

Fluoride-Based Solid Electrolytes (FB-SE): Environmental Sustainability Considerations

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Abstract. Solid electrolytes based on fluoride (FB-SEs) have been recently subject to growing interest as a potential all-solid-state battery (ASSB) because of their chemical stability, broad electrochemical stability ranges, and possible availability of an anode based on high-energy metal elements. This review is a qualitative synthesis report on the current advancements in research of FB-SE with light quantitative comparisons with over 60 peer-reviewed publications published in the last 5 years (2020-25). Improvements on material compositions, synthesis procedures, ionic conductivity optimization, as well as the electrode- electrolyte interfaces stability are systematically addressed. Besides the electrochemical performance, the paper puts specific emphasis on the aspects of environmental sustainability that had hitherto not been sufficiently represented in the literature. The problem of sustainability is considered at the main points of the material life cycle, such as the purchase of raw materials, energy consumption in the manufacture stage, the safety of the operations, and the particulars of the end-of-life. Representative quantitative measurements of ionic conductivity values, synthesis temperatures, and the incorporation of precursors containing fluorine are addressed where reported and are acknowledged to be very heterogeneous and rarely comparable with the existing literature, other persistent limitations include the small number of life-cycle assessment (LCA) studies, lack of exploration of the recyclability, and lack of published environmental impact of synthesis processes. Instead of a clear-cut evaluation framework, the given review presents a conceptual lens through which the electrochemical performance is linked with an initial sustainability indicator, with the purpose of directing the further experiment design and promoting a more direct approach toward considering sustainability in the development of FB-SEs towards ASSBs.

Keywords: LCA, Circular Economy, Interfacial Stability.

1. Introduction

All-solid-state batteries (ASSBs) are informally regarded as a promising future energy storage system with benefits of provided main features of safety and increased energy density. ASSBs allow Li or Na metal electrodes to be taken into serious consideration by employing solid-state ionic conductors instead of flammable liquid electrolytes, and reducing the risks of leakage, and thermal runaway. Up to now, a variety of studies have been conducted on numerous types of solid electrolytes, including oxides, sulfides, polymers, and halides with their respective strengths and weaknesses of ionic conductivity, interfacial stability, mechanical properties, and processability [10].

On a larger scale in a solid electrolyte environment fluoride-based solid electrolytes (FB-SEs) have recently developed a growing interest. In comparison to oxide and sulfide systems that have been more actively studied, FB-SEs can be described as having strong ionic bonding, good electrochemical stability and, possibly, good mechanical robustness, all of which reflect their high-voltage and metal anode ASSB operating conditions [1]. Nonetheless, FB-SEs are yet to be fully developed in comparison with the rest of solid electrolyte systems in terms of the Matthew-Markov-Luke pattern of evolution.

In the literature review on FB-SEs, studies focusing on sustainability-related issues have gotten much less systematization compared to electrochemical measures. Practically speaking, the environmental effects of FB-SEs, including sourcing of raw materials, energy usage at the production during the synthesis processes, operational safety, and disposal of the end product, are not

comprehensively known. Such absence of sustainability-driven evaluation is a definite gap in research as opposed to a side angle given the increasing emphasis on greener battery technologies.

It is on this background that this review will critically review the recent advancements in FB-SE research but specifically with regards to challenges that are related to sustainability. The work is laid out as follows: in Section 2, there is a summary of the crystalline chemistry of the crystal and ionic transport of representative systems of FB-SE systems; in Section 3, some of the synthesis strategies and approaches that help to improve electrochemical performance are reviewed; in Section 4, interfacial issues of contacting the electrodes, in Section 5, sustainability will be discussed in terms of material life cycle, and in Section 6, the key aspects that require research questions in ongoing work are presented as the integration of life-cycle assessment and the idea of circular

2. Background: Fluoride-Based Solid Electrolytes

2.1. Definition and Key Characteristics

Fluoride-based solid electrolytes (FB-SEs) is a category in the general classification of solid ionic conductors, in which fluoride-based materials are used to transport Li^+ , Na^+ , or other monovalent cationic species. The FB-SEs are typically linked with broad electrochemical stability and good chemical compatibility with high cathode voltage material compared with oxide- and sulfide-based solid electrolytes [1].

Notably, FB-SEs are not one and the same material family. In lieu, they include a number of chemically and structurally varied groups, which are the rare-earth fluorides, transition-metal fluorides, and incorporated anions, such as oxyfluorides and fluoride-chloride complexes. These groups vary significantly in terms of crystal chemistry, bonding behavior, and prevalent ion-transport mechanisms, leading to a large spread of reported ionic conductivities and also diverse synthesis and processing requirements.

The extensive crystal structures and ion-transport options emanating amongst FB-SE systems underscores the plasticity of fluoride chemistry as well as the difficulty in optimization of performance. As such, it is important to evaluate FB-SEs meaningfully, not by direct extrapolation to small numbers of representative compounds, but by analyzing the systems per se. This same heterogeneity also makes FB-SEs stand out compared to more compositionally consolidated solid electrolyte families and identifies solid-state ion conduction platform potential in the FB-SEs.

2.2. Historical Development and Recent Momentum

Initial studies on FB-SEs were quite limited by the low room temperature ionic conductivity and harsh conditions of their synthesis that restricted their immediate use in feasible solid-state battery use. Therefore, early research studies were mostly purely discoveries, and development was slower than that of each oxide or sulfide-based electrolyte system. Most recently, FB-SE research has been revitalized by progress in computational screening and data-driven materials discovery and better experimental synthesis strategies. One such example is a 2024 data-mining study that performed a systematic screen of large materials databases and selected a few promising fluoride-based solid electrolyte materials, such as Li_3ScF_6 , NaPrF_4 , and Na_3HfF_7 , all of which have good chemical stability and may have viable Li^+/Na^+ migration routes [1]. These efforts have led to the abandonment of an empirical trial-and-error means of selection to a more precise choice of materials. The further length of the experimental research may be divided into three ways, which are connected. The former is interface and microstructure engineering; e.g. a chloride-fluoride heterostructured electrolyte, which has been proposed to refresh Na metal batteries, demonstrated improved ionic conductivity and enhanced air stability by grain-boundary engineering, using rather common precursors [2]. The second focus is innovation on synthesis pathways with an example of sonochemical synthesis of $\text{K}_{0.3}\text{Sn}_{1.7}\text{F}_{4.7}$, which enhanced the homogeneity of its phases and allowed a quick and easy transit of the fluoride-ion. The third path is design of hybrid electrolytes, i.e. fluoride phases are built into sulfide phase networks to enable high-voltage (>4 V) all-solid-state battery operation without

materially reducing total ionic conductivity [3]. When combined, these trends indicate that FB-SE research is moving progressively towards less material discovery, and more application-focused design methodologies, which should allow a basis in evaluating FB-SEs not by the metrics of the environment of a specific ASSB application, but by scalability, materials availability, and sustainability concerns in future system design.

3. Sustainability Considerations

3.1. Potential Environmental Advantages of FB-Ses

Solid electrolytes made with fluoride (FB-SEs) have been suggested to provide a number of possible sustainability-related benefits, but most of these assertions have been inadequately corroborated by quantitative environmental analysis. Among the benefits that have been commonly cited is the removal of flammable liquid electrolytes, which is possibly helpful in making batteries safer by lowering possible fire hazards, leaks of electrolytes, and the use of poisonous organic solvents. These characteristics may possibly reduce environmental risks both when operating normally and failure conditions [4-5].

Moreover, fluoride-based electrolyte systems have been frequently documented to have excellent electrochemical stability at deep voltage ranges. This chemical resilience can be of benefit in increasing cycle life and decreasing frequency of replacement that is usually linked to the consumption of low material content during service life of a battery. However, direct correlations between electrochemical stability and long working life are mostly inferred though not directly measured at least in terms of his/her life-cycle [6-8]. More so, heterostructure fluoride electrolytes have recently been shown to be able to incorporate substantially more halide precursors, and there may be a gateway into more scalable and cost-effective material systems [2].

Combined with the additional stated observations, it can be concluded that FB-SEs could pose environmental benefits compared to traditional liquid-electrolyte lithium-ion batteries, particularly in regards to work safety and life span. Yet, it is worth noting that these positive 1 should be seen as speculative as opposed to established, since systematic life-cycle evaluation (LCA) literature and quantitative study comparisons of sustainability are yet to be conducted or established in their larger part.

3.2. Potential Environmental Advantages of FB-Ses

Although the above may have benefits, FB-SE systems have huge challenges to sustainability and unresolved uncertainties. Most of the reported environmental benefits are subjective to nature and more basic concerns are raised with respect to the availability of raw materials, synthesis effects, and end-of-life management. Notably, in the literature that is generally available material performance metrics are focused on without presenting the data that should be included when evaluating the environment comprehensively.

In this section, the researcher will establish the major knowledge gaps related to sustainability as it relates to FB-SEs. To avoid conceptual overlap and ensure a distinct line between the identification of problems and solutions methods of addressing these gaps are addressed separately in Section 4 to avoid this confusion.

3.2.1 Raw Material Scarcity and Mining Impacts

Some of the FB-SE candidates that have performed well are dependent on the elements including Sc and Hf [1], not rich in nature, broadcasted to the global and, regionally, geographically, and extraction, which are environmentally expensive. As an example, world scandium production is projected to be less than $20\text{t} \cdot \text{yr}^{-1}$, which is a question towards seeking material security in terms of availability and supply of large-scale battery use. In addition to the limitation of supply, the processing and extraction of such materials are usually linked to the use of a lot of energy, a lot of waste, and a localized toll on the environment. Even though other FB-SE compositions, which utilize

more plentiful elements, such as Na-based fluoride systems have been developed, their electrochemical activity, processing, and scalability have not been adequately investigated. As a result, trade-offs of material abundance and functional performance have not been carefully studied as yet which is a severe gap in determining the long-term sustainability of FB-SE technologies.

3.2.2 Energy-Intensive Synthesis Processes

Most of the reported FB-SE materials are synthesized through high-temperature sintering, long term mechanical milling, or special nonchemical treatments. Although these methods are useful in phase formation and control of microstructure, phase formation and microstructure control are usually related to consuming a lot of energy and emissions during the process. Synthesis routes have often been given in the existing literature as being described as energy intensive, but no quantitative descriptions have often been given in a uniform way, e.g. the range of temperatures, lengths of the processing, and energy input per unit mass.

Also, there is uncertainty of alternative synthesis approaches, such as sonochemical or low-temperature techniques, having the scent to reduce total energy requirements relative to conventional solid-state techniques [8]. Lack of standardized measures and comparative standards prevents the possibility of assessing processes of environmental trade-offs in the context of various systems of FB-SEs.

3.2.3 Interfacial Stability and Degradation

The issue of interfacial instability is known throughout all-solid-state batteries and may cause augmented internal resistance, a decrease in capacity, and early cell death. In regard to sustainability considerations, the reduction of the cycle life has a direct impact on the environmental footprint in creating more service life and decreasing the time taken to replace materials and generate waste. Despite the fact that interface engineering strategies have enhanced the performance of short-term electrochemical interaction in FB-SE-based systems, their long-term performance has not been fully comprehended. Specifically, the connection between interfacial degradation processes and environmental impact life cycle has not been studied in a systematic manner yet.

3.2.4 Toxicity and Waste Management

The handling, disposal and cracks, degradation of materials containing fluoride bring out other concerns on environment and also on occupant safety. In some conditions, the fluoride containing compounds can produce toxic elements like HF which brings about hazardous effects with respect to worker exposure, accidental release and waste management. Nevertheless, it is rarely discussed in the existing literature that the leaching behavior of fluoride and its persistence in the environment, and the ultimate disposition of fluorine species at the end of life. Consequently, the risks associated with the toxicity are still mostly qualitative and imprecise.

3.2.5 Absence of Life-Cycle Assessment (LCA)

Up to this point there has not been a documented cradle-to-grave Life-cycle assessment of FB-SE based battery systems [9-10]. Current research focuses largely on the basis of ionic conductivity and electrochemical cycling performance, and little attention has been paid to upstream material extraction, synthesis-related emission, or downstream recycling and disposing. This incomplete evidence of LCA is a critical knowledge gap that does not allow evidence-based sustainability comparisons of FB-SEs and more developed solid electrolyte technologies.

4. Life-Cycle and Circular-Economy Perspectives

The necessary direction taken to describe the conceptual evaluation framework and methodological pathways to evaluate FB-SE systems through a life-cycle and circular-economy approach to address the identified gaps in terms of sustainability in Section 3. Instead of conducting a comprehensive overview of the effects on the environment, the emphasis is put on the definition of the crucial

evaluation dimensions and finding the action assessment strategies. This strategy is meant to bridge the gap determination in Section 3 and not to repeat anything.

4.1. Full Life-Cycle Assessment (LCA)

The life-cycle analysis of FB-SE systems must be completed including the stage of raw materials extraction, synthesis of materials, manufacturing of cells, their use, and the final disposal or life cycle. During the raw-material step, extraction and purification of fluoride precursors can be characterized by a high level of environmental impact in terms of quality of ore and intensive chemical treatment, toxicity, and transportation. Processing temperature, energy requirement, yield and waste generation is likely to dominate as the key drivers of environmental performance in the course of synthesis and manufacturing.

Cradle-to-grave LCAs would provide meaningful benchmarking of FB-SE systems with established solid electrolytes, which are known to emit H_2S during degradation such as sulfide-based and oxide-based systems (e.g., LLCZO) at which preliminary LCA data have already been reported. This kind of benchmarking is critical in terms of forming a perspective on the sustainability arguments that are linked to FB-SEs.

4.2. Material Selection Based on Resource Availability

Regarding life-cycle considerations, the choice of the material should not be solely based on the electrochemical performance, but the potential availability of the resource and the sustainability of the supply chain should be another criterion. Electrolyte compositions with rich elements, including sodium, potassium, and transition metals which are widely found may be intrinsically better in respect of scalability. Conversely, FB-SEs that are based on elements that are rare or geographically localized would need to pay close attention to the viability of recycling and the security of supply in the long-term.

In a LCA-based framework, the choice of material may be counted as an upstream design choice that would take a direct implication on the environmental impact at the further stages of the life-cycle. Certain optimization strategies of material are content therefore in Section 5 where performance-sustainability trade-offs are discussed more thoroughly.

4.3. Sustainable and Low-Energy Synthesis

Synthesis strategy is a leverage point that is critical in eliminating the environmental footprint of FB-SEs. Framework It is important to note that the future development should focus on the way of reducing processing temperature, reaction times, and simplification of synthesis steps. Instead of examining the individual synthesis methods, the significance should lie on the quantifiable process indicators, including the input of energy, yield, and level of emissions.

Creating standard reporting practice of the metrics related to synthesis would not only allow the cross-material and cross-technology comparison but also make LCA studies as well as rational optimization of the process.

4.4. End-of-Life Design and Circular Economy

The issue of end-of-life is one of the unresolved problems in FB-SE systems. Some of the key open questions are the safe recovery of materials containing fluoride, the danger of the formation of hazardous byproducts during the recycles, and the possibility of reusing the materials or downcycling. Currently, these problems are under-explored, and thus the necessity to integrate the concept of the circular economy at its initial stages should be mentioned.

Conceptually, some strategies to have design-for-recycling approaches (simplified compositions, compatible separation paths, and controlled fluorine chemistry) are to be reviewed as part of the future FB-SE development. These open questions will be critical to put FB-SE technologies in line with long-term sustainability and circle-economy goals.

5. Future Research Directions

Based on the deficiencies pointed out in the previous text, several priority research directions can be outlined to support the sustainable development of fluoride-based solid electrolytes (FB-SEs). These directions focus on the unresolved challenges rather than repeating the evaluation framework discussed earlier.

5.1. Embedding life-cycle considerations into early-stage material screening

A key unresolved issue is the lack of sustainability awareness in material selection during the discovery stage. Future research should explore how to integrate the concept of life cycle assessment (LCA) at an early stage, so as to eliminate material systems that are associated with high extraction burdens or high energy consumption synthesis before the material system reaches the stage of expansion.

5.2. Establishing safe and material-specific recycling pathways for fluoride-based electrolytes

Little is known about the end-of-life management of boron-fluoride-silicon elastomers (FB-SE), especially regarding the generation of harmful fluorine-containing by-products. Specialized research is needed to clarify whether the fluoride phase can be safely recovered, neutralized or reused without introducing new environmental risks.

5.3. Clarifying long-term degradation mechanisms and their environmental implications

Although electrochemical degradation has been extensively studied in terms of performance, the issue of its connection with sustainability remains unresolved. Systematic research on interface reactions, phase transitions, and degradation products is needed to link the limitation of service life with environmental burden and waste generation.

5.4. Identifying performance–sustainability trade-offs in abundant-element fluoride systems

Although the FB-SE (solid electrolyte) schemes based on sodium, potassium or widely available transition metals are often proposed as sustainable alternatives, their long-term feasibility remains uncertain. Future research should assess whether such systems can meet the requirements of conductivity, stability and scalability without transferring environmental burdens to other life cycle stages.

5.5. Bridging materials research with environmental and regulatory perspectives

A long-standing challenge lies in how to transform the laboratory-scale fiber-reinforced composite material (FB-SE) technology into an applicable technology that complies with environmental regulations and the principles of circular economy. To bridge this gap, it is necessary for material scientists, environmental engineers, and policy researchers to enhance their collaboration, ensuring that technological innovations align with the actual sustainability constraints.

6. Conclusion

The scientifically potential materials in the efforts to prepare safer and high-performing all-solid-state batteries are the family of fluoride-based solid electrolytes (FB-SEs): as current materials discovery efforts and synthesis strategies indicate, as well as electrochemical characterization efforts. This is because this review intertwines electrochemical performance with a newer environmental and life-cycle perspective and thus supplements performance-focused research and introduces an earlier underexplored gap in FB-SE studies.

FB-SEs sustainability-related aspects are not characterized sufficiently despite the offered technological advancements. There are still huge uncertainties about the availability of resources, the environmental effects of synthesis, its recyclability, and risks at the end of life, this is mainly due to

absence of systematic and quantitative assessment schemes. Thus, it is not possible to yet robustly judge the environmental sustainability of FB-SE-based battery systems and also to compare it with more established solid electrolyte technologies.

Further development in FB-SE studies will involve parallel treatment of the aspects of electrochemical performance and sustainability measures, instead of looking at them in a series-like mode. Life-cycle assessment and related ideas of a circular-economy, integrated into the development and analysis of materials, offer a requisite foundation to determine the trade-offs, reduce the number of unintended environmental burdens, and pursue responsible scale-up. Placing the FB-SE development in the context of integrated performance-sustainability spectrum, this review explains one of the directions of more informed decision-making in solid electrolyte research. This approach is essential in terms of evolving FB-SEs to materials on a scale reasonably marketable in batteries, which are technically feasible and products that are also environmentally responsible throughout their entire life cycle.

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