}$  S/cm at RT, which is well beyond the garnet based solid electrolytes for LIBs.<sup>20</sup> Apart from a high ionic conductivity, the electrolyte in a battery should fulfill certain criteria: Suitable electrolyte candidates must exhibit high ionic conductivity with a negligible electronic conductivity to avoid self-discharging of the cell.<sup>21</sup> They should possess a high electrochemical stability window, i.e., they must be electrochemically stable within the operating voltage of the cell. The electrolyte must be chemically compatible with the electrode materials (cathode and anode) to ensure fast ion transport of the charged species across the interfaces, which does not only require stability towards redox reactions, but also an ion exchange within acid-base type of reactions. Further, SEs should possess certain mechanical properties, e.g., sufficient flexibility and softness, required for the fabrication of a solid state battery.

Most of the studies on fluoride-conducting electrolytes were carried out on single crystals. Some of the fluoride conducting single crystals show a high ionic conductivity. For example, barium doped lanthanum fluoride shows a fluoride ion conductivity in the order of  $10^{-4}$  S/cm, which is suitable to operate solid-state batteries with respect to the commonly encountered aspect ratios and charging/discharging rates. However, single crystals are expensive, difficult to grow and they are difficult to be integrated into an all-solid-state battery configuration. Thus, polycrystalline solid electrolytes are a more appropriate and realistic option. However, ionic transport in polycrystalline materials is significantly different due to the presence of grain boundaries (GB) and an increase in surface to volume ratio. Thus, ionic transport mechanisms are more complex in nanocrystalline samples due to the surface charge regions.

In solid electrolytes, ionic transport generally depends on the structural framework, the intrinsic mobility of conducting ions and their thermal activation, the concentration of intrinsic and/or extrinsic defects, and further on the crystal field impact of the mobile ions. Ion diffusion mechanisms are mostly based on Schottky and anti-Frenkel point defects, comprising the vacancy mechanism, interstitial mechanism, and interstitial–substitutional exchange mechanism.<sup>22</sup> However, some materials with fluorite or tysonite type structure can achieve high ionic conductivities without a high defect concentration.<sup>23, 24</sup> Geometric frustration from size mismatch of the cation lattice was recently also discussed to play an important role for the conductivity of multinary fluorides with fluorite type structure.<sup>25</sup> In general, only a few stable fluorides exhibit significant ionic conductivity, while being insulators for the transport of electrons due to a wide bandgap.

Different fluoride conducting solid-electrolytes were reported in the literature. These solid electrolytes can be broadly categorized into two classes of compounds: tysonite-type ( $\text{LaF}_3$  prototype) and fluorite-type ( $\text{CaF}_2$  prototype). A considerable number of possibilities to achieve improved solid-state electrolyte/separator approaches for FIBs have been developed and will be addressed in this chapter. Different materials are discussed and grouped according to their structure type (e. g., rare-earth fluorides (tysonite-type structure) doped with alkaline-earth or alkaline-earth fluorides (fluorite-type structure) doped with rare-earth fluorides). This discussion also comprises further design aspects, such as the creation of surface defects by vapor pressure treatment ( $\text{CaF}_2$ -Hum), grain boundary activation using Lewis acids ( $\text{BF}_3$ ), or critical geometry frustrations due to crystal deformations by multiple-phase systems.

#### 4.1 Design of all-solid-state cells used for FIBs

FIBs have often been made in an all-solid-state modification. For all-solid-state FIBs, the most popular strategy is to make bulk pellets by cold (uniaxial) pressing of the powder precursors (cathode/electrolyte/anode). For this approach, it is important to note that most of the used active electrode materials for FIBs suffer from low electronic and ionic conductivity. For the powder-based electrodes, a suitable electron conduction pathway needs to be provided, which is commonly achieved by additives such as carbon black, graphite, nanotubes, metal surplus, etc.<sup>23, 26</sup> The ionic conductivity is increased by the introduction of electrolyte materials. In most studies, the FIB active electrode materials are mixed with the electrolyte material and carbon black or nanotubes to form composite electrode materials.<sup>8, 23, 26-28</sup> Ball milling is by far the most used technique to prepare the composite electrodes and solid-state electrolytes. For the assembly of all-solid-state battery cells, Swagelok-type electrochemical cells are very common.<sup>8, 23, 29</sup> Figure 3 represents a typical Swagelok-type cell. Due to the low ionic conductivity of the most solid-state electrolytes for FIBs, the electrochemical cell setup should be heated often up to 150 – 200 °C, and the cell-design helps to protect the Teflon-based sealings from plastic deformation or heat-induced degradation. Recently thin-film strategies have also been introduced to make FIB cells. For instance, Zhang et al. reported<sup>30</sup> on implementing a thin-film of Ba doped  $\text{LaF}_3$  electrolyte by spin coating technique on a  $\text{CaF}_2$  or  $\text{MgF}_2$  anode composite as a substrate. Further, coin cell based systems were proposed by Grenier et al., where a high temperature stable epoxy resin can be used for sealing, facilitating improved longer-term operability.<sup>31</sup>



There also exist some reports<sup>32, 33</sup> on FIBs, which are based on liquid electrolytes, which can then be investigated in the most common Swagelok-type setup. For instance, Davis et al. reported<sup>33</sup> on standard three electrode systems for FIBs based on a liquid electrolyte. In this study, copper nanoparticles or Cu@LaF<sub>3</sub> core-shell nanoparticles were made into a paste with polyvinylidene fluoride (PVDF) to prepare the working electrode platinum, and silver wires were used as the counter electrode and reference electrode, respectively. Moreover, bismuth, lead, cerium and calcium thin strip foils were used as the working electrode.

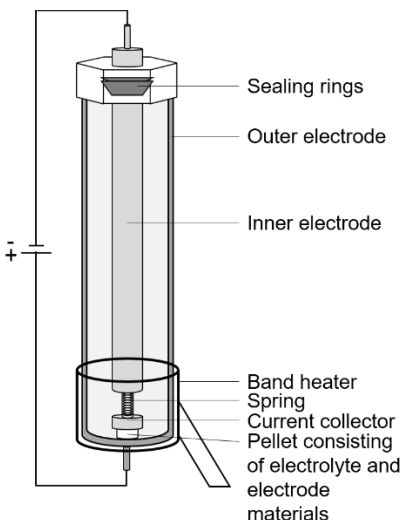


Figure 3. A schematic of a high-temperature cell used for the electrochemical measurements conducted on all-solid-state FIBs. The figure has been reproduced from ref. <sup>34</sup>.

#### 4.2 Ionic conductivity of rare-earth fluorides with tysonite-type structure

Tysonite-type RE<sub>1-x</sub>M<sub>x</sub>F<sub>3-x</sub> (RE = La, Ce, Sm, and M = Ba, Ca, Sr) fluorides are promising as SEs for FIBs as they show high ionic conductivities and large electrochemical stability window.<sup>8, 35</sup> In an undoped state, rare-earth fluorides show insufficient conductivities even for lab-scale operation. To improve the ionic conductivity in solid-state electrolytes defects are introduced into the crystal structure by increasing the concentration of mobile ionic species via aliovalent doping. It was shown that the doping of LaF<sub>3</sub> by BaF<sub>2</sub> enables the creation of fluoride vacancies.<sup>36</sup> These F<sup>-</sup> vacancies promote a higher ionic mobility within the fluoride sublattice, leading to an increase of the fluoride conductivity by two orders of magnitude as compared to the stoichiometric compound.<sup>37</sup> Thus, the conduction mechanism in tysonite-type structures relies on a purely vacancy-type mechanism due to Schottky defects.<sup>22, 38, 39</sup> Reddy and Fichtner used Ba-doped La<sub>1-x</sub>Ba<sub>x</sub>F<sub>3-x</sub> (0 ≤ x ≤ 0.15) (LBF) as the SEs in FIBs in their initial studies (Figure 4a). They found a maximum conductivity for La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub>. Further, LBF prepared by high energy ball milling method can be improved via sintering at high temperature.<sup>8, 39, 40</sup> The ionic conductivities of compacted, unsintered La<sub>0.90</sub>Ba<sub>0.10</sub>F<sub>2.90</sub> (1.6 × 10<sup>-4</sup> S·cm<sup>-1</sup> at 160 °C) can be significantly improved by a further sintering step at 800 °C for 2 h to 10<sup>-5</sup> S·cm<sup>-1</sup> at room temperature (Figure 4b). This observation within tysonite-type LBF fluoride ion conductors is explained by the differences in the grain boundary structure, which can result in a partial blocking of the migration pathways, and has been observed for various anion conducting compounds.<sup>41</sup> Thus, sintering treatments are viable methods to increase the ionic conductivity at the cost of the ease of cell fabrication. It is also worth

acknowledging that the grain boundary influence can be compensated without increasing the grain size: In the case of a co-precipitated electrolyte, a slight increase of conductivity was attributed to reduced amounts of impurities during the synthesis process as compared to mechanical milling.<sup>42</sup>

In 2017, Chable et al. investigated the ionic conductivity of  $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$  (LBF) synthesized by various methods, among them high-temperature solid-state reactions under inert atmosphere.<sup>43</sup> It was found (see Figure 4c) that the ionic conductivity at room temperature for the Ba-doped samples ( $\approx 6 \times 10^{-5}$  vs.  $10^{-4}$   $\text{S}\cdot\text{cm}^{-1}$  at RT for  $\text{La}_{0.93}\text{Ba}_{0.07}\text{F}_{2.93}$ ) approaches the limit of the single crystalline state of pure  $\text{LaF}_3$ .<sup>44</sup> The observed conductivity was two orders of magnitude higher than observed earlier on cold-pressed pellets, with activation energies between 0.2 and 0.4 eV.<sup>43</sup> Still, compositional dependence is maintained, with the maximum conductivity at room temperature for a composition close to  $x=0.05 - 0.07$  (see Figure 4d).<sup>43</sup> In addition, the compacted  $\text{La}_{0.95}\text{Ba}_{0.05}\text{F}_{2.95}$  samples were tested and compared to powders that underwent the process at 900 °C with different combinations of cold uniaxial pressing and cold uniaxial plus isostatic pressing. From these experiments, the authors conclude that rare earth fluorides should be treated by a sintering process before or after the ball-milling to improve the ionic conductivity.

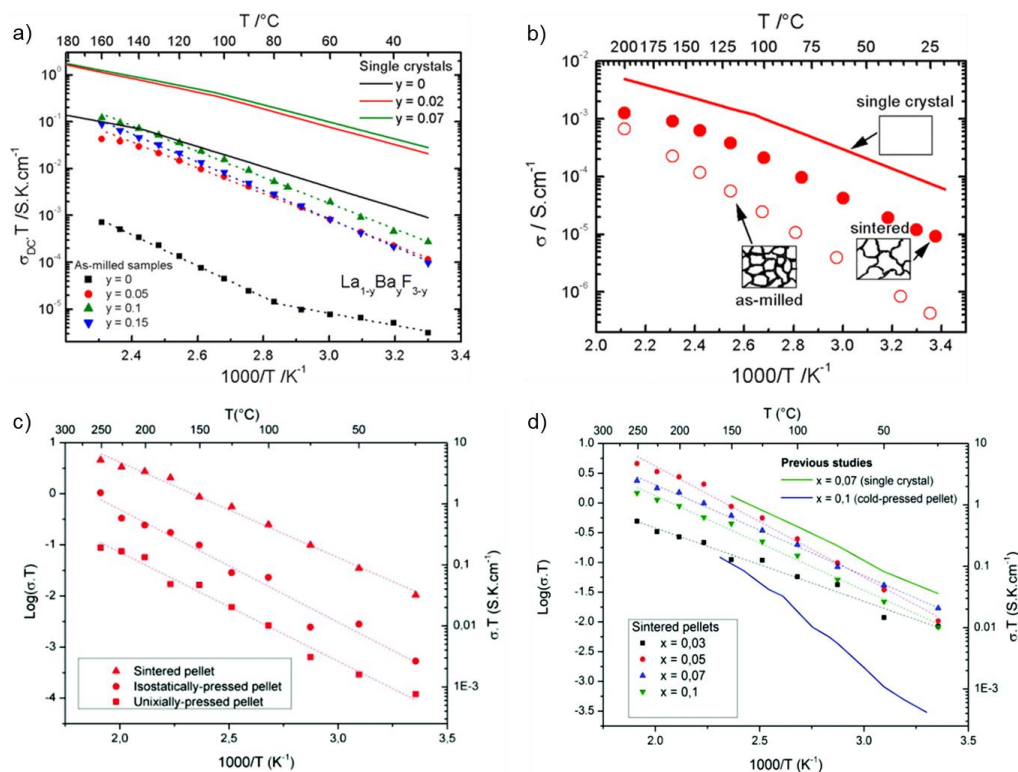


Figure 4. (a) and (b) Arrhenius plots of the ionic conductivities of  $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$ . Parts (a) and (b) are reproduced from ref.<sup>36</sup> with permission<sup>ii</sup>. (c) and (d)  $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$  ( $x=0.03, 0.05, 0.07, 0.1$ ) samples after cold-uniaxial pressing, cold isostatic pressing, and sintering of the pellets. Parts (c) and (d) are reproduced from ref.<sup>45</sup> (an original RSC publication). In part (d) the blue and green lines from the single crystal of  $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$  ( $x=0.07, 0.1$ ). Different pressing method applied for the  $\text{La}_{0.95}\text{Ba}_{0.05}\text{F}_{2.95}$  sample for the ionic conductivity for cold-uniaxial pressed pellet, a cold-uniaxial, cold-isostatic pressed pellet and a sintered pellet are reported.

Zhang et al.<sup>46</sup> investigated the ionic conductivity of  $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$  ( $0 \leq x \leq 0.15$ ) thin-films synthesized by a sol-gel assisted spin coating method based on mixtures of metal trifluoroacetate salts. They observed that the conductivity of the thin films could be significantly improved by increasing the sintering temperature and time. The conductivity value of the film was  $1.6 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ , a significant improvement in comparison to porous films<sup>35, 46</sup>, and an optimized thermal treatment condition was determined to be at  $450 \text{ }^\circ\text{C}$  for 4h. When compared to the bulk-type electrolyte, the overall conductance of the film was improved by a factor of  $\sim 65$ . The thin film morphology is of special importance, since the overall resistance was significantly reduced due to the low thickness of the thin films. A comparison shows that the conductance of a bulk type electrolyte at  $170 \text{ }^\circ\text{C}$  is similar to that of a thin-film electrolyte at  $80 \text{ }^\circ\text{C}$ , which could help to build all-solid-state fluoride ion batteries working at more viable conditions.<sup>35</sup>

Not only lanthanum-based fluorides can be used as a solid electrolyte. Dieudonné et al. investigated the ionic conductivity of  $\text{SrF}_2$  doped  $\text{CeF}_3$  ( $\text{Ce}_{1-x}\text{Sr}_x\text{F}_{3-x}$ ), synthesized by solid-state reaction at  $900 \text{ }^\circ\text{C}$  for 24h.<sup>47</sup> A high ionic conductivity of  $3 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$  was obtained for  $\text{Ce}_{0.975}\text{Sr}_{0.025}\text{F}_{2.975}$  at RT, which is close to the conductivity of a corresponding single crystal and better than previously reported fluoride compounds.<sup>47</sup> At room temperature, the ionic conductivity observed in various fluorides adopting the fluorite-type structure reached a maximum value at  $x$

<sup>ii</sup> Copyright (2014) American Chemical Society

= 0.025 with one of the lowest activation energies of 0.31 eV. The  $\text{Sr}^{2+}$  substitution for  $\text{Ce}^{3+}$  ions in this network associated with the creation of anionic vacancies modifies the fluoride ion mobility drastically. A maximum  $\text{F}^-$  conductivity for  $x = 0.025$  corresponds to the largest difference in bond distances between the F2 (4d site) and F3 (2a site) ion to the surrounding Sr/Ce ion and the highest buckling of the  $\text{RE}_{1-x}\text{AE}_x\text{F}_{3-x}$  layers, which appears to result in low activation energy in addition (Figure 5a). They further concluded that in tysonite-type  $\text{RE}_{1-x}\text{AE}_x\text{F}_{3-x}$  (RE = rare-earth and AE = alkaline-earth) the difference in the ionic sizes of the host element (RE) and the dopant (AE) plays a vital role for achieving high ionic conductivity: When the ionic sizes are comparable, the conductivity reaches to the maximum at a low substitution rate due to network relaxation of the  $\text{RE}_{1-x}\text{AE}_x\text{F}_{3-x}$  slabs in competition with the chemical pressure, which leads to a strong variation of sheet thickness.

Further detailed investigations have been carried out on tysonite-type Ca-doped  $\text{SmF}_3$ ,  $\text{Sm}_{1-x}\text{Ca}_x\text{F}_{3-x}$  ( $0.05 \leq x \leq 0.17$ ) again by Dieudonné *et al.*<sup>48</sup> The SEs were prepared using solid-state synthesis followed by sintering at 1000 °C. Analysis of the XRD data showed a reduction in the unit cell volume with an increasing amount of Ca dopant. This volume reduction of the cell has been attributed to the creation of anionic vacancies that decrease cationic coordination, and could further be explained by increased cation repulsion due to the loss of shielding. The best ionic conductivity as high as  $1.0 \times 10^{-4} \text{ S cm}^{-1}$  was obtained for  $\text{Sm}_{0.95}\text{Ca}_{0.05}\text{F}_{2.95}$  at RT. In  $\text{Sm}_{1-x}\text{Ca}_x\text{F}_{3-x}$ , the difference (+0.05 Å) of ionic radii for nine-fold coordination between  $\text{Ca}^{2+}$  (1.18 Å) and  $\text{Sm}^{3+}$  (1.13 Å) leads to a predominant influence of the network relaxation with a decrease of cell volume related to segregation of anionic vacancies. Both the thickness of  $[\text{Sm}_{1-x}\text{Ca}_x\text{F}_{3-x}]$  layers ( $\approx 1.20 \text{ Å}$ ) and the ionic conductivity are maximal for a composition of  $x = 0.05$ . This observation was explained by a modification of the fluorine environments and segregation of the vacancies around the calcium by increasing the  $x$  values. In contrast, for  $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$ , the large difference of cationic radii (+0.25 Å) introduces a significant chemical pressure and microstrain together with a significant increase in the cell volume. Comparison with  $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$ ,  $\text{Ce}_{1-x}\text{Sr}_x\text{F}_{3-x}$ , and  $\text{La}_{1-x}\text{Sr}_x\text{F}_{3-x}$ , shows that the higher the buckling effect of  $\text{RE}_{1-x}\text{AE}_x\text{F}_{3-x}$ , which affects the distortion of the F1 site, the higher the ionic conductivity. This explains the evolution with  $x$  of the RT ionic conductivity of different solid electrolytes (Figure 5b), which hardly correlates with simple volume changes only. They suggested that a moderate ionic radii difference serves to optimize the ionic conductivity: Y-Ca, Eu-Ca and Gd-Ca could fulfill this requirement. However, there are no experimental results on the suggested systems so far. Most recently,  $\text{Sm}_{1-x}\text{Ca}_x\text{F}_{3-x}$  solid electrolytes were prepared by high-energy planetary ball-milling as an alternative method and studied with NMR by Molaiyan *et al.*<sup>49</sup>, which helped to correlate the ionic conductivity to the detailed structural arrangements and relaxations taking place within this compound.

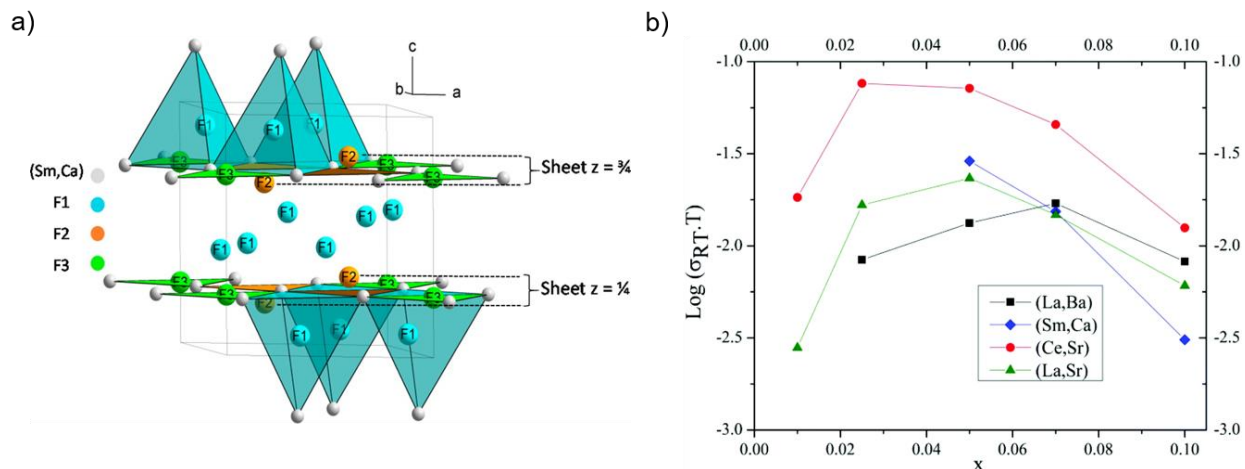


Figure 5. (a) The crystal structure representation of the tysonite-type structure. (b) Impedance plot and complex fits of the  $\text{Sm}_{0.95}\text{Ca}_{0.05}\text{F}_{2.95}$  at room temperature. (a, b: Reproduced from ref. <sup>48</sup> with permission<sup>iii</sup>) (c) Variation of the ionic conductivity vs temperature for  $\text{Ce}_{1-x}\text{Sr}_x\text{F}_{3-x}$  ( $x = 0, 0.01, 0.025, 0.05, 0.07, 0.10$ ). (d) Evolution with  $x$  of the room temperature ionic conductivity of  $\text{RE}_{1-x}\text{AE}_x\text{F}_{3-x}$  ( $\text{RE} = \text{La}, \text{Ce}, \text{Sm}$ ;  $\text{AE} = \text{Ba}, \text{Sr}, \text{Ca}$ ). (c, d: Reproduced from ref. <sup>47</sup> (an original RSC publication)).

### 4.3 Alkaline-Earth Fluorides with Fluorite-type Structure

#### 4.3.1 $\text{AE}_{1-x}\text{RE}_x\text{F}_{2+x}$ Compounds

Solid-state fluorite-type electrolyte systems are found at the alkaline earth richer end of the series with a general chemical formula of  $\text{AE}_{1-x}\text{M}_x\text{F}_{2+x}$  ( $\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}$ ;  $\text{M} = \text{RE}$ ), and also for a binary mixture between two alkaline earth fluorides. Most of these fluoride-conducting electrolytes have been synthesized by a high energy ball-milling method, e. g., for the formation of the series  $\text{Ba}_x\text{Ca}_{1-x}\text{F}_2$ .<sup>38, 50, 51</sup> An ionic conductivity of  $1.16 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$  for  $\text{Ba}_x\text{Ca}_{1-x}\text{F}_2$  at 413 K was reported,<sup>51</sup> which is lower than for the tysonite type systems. Apart from isovalent doping, also aliovalent series of  $\text{BaF}_2$  doped with  $\text{LaF}_3$  were taken into consideration.<sup>41, 52</sup>  $\text{Ba}_{0.6}\text{La}_{0.4}\text{F}_{2.4}$  shows the highest conductivity among the  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  solid solutions (Figure 6a). Ball-milling of coarse-grained  $\text{BaF}_2$  yields a nano-crystalline sample, which shows a conductivity of almost two orders of magnitudes higher as compared to non-milled material. The ionic conductivity can be further improved by further addition of calcium<sup>53</sup>, by which a non-equilibrium phase is obtained. In contrast, the increase of conductivity was explained here from the increase of disorder and strain introduced when the cations are of different sizes.<sup>54, 55</sup>

Düvel et al.<sup>56</sup> reported a detailed NMR study of  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  ( $0 \leq x \leq 1$ ) compositions synthesized by a ball milling method at ambient temperature. The  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  compounds crystallized in the fluorite-type structure from  $0 \leq x \leq 0.775$ , with phase mixtures beyond this range and tysonite-type structures for  $x > 0.85$ . From  $x \approx 0.70$  to  $x \approx 0.85$ , the NMR spectra indicate structural aspects of both crystal structures, though there is still a decrease of the chemical shift of the fluoride ions on the F2/3 sites with increasing  $\text{BaF}_2$  content (Figure 6b). The authors showed that changes of chemical shifts associated with the structural transition can be correlated with the transitions in the bond distances  $d(\text{M}-\text{F})$ . Further, there seems to be an intrinsic change of bonding to the F1

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ion in the range from  $x = 0.55$  to  $x = 1$  making the fluoride site in the fluorite-type structure more similar to the F1 ion in the tysonite-type structure (Figure 6b).

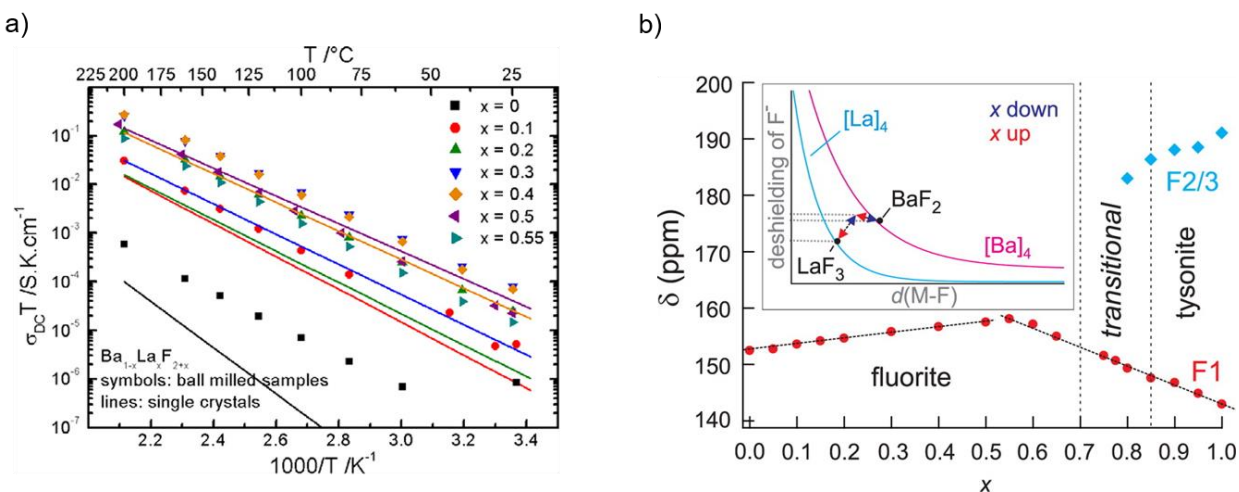


Figure 6. (a) Ionic conductivity for  $Ba_{1-x}La_xF_{2+x}$  ( $0 \leq x \leq 0.55$ ) solid solutions in comparison with ball-milled and single crystals of  $Ba_{1-x}La_xF_{2+x}$ . The best performance of ionic conductivity was reported for the sample  $x = 0.40$ . (Reproduced from ref. with permission<sup>iv</sup>). (b) <sup>19</sup>F Nuclear Magnetic Resonance (NMR) studies reported for the chemical shift changes of  $Ba_{1-x}La_xF_{2+x}$  with  $x$ . The red points indicate that the fluoride ions on the anion site in the fluorite-type structure and F1 sites in the tysonite structure appear to show a transition between each other. The NMR lines of  $Ba_{1-x}La_xF_{2+x}$  ( $x \geq 0.80$ ) corresponding to F1 on F2 and F3 sites with the tysonite-type structure as blue rhombs. (Reproduced from ref. <sup>56</sup> with permission<sup>v</sup>).

#### 4.3.2 Tetragonal BaSnF<sub>4</sub> and Interlayer Electrolytes (La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub>/BaSnF<sub>4</sub>)

SnF<sub>2</sub> containing compounds like MSnF<sub>4</sub> (M = Pb, Ba, Ca, Sr) can show ordering between the M and the Sn site cations in an otherwise fluorite-type structural setting. Such ordering can lead to a high conductivity even at room temperature.<sup>57-59</sup> The high ionic conductivity in SnF<sub>2</sub> containing compounds results from the presence of the 5s<sup>2</sup> lone pair on the Sn<sup>2+</sup> atom, which requires space (the lone pair is known to require as much space as a fluoride ion itself<sup>60, 61</sup>). This strongly distorts the fluoride sublattice in combination with the ordering of cations. The crystal structure of tetragonal BaSnF<sub>4</sub> (Figure 7a) can be derived from the cubic fluorite-type structure by ordering of the Sn and Ba cations in Sn-Sn, Ba-Sn, and Ba-Ba layers, along the  $c$ -direction of the tetragonal cell. This ordering results in three different fluoride sites, termed as F1 ( $3/4, 1/4, 0.19$ ), F2 ( $3/4, 1/4, 1/2$ ), and F3 ( $1/4, 1/4, 0.68$ ), and they reside in Sn-Sn, Ba-Sn, and Ba-Ba layers, respectively. The stereoactive lone pair induces a repulsive interaction between the lone pair electron and negatively charged fluoride ion, which leads to a depletion of the fluoride ions in the Sn-Sn and Sn-Ba layers of the BaSnF<sub>4</sub> crystal structure. Hence, the fluoride ions between Sn-Sn and Sn-Ba layers become mobile since the lone pair is polarizable and can reorient on movement, thus becoming involved in the conduction process. The ionic conductivity of BaSnF<sub>4</sub> is in the order of  $1 \times 10^{-4}$  S cm<sup>-1</sup> at RT.<sup>62</sup> Interestingly, its cold-pressed powders also exhibit high conductivity at RT, which makes it suitable candidates as solid electrolytes for fluoride ion batteries. Recently,

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Mohammad et al. have demonstrated rechargeable RT-FIBs utilizing  $\text{BaSnF}_4$  as a solid electrolyte<sup>63</sup>, where the electrode materials were chosen to take into account the limited electrochemical stability of the electrolyte. The ionic conductivity of  $3.5 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$  at RT for the electrolyte (see Figure 7b) can be sufficient for RT fluoride-ion battery applications. The cells were based on  $\text{BaSnF}_4$  as the electrolyte,  $\text{BiF}_3$  as the cathode, and Zn or Sn as the anode. The electrochemical results on Zn/ $\text{BaSnF}_4$ / $\text{BiF}_3$  cell are displayed in Figure 7c,d. The cyclic voltammetry profile of the cell features a cathodic and anodic peak confirming the reduction of  $\text{BiF}_3$  and oxidation of Bi, respectively (Figure 7c). The cell exhibits a first discharge and charge capacity of 56 and 43  $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ , respectively (Figure 7d). At subsequent discharging and charging, the capacity is found to increase slightly, which can be explained by increased electrochemical accessibility of the Zn anode.

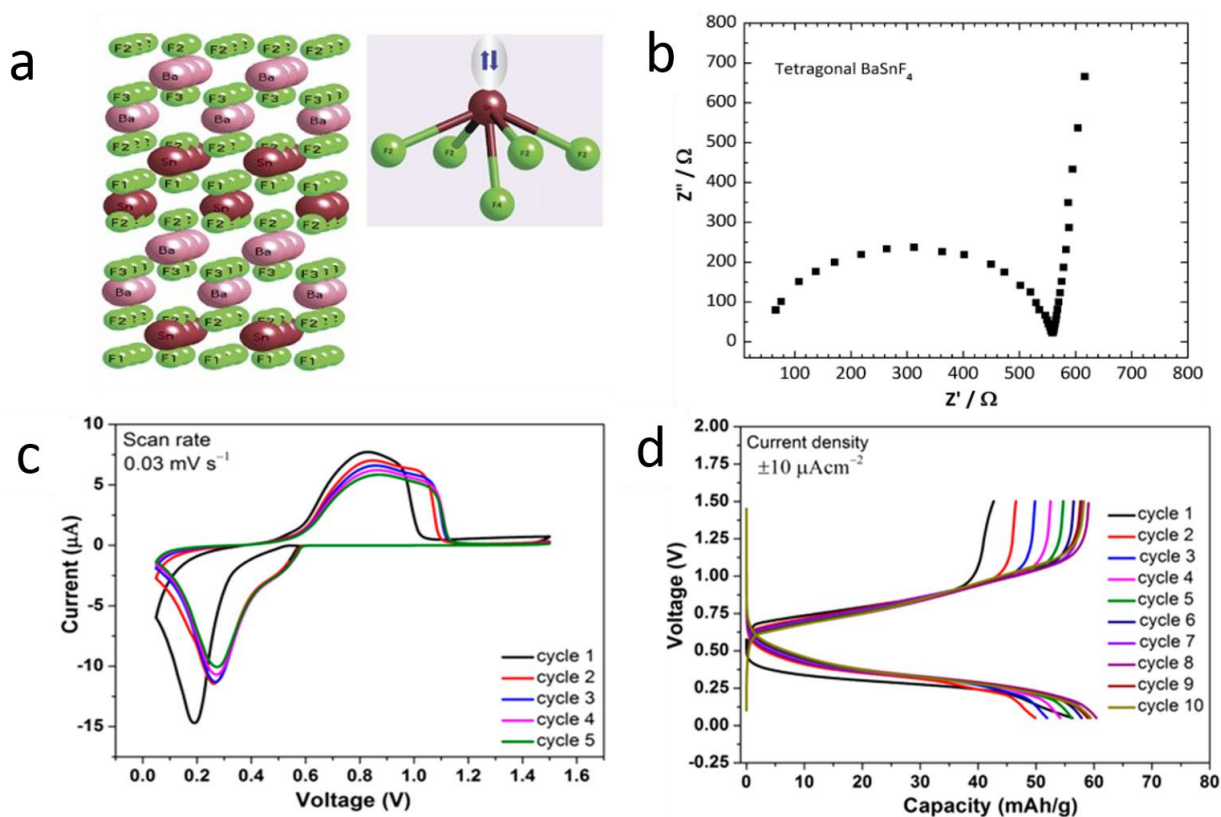


Figure 7. (a) Layered structure of tetragonal  $\text{BaSnF}_4$  displaying different cation layers and fluoride ions with Sn coordination environment of  $\text{BaSnF}_4$  showing lone pairs on  $\text{Sn}^{2+}$  pointing in the c-direction (figure a is reproduced from ref.<sup>57</sup> with permission<sup>vi</sup>); (b) Nyquist plot of tetragonal  $\text{BaSnF}_4$  obtained at 25 °C, (c) Cyclic voltammogram profiles of Zn/ $\text{BaSnF}_4$ / $\text{BiF}_3$  cells obtained at 25 °C (reproduced from ref.<sup>63</sup> with permission<sup>vii</sup>).

Currently, the low electrochemical stability of  $\text{BaSnF}_4$  limits the use of highly reductive anode materials or highly oxidizing cathode materials, due to the fact that  $\text{Sn}^{2+}$  can both be oxidized or reduced at intermediate potentials already. To build high potential FIBs, high electropositive metals (Ce, Mg, La) should be used as anodes, which are compatible with electrolytes like tysonite-type  $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$ .  $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$  electrolytes with low RT conductivity ( $4 \times 10^{-7} \text{ Scm}^{-1}$ ). To

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overcome these limitations of the low electrolyte stability and low ionic conductivity, Mohammad et al. developed an interlayer electrolyte concept to build high-potential RT-FIBs.<sup>64</sup> The use of low conductive  $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$  succeeded in maintaining the high total conductivity of the electrolyte, and in physically isolating the less stable and highly conductive electrolyte ( $\text{BaSnF}_4$ ) from the electropositive anode. Figure 8a shows the cross-sectional SEM image obtained for an inter-layer electrolyte pellet (20 mg of  $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$  and 120 mg of  $\text{BaSnF}_4$ ), which highlights that both layers stick uniformly to each other without intermixing. Impedance analyses are used to investigate the conductivity and interface stability of the interlayer electrolyte as shown in Figure 8b and c. The figure compares the Nyquist plots of interlayer electrolyte with different relative thicknesses of  $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$  obtained at 25 °C, and show a strong difference on to which extent grain, grain boundary and electrode responses are expressed, though the resistance appears to scale linearly with the thicknesses of the different layers. The authors conclude that with improved coating methods, it might be possible to achieve high ionic conductivities similar to that of  $\text{BaSnF}_4$  while extending its electrochemical stability window. Electrochemical performance testing of the interlayer electrolyte was conducted using  $\text{BiF}_3$  as a cathode and Ce as an anode. The charge-discharge profiles of the interlayer electrolyte-based cell is displayed in Figure 8d. The cell shows an open circuit voltage of 2.6 V at room temperature. It delivered a first discharge capacity of 27  $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$  at an average voltage of 1.4 V. During the second and subsequent cycles, the discharge and charge profiles show high average voltage plateau. In the following cycling, quick capacity fading was observed, resulting in 3  $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$  after five cycles Figure 8d).



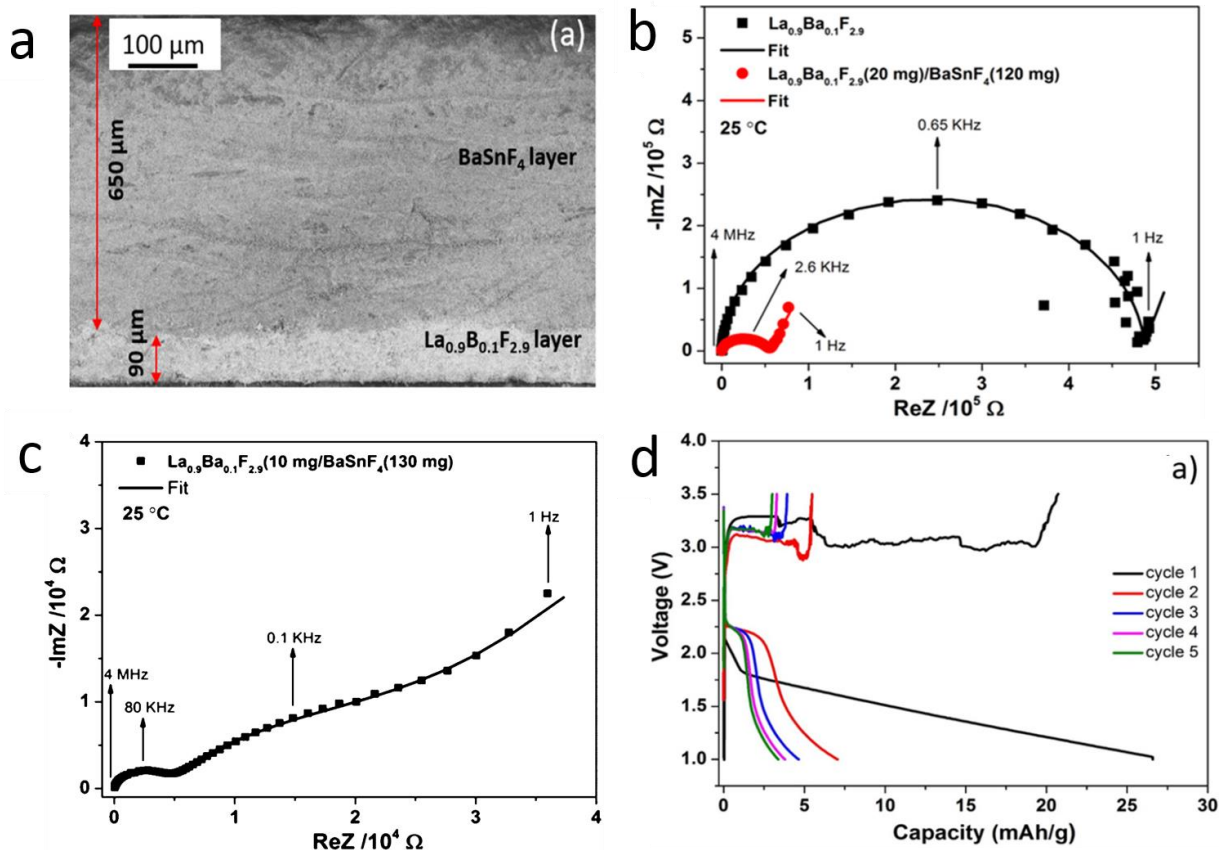


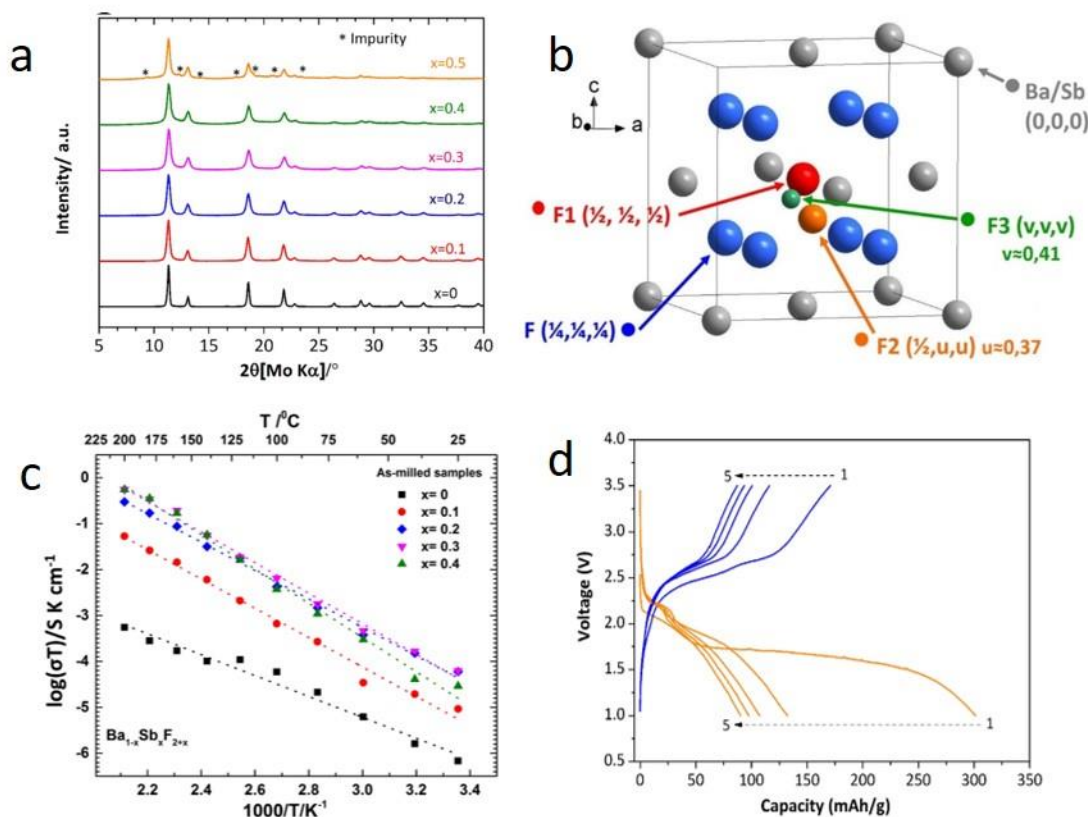
Figure 8. (a) Cross-sectional SEM image of  $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$  (20 mg)/ $\text{BaSnF}_4$  (120 mg) pellet, (b) Nyquist plots (symbols) and the corresponding fit (lines) of  $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$  (20 mg)/ $\text{BaSnF}_4$  (120 mg) and  $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$  obtained at 25 °C, (c) Nyquist plots (symbols) and corresponding fit (line) for  $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$  (10 mg)/ $\text{BaSnF}_4$  (130 mg) electrolyte obtained at 25 °C, (d). Voltage-composition profiles of  $\text{Ce}/\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}/\text{BaSnF}_4/\text{BiF}_3$  cell obtained at 25 °C with a current density of  $\pm 10 \mu\text{A}\cdot\text{cm}^{-2}$  (reproduced from ref.<sup>64</sup> with permission<sup>viii</sup>).

#### 4.4 Nano-crystalline Fluorite-type $\text{Ba}_{1-x}\text{Sb}_x\text{F}_{2+x}$ ( $0 \leq x \leq 0.4$ )

Besides  $\text{Sn}^{2+}$ , there are other cations containing lone pairs of electrons such as  $\text{Sb}^{3+}$ ,  $\text{Bi}^{3+}$ , and  $\text{Tl}^+$ , which might have a similar effect on the ionic conductivity. In an attempt to mimic the idea of the lone pair effect for the ionic conductivity enhancement, Mohammad et al. have recently synthesized  $\text{SbF}_3$ -doped  $\text{BaF}_2$  via ball-milling, assuming that  $ns^2$  configured  $\text{Sb}^{3+}$  might strongly participate to an increase the ionic conductivity of  $\text{BaF}_2$ .<sup>65</sup> The doping of  $\text{SbF}_3$  in the  $\text{BaF}_2$  crystal was limited to  $x < 0.5$ , confirmed by an XRD analysis (displayed in Figure 9a). This means a comparably lower amount of  $\text{SbF}_3$  is sufficient in order to obtain a higher occupancy of the interstitial site. In the crystal structure of  $\text{Ba}_{1-x}\text{Sb}_x\text{F}_{2+x}$  ( $0 \leq x \leq 0.4$ ), Ba and Sb (represented in grey) form an *fcc* array in which fluoride ions (represented in blue) occupy all tetrahedral sites (Figure 9b). During doping, extra fluoride ions due to the higher valancy of the dopant  $\text{Sb}^{3+}$  occupy the interstitial positions such as F2 and F3. The interstitial site F1 ( $1/2, 1/2, 1/2$ ) is being occupied at a lower concentration of the dopant, whereas the related sites with off-centre shifts, F2 ( $1/2, 0.37, 0.37$ ) and F3 ( $1/2, 0.41, 0.41$ ), are occupied at higher concentrations of the dopant. The ion conductivity of the solid solution was increased with increasing dopant concentration, indicating

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that these off-centre shifts can be considered crucial for obtaining functional ceramics. Further, the temperature dependent evolution of the ionic conductivity of  $Ba_{1-x}Sb_xF_{2+x}$  ( $0 \leq x \leq 0.4$ ) was investigated (Figure 9c). By this, it was found that it can reach twice the conductivity of the isostructural  $Ba_{0.7}La_{0.3}F_{2.3}$  ( $1.55 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$  at  $160 \text{ }^\circ\text{C}$ ), meaning that the additional increment of conductivity might result most plausibly from the stereochemical impact of the  $ns^2$  cation. The material can also be used within a full battery against Ce anodes. Figure 9d shows the electrochemical profiles of the cell for the first five cycles, showing high electrochemical accessibility of the active electrode material of  $\sim 66\%$  of the theoretical specific capacity of  $SbF_3$  ( $450 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ ). However, rapid capacity fading was observed for prolonged cycling. This considerable capacity fading is probably due to large volume and structural changes in the electrode materials and not necessarily linked to the electrolyte itself.



**Figure 9** (a) XRD patterns of  $Ba_{1-x}Sb_xF_{2+x}$  ( $0 \leq x \leq 0.5$ ) compounds, (b) Representative structural view of  $Ba_{1-x}Sb_xF_{2+x}$  (doped fluorite), (c) Arrhenius plots of the ionic conductivity of  $Ba_{1-x}Sb_xF_{2+x}$  ( $0 \leq x \leq 0.4$ ) compounds (symbols) and their fits (dotted lines). (d) Voltage-capacity profiles of  $Ba_{0.7}Sb_{0.3}F_{2.3}/La_{0.9}Ba_{0.1}F_{2.9}/Ce$  cell obtained at  $150 \text{ }^\circ\text{C}$  with a current density of  $10 \mu\text{A}\cdot\text{cm}^{-2}$  (figures are reproduced from ref. <sup>65</sup> with permission <sup>ix</sup>).

#### 4.5 PbSnF<sub>4</sub> based Solid Fluoride Electrolytes

In-depth investigations and improvements of the ionic conductivities of solid-state electrolytes are emerging areas of FIBs. So far,  $Pb_xSn_{2-x}F_4$  (Figure 10a) is one the best superionic fluoride conductors.<sup>66</sup>  $^{19}\text{F}$  MAS NMR results show that mechanochemical synthesis drives the system mainly into the cubic  $\beta$ -phase, with the introduction of surface defects, which exchange with the

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nanoparticle core.<sup>66, 67</sup> This interaction also promotes conductivities within the crystallite and at the particle boundaries, with ion mobility at the macroscopic material level, which is in slight contrast to what is reported in previous studies.<sup>68-70</sup> Low activation energies result in high ionic conductivities at room temperature (Figure 10b), with values close to single crystals and better than what was found previously for fluorite type materials.<sup>71, 72</sup> The solid electrolytes of  $Pb_xSn_{2-x}F_4$  were also prepared by high-energy planetary ball-milling.<sup>73</sup> Such electrolytes showed a fluoride ion conductivity equal to that of the electrolytes synthesized using a melting method with an activation energy of 0.30 eV for  $x = 1.1$ .

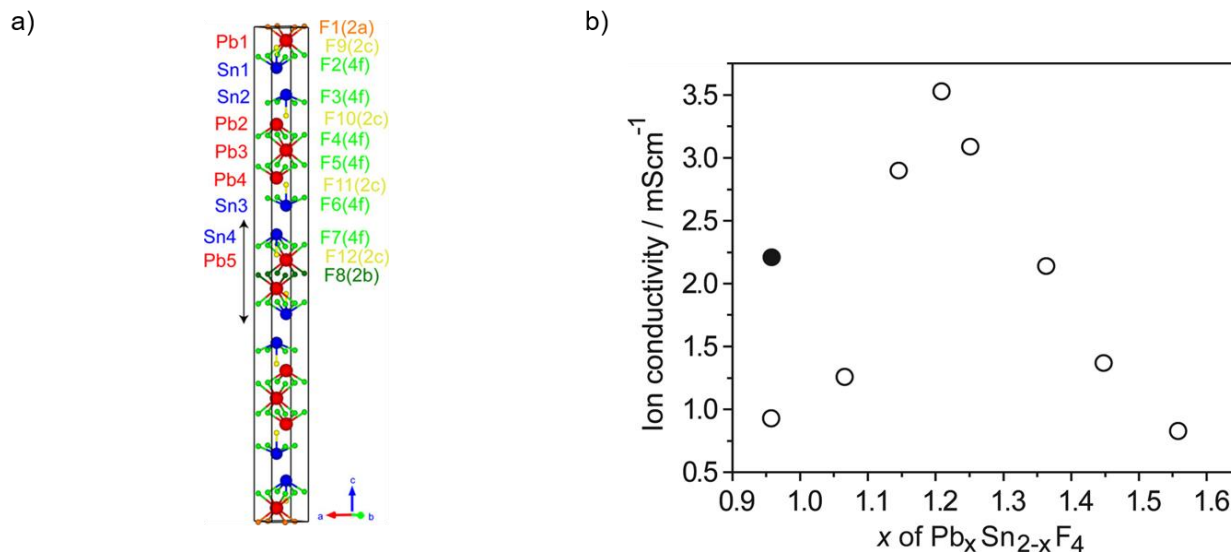


Figure 10. (a) Packing of  $\beta^+$ - $PbSnF_4$  in the unit cell. Blue and red balls are Sn and Pb, respectively. (b) Dependence of the conductivity at room temperature on the Pb/Sn molar ratio in the  $Pb_xSn_{2-x}F_4$  pressed-powder samples ( $x = 0.96$ – $1.56$ ) annealed at 400 °C (open circle) and 200 °C (filled circle) (figures are reproduced from ref.<sup>74</sup> with permission\*).

#### 4.6 $CaF_2$ based Solid Electrolytes for FIBs

$CaF_2$  would be a cheap electrolyte material with a high electrochemical stability; however, pure  $CaF_2$  is a bad ionic conductor, due to the hard nature of  $Ca^{2+}$  ion.<sup>75</sup> Yuria Saito et al. reported that an ionic conductivity enhancement of the  $CaF_2$  could be achieved using Lewis acids<sup>76</sup>, but not via the creation of grain conductivity on doping. The effect of the addition of a Lewis acid, e. g.,  $SbF_5$  or  $BF_3$ , on the fluoride ion conductivity in  $CaF_2$  indicated a surface activation of the particles. The conductivity enhancement mechanism is based on the adsorption of Lewis acids, which attract fluoride ions out of the  $CaF_2$  boundary regions to create vacancies at the  $CaF_2/SbF_5$  or  $CaF_2/BF_3$  interfaces, giving rise to a strong increase of the ionic conductivity. The conductivity results based on  $CaF_2$  thin films also confirmed the presence of space-charge regions as a consequence of the attractive forces of the adsorbed Lewis acid.<sup>76</sup>

Molaiyan et al. have recently reported that the surface activation and conductivity enhancement of calcium fluoride synthesized via ball milling is possible.<sup>77</sup> The pure  $CaF_2$  powder was exposed to salt water with a relative humidity (RH) of 88%, and ball-milled subsequently. The reported ionic conductivity of synthesized humidified  $CaF_2$  electrolyte was around  $1.9 \times 10^{-5} S\cdot cm^{-1}$  at room

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temperature. The reported values are several orders of magnitude higher than pure and ball-milled  $\text{CaF}_2$  ( $2 \times 10^{-7}$  to  $1.6 \times 10^{-11} \text{ S}\cdot\text{cm}^{-1}$ ).<sup>78</sup> The reported activation energy of the humidified  $\text{CaF}_2$  was around 0.35 eV, which was related to the surface formation of interstitial fluoride sites with suggested formation energies of around 0.25 eV,<sup>79, 80</sup> making the material applicable in fluoride ion batteries.<sup>81</sup> The ionic conductivity increases with higher temperature up to a certain critical temperature, after which the decomposition of the defect structure is promoted and the conductivity decreases. From this study, it can be concluded that crystal surface defects strongly influence overall bulk conductivities<sup>82, 83</sup> and can provide an alternative route as compared to bulk modifications<sup>84, 85</sup>.

#### **4.7 Synthesis of Solid Electrolytes: Ball-Milling Method and other methods**

Solid-state reactions generally occur at higher temperatures and often lead to powder morphologies that are unfavorable for battery cell fabrication. In favorable cases, reactions can be carried out merely by grinding the reagents via mechanochemical synthesis<sup>86</sup>, and this method has been widely studied for the preparation of multinary fluorides.<sup>41, 51, 56, 70, 87-90</sup> On the lab-scale level, such synthesis will be done with a high-energy milling method. The crystalline reagents are being impacted with the milling balls at high kinetic energies, which causes high impact energies and can reduce the crystalline regions down to nanometer size with the introduction of crystal defects also.<sup>41</sup> Thus, mechanochemical synthesis may become an essential method for the synthesis of new nanomaterials and nanocomposite materials, as it is a relatively cheap and energy-efficient. In addition, further advantages of mechanochemical synthesis comprise a more reliable, easy operation to ensure reproducibility and large scale synthesis. As a disadvantage, one must acknowledge that due to high-speed rotation of the vial usually for long hours, contamination might be introduced to the system. This can be even more severe for fluoride-based materials, which can be reactive towards many milling vials (e.g., silica or alumina based materials).

As discussed in the previous section, post-ball-milling treatments such as high-temperature sintering can often be required to reach the highest ionic conductivities, where the increase of conductivity must be balanced against particle growth, which can be unfavorable for cell fabrication. The ionic conductivity is highly dependent on the microstructure of the polycrystalline material, as conduction properties are different within the grain boundaries and in bulk.<sup>91</sup> In polycrystalline solid electrolytes, especially when milled to the nanoscale, the conduction properties can be radically different from their single-crystalline counterparts. This is due to the fact that high amounts of grain boundaries must be surpassed and since such powders are often richer in defects.<sup>92</sup> From a microscopic viewpoint, properties are different for the bulk, which generally presents the same conduction properties as a single crystal, and for the surface, where many defects are present at the grain boundaries.<sup>47</sup> While the conduction is limited by the migration of the ionic species in the grain boundaries, if the powder processed by uniaxial pressing, the sintered samples are normally dominated by bulk conduction.<sup>93</sup>

Apart from ball-milling, only a few reports exist which emphasize on the preparation of nano-crystalline materials via other approaches. Since most electrolytes are based on alkaline earth or lanthanide metals, precipitation routes are feasible for the fabrication of nano-crystalline defect rich powders. This is based on the low solubility of these fluorides, even in an aqueous solution.

Bhatia et al.<sup>42</sup> found that this fabrication method can give similar properties as the ball-milling procedure. Due to the similar solubility of  $\text{LaF}_3$  and  $\text{BaF}_2$ , this method can be even used for the preparation of mixed crystals of higher complexity, such as  $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$ . Further, up-scaling of powder production could also be considered easier for wet-chemical approaches in contrast to milling based reaction routes.

#### **4.8 Temperature-dependence of Fluoride conducting Materials – A comparison**

From the early days until now, the detailed understanding of structural and conductivity features of inorganic fluorides has opened the path for the development of many solid fluoride electrolytes with improved ionic conductivity and their use in lab-scale batteries in various electrochemical studies. In a nutshell, the doping of pure fluoride electrolytes with aliovalent fluorides (e.g.,  $\text{BaF}_2$ -doped  $\text{LaF}_3$ ,  $\text{KF}$ -doped  $\beta\text{-PbF}_2$  or  $\text{BiF}_3$ -doped  $\beta\text{-PbF}_2$ ) leads to an increase in the ionic conductivity of the doped material due to the creation of fluoride point defects most often. Defects present in the crystal structure provide fast diffusion pathways for fluoride ions and result in the conductivity enhancement required to obtain reasonable charging times. An overview of ionic conductivities reported previously for a variety of materials is given in Table 1.

**Table 1.** Summary of synthesis methods for different Solid-state fluoride electrolytes. RT refers to room temperature.

Solid-state Fluoride electrolyte	Ionic conduct: $\sigma$ (S-cm <sup>-1</sup> )	Synthesis Method	Reference
La <sub>0.95</sub> Ba <sub>0.05</sub> F <sub>2.95</sub>	4.50 × 10 <sup>-6</sup> (RT)	Annealing + high energy ball-milling + sintering	65
La <sub>0.95</sub> Ba <sub>0.05</sub> F <sub>2.95</sub>	1.26 × 10 <sup>-4</sup> (60°C)	Co-precipitation method	42
La <sub>0.95</sub> Ba <sub>0.05</sub> F <sub>2.95</sub> @PEO	5.75 × 10 <sup>-4</sup> (90°C)	Co-precipitation method	94
La <sub>0.90</sub> Ba <sub>0.10</sub> F <sub>2.90</sub>	2.75 × 10 <sup>-6</sup> (RT)	High energy ball-milling + sintering	43, 65
La <sub>0.90</sub> Ba <sub>0.10</sub> F <sub>2.90</sub>	1.20 × 10 <sup>-6</sup> (RT)	High energy ball-milling + sintering	95
La <sub>0.90</sub> Ba <sub>0.10</sub> F <sub>2.90</sub>	4 × 10 <sup>-7</sup> (RT)	High energy ball milling	64
La <sub>0.90</sub> Ba <sub>0.10</sub> F <sub>2.90</sub>	2.36 × 10 <sup>-4</sup> (200°C)	High energy ball milling	96
La <sub>0.95</sub> Ca <sub>0.05</sub> F <sub>2.95</sub>	2.0 × 10 <sup>-6</sup> (RT)	Single crystal	97
La <sub>0.8</sub> Ca <sub>0.2</sub> F <sub>2.8</sub>	1.0 × 10 <sup>-6</sup> (RT)	Ball-milling + annealing	54
La <sub>0.95</sub> Sr <sub>0.05</sub> F <sub>2.95</sub>	3.0 × 10 <sup>-5</sup> (RT)	Single crystal + high energy ball-milling + sintering	98
Sm <sub>0.95</sub> Ca <sub>0.05</sub> F <sub>2.95</sub>	1.0 × 10 <sup>-4</sup> (RT)	Sintering + solid state synthesis + mixing	48
Sm <sub>0.95</sub> Ca <sub>0.05</sub> F <sub>2.95</sub>	2.8 × 10 <sup>-5</sup> (RT)	High energy ball-milling	49
Ce <sub>0.975</sub> Sr <sub>0.025</sub> F <sub>2.975</sub>	3.0 × 10 <sup>-4</sup> (RT)	Sintering + solid state synthesis + mixing	47, 99
Ce <sub>0.95</sub> Ca <sub>0.05</sub> F <sub>2.95</sub> Ce <sub>0.95</sub> Sr <sub>0.05</sub> F <sub>2.95</sub> Ce <sub>0.95</sub> Ba <sub>0.05</sub> F <sub>2.95</sub>	~1 × 10 <sup>-4</sup> (100°C)	High energy ball-milling + Annealing	99
Ba <sub>0.6</sub> La <sub>0.4</sub> F <sub>2.4</sub>	5.0 × 10 <sup>-6</sup> (RT)	Annealing + solid- state synthesis + mixing	38,51
Ba <sub>0.6</sub> La <sub>0.4</sub> F <sub>2.4</sub>	1.9 × 10 <sup>-4</sup> (160 °C)	High energy ball-milling + Annealing	100
Ba <sub>0.7</sub> Sb <sub>0.3</sub> F <sub>2.3</sub>	4.4 × 10 <sup>-4</sup> (160 °C)	High energy ball milling	65
Ba <sub>0.6</sub> Sb <sub>0.4</sub> F <sub>2.4</sub>	3.9 × 10 <sup>-4</sup> (160 °C)	High energy ball milling	65
H-CaF <sub>2</sub>	1.88 × 10 <sup>-5</sup> (RT)	Humidified + ball-milling	77,101
β-PbSnF <sub>4</sub>	1.20 × 10 <sup>-3</sup> (RT)	Sintering + mixing	84,71
Pb <sub>0.55</sub> Sn <sub>0.45</sub> F <sub>2</sub>	2.53 × 10 <sup>-3</sup> (RT)	High energy ball-milling	73
Pb <sub>x</sub> Sn <sub>2-x</sub> F <sub>4</sub> (x = 1.21)	3.53 × 10 <sup>-3</sup> (RT)	High energy ball-milling + Annealing	74

## 5 Liquid and Polymer-based Electrolytes for Fluoride-Ion Batteries

Fluoride ion batteries have been studied mostly using solid electrolytes, mainly leading to operating temperatures of 150 °C or even above. However, more and more reports have been demonstrating the fluoride ion battery concept using a liquid electrolyte in very recent years.

The preparation of liquid electrolytes for FIBs is significantly different as compared to LIBs. For Li-ion batteries, liquid electrolytes typically consist of simple lithium salts such as  $\text{LiPF}_6$  or  $\text{LiClO}_4$  in organic solvents. However, this cannot be mimicked for fluoride ion batteries because simple fluoride salts such as  $\text{KF}$  and  $\text{CsF}$  are almost insoluble in organic aprotic solvents. So far, two strategies were adopted to prepare fluoride ion conducting liquid electrolytes: The first one is by dissolving fluoride salts in organic solvents, and the second one is by mixing organic fluorides into ionic liquids (ILs). For the latter, only one patent has claimed the fabrication of a FIB cell using an IL based electrolyte, which was composed of tetramethylammonium fluoride (TMAF) and 1-methyl-1-propylpiperidinium bis(tri-fluoromethanesulfonyl)imide (MPPTFSI).<sup>102</sup> The assembled cell showed an electrochemical performance for two cycles with an initial capacity of 103 mAh  $\text{g}^{-1}$ , but the structural data of electrodes before and after discharge was not reported. To date, several patents have been reported, claiming the feasibility of FIBs containing a liquid electrolyte.<sup>103-106</sup> Thus, several attempts have been made in order to develop liquid fluoride conducting electrolytes and test them in battery setups. In an initial report, Gschwind et al. prepared a non-inorganic electrolyte based on ammonium bifluoride-doped polyethylene glycol (PEG) matrix.<sup>32, 107</sup> Their objective was to form a hydrogen-bonded PEG matrix to trap difluorides for fluoride conduction. Figure 11a shows a schematic drawing of the possible hydrogen bonding, which could be expected in a polymer electrolyte containing bifluoride ions ( $\text{FHF}^-$ ). The electrolyte showed an ionic conductivity of 2.1  $\text{mS cm}^{-1}$  at room temperature for an optimized concentration of 0.02 M. The assembled cell with  $\text{BiF}_3$  as the cathode, Mg as the anode and this polymer electrolyte showed a good first discharge capacity. However, it fails to deliver any reversible capacity (Figure 11b). To find the exact reason of the non-reversibility of the cell, SEM analysis was performed on the Mg electrode before and after discharging, which reveals a snowflake-like formation of  $\text{MgF}_2$  layers on the Mg surface.<sup>107</sup> This is a very poor ionic conductor and acts as a passivation layer for  $\text{F}^-$  diffusion, and can be considered as the main reason for irreversibility. Recently, a new fluoride ion-conducting polymer system consisting of poly(ethylene)oxide (PEO), metal fluoride salts, and anion acceptors has been reported.<sup>108</sup> The polymer electrolyte exhibited the ionic conductivity of  $1 \times 10^{-6} \text{ S cm}^{-1}$  at 303 K, with fluoride transference numbers as large as 0.8. A FIB utilizing a liquid electrolyte for fluoride transport was reported recently by Ogumi et al., where the electrolyte was made from mixing an organic fluoride (1-methyl-1-propylpiperidinium fluoride: MPPF) in an ionic liquid (N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)amide: TMPA/TFSA).<sup>109</sup> The electrolyte shows a conductivity of 2.5  $\text{mS cm}^{-1}$  at room temperature for a concentration of 0.35 M. The electrochemical stability of the electrolyte was investigated by cyclic voltammetry using Pt or Bi as working electrode, and a fluorinated Pb plate as counter and reference electrode (Figure 11c), indicating a small electrochemical stability window of 0.7 V vs  $\text{Pb/Pb}^{2+}$ . The full cell assembly utilizing the electrolyte showed significant charge and discharge capacities for few cycles at low operating voltage (~ 0.2 V) (Figure 11d).

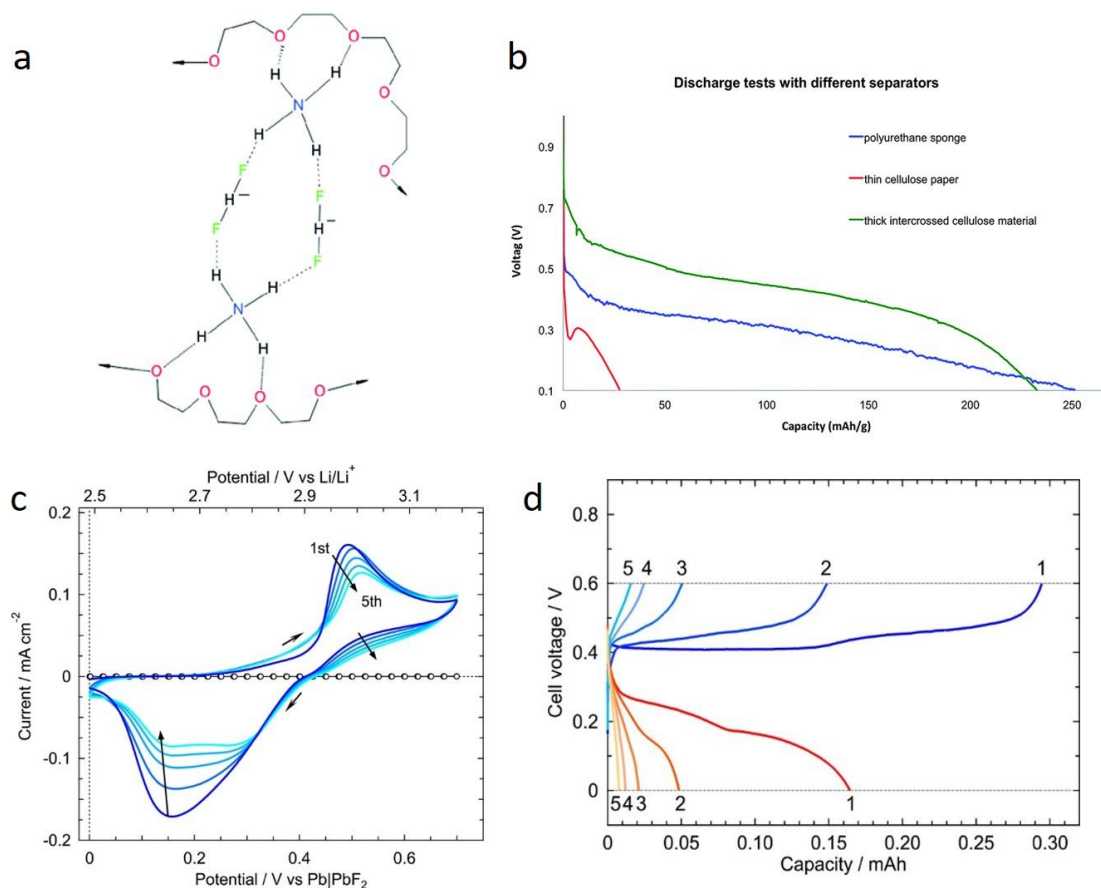


Figure 11 (a) A schematic drawing of possible hydrogen bonds, which could occur in a hydrogen bifluoride-doped PEG matrix (reproduced from ref.<sup>32</sup> (an original RSC publication)), (b) Discharge curves of  $\text{BiF}_3$  against Mg using PEG matrix based electrolyte with three different separators (reproduced from ref.<sup>107</sup> (an original RSC publication)), (c) CVs of the Bi and Pt electrodes in  $\sim 0.07 \text{ mol.dm}^{-3}$  MPPF/TMPA-TFSA at a scan rate of  $1.0 \text{ mV.s}^{-1}$  (Blue lines: Bi. Gray lines with circles: Pt), (d) Cycling test of the bismuth electrode in  $\sim 0.35 \text{ mol dm}^{-3}$  MPPF/TMPA-TFSA at current densities of  $20 \mu\text{A.cm}^{-2}$  (parts b and c are reproduced from ref.<sup>109</sup> with permission<sup>xi</sup>).

Later, the same group has further developed FIBs by introducing a new type of electrolyte synthesized by dissolving a fluoride salt in an organic solvent with the help of an anion acceptor.<sup>110</sup> The idea was to develop an electrolyte that can dissolve and deposit the active material to facilitate the electrochemical reaction of FIBs. The electrolyte solution was prepared by using bis [2-(2-methoxyethoxy) ethyl] ether (tetraglyme:G4) as the solvent containing 0.45 M cesium fluoride ( $\text{CsF}$ ) with addition of  $0.5 \text{ mol L}^{-1}$  of a boron-based ion anion acceptor (fluorobis (2,4,6-trimethylphenyl) borane: FBTMPPhB). The anion acceptor was added mainly to enhance the solubility of  $\text{CsF}$  in the tetraglyme solvent by reducing the cation-anion interaction between  $\text{Cs}^+$  and  $\text{F}^-$ . DFT calculations confirm the capability of FBTMPPhB as anion acceptor to bind fluoride ions. Figure 12a shows the most stable binding site for the fluoride ion at the boron atom. The electrochemical stability of this liquid electrolyte was investigated by cyclic voltammetry (displayed in Figure 12b), where the  $\text{CsF}(0.45)\text{-FBTMPPhB}(0.5)\text{-G4}$  composition shows a stability window between  $-2.2$  to  $-0.3 \text{ V vs. Ag/Ag}^+$ . Furthermore, the performance of this electrolyte was demonstrated in a FIB half cell constituting of  $\text{BiF}_3$  as a working cathode and a Pt mesh as a counter electrode. The cell delivered a first discharge capacity of  $316 \text{ mAh g}^{-1}$  (slightly higher than

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the theoretical capacity, indicating some side reactions), but in the subsequent cycles the capacity faded rapidly and decreased close to zero after 10 cycles. The electrochemical performance of  $\text{PbF}_2$  as an active material has also been investigated within a FIB system with the same liquid electrolyte.<sup>111</sup> In this work, the discharge capacity reduced to almost half only after three cycles, though, the XRD measurements confirm occurrence of the charge/discharge reactions within the second and third cycles.

Later, the effect of two other boron-containing compounds, triphenylboroxine (TPhBX) and triphenylborane (TPhB), as anion acceptors was investigated.<sup>112</sup> The authors concluded that the addition of TPhBX and TPhB can significantly increase the solubility of CsF in G4. Still, a significant capacity fading (from  $\sim 350 \text{ mAh g}^{-1}$  in the first cycle to  $\sim 75 \text{ mAh g}^{-1}$  in the third cycle for CsF-TPhB-G4) can be observed during the cell operation. A similar argument holds true when  $\text{PbF}_2$  is used as the electrode material instead of  $\text{BiF}_3$ .<sup>113</sup> This poor behavior of TPhBX has been related to the dissolution of  $\text{Bi}^{114}$  and  $\text{Pb}^{113}$  ions. It is also shown that the amount of CsF in the solution can influence the cycling stability: The discharge capacity of the system based on the electrolyte with G4 containing saturated CsF and 0.50 M TPhBX can increase the discharge capacity of  $\text{BiF}_3$  in the second and third cycles to almost 100 % as compared to that within the system based on the electrolyte with G4 containing 0.45 M CsF and 0.50 M TPhBX.<sup>114</sup> In the same system, other factors such as microparticulation of the  $\text{BiF}_3$  and adhesion of the conductive material to  $\text{BiF}_3$  by ball milling were investigated later, showing that while reducing the particle size only slightly affects the practical capacity, adhesion of the  $\text{BiF}_3$  to carbon particles can significantly increase the charge/discharge capacities.<sup>115</sup> To further improve the cycling performance, a  $\text{PbF}_2$  electrode was later used by the same research group to build up a FIB cell based on bis[2-(2-methoxyethoxy)ethyl] ether containing cesium fluoride and TPhB as the electrolyte.<sup>116</sup> This resulted in a better capacity retention during the first three cycles ( $\sim 210 \text{ mAh g}^{-1}$  and  $\sim 100 \text{ mAh g}^{-1}$  at the first and third cycles, respectively) as compared to that with  $\text{BiF}_3$  as the electrode material.<sup>117, 118</sup> In another study,<sup>119</sup>  $\text{PbF}_2$  has been investigated using a similar liquid-based electrolyte but with the addition of TPhBX as the anion acceptor. There, the effects of pulverization of  $\text{PbF}_2$  and carbon additive were elaborated and the authors conclude that a mixture of  $\text{PbF}_2$  and carbon, which is pulverized by ball milling, can increase the capacity of the cell.

A liquid fluoride conducting electrolyte with high ionic conductivity and wide electrochemical stability was designed and developed by Davis et al.<sup>33</sup> A highly concentrated ( $>2.2 \text{ M}$ ) electrolyte was synthesized by dissolving dry N,N,N-trimethyl-N-neopentylammonium fluoride (Np1F) in the organic solvent Bis(2,2,2-trifluoroethyl) ether (BTfE) (Figure 12c). They also investigated the solubility of Np1F in several non-aqueous solvents in order to find suitable electrolyte for FIBs.<sup>120</sup> The 0.75 M Np1F/BTfE electrolyte, in particular, displays ionic conductivity of  $7.95 \text{ mS cm}^{-1}$  at room temperature. The electrochemical stability window of 0.75 M Np1F/BTfE electrolyte was determined by linear sweep voltammetry, showing a potential window between 0.7 V (cathodic voltage limit) and 4.8 V (anodic voltage limit) versus  $\text{Li}^+/\text{Li}$  (Figure 12d). However, the electrochemical cycling of various metallic electrodes (such as: Cu, Pb, Bi, Ce and Ca) revealed that there is a considerable amount of metal dissolution into the electrolyte, which leads to poor performances. To avoid the electrolyte breakdown due to direct contact with the metal, a fluoride conductive layer protecting the electrode materials was introduced. The Ce electrode was engineered with a fluorinated solid electrolyte interphase (SEI) layer, whereas Cu particles were encapsulated in a thin layer of  $\text{LaF}_3$  in a core-shell setup, referred to as  $\text{Cu@LaF}_3$ . The fabricated

cell comprised of the modified electrodes and the liquid electrolyte was cycled reversibly at room temperature with a reversible capacity of around  $60 \text{ mAh g}^{-1}$ , which is 8 times less than the theoretical capacity of  $\text{CuF}_2$  ( $528 \text{ mAh g}^{-1}$ ), meaning an incomplete reaction occurred at the electrodes. Another report describes a new electrolyte based on fluorohydrogenate ionic liquid [C2C1im][[FH)2.3F] (C2C1im = 1-ethyl-3-methylimidazolium), with an ionic conductivity as high as  $100 \text{ mS cm}^{-1}$  at  $25 \text{ }^\circ\text{C}$ .<sup>121</sup> Here, the FIB cell with  $\text{CuF}_2$  cathode delivered an excellent first discharge capacity of  $500 \text{ mAh g}^{-1}$ , which is close to the theoretical capacity of  $\text{CuF}_2$ . The reversible capacity reaches to  $475 \text{ mAh g}^{-1}$  during the first cycle, resulting in a Coulombic efficiency of 92 %, which is already higher than the value observed in previous reports. In the following cycles, the performance of the cell degraded gradually; as result, the 10<sup>th</sup> reversal capacity reaches to  $264 \text{ mAh g}^{-1}$ . Thus, one can conclude that realizing full utilization of active material at room temperature is a very challenging task, whose implementation requires the development of other electrolytes.

Apart from using organic solvents to develop liquid electrolytes for FIBs, aqueous solutions have also been considered for the same purpose. For instance, cells based on fluoride and sodium ion (dual) transfer were proposed by Zhang et al.<sup>122</sup> In their study, aqueous sodium fluoride was used as a liquid electrolyte while  $\text{BiF}_3$  and sodium manganese oxides (NMO) were used as the positive and negative electrodes, respectively. The cell delivered a reversible and stable discharge capacity of  $47.3 \text{ mAh g}^{-1}$  after 40 cycles. A NaF salt solution has also been used as a liquid electrolyte to build up a FIB cell by Hou et al.<sup>123</sup> In this study,  $\text{BiF}_3$  has been used as an anode and cycled against a 4-hydroxy-TEMPO cathode, i.e., a persistent radical that is sterically protected by four  $\alpha$ -methyl groups and undergoes one electron oxidation.<sup>123</sup> The electrodes were implemented as a paste (slurry method) on graphite paper and a high-quality anion exchange membrane was used to prevent side effects of insoluble compounds ensuring only fluoride ions are transported during the operation of the cell. Here the results show stable cycling performance at least for 85 cycles with a reversible capacity of around  $90 \text{ mAh g}^{-1}$ . However, a relatively large voltage hysteresis ( $\sim 1.0 \text{ V}$  on average) can be observed.

A summary of the reported liquid electrolytes and their electrochemical properties can be found in Table 2.

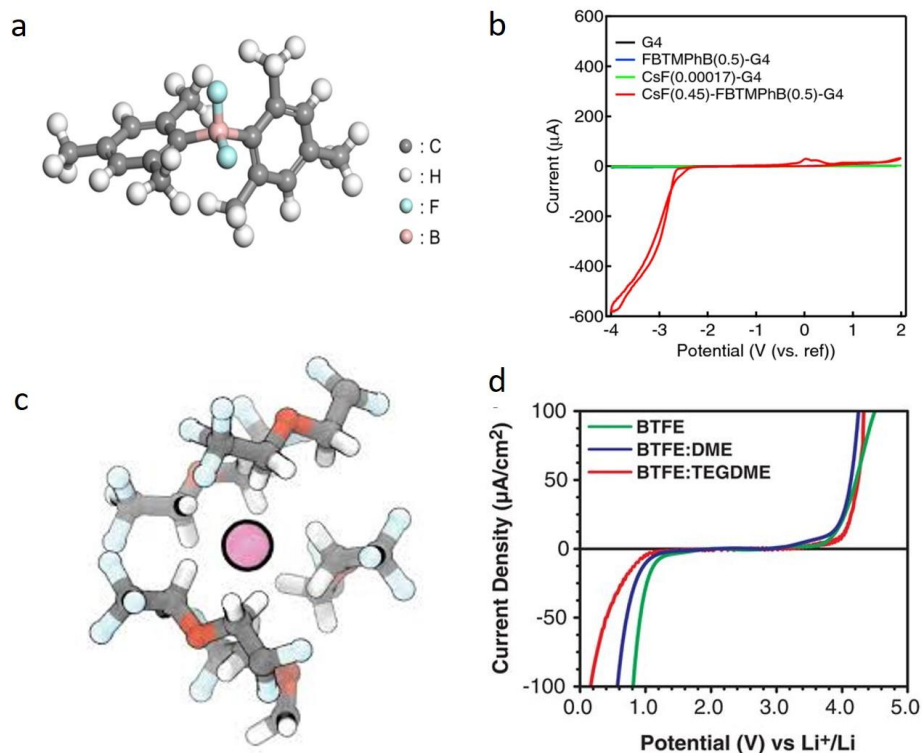


Figure 12. (a) Optimized molecular structure of FBTMPbB-F<sup>-</sup>, (b) Cyclic voltammograms of the CsF(0.45)-FBTMPbB(0.5)-G4 (parts a and b are reproduced from ref.<sup>110</sup> with permission<sup>xii</sup>); (c) Simulated solvation shell of BTFE molecules surrounding F<sup>-</sup> (pink sphere) (d) Linear sweep voltammograms for 0.75 M Np1F in BTFE, collected using a scan rate of 1 mV.s<sup>-1</sup>. (parts c and d are reproduced from ref.<sup>33</sup> with permission<sup>xiii</sup>)

Table 2. Liquid electrolytes for FIBs and their electrochemical property.

Electrolyte	Conductivity (mS cm <sup>-1</sup> )	Stability-Window (V)	Capacity (first discharge)	Ref.
0.1M TMAF/MPPTFSI	1	-3.5 to 4.0 (vs Ag/Ag <sup>+</sup> )	103 mAh g <sup>-1</sup>	102
0.02M FHF <sup>-</sup> doped PEG	2.1	-	250 mAh g <sup>-1</sup>	32
0.35M MPPF/TMPA-TFSA	2.5	0 to 0.7 (vs Pb/PbF <sub>2</sub> )	0.16 mAh	109
CsF(0.45M)-FBTMPbB(0.5M)-G4	-	-2.2 to -0.3 (BiF <sub>3</sub> /Bi)	316 mAh g <sup>-1</sup>	110
0.75 M Np1F/BTFE	7.95	0.7 to 4.8 (vs Li/Li <sup>+</sup> )	60 mAh g <sup>-1</sup>	33
[C2C1im][F(2.3F)]	100	-0.3 to 0.7 (vs CuF <sub>2</sub> /Cu)	517 mAh g <sup>-1</sup>	121
1M LiPF <sub>6</sub> in EC/DME	-	0 to 3.0 (vs Mg/MgF <sub>2</sub> )	-	124
P(EO/PO)/MF/AA	1000	-	-	108
Aqueous 0.8 M NaF	-	0 to 1.5 (Ag/AgCl)	137 mAh g <sup>-1</sup>	122

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## 6 Electrode Materials

### 6.1 Conversion Vs. Intercalation Mechanism

In fluoride ion battery systems, storage of the ions in electrodes can take place through two main types of reaction mechanisms. As it was highlighted in section 3, the suitability of FIBs for reversible energy storage systems has been first demonstrated for cells containing conversion-based electrode materials. Such conversion-based electrodes generally offer the highest specific capacities due to their ability to accommodate more electrons per redox-active metal species and often lower molar mass of the active electrode material. However, in a conversion-reaction, the electrode material undergoes a redox reaction during fluorination/de-fluorination, which is accompanied by a change in the crystalline structure leading to breaking and recombining of the chemical bonds and often a large volume change in the active electrode material.<sup>1</sup> This large volume change results in a loss of physical contact between the active electrode material, the conductive particle and the ion conductor (see the scheme in Figure 13), which can lead to a significant deterioration in the electrochemical performance of the electrode material.

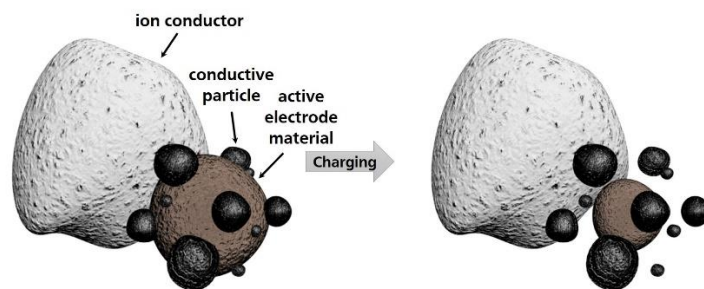


Figure 13. Schematic illustration of the volume changes in the contact surface area of the active anode material/electrolyte/carbon grains taking place during electrochemical charge/discharge. Reproduced from ref.<sup>27</sup>.

The second reaction for storage of the fluoride ions is based on the intercalation mechanism (sometimes also called insertion or solid solution reactions,<sup>125</sup> depending on the detailed structural arrangement of the host and the substructure of the incorporated species and nature of bonding therein). In the following, we refer to an intercalation-based electrode material for FIBs as a solid host network, which can store guest ions within the vacant positions in the host lattice, without referring to the dimensionality of this host sublattice explicitly. In other words, the guest species are inserted into normally unoccupied interstitial sites or anion vacancies in the crystal structure of a stable host material. The great advantage of the intercalation-based electrode materials lies within the fact that the ions can be inserted or removed into/from the host network reversibly with much lower volume changes during the redox reaction (e.g., in the order of 2 % for  $\text{LiCoO}_2$ <sup>126</sup> as an intercalation-based cathode for lithium-ion batteries) while the basic crystal structure or amounts of the phase in the microstructure do not change significantly.<sup>125</sup> Therefore, intercalation-based electrode materials can often provide a better cycling performance as compared to conversion-based electrode materials, with improved charging and discharging rates. However, this normally comes at the cost of lower specific capacities<sup>1</sup>, as intercalation-based materials are usually heavier in weight than the conversion-based electrode materials due to the existence of redox-inactive lattice atoms within the materials and the capability of accommodating fewer ions per redox-active species (for instance, theoretical capacity for intercalation-based  $\text{LiCoO}_2$  is

calculated to be  $140 \text{ mAh g}^{-1}$ , for lithiation/de-lithiation of 0.5 Li-ions <sup>127</sup> in comparison to conversion-based  $\text{Li/Li}_2\text{S}^1$  with a theoretical capacity of  $1675 \text{ mAh g}^{-1}$ ).

The following sections aim to provide an overview of the different electrode materials investigated previously.

## 6.2 Conversion-based Cathode Materials

$\text{BiF}_3$  and  $\text{CuF}_2$  are by far the most used cathode materials in conversion-based FIBs.<sup>8, 23, 32, 33, 63, 128</sup> Reddy and Fichtner reported on the cycling behaviour of  $\text{BiF}_3$  as cathode material against a Ce anode material in an all-solid-state cell modification the solid-state electrolyte  $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$ .<sup>8</sup> In addition, they reported the first discharge behaviour of several metal fluorides. Figure 14 summarizes the first discharge profile of various metal fluorides as cathode materials (against Ce anode material) compared to  $\text{BiF}_3$  and  $\text{CuF}_2$ . It is worth mentioning that in this study the cathode materials were made in a charged state (i.e.,  $\text{MF}_x$ ). The results revealed that for the  $\text{CuF}_2$  composite material the highest discharge capacity of  $322 \text{ mAh g}^{-1}$  (in the first cycle) with a flat discharge potential of around 2.7 V could be obtained when the cell was discharged at  $150 \text{ }^\circ\text{C}$  using a current density of  $10 \text{ } \mu\text{A/cm}^2$ . The high discharge capacity of  $\text{CuF}_2$  is due to the high theoretical capacity of  $\text{CuF}_2$ , which arises from the low molar mass of Cu (e.g. theoretical capacities of  $\text{Cu/CuF}_2$  and  $\text{Bi/BiF}_3$  are calculated to be  $\sim 843$  and  $384 \text{ mAh g}^{-1}$ , respectively). The  $\text{Cu/CuF}_2$  redox couple has been used as a conversion-based cathode in a nanostructure core-shell modification,<sup>33</sup> as discussed in section 5. For the  $\text{BiF}_3$  cathode composite, a flat plateau around 2.5 V with a discharge capacity of  $126 \text{ mAh g}^{-1}$  was observed. The discharge capacity could be further increased up to  $190 \text{ mAh g}^{-1}$  by synthesizing a  $\text{BiF}_3$  (tysonite-type) solid solution (via mechanical milling of the  $\text{BiF}_3$  active cathode material together with the electrolyte material with increased rotational speed up to 600 rpm). However, the average discharge potential slightly reduced to  $\sim 2.15 \text{ V}$  for the  $\text{BiF}_3$  solid solution. The improvement of the discharge capacity has been attributed to a higher fluoride ion mobility within the  $\text{BiF}_3$  solid solution as compared to a  $\text{BiF}_3$  composite.

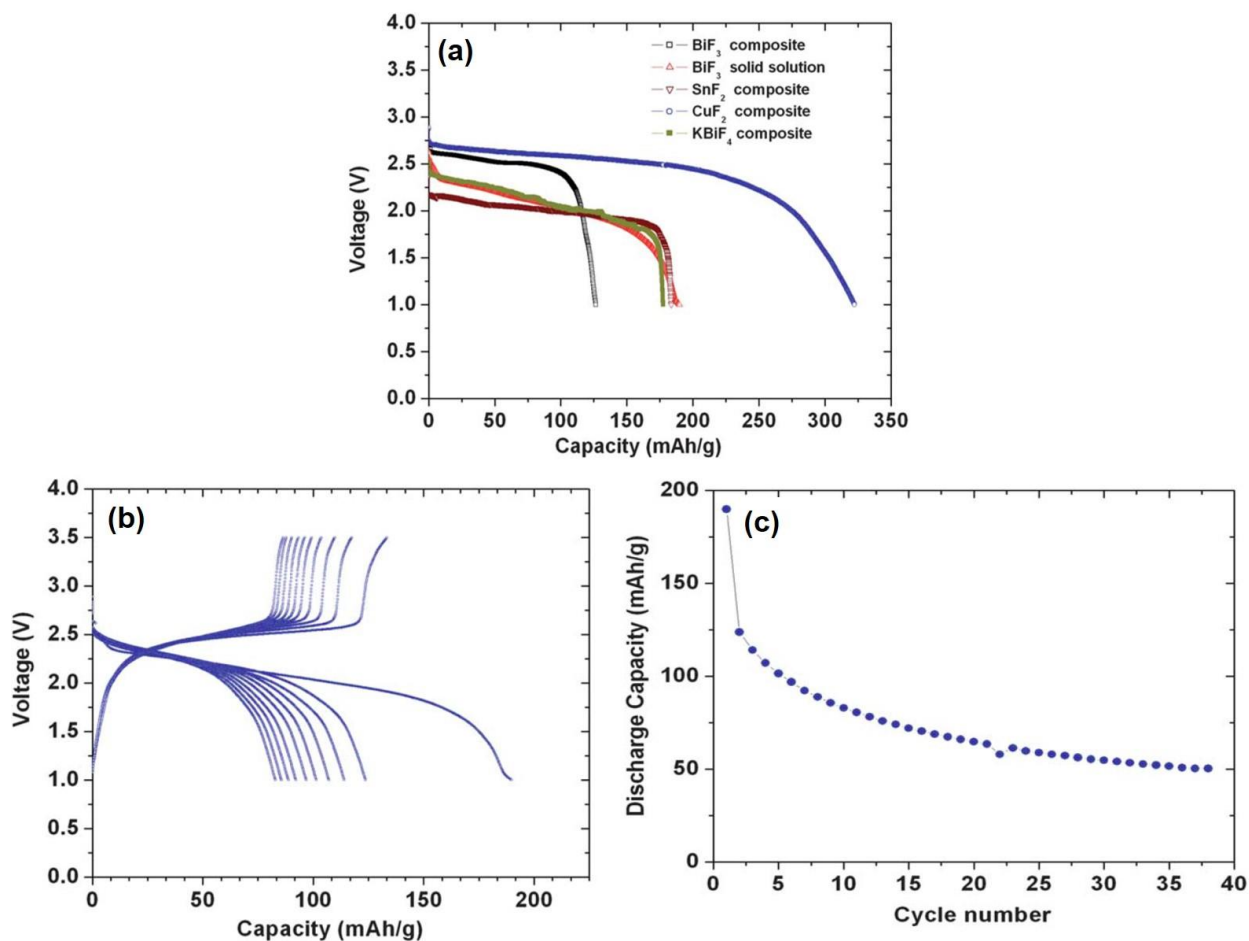


Figure 14. (a) Voltage-capacity profiles of various metal fluorides vs. Ce metal. The discharge curves were obtained at 150 °C with a current density of 10 mA/cm<sup>2</sup>; (b) Cycling performance of the BiF<sub>3</sub> (solid solution)/Ce cell for the first 10 cycles; (c) changes of discharge capacity with cycle numbers for the same electrochemical cell. The figures have been reproduced from ref.<sup>8</sup> with permission <sup>xiv</sup>).

The cycling performance of BiF<sub>3</sub> against Ce reveals a large capacity loss (~ 35 %) already after the first cycle, followed by rapid capacity fading over the next cycles, leading to only ~ 26 % capacity retention after 40 cycles (see Figure 14b, c). Interestingly, it was found that synthesizing the La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> solid electrolyte by co-precipitation method could lead to a significant increase in the discharge capacity of a BiF<sub>3</sub>|Ce electrochemical cell of up to 250 mAh g<sup>-1</sup>. Though the cell still suffered from a strong capacity fading upon cycling (the discharge capacity reached to 90 mAh g<sup>-1</sup> after only 8 cycles, when the cells were cycled at 150 °C), these findings indicate that the performance of certain electrode materials can highly depend on the detailed morphological and compositional aspects of the solid electrolyte used in the electrode composite mixture.<sup>42</sup>

Cathode composites of Bi+BiF<sub>3</sub> were also studied in detail by Grenier et al.<sup>129</sup> by means of pair distribution function analysis of synchrotron data, revealing a complex transformation reaction comprising also the formation of oxyfluoride compounds at intermediate cycling states. Further,

they could show that such oxide impurities cannot migrate through the fluoride conducting electrolyte, and thus remain at the respective electrode side.

In another report,<sup>23</sup> electrochemical activities of Bi and Cu (active cathode materials in discharged states) against  $\text{CeF}_3$ ,  $\text{CaF}_2$ ,  $\text{MgF}_2$  and  $\text{Mg}+\text{MgF}_2$  anode composites have been studied. The results suggested that the electrochemical fluorination of Bi against  $\text{CeF}_3$  (during charging) takes place in several steps as was found by Grenier et al.<sup>129</sup> and that the transformation process can be very complex: First, traces (remaining from the starting powder) of  $\text{Bi}_2\text{O}_3$  were fluorinated, and  $\beta\text{-BiF}_{3-2x}\text{O}_x$  is formed, which was accompanied by a charge plateau below 2.4 V. In the second step,  $\text{BiF}_3$  forms from Bi (desired reaction) and a plateau between 2.5 – 2.7 V could be observed. The last step was referred to as the formation of  $\text{BiF}_5$  from previously formed  $\text{BiF}_3$ . Considering the theoretical capacity related to the reaction of three fluoride ions with Bi ( $385 \text{ mAh g}^{-1}$ ), the first charge capacity was  $\sim 404 \text{ mAh g}^{-1}$ , indicating that a reaction of  $\text{BiF}_3$  to  $\text{BiF}_5$  might be partly involved in the redox process. Other possibilities such as carbon or electrolyte decomposition were not evaluated as the source of the side reaction related to the observed excessive charge capacity. When using the other mentioned anode materials, similar charging behaviors were found. However, a considerable reversibility upon discharging could only be obtained when using  $\text{CeF}_3$  and  $\text{MgF}_2$  based anode composites. A significant improvement of the cyclability was further observed when a  $\text{Mg}+\text{MgF}_2$  anode composite, containing a mixture of Mg and  $\text{MgF}_2$ , was used (see also section 6.3).

A slightly improved cycling stability has been reported<sup>30</sup> for  $\text{Bi}|\text{CaF}_2$  cells using a thin film  $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$  electrolyte (see also section 4.2). In this study,  $\text{SnO}_2$  and indium tin oxide (ITO) instead of carbon nanotubes as the electronic conductor have been investigated to study the role of the electron-conducting additive for the electron transfer to the active electrode material. It was observed that the best cycling behavior could be observed using carbon nanotubes as the electronic conductor. Despite of a low Coulombic efficiency in the first cycle (the cell has been initially charged up to ca.  $320 \text{ mAh g}^{-1}$  but only  $120 \text{ mAh g}^{-1}$  could be reversed), in the next cycles, the capacity fading was less severe compared to the first cycle. Nevertheless, the discharge capacity reached to ca. 66% of its initial value ( $\sim 120 \text{ mAh g}^{-1}$ ) within only 10 cycles. Recently, Konishi et al. showed<sup>115</sup> that pulverization of  $\text{BiF}_3$  with the conductive material by ball milling can improve the practical capacity of the FIB system. This has been explained by the reduction of the particle size and a stronger adhesion of the conductive particle to the  $\text{BiF}_3$  electrode material. Another approach to improve the capacity retention of  $\text{BiF}_3$  was proposed very recently by Konishi et al.<sup>130</sup> In this publication, it was shown that a solid solution of  $\text{BiF}_3$  and  $\text{BaF}_2$  ( $\text{Bi}_{1-x}\text{Ba}_x\text{F}_{3-x}$ ,  $0 < x < 0.4$ ) as the cathode material made by mechanical alloying, offers a higher capacity retention during cycling for  $x = 0.4$ . However, the overall capacity was reduced to almost 50 % of the one for pure  $\text{BiF}_3$ . This has been claimed to be due to an excess amount of barium fluoride that did not contribute to the redox reaction.

Apart from using  $\text{Bi}/\text{BiF}_3$  as a cathode in an all-solid-state modification, it has also been used as the cathode in a liquid electrolyte system. In 2019 Yamanaka et al. reported<sup>131</sup> on using orthorhombic- $\text{BiF}_3$  microparticles in a gold plating film as a cathode material against Pb wire as the counter electrode. Then the structural transformation and reaction mechanisms within  $\text{BiF}_3$  as the active electrode material were studied by means of in-situ Raman microscopy. In this paper, the authors showed that by discharging the cell within a potential range of 0.45 – 0.2 V (against Pb), a part of the orthorhombic- $\text{BiF}_3$  is deposited as Bi on the gold plate, which is indicative for a

direct de-fluorination process while the rest of the orthorhombic-BiF<sub>3</sub> was transformed to cubic-BiF<sub>3</sub>. The de-fluorination of the cubic-BiF<sub>3</sub> was observed only below 0.2 V (vs. Pb) and with a slower rate as compared to orthorhombic-BiF<sub>3</sub>. Moreover, it is suggested<sup>132</sup> that electronic diffusion is the rate-limiting process during the de-fluorination: The de-fluorination of orthorhombic-BiF<sub>3</sub> starts from the cluster that is in contact with conductive gold plate and not from the cluster that is in contact with the liquid electrolyte. This non-uniformity in the de-fluorination would not have been observed if the electronic diffusion at the surface of the BiF<sub>3</sub> cluster in contact with the liquid electrolyte was as fast as the ionic diffusion at the surface of BiF<sub>3</sub>. In a recent attempt<sup>33</sup> to build up a room-temperature FIB, Cu/CuF<sub>2</sub> redox couple has been used as a conversion-based cathode in a nanostructured core-shell modification with a redox-inert thin shell of LaF<sub>3</sub> (Cu@LaF<sub>3</sub>) around the active material. The cell was prepared as a standard three-electrode with a liquid electrolyte (also see section 5 for the view-point of the liquid electrolyte design). The results reveal that the Cu has been charged up to at least 80 mAh g<sup>-1</sup>, of which 50 mAh g<sup>-1</sup> could be reversed during the first cycle. With respect to the theoretical capacity of Cu/CuF<sub>2</sub> (843 mAh g<sup>-1</sup>) the obtained discharge capacity is much lower than the theoretical capacity. The capacity within the first 7 cycles seems to be stable, though, the Coulombic efficiency appeared to be low (<50%).

Very recently, Takami et al. have introduced the use multinary oxyfluorides as active electrode materials.<sup>133</sup> In this report, by chemical fluorination with PVDF, a new quaternary Bi<sub>0.7</sub>Fe<sub>1.3</sub>O<sub>1.5</sub>F<sub>1.7</sub> was synthesized, and then the phase was used as a charged cathode material. The Bi<sub>0.7</sub>Fe<sub>1.3</sub>O<sub>1.5</sub>F<sub>1.7</sub> cathode material has been discharged against Pb+PbF<sub>2</sub> composites, and a discharge capacity of 500 mAh g<sup>-1</sup> has been obtained. However, this capacity is much larger than the theoretical capacity corresponding to a de-fluorination of 1.7 F<sup>-</sup> ions. Nevertheless, during the charge step, an effective charge plateau of about 190 mAh g<sup>-1</sup> can be observed, which is in the order of the theoretical capacity. No subsequent cycling experiments were possible for the cell, which the authors assigned to a poor reaction activity and low electronic conductivity of the active cathode material itself.<sup>133</sup>

### 6.3 Conversion-based Anode Materials

Due to the strong interplay between the cathode and anode, a strict separation of the influences of individual electrode materials on the cycling performance and the overall improvement of FIBs is challenging. As already introduced in the previous section, significant contributions to the development of conversion-based electrodes have been made by the research groups of Reddy and Fichtner. On the anode side, composites based on the Ce/CeF<sub>3</sub><sup>8, 23</sup>, Ca/CaF<sub>2</sub><sup>23, 30</sup> and Mg/MgF<sub>2</sub><sup>23</sup> redox couples have been intensively studied. For Ce/CeF<sub>3</sub>, experiments were conducted starting from the charged state of Ce<sup>8</sup> as well as the discharged state of CeF<sub>3</sub>.<sup>23</sup> As reported by Rongeat et al.<sup>23</sup>, the use of an anode composite in a “half-discharged” state, containing a mixture of the discharge and charge products leads to the presence of more reactive interfaces within the composite and, therefore, to a better reactivity during charging (MF<sub>x</sub>→M) and discharging (M→MF<sub>x</sub>). This is shown for the cell Bi/La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub>/Mg+MgF<sub>2</sub> in comparison to the cell Bi/La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub>/MgF<sub>2</sub> in Figure 15. While for the cell containing the Mg+MgF<sub>2</sub> anode, reversibility upon discharging could be observed and cycling was possible, the cell with the pure MgF<sub>2</sub> anode showed a very low discharge capacity, and cycling could not be achieved. A strong capacity fading was also observed for the Bi/La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub>/Mg+MgF<sub>2</sub> cell with increasing cycling



number. Further, the use of composite mixtures as the starting point already indicates that the fully charged or fully discharged state might be unfavourable for maintaining the overall integrity of the electrode.

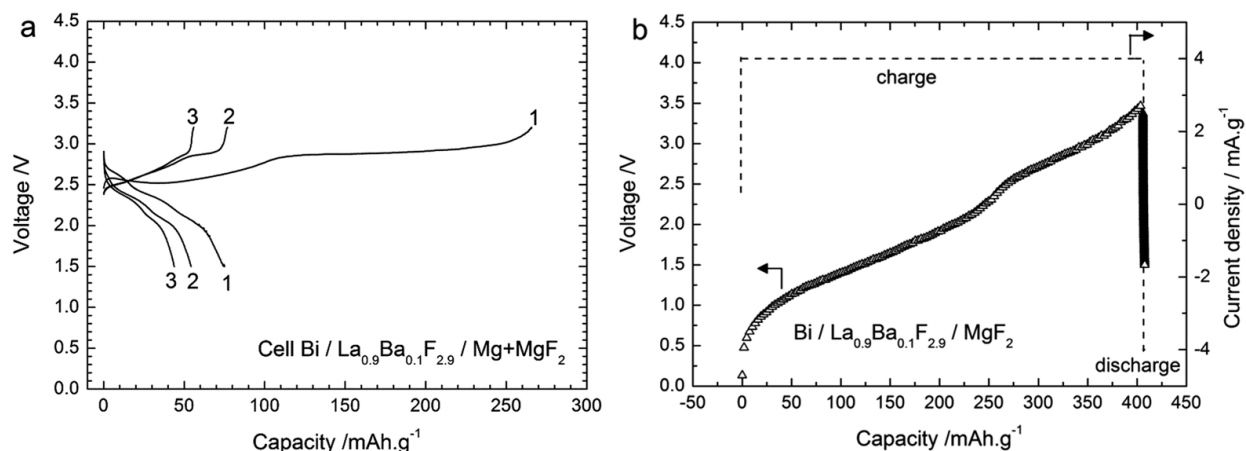


Figure 15: Voltage profiles of the first three cycles of a cell  $\text{Bi/La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}/\text{Mg}+\text{MgF}_2$  (a) and of the first charging and discharging of a cell  $\text{Bi/La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}/\text{MgF}_2$ . The cells were heated to  $150\text{ }^\circ\text{C}$ , a current density of  $4\text{ mA.g}^{-1}$  ( $10\text{ mAcm}^{-2}$ ) was applied. (The figures have been reproduced from ref.<sup>23</sup> (an original RSC publication)).

The successful application of a  $\text{Pb}+\text{PbF}_2$  anode composite in combination with an intercalation-based  $\text{LaSrMnO}_4$  cathode in a FIB was firstly demonstrated by Nowroozi et al.<sup>134</sup> DFT based calculation predicted a redox potential of  $2.26\text{ V}$  vs.  $\text{Li/LiF}$  for the  $\text{Pb}/\text{PbF}_2$  redox couple, making it a suitable material for its use as anode material. Upon charging of the cell, a transformation of  $\text{PbF}_2$ , contained in the anode composite, into  $\text{Pb}$  takes place. As it was observed for  $\text{Mg}+\text{MgF}_2$  anodes, when using this  $\text{Pb}+\text{PbF}_2$  anode composite instead of a composite, containing only  $\text{PbF}_2$ , lower overpotentials and better cycling performances with much more pronounced charging plateaus and higher phase fractions of the fluorinated  $\text{LaSrMnO}_4\text{F}_{2-\delta}$  could be identified, even though the involved redox couple remained the same. This shows that the complex conversion process taking place within the anode has a significant influence on the charging (and discharging) behavior of the cells. To gain a deeper understanding of the influence of such conversion-based anode materials on the cycling stabilities, the authors conducted an additional study, addressing the conversion reactions and determined limiting factors, including volume changes upon the occurring phase transformations.<sup>135</sup> Different conversion-based anodes, containing  $\text{Pb}$  and  $\text{PbF}_2$ ,  $\text{Zn}$  and  $\text{ZnF}_2$ , and  $\text{Mn}$  and  $\text{MnF}_2$  were investigated against an intercalation-based cathode composite containing  $\text{La}_2\text{CoO}_4$  as an active material. In particular, for cells with a  $\text{Mn}+\text{MnF}_2$  anode, a strong change in the impedance response due to increasing capacitive behavior was found upon charging above a certain capacity. This change was related to the strong volume decrease of  $\text{MnF}_2$  when transformed to  $\text{Mn}$  ( $\Delta V > 300\%$ ), which leads to a loss of contact between the active material and the electrolyte and carbon additive. This general dependency of cycling stabilities on the volume changes could also be confirmed based on the investigation of symmetrical cells. It was found that overpotentials increase much stronger for symmetrical cells with  $\text{Zn}+\text{ZnF}_2$  electrodes over prolonged cycling in comparison to the observed stable overpotentials for respective  $\text{Pb}+\text{PbF}_2$  cells, as the  $\text{Zn}$  and  $\text{ZnF}_2$  undergo stronger volume changes. Overall, it appears that large and soft cations, with corresponding low melting points of

the metal and high ionic conductivity within the metal fluoride state, seem to be preferable for maintaining structural integrity, which can be key for reversibility.

#### 6.4 Intercalation-based Cathode Materials

Investigations on fluorine insertion in oxides via electrochemical fluorination have been performed even before the recent development of FIBs. For instance,  $Y_1Ba_2Cu_3O_{7-x}$  has been electrochemically fluorinated in an all-solid-state configuration in 1991 by MacManus et al.<sup>136</sup> using a single crystal of Eu-doped in  $LaF_3$  as the ion conductor and  $Cu/CuF_2$  as the counter electrode at very high temperatures of  $\sim 300$  °C. After careful evaluation of the structural changes upon fluorine insertion, they reached the conclusion that the electrochemical process resulted in a shrinkage of the  $c$  parameter of the unit cell, which has been explained by the occupation of oxygen sites by fluoride in the basal plane of the lattice. The other example is the electrochemical fluorination of  $La_2CuO_4$  in a classic three-electrode configuration using organic fluorinated electrolytes (in liquid state) and gold foil and Pt wire as counter and reference electrodes, respectively.<sup>137</sup> In this work, it was reported that 0.18 fluoride ions had been electrochemically inserted in the vacant interlayers of  $La_2CuO_4$ , resulting in an increase in the parameter  $c$  of the cell from 13.141 Å to 13.205 Å. The results were in good agreement with what was found using chemical fluorination methods using  $F_2$  gas. It should be taken into consideration that in both mentioned cases, no electrochemical reversibility has been reported since the investigations were solely devoted to the fluorine insertion (intercalation).

Attempts to develop all-solid-state FIBs based on the intercalation mechanism was first reported by Clemens et al. in 2014 on anion deficient perovskite-related  $BaFeO_{2.5}$ , which showed low uptake of fluoride and poor performance as a cathode material.<sup>138</sup> As today, the three structure types of Ruddlesden-Popper ( $K_2NiF_4$ -type structure), Schafarzikite ( $MSb_2O_4$ ) and (anion deficient) perovskite ( $AMO_{3-y}$ ) have been investigated as potential intercalation-based cathode materials for FIBs. Among these, Ruddlesden-Popper-type compounds (e.g.,  $La_2MO_4$  and  $LaSrMO_4$ ) appeared to be the most promising candidates.

The Ruddlesden-Popper structure type can be regarded as a perovskite-related structure with a general formula of  $A_{n+1}M_nO_{3n+1}$  (or  $(AMO_3)_nAO$ ),<sup>139</sup> where  $n$  shows the number of connected layers of vertex sharing  $MO_6$  ( $n$  perovskite layers are stacked between rock-salt AO layers along the  $c$ -axis). Figure 16 schematically illustrates the Ruddlesden-Popper-type structure with  $n = 1$  and formula of  $(ABO_3)_nAO$  (also known as  $K_2NiF_4$ -type structure). In a  $K_2NiF_4$  ( $A_2MO_4$ ) structure  $MO_6$  octahedra share corners with each other to form  $AMO_3$  (two-dimensional) perovskite layers and the AO rock salt units exist between multiple layers of the perovskite along the  $c$ -axis, resulting in a tetragonal unit cell with an aristotype symmetry of  $I4/mmm$ <sup>139</sup>; for compositions close to  $A_2BO_4$  the lattice parameter  $c$  normally ranges between  $\sim 12.6 - 13.2$  Å.<sup>140-144</sup> The vacant anion positions within the rock salt-type interlayers are suitable for the accommodation of fluoride ions (Figure 16):  $K_2NiF_4$ -type compounds are capable of accepting up to 2 fluoride ions per formula unit, resulting in theoretical capacities (normally between  $130 - 160$  mAh  $g^{-1}$ ) comparable to various state of the art materials for LIBs (intercalation cathodes in mAh  $g^{-1}$ ,  $LiMn_2O_4$ : 120 mAh  $g^{-1}$ , and  $LiFePO_4$ : 165 mAh  $g^{-1}$ <sup>145-147</sup>). This fluorine insertion most often, but not always, results in an expansion of the lattice along the  $c$ -axis. For instance, fluorination of  $LaSrMnO_4$  leads to an increase in lattice parameter  $c$  to around  $\sim 14.2$  Å for the occupation of only one interlayer ( $A_2MO_4F$ ) and 15.5 Å for an ideal full occupation of both anion sites ( $A_2MO_4F_2$ ).<sup>148</sup>

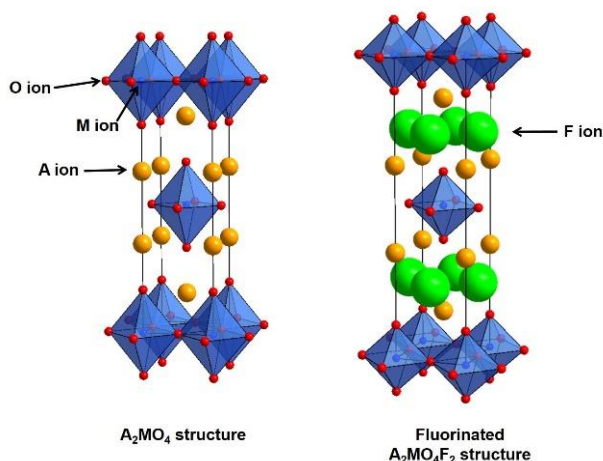


Figure 16. Schematic illustration of the  $n = 1$  Ruddlesden-Popper ( $A_2MO_4$ ) structure (left) and fully fluorinated  $A_2MO_4F_2$  structure (right).

The reversible electrochemical intercalation and deintercalation of fluoride ions into the Ruddlesden-Popper type compound  $LaSrMnO_4$  using a  $Pb/PbF_2$  counter electrode (anode) was reported by Nowroozi et al.<sup>134</sup> in 2017. In this work, it has been shown that the structural changes upon electrochemical fluorination are in principle agreement with the results of chemical fluorination experiments of  $LaSrMnO_4$ <sup>148, 149</sup>: The fluorination process occurs in two steps, in the first step partially fluorinated  $LaSrMnO_4F$  with a  $c$ -parameter of  $\sim 14.2$  Å forms and in the second step a new phase with an extended  $c$ -parameter up to  $\sim 15.6$  Å is obtained which is an indication for formation of the rich-fluoride content phase of  $LaSrMnO_4F_{2-6}$ . The initial structure could be recovered by discharging the cell (electrochemical de-intercalation) to negative potentials (down to  $-3.5$  V against  $PbF_2$ ). This indicates that for the recovery of initial  $LaSrMnO_4$ , the overpotentials which were created during the charging step could only be overcome at negative potentials. Such large overpotentials were attributed to the decomposition of the carbon conductive matrix during the charging step.<sup>134</sup> Successful insertion/removal of the fluoride ions into/from the anion interlayers of Ruddlesden-Popper type  $LaSrMnO_4$  serves as proof of principle for developing intercalation-based cathodes for FIBs, and meanwhile, reversed cycling at low capacities could be found for higher-order manganates.<sup>150</sup> The need to optimize cycling conditions has been related to the deterioration of the conductivity of the cell as a result of decomposition of the conductive carbon.<sup>134</sup>

Unlike the fluorination of  $LaSrMnO_4$ , which takes place in a layer-wise manner, the transformation of the Ruddlesden-Popper-type compounds  $La_2NiO_{4+d}$  and  $La_2CoO_{4+d}$  to  $La_2MO_{4+d}F_y$  ( $1 \leq y \leq 2$ ) occurs in only one step, and no stage-ordered fluorinated  $La_2MO_{4+d}F_1$  phase could be observed during the charging (electrochemical fluorination) step.<sup>29, 151</sup> For the charged  $La_2NiO_{4+d}$  particles, the data obtained from electron diffraction tomography (ADT) suggests that 1.59 to 1.72 fluoride ions can be inserted within the interlayers of a  $La_2NiO_{4+d}$  unit cell, which corresponds to a change in the oxidation state of Ni from close to +2 for un-fluorinated particles to almost +4 for the fluorinated particles. This change in the oxidation state of Ni is also confirmed by XANES analysis.<sup>151</sup> In the case of  $La_2CoO_{4.16}$ , the number of inserted fluoride ions calculated (based on the effective charge capacity) is around 1.2  $F^-$  per formula unit. Furthermore, a separation between the side reaction of the carbon additive and the desired electrochemical redox reaction

can be observed in the charge curves of  $\text{La}_2\text{CoO}_{4+d}$  which has been reported to be in favor of controlling the degree of the side reactions taking place.<sup>29</sup>

Based on the extended cycling experiments on  $\text{La}_2\text{NiO}_{4+d}$  and  $\text{La}_2\text{CoO}_{4+d}$ , it is reported<sup>29, 151</sup> that the choice of the cutoff criteria (capacity and potential) can significantly influence the cycling stability of cathodes with Ruddlesden-Popper-type structures. For instance, higher charging cutoff capacities such as 120 or 80  $\text{mAh g}^{-1}$  would significantly deteriorate the cyclic stability of  $\text{La}_2\text{NiO}_{4+d}$  (as can be seen in Figure 17a), while at a lower cutoff capacity of 50  $\text{mAh g}^{-1}$  the cyclic stability becomes much better ( $\sim 60$  cycles) and a cycle life of more than 220 cycles with a Coulombic efficiency of close to 100 % is reported for the cutoff capacity of 30  $\text{mAh g}^{-1}$  (see Figure 17a). A similar dependency on the cutoff criterion of the cycling behavior has also been observed for  $\text{La}_2\text{CoO}_{4.16}$ <sup>29, 135</sup>: The Coulombic efficiency at the first cycle of the  $\text{La}_2\text{CoO}_{4.16}|\text{Pb}+\text{PbF}_2$  cell that was charged up to 65  $\text{mAh g}^{-1}$  is calculated to be almost 50 % while it is only  $\sim 18$  % for the cell charged up to 130  $\text{mAh g}^{-1}$ . The discharge capacity decreases less than 10  $\text{mAh g}^{-1}$  starting from the second cycle for the charge cutoff capacity of 130  $\text{mAh g}^{-1}$ , showing the severity of the capacity fading for this cell. On the other hand, the discharge capacity for the cell that was initially charged up to 65  $\text{mAh g}^{-1}$  was still above 15  $\text{mAh g}^{-1}$  after 20 cycles, which is roughly half of the discharge capacity at the first cycle (Figure 17b). The reason for the stability upon limiting the cutoff criteria can be understood as a result of limited oxidation of carbon facilitating the maintenance of electrically conducting interfaces.<sup>151</sup>

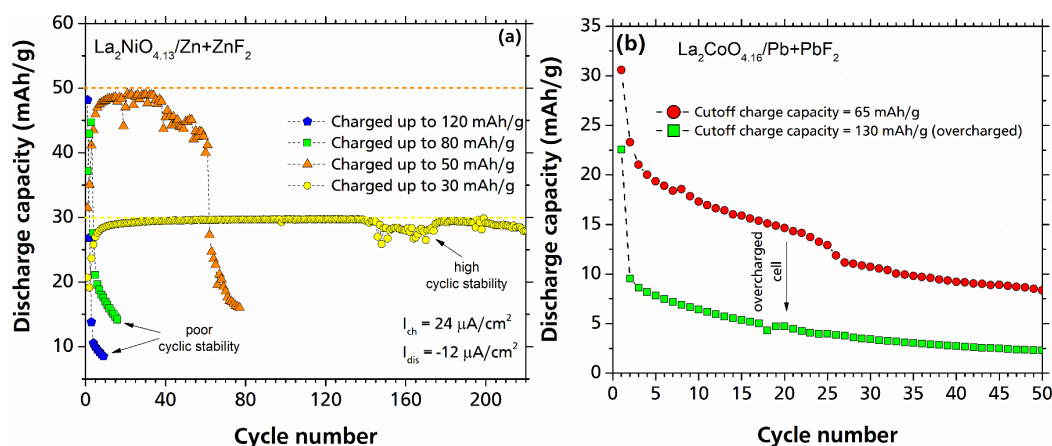


Figure 17. (a) Cycling stability of the  $\text{La}_2\text{NiO}_{4.13}|\text{Zn}+\text{ZnF}_2$  cell at different cutoff capacities<sup>151</sup>; (b) the effect of overcharging on cycling stability of a  $\text{La}_2\text{CoO}_{4.16}|\text{Pb}+\text{PbF}_2$  cell. All cells were heated at 170 °C and charged/discharged at a current of 24/-12  $\mu\text{A}/\text{cm}^2$ . Reproduced from ref.<sup>29</sup>.

The effect of the counter electrode (anode material) on the hysteresis potentials have also been found for the  $\text{La}_2\text{NiO}_{4+d}$  intercalation-based system.<sup>151</sup> In fact, by using anode materials with a lower intrinsic volume change during the redox reactions, less overpotentials would be introduced to the  $\text{La}_2\text{NiO}_{4+d}$  system, and therefore the cycling stability of the cell may be improved especially at higher cutoff capacities (Figure 18a). However, such a strategy does not improve the cycling stability of the  $\text{La}_2\text{CoO}_{4.16}$  cathode material. This inconsistency between the effect of the anode material on  $\text{La}_2\text{NiO}_{4+d}$  and  $\text{La}_2\text{CoO}_{4+d}$  may arise from a higher internal resistivity of the  $\text{La}_2\text{CoO}_{4+d}$  composite material, which might originate from some unknown low-potential side reactions.<sup>135</sup>

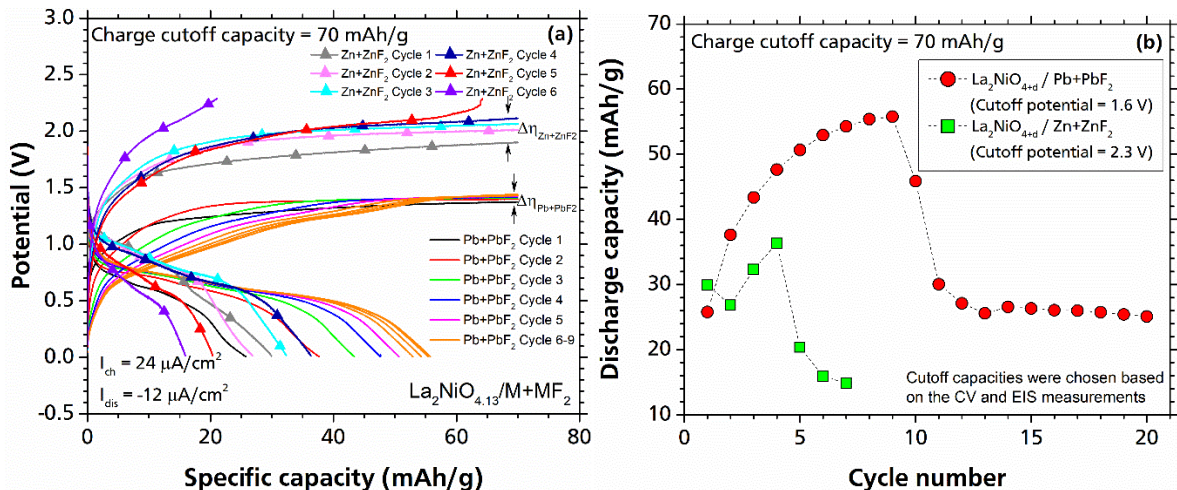


Figure 18. The effect of anode material on the overpotential and cycling behavior of  $\text{La}_2\text{NiO}_{4+d}$  by showing (a) the first few cycles of  $\text{La}_2\text{NiO}_{4+d}$  against  $\text{Zn}+\text{ZnF}_2$  and  $\text{Pb}+\text{PbF}_2$  anode materials (b) discharge capacities of  $\text{La}_2\text{NiO}_{4+d}$  against  $\text{Zn}+\text{ZnF}_2$  and  $\text{Pb}+\text{PbF}_2$  anode materials. Reproduced from ref.<sup>151</sup>.

Electrochemical cycling of the  $n = 2$  Ruddlesden-Popper-type  $\text{La}_{1.3}\text{Sr}_{1.7}\text{Mn}_2\text{O}_7$  has been performed by Vasala et al.<sup>150</sup> in order to reversibly tune the ferromagnetic properties of the compound. For this,  $\text{La}_{1.3}\text{Sr}_{1.7}\text{Mn}_2\text{O}_7$  has been charged up to 0.45 or 0.6 V against  $\text{Pb}+\text{PbF}_2$  corresponding to specific capacities of  $\sim 15$  and  $\sim 25$  mA/g during the charging step and down to -0.3V during the discharging. Over a span of 10 – 45 cycles, the electrochemical behavior of the cells is very stable without any significant capacity fading during the cycling. Upon cycling, the compound shows a change of the ferromagnetic behavior from strong (defluorinated state) to weak (fluorinated state) ferromagnetism.

Besides Ruddlesden-Popper type oxides, Ruddlesden-Popper-type oxyfluorides  $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1-x}\text{F}_{2x}\square_{2-x}$  with  $x < 2$  were also found to be suitable as intercalation-based cathode materials. Such oxyfluorides can be prepared via low-temperature topochemical fluorination reactions of the respective Ruddlesden-Popper type oxide using fluorine-containing polymers such as polyvinylidene difluoride (PVDF) as fluorination reagent<sup>34, 152-155</sup>. The fluorination takes place via a coupled substitution and intercalation process, in which for each substituted oxide ion, two fluoride ions are intercalated under the maintenance of the oxidation state. When used as active cathode materials for FIBs (the oxyfluoride represents the discharged state), additional fluoride ions are intercalated into these oxyfluorides upon charging. Therefore, anion vacancies  $\square$  have to be present after the topochemical fluorination in order to enable oxidative fluorination of these compounds during the electrochemical fluorination. This is, for example, given for non-oxidatively fluorinated  $\text{A}_2\text{BO}_3\text{F}_2\square$ , derived from an  $n = 1$  Ruddlesden-Popper type oxide  $\text{A}_2\text{BO}_4$ .

The topochemical fluorination of  $\text{La}_2\text{NiO}_{4+d}$  using PVDF leads to the formation of  $\text{La}_2\text{NiO}_3\text{F}_2\square$ .<sup>156</sup> In this compound, only half of the interstitial anion sites are occupied. Thus, additional fluoride intercalation of up to one ion per formula unit is possible, leading to the formation of  $\text{La}_2\text{NiO}_3\text{F}_3$  within the charged cathode composite.<sup>34</sup> As for the cycling of cells  $\text{La}_2\text{NiO}_{4+d}|\text{Zn}+\text{ZnF}_2$ , the choice of the cutoff capacity has a significant influence on the cycling stabilities. For cells  $\text{La}_2\text{NiO}_3\text{F}_2|\text{Pb}+\text{PbF}_2$ , best performances are found when using a cutoff capacity of  $30 \text{ mAh g}^{-1}$  (Figure 19). For these cells, comparatively stable cycling can be observed over at least 50 cycles. However, the Coulombic efficiency is considerably reduced compared to the cells

$\text{La}_2\text{NiO}_{4+d}|\text{Zn}+\text{ZnF}_2$  of the pure oxide compound, even though a steady increase of the efficiency occurs with increasing cycling numbers. In contrast to the high cycling stabilities of the cells  $\text{La}_2\text{NiO}_{4+d}|\text{Zn}+\text{ZnF}_2$ , cycling of  $\text{La}_2\text{NiO}_3\text{F}_2$  against  $\text{Zn}+\text{ZnF}_2$  leads to an early onset of capacity fading. Further, it was found that apart from the importance of this synthesis route for new battery technologies, such routes can play a vital role for the synthesis of metastable oxyfluoride: a chemical preparation of  $\text{La}_2\text{NiO}_3\text{F}_3$  via common topochemical reaction approaches using  $\text{F}_2$  gas has not been successful.<sup>34</sup> For the electrochemical route, the controllability is obtained by adjusting the potential, whereas the chemical potential of chemical reactants cannot be altered.

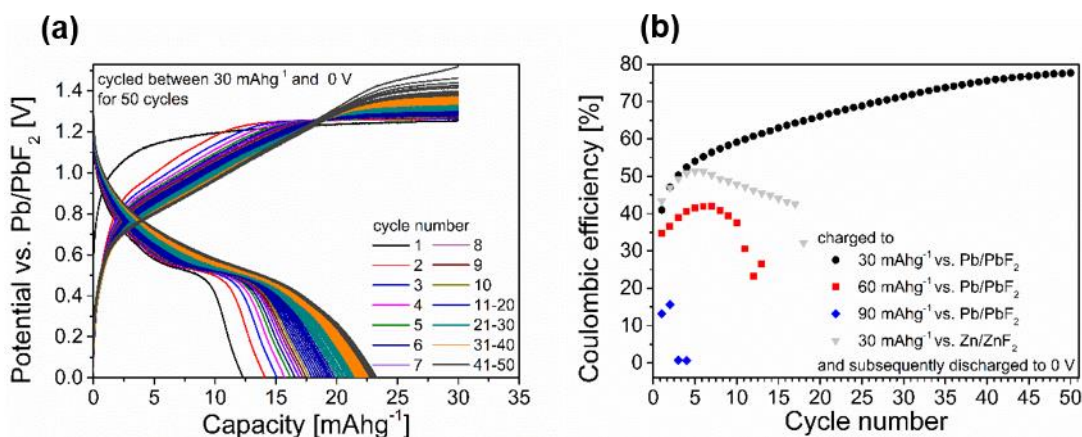


Figure 19. a) Cycling curves of a cell  $\text{La}_2\text{NiO}_3\text{F}_2$  against  $\text{Pb}+\text{PbF}_2$ . The cell was cycled between a charging cutoff capacity of  $30 \text{ mAh g}^{-1}$  and a discharging cutoff potential of  $0 \text{ V}$ , b) Coulombic efficiencies of cells  $\text{La}_2\text{NiO}_3\text{F}_2$  against  $\text{Pb}+\text{PbF}_2$  and  $\text{La}_2\text{NiO}_3\text{F}_2$  against  $\text{Zn}+\text{ZnF}_2$  charged to different cutoff capacities. The cells were heated to  $170 \text{ }^\circ\text{C}$ , a current of  $\sim 2.5 \text{ mAg}^{-1}$  ( $\sim C/25$  rate) was applied. Reproduced from ref.<sup>34</sup>.

The one-dimensional tunnel structure of Schafarzikite-type compounds with a general composition of  $\text{MSb}_2\text{O}_4$ <sup>157</sup> has recently attracted some attentions for the application of intercalation-based electrodes for FIBs.<sup>158, 159</sup> Schafarzikite type compounds possess a tetragonal symmetry (space group  $P4_2/mbc$ ), and the structure can be understood as being built up of chains of edge-linked  $\text{MO}_6$  octahedra running along the  $[0 0 1]$  direction; the chains are connected via trigonal pyramidal  $\text{SbO}_3$  units (Figure 20). Recent studies have shown that it is possible to fluorinate variants of this material, which contain  $\text{Fe}^{2+}$  on the M site, via topochemical reactions.<sup>160</sup> This material can thus be of interest for making electrode materials for FIBs because of the mechanism for the inclusion of excess fluoride ions within the channel of the structure (Figure 20). Therefore, it can be considered to be a 1D intercalation material, like olivine type materials for lithium-ion batteries.<sup>161</sup> This is in contrast to the layered ordering of intercalated fluoride ions within Ruddlesden-Popper-type compounds that has been discussed in the previous sections, which are 2D intercalation materials.

Nowroozi et al. reported<sup>158</sup> on the successful electrochemical fluorination/de-fluorination of Schafarzikite-type compounds  $(\text{Co/Mn})_{0.5}\text{Fe}_{0.5}\text{Sb}_2\text{O}_4$  at  $170 \text{ }^\circ\text{C}$ . Recently, Zaheer et al. reported<sup>159</sup> on room temperature topochemical fluorination and defluorination of  $\text{FeSb}_2\text{O}_4$  by stirring the Schafarzikite-type and  $\text{XeF}_2$  within an acetonitrile solution showing the principle of fluoride ion insertion/removal in Schafarzikite-type structures at room temperature. Though the Schafarzikite compounds<sup>158</sup> showed poor cycling performance in FIBs using solid electrolytes, this might

highlight the potential of these materials to be used in a liquid electrolyte based battery systems at ambient conditions.

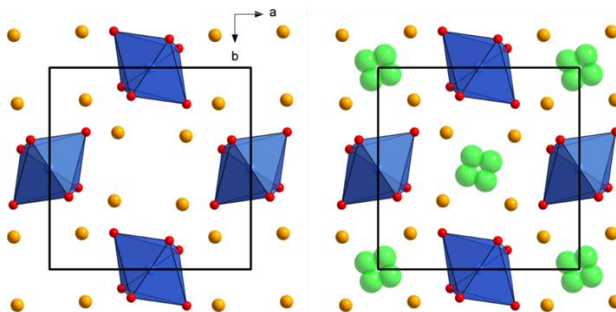


Figure 20. Schematic presentation of the non-fluorinated  $MSb_2O_4$  (left) and fluorinated  $MSb_2O_4F_y$  (right) Schafarzikite-type structure. Sb orange, M (Fe, Co) blue, O red, F (partially occupied to ~15 %) green. Reproduced from ref.<sup>158</sup> (open source publication).

Anion-deficient perovskite-type compounds such as  $BaFeO_{2.5}$ <sup>138</sup> and  $SrFeO_2$ <sup>27</sup> have also been investigated as potential intercalation-based cathode materials for FIBs. It is reported that  $SrFeO_2$  has insufficient chemical stability towards the other components used in the electrode composite at the applied experimental conditions ( $T = 170\text{ }^\circ\text{C}$ ) and the active cathode material undergoes an oxidation reaction resulting in the formation of a compound with high similarity to  $SrFeO_2F$ . It is not clear how this oxidation takes place and it seems that  $SrFeO_2$  can only be stabilized under highly reductive conditions (such as in the presence of excess of  $CaH_2$  used during its synthesis).<sup>162</sup>

In another effort by Clemens et al.<sup>27</sup>,  $BaFeO_{2.5}$  has been investigated against  $Ce/CeF_3$  or  $Mg/MgF_2$  (conversion-based anode) materials using  $La_{0.9}Ba_{0.1}F_{2.9}$  electrolyte (at  $150\text{ }^\circ\text{C}$ ). The cell has been charged up to  $4.0\text{ V}$  (vs.  $CeF_3$ ), corresponding to  $\sim 80\text{ mAh g}^{-1}$ , which is slightly larger than the theoretical capacity of  $BaFeO_{2.5}/BaFeO_{2.5}F_{0.5}$  ( $57.5\text{ mAh g}^{-1}$ ). This was claimed to be arising from side reactions. Diffraction experiments revealed that upon the electrochemical fluorination (charging), a decrease in the cell volume per  $BaFeX_{3-y}$  unit, down to the range where oxidatively fluorinated compounds are expected, could be observed together with a symmetry change from a vacancy ordered modification to a cubic perovskite. These structural changes upon electrochemical fluorination are in agreement with what was found on fluorinating  $BaFeO_{2.5}$  via chemical fluorination using  $F_2$  gas. Although the chemical fluorination was successful, only negligible discharge capacities of around  $6\text{ mAh g}^{-1}$  could be obtained upon discharging the cell against  $CeF_3$ <sup>27</sup>

Figure 21 sums up the discharge profiles (after the first charging cycle) of some intercalation-based cathodes that have been discussed in this chapter. The discharge capacity for Ruddlesden-Popper-type  $La_2NiO_{4+d}$  appeared to be the highest among all other cathodes: The highest stable discharge capacity that has been so far obtained for an intercalation-based cathode material for FIB was measured to be about  $70\text{ mAh g}^{-1}$  (accompanied by a high average discharge potential of  $\sim 1.2\text{ V}$ ) for  $La_2NiO_{4+d}$  against a  $Zn+ZnF_2$  anode composite material. The discharge capacity for  $La_2CoO_{4+d}$  and  $LaSrMnO_4$  cathode materials was found to be in a similar range, around  $30\text{ mAh g}^{-1}$  (however,  $LaSrMnO_4$  provides a higher potential as compared to  $La_2CoO_{4+d}$ ), while  $LaSr(Co/Fe)O_4$  cathode materials showed only a poor performance in respect to their discharge

capacity (Figure 21). A much poorer performance of the  $\text{LaSr}(\text{Co}/\text{Fe})\text{O}_4$  cathode is indicated<sup>27</sup> to result from a structural instability of the active cathode material upon electrochemical fluorination, though these materials might require further elaboration. The lowest discharge capacity is observed for the Schafarzikite-type structure ( $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Sb}_2\text{O}_4$ ) around  $5 \text{ mAh g}^{-1}$ , which is in the same capacity range as that of the anion-deficient perovskite structure of  $\text{BaFeO}_{2.5}$ . This comparison reveals the great potential of the Ruddlesden-Popper-type compounds (especially  $\text{La}_2\text{MO}_{4+d}$ ) as promising intercalation-based cathode materials for FIBs. Furthermore, a high degree of structural reversibility has been observed over a routine discharging process for  $\text{La}_2\text{NiO}_{4.13}$  and  $\text{La}_2\text{CoO}_{4.16}$ : After a discharge step, there is no sign of the high fluorine content phase with an extended  $c$ -parameter (up to  $\sim 15.2 \text{ \AA}$ ) and the initial  $\text{La}_2\text{MO}_{4+d}$  structure could be recovered.<sup>29, 151</sup>

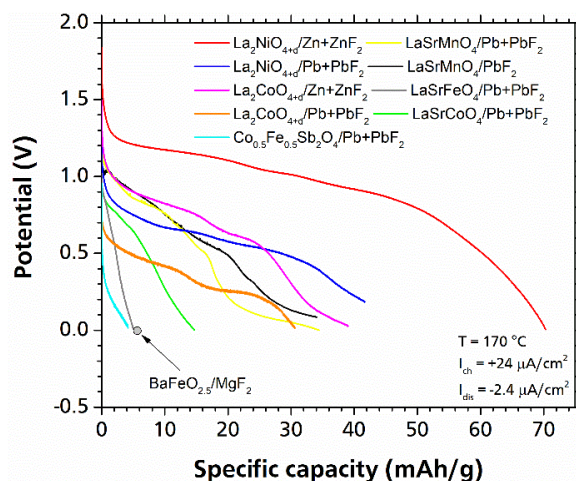


Figure 21. Discharge profiles of some of the so far proposed intercalation-based cathode materials for FIBs. Reproduced with some modifications from ref.<sup>27</sup>.

## 6.5 Intercalation-based Anode Materials

So far, only a few reports about intercalation-based anode materials exist. A suitable active anode material should be a strong reductant in its charged (defluorinated) state, i.e., the redox-active cation should have an unusually low oxidation state. Thus, the involved redox couple should have a low potential against  $\text{Li}|\text{LiF}$ . As has been described in the previous section, compounds with Ruddlesden-Popper-type structure offer great potential for their use as intercalation-based active cathode materials since the structure shows flexibility towards reversible oxidative intercalation of fluoride ions upon charging and discharging of FIBs. The topochemical modification of Ruddlesden-Popper-type oxides  $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$  via non-oxidative fluorination reactions, leading to the formation of oxyfluorides  $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1-x}\text{F}_{2x}\square_{2-x}$  with  $x < 2$  offers possibilities for the development of intercalation-based anode materials.<sup>34</sup> Such oxyfluorides represent the discharged states of potential anode materials, while electrochemical charging leads to reductive defluorination reactions. Apart from Ruddlesden-Popper-type compounds, layered electride materials such as  $\text{Ca}_2\text{N}$  or  $\text{Y}_2\text{C}$  and their transformation to the fluorinated states  $\text{Ca}_2\text{NF}$  or  $\text{Y}_2\text{CF}$  were recently studied by Hartman et al.<sup>163</sup>, indicating that these materials could work as high-energy anode materials, if stability towards other battery components can be achieved.



A synthesis process for the chemical low-temperature preparation of the charged states of Ruddlesden-Popper-type anode materials has been recently introduced by Wissel et al.<sup>164</sup> This strongly reductive process allows for an in-depth structure and property analysis of the anode materials in their charged states. It is based on a reaction between the Ruddlesden-Popper-type oxyfluoride and sodium hydride, resulting in selective extraction of fluoride ions from the oxyfluoride. So far, the chemical defluorination behavior of  $n = 1$   $\text{Sr}_2\text{TiO}_3\text{F}_2$ ,  $n = 2$   $\text{Sr}_3\text{Ti}_2\text{O}_5\text{F}_4$  and  $n = 1$   $\text{La}_2\text{NiO}_3\text{F}_2$  has been investigated.<sup>34, 164-166</sup> This defluorination reaction is favoured by the high lattice energy of NaF, which helps to prepare anode materials in the charged state down to a potential of  $< \sim 1\text{V}$  against Li/LiF.

The feasibility of topochemical modifications of these Ruddlesden-Popper-type oxyfluorides, when used as active anode materials, via electrochemical defluorination reactions in FIBs have also been investigated.<sup>34</sup> A significant redox-activity of the active materials has been only found for the Ni-based compound. Electrochemical charging of cells with a  $\text{La}_2\text{NiO}_3\text{F}_2$ -containing anode and a  $\text{Pb}+\text{PbF}_2$ -based cathode resulted in the formation of a  $\text{Ni}^+$ -containing phase with reduced monoclinic symmetry (space group  $C12/c1$ ) and an approximate composition of  $\text{La}_2\text{NiO}_3\text{F}_{1.9}$  (i.e., containing 10 % of monovalent Ni species). Changes in the crystal structures due to the successful deintercalation of fluoride ions can be related to the chemically formed reduced phases and are also found for electrochemical reactions (Figure 22).

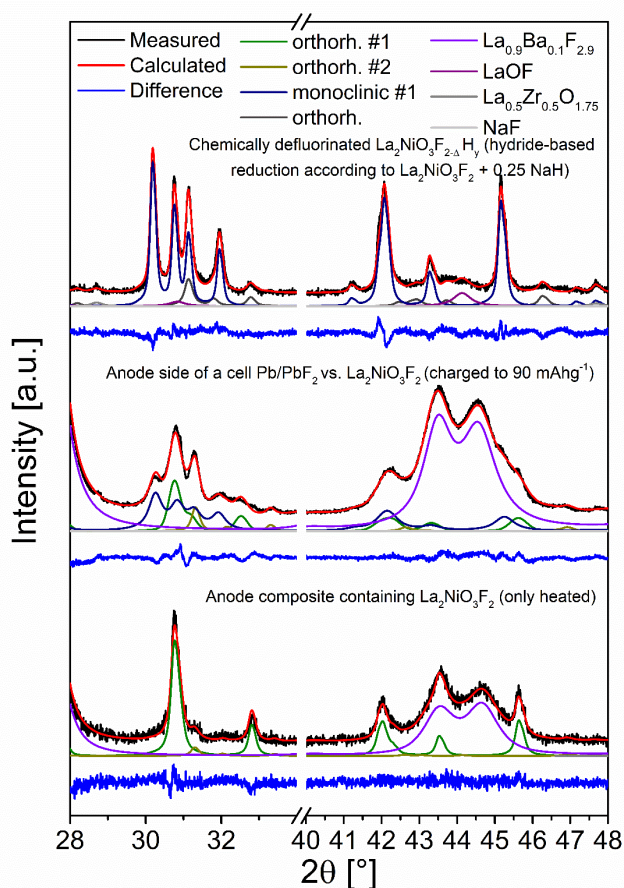


Figure 22: Comparison of selected angular ranges of XRD patterns of chemically (top) and electrochemically (middle) defluorinated  $\text{La}_2\text{NiO}_3\text{F}_{2-x}$ . The chemical defluorination was obtained via a hydride-based reduction, the electrochemical

defluorination within a FIBs, in which an anode material containing  $\text{La}_2\text{NiO}_3\text{F}_2$  was used. In addition, an XRD pattern of the anode composite before electrochemical treatment (bottom) is given, highlighting the change in the reflection patterns of the reduced  $\text{La}_2\text{NiO}_3\text{F}_{2-x}$  and the precursor phase  $\text{La}_2\text{NiO}_3\text{F}_2$ . Reproduced from ref.<sup>34</sup>.

A typical charging curve of a cell of  $\text{Pb}+\text{PbF}_2$  against  $\text{La}_2\text{NiO}_3\text{F}_2$  is given in Figure 23a. A comparison between the theoretical capacity related to the extraction of one fluoride ion from  $\text{La}_2\text{NiO}_3\text{F}_2$  to the actually observed capacities illustrates that substantial side reactions are taking place in parallel to the reduction of  $\text{La}_2\text{NiO}_3\text{F}_2$  (see also section 6.6) and can be assigned to changes in the carbon matrix. Moreover, large overpotentials and low Coulombic efficiencies have been found (Figure 23b), resulting in negligible reversible capacities on discharging to 0 V. Nevertheless, by discharging to negative potentials, full reversibility of the structural changes has been reported. This is similar to what is reported for  $\text{LaSrMnO}_4$  in section 6.4.

Overall, a closer examination of the origin and influence of the side reactions, which seem to play a crucial role in the defluorination process, has been found to be very important. This has also become obvious with regards to the unsuccessful electrochemical reduction of the Ti-based compounds<sup>89</sup> (see also section 6.6).

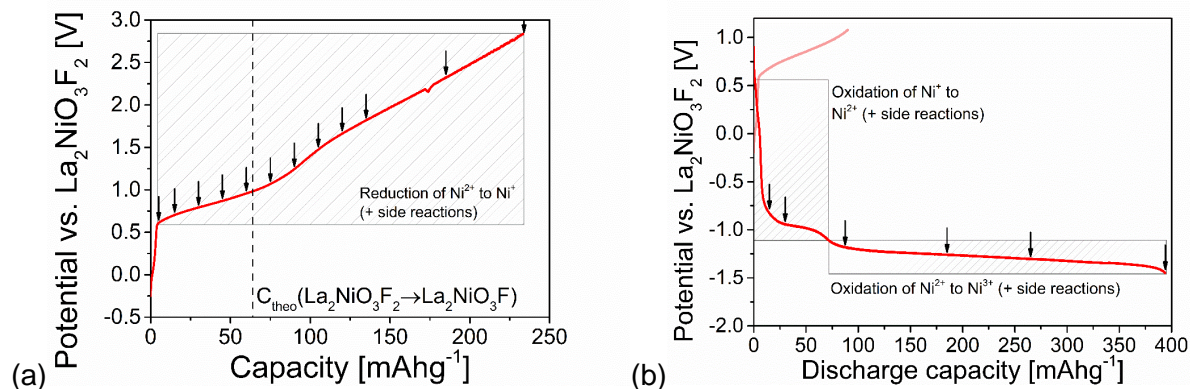


Figure 23: a) Charging curve of a cell  $\text{Pb}+\text{PbF}_2$  against  $\text{La}_2\text{NiO}_3\text{F}_2$ , b) Charging and discharging curves of a cell  $\text{Pb}+\text{PbF}_2$  against  $\text{La}_2\text{NiO}_3\text{F}_2$ . The cell was charged to  $90 \text{ mAh g}^{-1}$  prior to the discharging. The cells were heated to  $170 \text{ }^\circ\text{C}$ , a current of  $\sim 2.5 \text{ mA g}^{-1}$  ( $\sim C/25$  rate) was applied. Reproduced from ref.<sup>34</sup>.

## 6.6 The Issue of Carbon Side Reactions for the Application of Electrode Materials

Due to the low electronic conductivity, usually the active electrode materials are mixed with carbon black/carbon nanotubes.<sup>8, 29, 134, 135, 138, 151, 158</sup> The possibility of the occurrence of the carbon side reaction has been reported by different research groups in several studies.<sup>47, 134, 138</sup> Dambournet et al.<sup>47</sup> carried out investigations on possible interactions of carbonaceous additives (as electronic conductor) with the fluoride conducting electrolyte. After the ball milling of the LBF electrolyte and carbon, no indication of the formation of insulating graphite fluoride ( $\text{CF}_x$ ) could be determined by NMR. However, according to impedance measurements, the conductivity of the mixed LBF-C composite (produced by ball milling) is lower by one order of magnitude ( $5 \times 10^{-8} \text{ S cm}^{-1}$  at  $30 \text{ }^\circ\text{C}$ ) as compared to milled  $\text{La}_{0.95}\text{Ba}_{0.1}\text{F}_{2.95}$  ( $5.4 \times 10^{-7} \text{ S cm}^{-1}$  at  $30 \text{ }^\circ\text{C}$ ). The authors have further investigated the presence of a reaction of carbon with the LBF electrolyte to yield  $\text{CF}_x$  by conducting cyclic voltammetry experiments on  $\text{Li}|\text{LBF}|\text{LBF-C}$  cells. They showed a rapid increase in the measured current at a potential range between  $4.2 - 4.8 \text{ V}$ . The standard potential of the electrochemical fluorination reaction of carbon (according to:  $1/3 \text{ LaF}_3 + \text{C} \rightarrow \text{CF} + 1/3 \text{ La}$ ) had

been calculated to be 4.19 V which is very close to the contribution to the current behaviour observed in the CV measurements of the LBF-C cell, suggesting that carbon probably undergoes electrochemical fluorination to form  $CF_x$ .

It was also shown<sup>27</sup> that cyclic voltammograms of a carbon electrode (as the positive electrode) feature an irreversible anodic peak (as can be seen in Figure 24a), which has been attributed to the irreversible oxidation (fluorination; e.g., formation of  $CF_x$ ) of the carbon.<sup>27</sup> Such irreversible anodic peaks can also be observed in the cyclic voltammograms of the  $La_2NiO_{4.13}$  cells. However, it slightly shifted towards the lower potential range (Figure 24a), which has been explained by a catalytic effect of the active cathode material towards the carbon side reaction.<sup>151</sup> Interestingly, reversible cathodic peaks corresponding to the de-fluorination of  $La_2NiO_{4.13}F_x$  in the cathode composite material can only be observed upon limiting the cycling voltage range below the range for the occurrence of the irreversible anodic peaks (Figure 24b), suggesting that oxidation reactions of C within the cathode composite result in electrochemical irreversibility of the cell.<sup>151</sup> Other characterization methods also support the oxidation of carbon during the charging step within the  $La_2MO_{4+d}$  systems. For instance, XPS measurements confirm an increase in the oxidation state of carbon within the  $La_2NiO_{4+d}$  systems during the charge step. Further, electrochemical impedance measurements show a rapid change in the impedance behavior of the  $La_2NiO_{4+d}$  cells from a Warburg-type behavior (indicative for electrochemical reactions) to a capacitive behavior, which is indicative for a blocking effect. This rapid change occurs within the region in which the irreversible cathodic reactions are seen within the cyclic voltammograms of  $La_2NiO_{4+d}$  cathode material. Moreover, electrochemical impedance spectroscopy (EIS) measurements reveal a sharp increase in resistivity of the cells after  $\sim 60 \text{ mAh g}^{-1}$  in the  $La_2CoO_{4+d}$  systems, which is explained as a significant deterioration in the conductivity of the cell due to carbon oxidation.<sup>29, 135</sup>

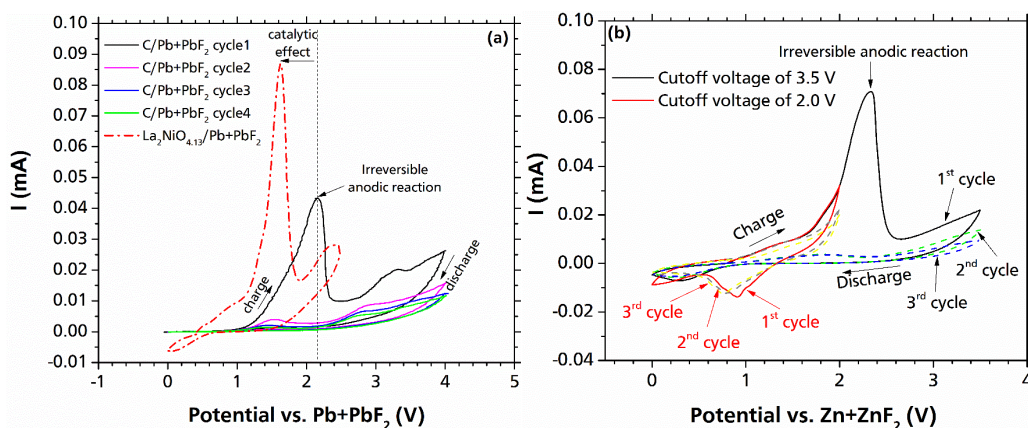


Figure 24. Cyclic voltammograms of a carbon electrode as compared to  $La_2NiO_{4+d}$  cathode material ( $Pb+PbF_2$  as counter electrode); (b) Cyclic voltammograms of  $La_2NiO_{4+d}$  cathode material vs.  $Zn+ZnF_2$  in two different potential range of 0 – 2 V and 0 – 3.5 V. Figures are reproduced with some modifications from ref.<sup>27</sup>.

On the anode side, there has also been an indication for the occurrence of side reactions in the form of a carbon reduction. The detailed nature of this reaction is yet to be understood and could involve the release of surface-adsorbed oxygen or a reaction of carbon with La or Ba of the electrolyte LBF (according to  $C + x LaF_3 \rightarrow CLa_x + 3F^-$ ).<sup>34</sup> Cyclic voltammetry measurements showed that these irreversible side reactions take place largely in parallel with the desired

reactions during the charging of the  $\text{La}_2\text{NiO}_3\text{F}_2$ -based anode composites. XPS measurement revealed, furthermore, that the carbon additive is reduced during this process. The carbon reduction and the associated destruction of the electronically conductive matrix within the electrode material also provides an explanation of why  $\text{Sr}_2\text{TiO}_3\text{F}_2$  and  $\text{Sr}_3\text{Ti}_2\text{O}_5\text{F}_4$  could not be defluorinated electrochemically when used as anode material. Due to the low potential of  $\text{Ti}^{3+}|\text{Ti}^{4+}$ , the carbon reduction sets in at much higher potentials compared to the desired reduction of the Ti-based compound. This impairs a reduction of the Ti-based compounds.

While the reaction of carbon within the FIB cells is often considered to be a side reaction<sup>26, 29, 151</sup> affecting the conductivity of the cell, fluorine-intercalated graphite has recently been proposed<sup>167</sup> as a cathode material (positive electrode) for FIBs. In this study, the active cathode material of  $\text{C}_x\text{F}$  has been made in a charged state by the reaction of graphite powder and fluorine gas in anhydrous HF at room temperature to form  $\text{C}_{2.8}\text{F}$ . The full cell was built up using  $\text{PbSnF}_4$  as the electrolyte and a Pb plate as the anode material. To increase the discharge capacity, the active cathode material was mixed with  $\text{CuF}_2$ . The highest discharge capacity of  $230 \text{ mAh g}^{-1}$  with a voltage plateau of  $0.6 - 0.55 \text{ V}$  is reported for the cathode composite with a  $\text{CuF}_2$  weight fraction of 80 %. The obtained capacity lies around half of the theoretical capacity of  $\text{C}_{2.8}\text{F}$  ( $521 \text{ mAh g}^{-1}$ ). However, since the active carbon cathode is mixed with  $\text{CuF}_2$ , it is not clear if all the obtained capacity is arising from the defluorination of carbon or a contribution of the  $\text{CuF}_2$  to the Cu conversion-type reaction exists, which could also be responsible for some fraction of the discharge capacity.

## 7 Conclusions and Future Challenges

In this review, the improvements of FIBs from the early 1970s until today have been discussed with respect to the development of the electrolytes as well as cathode and anode materials.

In contrast to LIBs, the first cells suggested for FIBs relied on the use of solid fluoride ion conductors due to the difficulty of transporting a “naked” fluoride ion in liquid conditions. The respective doped binary fluorides are easy to make and commercially available but have limited conductivities at room temperature and thus require heating to  $\sim 150$  °C or above in order to be charged/discharged with reasonable C-rates. Therefore, in the future, a critical focus must be based on the development of RT-FIB systems with either solid or liquid electrolytes, which could make the technology a real alternative to the current commercial batteries, especially for localized storage applications. In particular, since less attention has been paid to develop FIBs based on liquid electrolytes, their further elaboration and determination of compatibility with various electrode materials can play an important future role in making efficient cells in the future.

A big advantage of solid ion conductors lies in a maximal transport number for a certain ionic species approaching a value of  $t \sim 1$ . For LIBs, it is considered that this can prevent certain polarization issues arising at high current densities,<sup>21</sup> and it is valid to assume similar behavior for FIBs. However, due to the intrinsically lower ionic conductivity of FIBs, the breakthrough of solid ion conductors can be measured primarily by the challenges of operating temperature and cell preparation before the consideration of high-performance issues should take place. The operating temperature can, in principle, be matched by few materials containing  $ns^2$  cations ( $PbSnF_4$  has the highest conductivity of around  $10^{-3} \text{ S}\cdot\text{cm}^{-1}$  at room temperature until present), which show a lower electrochemical stability window. Again, this gives some similarity to solid lithium-ion conductors, such as thiophosphate based compounds, which have high conductivities, but low electrochemical stability.<sup>168</sup> In many cases, such instabilities can be circumvented by applying coating to electrode materials or using interlayer approaches. Clearly, the design strategies cannot be adopted one by one, but a certain similarity might also account here. The cathode side might be easier to be handled in such a case, since known solid ion conductors such as  $La_{0.9}Ba_{0.1}F_{2.9}$  have high stability towards oxidizing reactions. In contrast, metals with low electronegativity such as Mg or Ce used on the anode side will be more difficult to be stabilized by coating since they perform conversion reactions with large volume changes and have similar redox potentials than  $La_{0.9}Ba_{0.1}F_{2.9}$ , which might imply a certain cross-reactivity.

Cell preparation is another important aspect of FIBs. Fluorides have in general lower melting temperatures than oxide materials and thus can show easier thermal handling in order to minimize grain boundaries. Other methods such as cold sintering or spark plasma sintering might bring into play new aspects for the preparation of ceramic conductors, which have been basically unexplored. Further, though some reports have considered the use of thin films, the exploration space provided in this field is large, with aspects such as the exploration of multilayers, interface studies, thin-film batteries, strain engineering, etc., deserving future focus.

Another point to be considered for future applications lies in the fact that rare earth fluoride conductors present challenges in terms of weight and material costs (for example, La, Ce, Sr). These materials neither possess a large availability for large scale applications nor a strong interest for applications such as electromobility. Though alkaline earth or lanthanide fluorides

possess good stability against humidity and do not release HF easily (e. g., LaF<sub>3</sub> can be precipitated from aqueous solutions), certain alkali metal fluorides are more sensitive to humidity and acidic conditions especially, and can release corrosive HF gas. Further, elements such as Pb and Sb imply certain environmental concerns, and would be desirable to be replaced or limited in use for real applications.

Regardless of the work that has to be done in the future, the authors of this review assume that solid electrolytes will still be of importance for the development of other cell components such as electrode materials within the upcoming years. Thus, it can be expected that many reports will be based on the development of solid-state FIB concepts. Further, we also think that solid-state batteries are in general less understood than the liquid electrolyte-based counterparts and that research performed in this context can lead to co-operative effects in creating a deeper understanding of the matter. The fluoride-ionic conductivities of the studied materials were in the range of between 10<sup>-3</sup> to 10<sup>-6</sup> S·cm<sup>-1</sup>, an outcome that is very comparable to what is found for inorganic or polymer-based electrolytes used in LIBs.

Recent developments of the electrode materials (both cathodes and anodes) for FIBs were discussed in the context of intercalation and conversion mechanisms. It is shown that conversion-based systems mainly provide large capacities, though, they often suffer from poor cycling stability. Therefore, the highest cycle life has been so far observed for intercalation-based cathode materials with Ruddlesden-Popper-type structure. It is worth mentioning that to overcome intrinsic problems with conversion-based electrode materials, several strategies have been derived for lithium-ion batteries, which might be conceptually adaptable to improve conversion-based electrodes for FIBs. These strategies comprise the preparation of cells in thin electrode configurations,<sup>1</sup> encapsulation of the electrode material in a hollow structure,<sup>169, 170</sup> or the infiltration of materials into porous carbon hosts.<sup>171</sup> Nevertheless, considering the limitations of the conversion-based electrode materials, even the state of the art of the LIBs still mainly relies on intercalation-based electrode materials. Thus, the solution to the problem of obtaining functional intercalation-based materials might not necessarily be fully chemistry-related but also include materials science and engineering aspects, such as the application of pressure during cycling. Therefore, by further improvement of the conversion-based electrode materials, they may enter into the market of reversible batteries, especially due to their high energy capacity required for large scale energy storage<sup>39</sup>.

With respect to intercalation-based systems, there is still a wide space for exploration, especially for anode materials, where the concept of oxide for fluoride substitution and subsequent reductive fluoride extraction could be adopted to metal cations such as Sn<sup>4+</sup>, In<sup>3+</sup>, Ru<sup>6+</sup>, etc. to stabilize them in more reductive, lower oxidation states, or by exploring electrifieds as suggested recently.<sup>163</sup> For intercalation materials, another issue lies in the replacement of heavy alkaline earths or lanthanides, such as Sr, Ba, or La by lower weight and higher abundant cations such as Ca or Sc for Ruddlesden-Popper based systems. In addition, topochemical reactions based on anions are not limited to Ruddlesden-Popper type compounds, but can also occur for other perovskite related materials.<sup>172</sup> Further, a lighter matrix could also be achieved by using fluoride in combination with polyanions such as phosphate or sulphate, by which the stabilization of the host matrix might occur via the polyanion instead of the alkaline / rare earth metals. In this respect, one must succeed in adopting topochemical fluorination routes away from perovskite-related systems<sup>153</sup> to other structural settings. On the other hand, the issues related to the carbon side reaction need

to be further investigated, and techniques to mitigate the negative effect of carbon should be developed. In this context, materials engineering can be highly important, where contact points between the different cell components might be optimized by using nano-rod morphologies, particle coating strategies and core-shell structures or by using thin films.

Though many improvements were made over the last years, FIBs are still at an early stage of development; their performance is not yet close to the state-of-the-art LIBs, but they can approach other alternative battery technologies such as chloride, magnesium or aluminum ion batteries. For certain applications, the development of room temperature solid-state and liquid electrolytes is an obligation in order to attract more interest in FIBs. However, high-temperature batteries might still fill a niche for certain applications,<sup>173</sup> might not be as critical considering electromobility (where the so-called ZEBRA battery been used already<sup>174</sup>), and might be unproblematic for large scale energy storage, for which the energy losses can be minimized using well-engineered thermal insulation.

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