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REVIEW

LiF: past, present, and future in advanced material applications—insights into battery technology: a review

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Abstract

Lithium fluoride has attracted considerable attention due to its distinctive properties, such as relatively high ionic conductivity, chemical stability, and compatibility with various battery components. Initially employed as a dosimeter for radiation dose measurement, the scope of LiF applications has significantly broadened over the years. This review delves into the historical and contemporary uses of LiF, with a particular emphasis on its role in the evolution of lithium-ion battery technology. The paper traces the material's progression from a dosimetric tool in the 1980s to an essential element in solid-state batteries, highlighting its surface properties, defect formation, and performance improvements. The advancement of LiF-based solid electrolytes presents numerous benefits, including enhanced safety, superior performance at high temperatures, and longer battery lifespan. Additionally, this review spotlights key research developments and technological innovations that emphasize LiF's potential for future applications in diverse areas such as optics, catalysis, and biomedicine.

Keywords Lithium fluoride (LiF) · Material science · Surface modification · Dosimetry · Solid electrolytes · Solid-state batteries

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Introduction

Today, the fourth generation of lithium-ion technology with enormous potential is on the verge of further development [1]. Due to its unique properties and advantages, such as inherent safety, relatively high ionic conductivity, chemical stability and compatibility, economic potential, and non-proliferation in nature, LiF has become the focus of significant attention for lithium-ion technology [2–4]. This study primarily reviews the history of research on LiF materials, including authors and active research centers. Then, the research status of LiF is presented, describing the current state of research, the scientific areas in which LiF is used, and the strategy of experimental research. In addition, the resulting novelties and challenges encountered when using LiF are discussed, including defect formation in materials, optimization of solid electrolyte component systems for energy control, interactions with other substances, and disposal and recycling methods. Based on the above, research directions in the field of LiF are discussed, and research areas are recommended for the future development of Li-ion technology. The purpose of this article is to provide the current state of research and expected future developments in the field of LiF-related materials.

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Methodology

To achieve our goal, we employed a content analysis approach based on the survey method. An extensive literature search was conducted across various platforms, including Scopus, Web of Science, Science Direct, Google Scholar, ResearchGate, and international agencies. Comprehensive searches were conducted using keywords such as: “lithium fluoride; LiF; surface of alkali halide crystals (AHC); surface of lithium fluoride crystals; defects in lithium fluoride crystals; lithium fluoride in solid-state batteries; lithium fluoride in solid electrolytes; issues, advantages, and applications, as well as pros and cons.” In our analysis, we used search queries for specific AHC (KCl, CsBr, RbCl, KBr, KF, CsI, etc.) rather than relying solely on the general term “AHC.” This approach helps prevent underestimation due to potential inconsistencies in terminology within the literature. However, search queries for LiF and NaCl were conducted separately, as a significant number of studies on NaCl exist, particularly due to its increasing use in sodium-ion batteries in recent years. For this reason, when summing the total number of publications on AHC, NaCl-related studies were excluded to avoid data distortion.

During this search process, numerous articles were identified. The literature evaluation involved a thorough analysis of titles, keywords, abstracts, article contents, and journal topics to select relevant references.

The review process was carried out in two distinct stages:

- Selection Method
- Review Results

The selection stage began with an extensive literature search, during which several dozen documents were identified. Subsequent evaluation, including key keywords and an assessment of titles, abstracts, topics, and materials, narrowed down the selection. Finally, factors such as impact factor, citation count, review process, and publication period were considered, leading to the selection of appropriate articles. These articles formed the basis for subsequent review, analysis, and critical discussion of lithium fluoride materials used in various industries. The topics discussed included an overview and comparison of properties and functions for use in different applications, the growing demand for such materials, structure, classification, advantages, optimization of various applications, as well as general issues. Following this, research directions and potential areas for future research to advance various technologies related to LiF materials are discussed.

The selection (inclusion and exclusion) of articles was carried out based on the criteria presented in Table 1:

The “Content Analysis” method was chosen as the most suiTable approach for reviewing LiF research, as it enables a systematic examination of existing literature to identify key trends, research gaps, and thematic patterns across multiple studies. This approach allows us to:

- Track the evolution of research: By analyzing both historical and recent publications, we can highlight how LiF applications have expanded over time.
- Identify research gaps: This approach helps uncover underexplored areas, such as defect formation mechanisms in LiF and its role in emerging battery technologies.
- Compare methodologies and findings: It enables a comparative analysis of experimental techniques and theoretical models used in LiF research.
- Highlight interdisciplinary applications: Since LiF is utilized in multiple fields (batteries, optics, dosimetry, catalysis), content analysis facilitates an integrated perspective across disciplines.
- Provide a forecast for the next decade: By tracking current trends and technological advancements, we can predict the potential applications of LiF over the next 10

AQ2 **Table 1** Criteria for article selection

Criteria Type	Description
Inclusion Criteria	
Peer-reviewed sources	Articles published in repuTable, peer-reviewed journals indexed in Scopus, Web of Science, ScienceDirect, and Google Scholar
Research focus	Studies focusing on LiF applications in batteries, optics, dosimetry, catalysis, and related fields
Publication timeframe	Studies published within the last 30 years to capture historical and recent advancements
Study type	Experimental, theoretical, and review articles contributing to the understanding of LiF properties and applications
Exclusion Criteria	
Non-peer-reviewed sources	Conference abstracts, unpublished manuscripts, preprints, and non-reviewed articles
Lack of relevant data	Studies without experimental validation, insufficient data, or no direct connection to LiF
Unrelated research scope	Articles focusing on different materials or applications unrelated to LiF

years, particularly in energy storage, advanced materials, and quantum technologies.

Results and discussion

Data obtained from the Scopus and ScienceDirect search engines indicate that after World War II, AHC became an active area of research. This surge in interest was driven by several factors. In particular, their high transparency in the ultraviolet (UV) and infrared (IR) ranges made them promising materials for optical systems, surpassing most available alternatives. Their unique properties led to widespread demand in military, optical, and scientific applications.

Even after the war, interest in AHC remained high as they continued to find applications in diverse fields, ranging from nuclear technology to optics and quantum physics. These materials played a crucial role in scientific discoveries and technological advancements. Below, we outline the key reasons behind the popularity of AHC in the second half of the twentieth century:

1. Nuclear Technology – Used in nuclear reactors (e.g., molten salt reactors) and radiation dosimetry due to their thermoluminescent properties.
2. Optical Research – High transparency in the UV and IR ranges, making them essential for optical systems. Studied for color centers and photorefractive effects, which are applied in lasers and optical instruments.
3. Fundamental Physics – Investigated for defects, vacancies, color centers, and quantum mechanical phenomena. Used in studies of electronic states and light-matter interactions.
4. Military Applications – Utilized in radiation-resistant military technologies and space applications for thermal protection and optical devices.
5. Ease of Processing – Simple to grow and process, enabling the production of large, high-quality single crystals. Their simple cubic structure makes them ideal model objects for research.
6. Advancement of Research Methods – Enabled the active development of new experimental and theoretical approaches, including IR and UV spectroscopy.

Table 2 presents the advantages, disadvantages, and applications of some of the most widely used AHC.

For the development of radiation-resistant materials and devices used in nuclear reactors, space technologies, and dosimetry systems, a detailed study of defect formation processes was required. Lithium fluoride became a model material for such research due to its simple cubic structure and high radiation sensitivity.

As shown in Table 2, LiF stands out as the most versatile and widely used material due to its high transparency, radiation resistance, and suitability for fundamental research. However, its hygroscopicity and brittleness have limited its application in certain fields.

Additionally, in the modern world, the demand for enhanced functional properties of materials across various scientific and technological applications has been steadily increasing [5–8]. Control over the surface properties of materials is of particular relevance, since it is the near-surface region that plays a key role in a number of physicochemical processes [9–11]. The physicochemical properties of any surface can be changed in three methods [12, 13], (see Table 3).

Table 2 Advantages, disadvantages, and applications of popular AHC (Based on Scopus and ScienceDirect search data)

AHC	Applications	Advantages	Disadvantages
LiF	Dosimetry, nuclear technology, optics, fundamental physics, space technology	High transparency in UV and IR, high radiation sensitivity, simple cubic structure, high thermoluminescence	Brittleness, high hygroscopicity, difficulty in mechanical processing
NaCl	Optics, infrared windows, laboratory research	Good transparency in IR, availability, easy processing	Hygroscopicity, low mechanical strength
KCl	IR optics, laser technologies	Good transparency in IR, easy to grow	Hygroscopicity, high solubility in water
CsBr	X-ray and gamma-ray spectroscopy, radiation detectors	High radiation sensitivity, low photon absorption threshold	High hygroscopicity, high cost
RbCl	Solid-state physics, ion conductivity research	High ionic conductivity, simple crystal structure	Limited industrial applications, high solubility
KBr	IR spectroscopy, laser technologies	High transparency in IR, easy to grow	Very high hygroscopicity, requires special storage conditions
KF	Laser technologies, nonlinear optics	High transparency in the UV range, nonlinear optical properties	Hygroscopicity, brittleness
CsI	Scintillation detectors, medical imaging	High absorption coefficient for X-ray and gamma radiation	Hygroscopicity, low mechanical strength

Table 3 Methods for changing the physical and chemical properties of a surface

Method	Description	Changeable properties	Examples applications
Physical methods			
Mechanical treatment	Grinding, polishing, sandblasting, shot blasting	Roughness, area surfaces, topography	Surface preparation before coating, improving adhesion
Physical etching	Treating a surface with substances to dissolve or remove part of the material	Chemical composition, topography, microstructure	Cleaning surfaces, formation microrelief
Ionic bombardment	Bombarding a surface with ions to change its composition and properties	Chemical composition, electrical conductivity, optical properties	Doping of materials, changing the electrical conductivity of semiconductors
Sputtering	vacuum deposition, magnetron sputtering, electrochemical deposition	Chemical composition, mechanical properties, electrical conductivity, optical properties, tribological properties	Creation of protective coatings, changing surface color, increasing wear resistance
Laser treatment	Surface treatment with laser radiation to change its properties	Roughness, topography, microstructure, optical properties	Material marking, micro-processing, surface color change
Chemical methods			
Modification surfaces reagents	Treatment of a surface with chemicals to change its chemical composition or functional groups	Chemical composition, wettability, adhesion, biocompatibility	Creation of hydrophobic and hydrophilic surfaces, changing the biocompatibility of materials
Stitching	The formation of covalent bonds between molecules on a surface to change its properties	Chemical stability, mechanical properties, biocompatibility	Increasing the strength and wear resistance of materials, modifying biomaterials
Chemical etching	Dissolving or removing part of a surface material using chemicals	Topography, microstructure, roughness	Formation of microrelief, removal of surface defects
Physico-chemical methods			
Plasma treatment	Plasma surface treatment to change its properties	Chemical composition, wettability, adhesion, biocompatibility	Surface cleaning, surface activation, modification of biomaterials
Treatment UV radiation	Irradiation of a surface with UV radiation to change its properties	Chemical composition, wettability, adhesion	Cleaning surfaces, modification polymers

As can be seen, the study of factors influencing the physicochemical properties of a surface is an important area of scientific research, which holds great significance for various fields of science and technology. Controlling these factors allows for the modification of surface properties of materials, improving their performance characteristics and creating new materials with specified properties for various applications [14, 15], such as catalysis [16], microelectronics [17, 18], corrosion protection [19], and biomaterials [20, 21]. The Table 3 shows that a sharp change in surface properties occurs during ion implantation [22–24], well as laser [25–27] and plasma treatment [28]. During implantation, bombardment of the surface with high-energy ions can lead to the formation of new phases, changing the chemical composition and structure of the surface [29, 30]. Plasma and laser processing can also lead to melting, evaporation, decomposition of the surface material, changes in the chemical composition, structure, and topography of the surface, as well as the formation of new functional groups and structures and changes in properties.

Thus, the primary result of surface formation from physical and chemical treatments is the creation of defects. With increasing time and intensity, these treatments lead to the accumulation and increase in the concentration of defects on the surface, which will undoubtedly affect its properties. Defects in the near-surface region can have both positive and negative effects on the properties of materials. For example, they can affect mechanical strength, electrical conductivity, optical characteristics, catalytic properties, corrosion resistance, etc. Below, Table 4 summarizes the key mechanisms of defect formation in AHC.

The control and optimization of defects in crystals, using lithium fluoride as an example, are critically important for ensuring optimal performance in various applications. Defects in the crystalline structure of LiF can significantly influence its optical, mechanical, and electrical properties. By managing the type, concentration, and distribution of defects, it is possible to deliberately modify the material's properties to meet specific application needs.

For instance, a study on the effect of low-energy electron irradiation on LiF nanofilms has demonstrated that defect engineering offers promising opportunities for modifying the properties of solid materials.

Thus, the development and application of defect control and optimization methods in LiF crystals are essential for enhancing their functionality and reliability in both scientific and industrial applications. Below, Table 5 summarizes the methods for controlling and optimizing defects in LiF crystals. These methods enable effective manipulation of the defect structure, thereby improving the operational characteristics of LiF in various applications.

Despite a significant amount of research devoted to the formation of defects in the near-surface region, many issues remain insufficiently studied. To develop effective methods for managing defects, a deeper understanding of the mechanisms of their formation and influence on the properties of materials is necessary. For example, in the primary interaction processes, the mechanism of exciton formation was theoretically predicted in 1930 [31]. However, excitons were experimentally detected using photoelectron emission spectroscopy and other methods [32, 33] only several decades later, after 1960. The development of materials with specified surface properties can lead to the creation of new materials with unique characteristics, which, in turn, can stimulate the development of various industries and improve the environment. Controlling the formation of defects in the near-surface region can increase the efficiency of material and product production, reduce the number of defects,

Table 4 Key mechanisms of defect formation in AHC

Defect Formation Mechanism	Description	Examples of Defects	Influencing Factors
Radiation-Induced Defects	High-energy radiation (gamma rays, electrons) creates defects such as F-centers (anion vacancies trapping an electron) and H-centers	Vacancies, F-centers, H-centers	Radiation intensity and energy, crystal temperature
Thermal (Intrinsic) Defects	At elevated temperatures, vacancies and interstitial atoms form spontaneously, known as Schottky and Frenkel defects	Anion and cation vacancies, interstitial ions	Temperature, crystalline lattice imperfections
Mechanical Deformation	Applied mechanical stress leads to the formation of dislocations and other structural defects, altering crystal properties	Dislocations, cracks, packing defects	Magnitude and direction of applied stress, deformation rate
Impurity Defects	Introduction of impurities leads to new defect structures or changes in the concentration of existing defects	Substitutional ions, impurity complexes	Impurity ion concentration, size, and charge

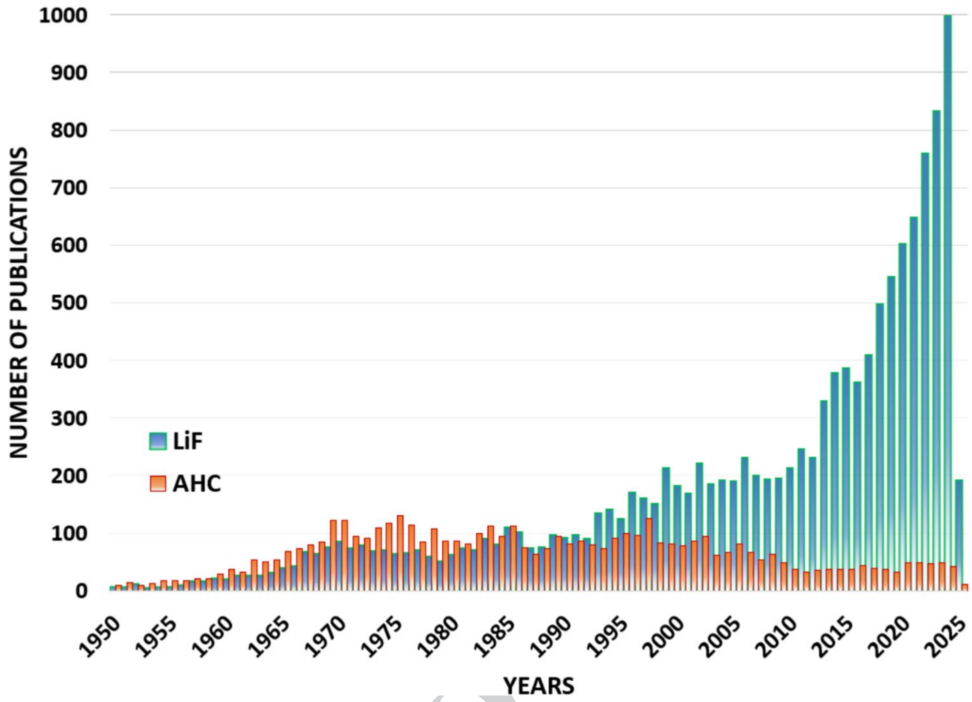
Table 5 Methods for controlling and optimizing defects in LiF crystals

Method	Description	Objective	Notes
Thermal Treatment (Annealing)	Heating LiF crystals to specific temperatures followed by controlled cooling	Reducing defect concentration, such as F-centers and dislocations; restoring crystal structure; improving optical properties	Optimal annealing parameters (temperature, duration) depend on the type and concentration of defects
Control of Irradiation Conditions	Regulating radiation dose and energy when using LiF in radiation environments	Minimizing the formation of undesirable defects; preventing material degradation	Understanding radiation-induced defect mechanisms allows for the development of effective defect prevention and mitigation strategies
Mechanical Processing	Careful control of cutting, grinding, and polishing processes	Reducing defect formation due to mechanical stress; minimizing the likelihood of dislocations and cracks	Use of optimal processing methods and appropriate equipment
Doping	Introducing specific impurities, such as magnesium or hydroxyl ions, into the crystal	Stabilizing the crystal structure; reducing the concentration of existing defects; enhancing specific material properties	The selection of impurity type and concentration should be justified based on the desired properties and potential side effects
Control of Crystal Growth Conditions	Optimizing growth parameters, including temperature, crystallization rate, and raw material composition	Producing LiF crystals with minimal defects; ensuring a more perfect crystal lattice	Careful monitoring of growth conditions promotes the formation of high-quality crystals

and enhance their competitiveness. The development of new materials with improved characteristics can lead to an improvement in people's quality of life. For example, materials with higher corrosion resistance can be used to construct more durable buildings and structures, and materials with improved biocompatible properties can be used to create more advanced medical implants.

In general, the study of defect formation in the near-surface region is an urgent scientific, technical, economic, social, and environmental problem. Based on this, in this work, we will carefully analyze research conducted over the entire period on defect formation and its influence on changes in the properties of material surfaces. Of course, we cannot cover the entire spectrum of defect formation on all existing crystals, which could include metals, semiconductors, and AHC. This would result in the accumulation of a large amount of data that needs to be processed. However, among all classes of crystals, AHC occupy a special place due to their unique properties and wide range of applications. AHC attract the attention of scientists due to their ability to easily form and modify defects under the influence of external factors, which opens up opportunities for targeted control of their properties. These crystals, including materials such as NaCl and LiF, are widely used in various fields of science and technology—from optics and electronics to biomedicine and nuclear energy. The data obtained from studies of defects in AHC are important not only for the development of technologies based on these materials but also for a broader understanding of defect formation processes in other classes of crystals, such as semiconductors and metals. Since the mechanisms of formation and evolution of defects are largely universal, the results obtained in AHC can be adapted to interpret similar processes in semiconductors and metals. This allows the knowledge gained to be used to improve material properties in electronics, where defects play a key role in determining conductivity and durability, and in metallurgy, where defect management is critical to mechanical properties and corrosion resistance. Thus, studies of defects in AHC open up new prospects for interdisciplinary application and advancement of technologies in various fields of science and technology. An in-depth study of defect formation specifically in AHC is a promising direction that can bring significant scientific and technical achievements. In the next section, we will consider the main achievements and current problems in the field of studying defects in AHC.

Recent data obtained from the Scopus and ScienceDirect search systems revealed an unusual trend based on studies on the surface of AHC and specifically LiF crystals (Fig. 1). As shown in Fig. 1, the number of studies conducted on the surface of alkali halide crystal samples per year until 2024 is illustrated. After 2000, the number of experimental and theoretical works carried out sharply decreases, reaching



AQ3 **Fig. 1** Number of publications devoted to processes on the surface of AHC (red) and lithium fluoride (blue) over time

approximately 50 works per year, whereas in 1996, the number reached 125 works (Fig. 1, red line).

However, if we search for publications specifically on the surface of LiF crystals, we observe the following trend shown by the blue line in Fig. 1. There is a sharp increase in the number of publications (by about 20 times) related to experimental and theoretical work on the surface of LiF. This surge is primarily due to the increased use of these materials as a key component of solid electrolytes for lithium-ion batteries [34].

According to scientific research, LiF has a number of attractive properties that make it a promising material for lithium-ion batteries. These properties include relatively high ionic conductivity, an important factor for high capacity and discharge rate of the battery, and stability [35], which contributes to long battery life. Additionally, LiF is compatible with other materials used in lithium-ion batteries, such as cathodes and anodes [34].

In recent years, the development of a new type of solid electrolytes based on LiF for lithium-ion batteries has begun, offering several advantages over traditional liquid electrolytes [36]. These benefits include increased safety, as solid electrolytes are non-flammable and non-explosive, reducing the risk of fire or battery explosion [37]. Performance is also improved at higher temperatures compared to liquid electrolytes, allowing for higher battery capacity. Moreover, solid electrolytes have a longer lifespan and are more resistant to degradation, which can extend battery life. Based on this, we are focusing on studies of defect formation in LiF crystals, as the number of publications on this material is growing daily.

Apart from its use in lithium-ion batteries, LiF also finds applications in other fields such as optics [38], catalysis, and biomedicine. Figure 2 shows that after the 1980 s, most research on the LiF surface was conducted for use in dosimetry, nuclear energy, and nuclear medicine. After the 1990 s, the graph indicates increased use in laser technology for optical applications. From the 2000 s onward, as shown by the red line, LiF has primarily been used as an electrolyte in lithium-ion batteries, highlighting the growing interest and publications in this area.

Indeed, from the presented graph, it can be seen that after the 1980 s, the number of studies on the LiF surface increased significantly since LiF is an ideal material for dosimeters. It can accurately measure X-ray [39] and and gamma radiation doses [40], making it a valuable tool for monitoring radiation exposure in various fields such as medicine, electronics, nuclear power, industrial, and space materials science.

In the 1990 s, LiF was such a popular material that entire scientific groups conducted research on it. One notable group is the laboratory led by Rosa Maria Montereali at the ENEA Institute—Frascati Research Center. To date, this group has published more than 300 articles devoted to LiF materials. In Fig. 3, you can see the number of articles by author dedicated to research on the surface of LiF crystals. Additionally, Horowitz, Yigal S. from the Israeli Ben-Gurion University, is still publishing on the topic of thermoluminescence in LiF dosimeters, and their number of publications is increasing (more than 100 publications).

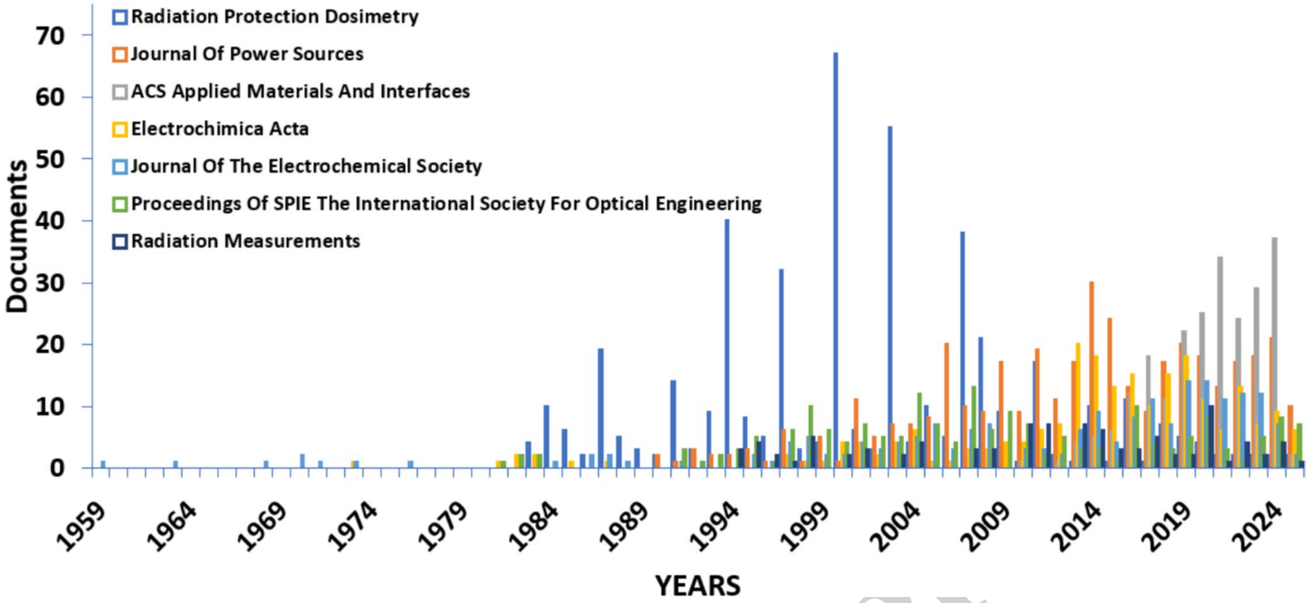


Fig. 2 Number of publications from various scientific sources concerning the surface of LiF crystals over time

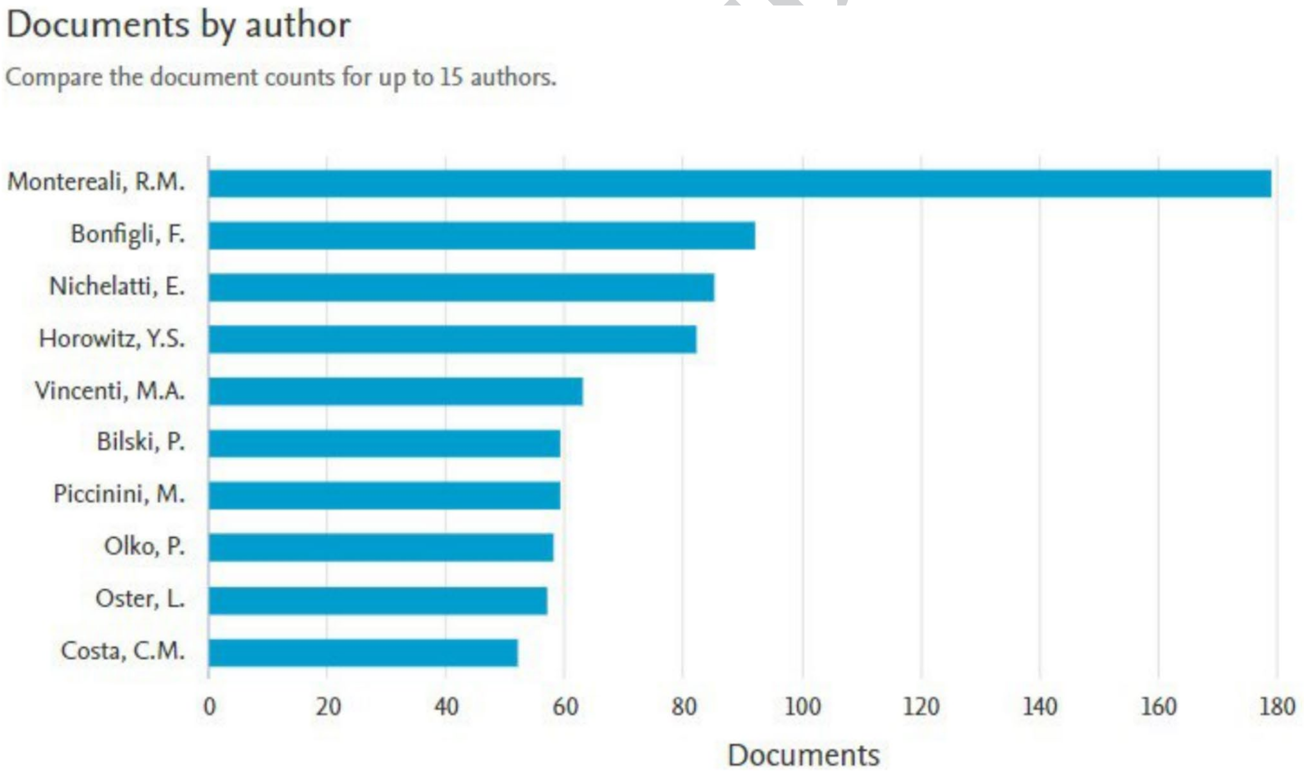


Fig. 3 Number of publications by author over the entire period devoted to research on the surface of LiF crystals

Significant contributions to the study of the optical properties of LiF crystals when exposed to radiation were made by RM Montereali, F. Bonfigli, and E. Nichelatti. They are leading specialists in the field of studying the physicochemical properties of LiF crystals, conducting extensive research on the luminescent properties of LiF crystals activated with various impurities under different types of radiation. They have also studied second harmonic generation, photorefraction, and other nonlinear optical phenomena in LiF crystals.

By the beginning of 2010, their research group had accumulated a vast amount of data on defects in LiF, their absorption, and photoluminescence (see Fig. 4). Their research has shown that these defects can be utilized in creating lasers in thin films and crystals.

Figure 4a displays the absorption and emission spectra of several color centers (CC) (F_2, F_3^+ F_2^+ etc.) in LiF crystals at room temperature. These peaks indicate that color centers absorb light at specific wavelengths and emit light at specific wavelengths after absorption.

Figure 4b illustrates the relationship between the average energy and tuning range of CC lasers operating at room temperature in pulsed mode in LiF crystals. The tuning range refers to the wavelengths that the laser can be adjusted to emit. These figures collectively suggest that CCs in LiF crystals can serve as sources for wavelength-tunable lasers. The specific laser wavelength and tuning range vary depending on the type of CC employed.

One of the key aspects of radiation-stimulated processes in LiF is the formation of point defects, such as F-centers, which arise under the influence of high-energy radiation [42–44]. The formation process consists of several sequential stages, resulting in the creation of anion vacancies in the crystal that capture electrons. The Fig. 5 clearly illustrates the main stages of this process:

1. Exciton Generation

Upon exposure to high-energy radiation (electrons, ions, X-rays, or gamma photons), electronic excitations occur in the crystal lattice. This leads to the formation of a free exciton, a bound state of an electron and a hole. The exciton represents an intermediate excitation state that exists on a timescale of approximately 10^{-13} s.

2. Electron–Hole Pair Formation

The exciton dissociates, leading to the creation of a free electron and a hole. If the process occurs near the crystal surface, it may contribute to structural modifications. The hole can localize at an anion site, weakening its interaction with the surrounding lattice and promoting defect formation.

3. F-Center Formation

The localized hole may facilitate the removal of an anion from its lattice site, generating an anion vacancy. This vacancy is subsequently occupied by a trapped electron, forming an F-center. This process occurs within a timeframe ranging from 10^{-13} to 10^{-3} s.

4. Secondary Processes: Luminescence and Desorption

The formation of F-centers is often accompanied by additional optical and structural effects:

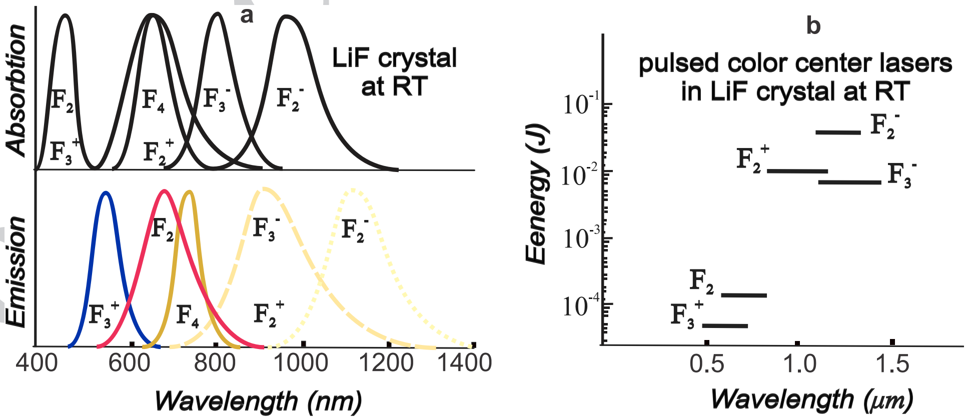


Fig. 4 **a** Absorption and emission bands, outlined as normalized Gaussian curves, of the known CCs which possess photoluminescence in LiF at RT. **b** Average energy and tunability range versus wavelength of the CC lasers operating at RT in LiF crystals in pulsed regime. Reproduced from [41] with permission

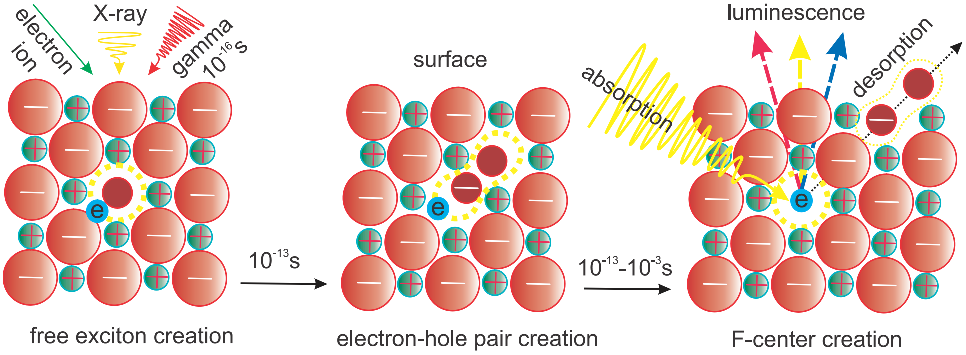


Fig. 5 The process of F-center formation in ionic crystals under high-energy radiation

- Photon absorption and luminescence, where electronic transitions within the defect states contribute to characteristic optical emissions.
- Desorption of anionic species, particularly at the surface, which can influence the overall defect concentration and material stability.

By the beginning of 2010, Tables detailing defects in LiF were compiled based on research data from this group. All the data obtained are presented in Table 6.

The Table 6 contains the spectroscopic properties and room temperature optical gain of laser-active CCs in LiF grown by nonstoichiometric crystal growth at n = 1.39.

Explanation of the Table 6:

λ_a (nm): Absorption wavelength of the CC.

λ_e (nm): Emission wavelength of the CC after absorbing light.

$\Delta\nu$ (10^{13} Hz): Energy difference between the absorption and emission states of the CC in units of 10^{13} Hz, related to the emitted light color.

τ_{eff} (ns): Effective lifetime of the excited state of the center, indicating how long the electron stays in the excited state before returning to the ground state.

η (%): Quantum yield of the CC, the percentage of absorbed photons converted into emitted photons.

g (cm^{-1}): Optical gain of the CC, indicating how much light is amplified when passing through the material.

Overall, the Table 6 demonstrates that defects in LiF crystals can serve as active media for lasers, with specific properties varying depending on the type of CC.

Their work has significantly contributed to understanding luminescence mechanisms, clarified the role of defects in the optical properties of LiF crystals, and opened new possibilities for their use in nonlinear optics. They conducted comprehensive studies on photoluminescence, electroluminescence, and thermoluminescence of LiF crystals with defect states. Additionally, LiF radiation detectors, based on the thermoluminescence method, exhibit a response where the luminescent detector's efficiency depends on the received dose magnitude, the detector's composition materials, and the method of dose transmission (i.e., the microscopic pattern of energy release), greatly affecting its effectiveness [45]. Therefore, precise understanding of these efficiency variations is crucial. Accurate estimation of measured radiation doses is essential for designing dosimeters based on fluorescent detectors. Table 7 below summarizes various methods for recording radiation emissions.

This Table 7 highlights the materials used in various radiation detection methods, providing insights into which materials are effective at detecting certain types of radiation and under what conditions they are used.

The Table 7 emphasizes the significant advantages of LiF detectors. LiF detectors offer high sensitivity to ionizing radiation and can detect various types of radiation, including α, β, γ radiation, and neutrons [46]. LiF detectors demonstrate a highly linear response to radiation intensity and have low background noise, enabling accurate measurement of radiation doses under diverse conditions. Additionally, LiF exhibits resistance to thermal and mechanical stress, ensuring reliability and durability in operation [47]. Its low cost, ease of processing, and usability make LiF a preferred choice for a wide range of applications, from personal dosimetry to scientific research and radiation monitoring in fields such as medicine, nuclear power plants, and space exploration. In contrast, other materials may be less convenient and mobile, limiting their application to narrow fields of science and technology. For example, some materials may be heavy or require complex cooling systems or specific environmental conditions [48], restricting their use in mobile or field settings [49]. LiF, due to its lightweight nature, convenience, and ease of use, enjoys widespread adoption. Recent research [50] has also shown that LiF has potential applications in UV dosimetry.

Now, let's examine key studies from the last 5 years. In [51] visible photoluminescence of CCs in LiF crystals was studied for advanced diagnostics of 18 and 27 MeV proton beams. Using a simple defect formation model that considers energy release in the material and saturation of defect concentration, researchers obtained a two-dimensional dose map from the image of transverse beam intensity distribution. They also reconstructed the full Bragg curve, enabling comprehensive characterization of proton beams produced by the accelerator. The high intrinsic spatial resolution and wide dynamic range of these new LiF detectors facilitated two-dimensional imaging of lateral beam intensity distribution. These findings are crucial for dose assessment in hadron therapy and for nuclear and space research at CERN (European Organization for Nuclear Research) [52].

Table 6 Spectroscopic properties and optical gain at room temperature of laser-active CCs in LiF

CCs	λ_a (nm)	λ_e (nm)	$\Delta\nu$ (10^{13} Hz)	t_{eff} (ns)	η (%)	g(cm^{-1})
F_3^+	448	541	6.5	11.5	100	7.6
F_2	444	678	7.5	17	100	7
F_3^-	800	900	8	10	10	1.9
F_2^+	645	910	7	15	50	7.6
F_2^-	960	1120	8	55	30	1.6

Table 7 Various methods for recording radiation

Method	Description and principle of work	Type of radiation	Basic materials	Applications
Geiger-Muller counter	Radioactive particles ionize the gas, creating an electrical impulse	α, β, λ	Gas (argon, helium, neon)	measuring radiation levels
Scintillation	They emit light when they absorb a radioactive particle. Light is converted into an electrical signal	α, β, λ, η	NaI, CsI, BGO, plastics, liquid scintillators	Medical diagnostics, particle physics
Ionization camera	Measures the current produced when a gas is ionized by radiation in an electric field	α, β, λ	Gas (usually air or argon)	Radioecology, medical physics
Proportional counter	Similar to an ionization chamber, but amplifies the signal to be proportional to the amplitude of the energy of the ionizing event	α, β, λ	Argon gas with methane admixture	Spectrometry, scientific research
Semiconductor	Radiation creates electron–hole pairs, generating an electrical signal	α, β, λ	Si, Ge, GaAs	High precision spectrometry
Thermoluminescent	The material stores energy from radiation and releases it as light when heated	α, β, λ, η, ρ	LiF, CaF_2	dosimetric equipment
Electron spin resonance	Measures the change in the state of electrons in materials caused by radiation	α, β, λ	Amino acids, carbonates, quartz	Dosimetry, radiation biology
Bubble camera	A liquid in a superheated state forms bubbles along the trajectory of charged particles	particles	Liquid hydrogen, liquid neon	Experimental physics
Spark camera	Sparks are created in a gas along the tracks of charged particles in an electric field	particles	Gas (usually argon or a mixture of gases)	Experimental physics

In [53], a comparative study of photoluminescence and modeling of F_2 and F_3^+ CCs in lithium fluoride irradiated at high doses with low-energy proton beams was conducted. In their work, the authors studied the photoluminescence (PL) of F_2 and F_3^+ CCs in lithium fluoride crystals irradiated with a proton beam with energies of 3 and 7 MeV (Fig. 6). Radiation doses varied from 10^3–10^6 Gy. Ionization caused by protons in LiF crystals led to the stable formation of CCs exhibiting broad PL bands in the red (F_2) and green (F_3^+) regions of the spectrum when optically pumped with blue light (~ 450 nm).

The main goal of the study was to investigate the dependence of PL intensity on the absorbed dose. It was found that at high doses (about 10^6—10^7 Gy) there is a decrease in the integral PL intensity for F_3^+ centers. The authors suggest that this phenomenon is associated with the formation of absorption or quenching centers that absorb or scatter PL. The study covers a wide range of radiation doses, allowing for a detailed examination of the effects that occur at different levels of radiation exposure. The work offers a separate analysis of the contribution of F_2 and F_3^+ CCs to the overall

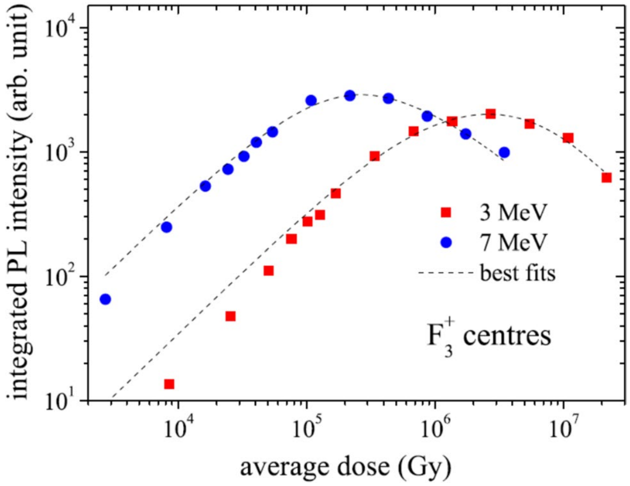


Fig. 6 Photoluminescence intensities were measured for several absorbed doses emitted from spots irradiated with protons with energies of 3 and 7 MeV. Here, the photoluminescence intensities are integrated over the F_3^+ emission band, and the doses are averaged over the irradiated volume. Reproduced from [53] with permission

PL, contributing to a better understanding of the processes occurring in irradiated LiF crystals.

The results may be useful for improving diagnostic and dosimetry techniques in radiation therapy, especially in the context of the use of protons and other heavy particles. In this work, there is a discrepancy between the model and the experimental data at low irradiation doses, which may be due to measurement inaccuracies or nonlinear effects of the formation of CCs. Additionally, the model used does not always accurately describe the behavior of the system, especially at high doses, which requires further research and possible modification of theoretical approaches.

The authors of the study [54] from ENEA studied the visible PL of CCs in thin films of lithium fluoride for use in detectors of low-energy proton beams at high doses. The article describes how irradiation of thermally evaporated LiF thin films with a proton beam with a nominal energy of 3 MeV in the fluence range from 10^{11}—10^{15} protons/cm^2 causes the formation of stable CCs, including primary F centers and aggregate defects F_2 and F_3^+. The authors showed that PL, measured in spectrally integrated form, depends on the absorbed dose and behaves linearly until saturation at high dose values ($> \approx 10^5$ Gy). It was found that the spectral contributions of F_2 and F_3^+ CCs in the red and green regions of the spectrum exhibit differences in their behavior at high irradiation doses.

The difference between this work and the previous one is that thin LiF films provide high spatial resolution, which is important for accurate mapping of radiation doses. The study also demonstrates the detectors'ability to operate in a wide range of doses, from low to high values, making them versatile for various applications. It has been shown that CCs remain stable at room temperature, simplifying their use and analysis. After irradiation, the detectors do not require complex processing, facilitating their operation.

This work does not take into account the influence of the proton beam energy on the formation of CCs, which requires consideration when calibrating detectors for various irradiation conditions. Additionally, the limited thickness of LiF films (about 1 μm) can affect their ability to detect deeper layers of materials, and signal saturation at high doses limits the capabilities of detectors under extremely high radiation doses. This necessitates further research to expand their applicability. However, ultimately, this and other studies from this group [55] demonstrate the promise of using LiF thin films to detect low-energy proton beams, offering new opportunities for radiation diagnostics and therapy while indicating the need for further research to optimize their performance and expand the range of applications.

In [56], solid-state radiation detectors using PL of stable point defects in LiF crystals were employed for advanced diagnostics during the commissioning of the TOP-IMPLART linear proton accelerator segment with energies up to 27 MeV for proton therapy. Here, LiF detectors provided high spatial resolution and a wide dynamic range, enabling the creation of two-dimensional images of the transverse distribution of beam intensity. They also accurately determined the position of the Bragg peak using a conventional optical fluorescence microscope. The term"Bragg peak"in the context of radiation therapy refers to the specific point within a material where maximum energy release from ionizing radiation, such as protons, occurs. This peak is displayed on a graph of absorbed dose versus radiation penetration depth. The critical point is that most of the radiation energy is released just before the particles come to a complete stop.

The study reports and discusses the results of proton beam characterization, including estimates of energy components and beam dynamics under various accelerator operating conditions. Figure 7 shows the dependence of PL intensity on the depth of proton penetration into LiF. Protons with an energy of 27 MeV are used to excite PL. The work shows that the intensity of PL in LiF depends on the depth of proton penetration. The maximum PL intensity is achieved at a certain penetration depth, after which it gradually decreases.

The continuation of this work allowed [57] based on this knowledge, the creation of solid-state dosimeters based on PL readings. The authors conducted a systematic study of the optical properties of LiF when exposed to 7 MeV proton beams and found that the PL of these CCs under optical pumping is proportional to the absorbed dose. A model was developed to reconstruct the Bragg curve and perform 2D dose mapping from PL images stored in LiF. The study presents results highlighting quantitative aspects of PL behavior in LiF at various doses, including cases of high CC saturation (Fig. 8). AQ4

The third most prolific author in publications on LiF surface research is Y.S. Horowitz and his group (Fig. 3).

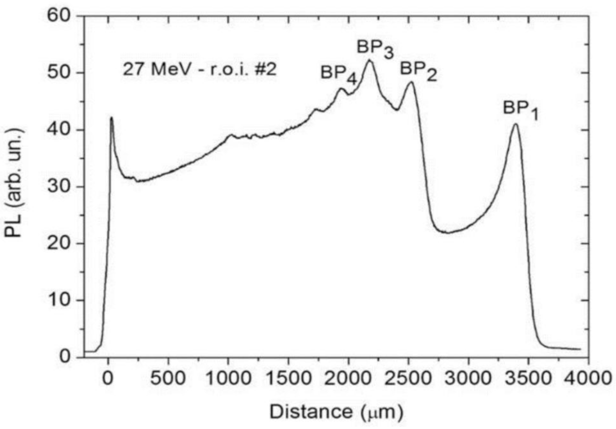
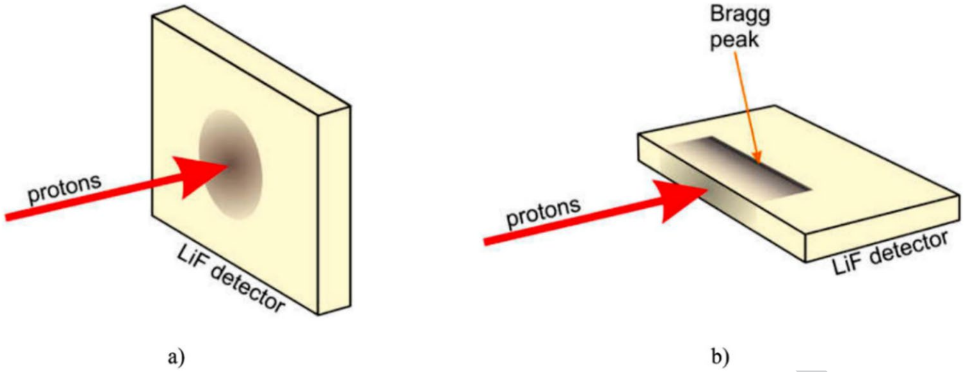


Fig. 7 PL intensity profile vs. proton penetration depth to LiF. Reproduced from [56] with permission

Fig. 8 Sketches of the two mounting geometries used for low-energy proton irradiation of LiF detectors: **a** larger surface perpendicular to the proton beam propagation direction, (**b**) larger surface parallel to the proton beam propagation direction. Reproduced from [57] with permission



Horowitz specializes in studying the effects of radiation on LiF crystals [58]. He has conducted several studies on the impact of various types of radiation on the optical properties of LiF crystals [59]. Horowitz's work is important for understanding the radiation resistance of LiF crystals [60] and their potential use in radiation-resistant optical devices [61].

M.A. Vincenti studies the photochemical properties of LiF crystals [62]. He has conducted a number of studies on the photochemical reactions occurring in LiF crystals under the influence of various types of radiation [63]. Vincenti's work is very important for understanding the photostability of LiF crystals and their potential use in photochemical devices [63]. He and his co-authors are the first to show promising results using LiF crystals as solid-state fluorescent nuclear tracking detectors under typical ion radiobiology conditions, and further experiments are ongoing to improve this promising application, especially at higher doses and energies.

These are just a few of the many authors who have made significant contributions to the study of the optical properties of LiF crystals when exposed to radiation. The studies of these authors have helped to clarify the fundamental mechanisms underlying the optical properties of LiF crystals and opened up new possibilities for the use of these materials in various fields such as optics [64, 65], laser technology [66], and medicine. It is important to note that the list of authors presented above is not exhaustive. Many other researchers have made significant contributions to this area. Apart from these main applications, LiF surface research is also being carried out in other fields such as electronics [66–68], and catalysis [69]. Due to its high sensitivity to radiation, LiF can detect very low levels of radiation [70–73], making it an attractive material for research. Given its many advantages, LiF is likely to remain an important material for research and development for many years to come.

The use of LiF in battery technology helps address important energy challenges, including improving battery efficiency, safety, and longevity, which in turn supports the energy boom and the transition to more sustainable energy sources. Accordingly, this has led to an increase in research due to technological breakthroughs and stimulates funding for such technologies in different countries. Data obtained from Scopus shows that the number of publications, by country and by affiliation, continues to increase (Figs. 9 and 10). From these two figures, you can see the distribution of the number of publications devoted to research on LiF crystals, across 10 countries and by affiliation for all time and for the last 10 years.

From the information presented in the graph, it is worth noting that:

China: Approximately 2700 publications, which is the largest number among all countries.

USA: Approximately 2400 publications, ranked second, and so on.

It can be seen that China and the USA are leaders in LiF crystal research, each with 2000 + publications. Japan, Germany, and the Russian Federation follow in the next positions in terms of the number of publications, indicating their active engagement in this area of research. Of course, this is a rough visual representation of the data. But overall (without considering the quality or impact of each publication), the graph provides a valuable overview of global activity in the field of LiF crystal research.

Recently, research has become increasingly interdisciplinary, combining fields such as physics, chemistry, materials science, and engineering (Fig. 11). The number of publications devoted to LiF surface research [43, 74] continues to grow. New research methods, such as computer modeling [75, 76] and nanotechnology, are opening up new possibilities for studying and using the LiF surface. LiF surface research is of great importance for the development of new technologies and the improvement of existing lithium production [77, 78].

Figure 11 shows the distribution of publications in the form of a pie chart on LiF crystal research as a percentage of the total number of publications in various scientific fields.

Several important conclusions can be drawn from the diagram:

The dominant areas of research are materials science (19.1%), physics and astronomy (18.3%), and chemistry

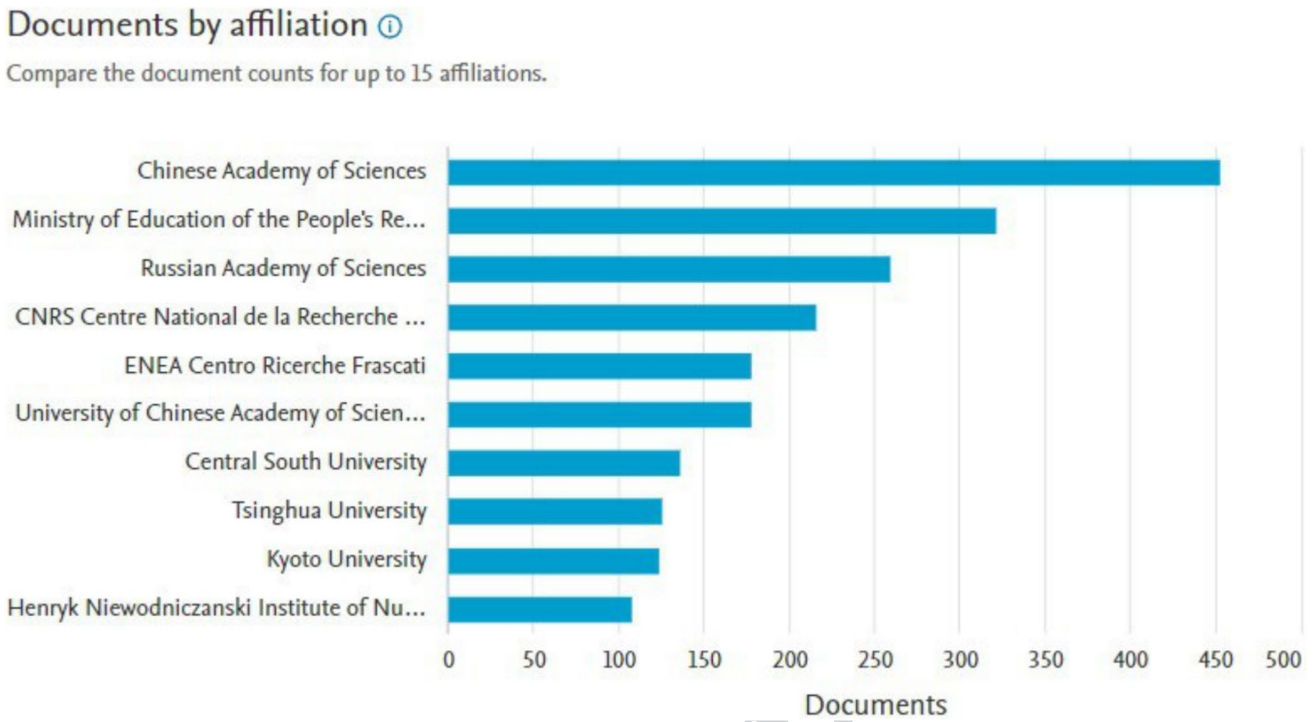


Fig. 9 Number of publications, by affiliation, over the entire period of time devoted to the study of LiF crystals

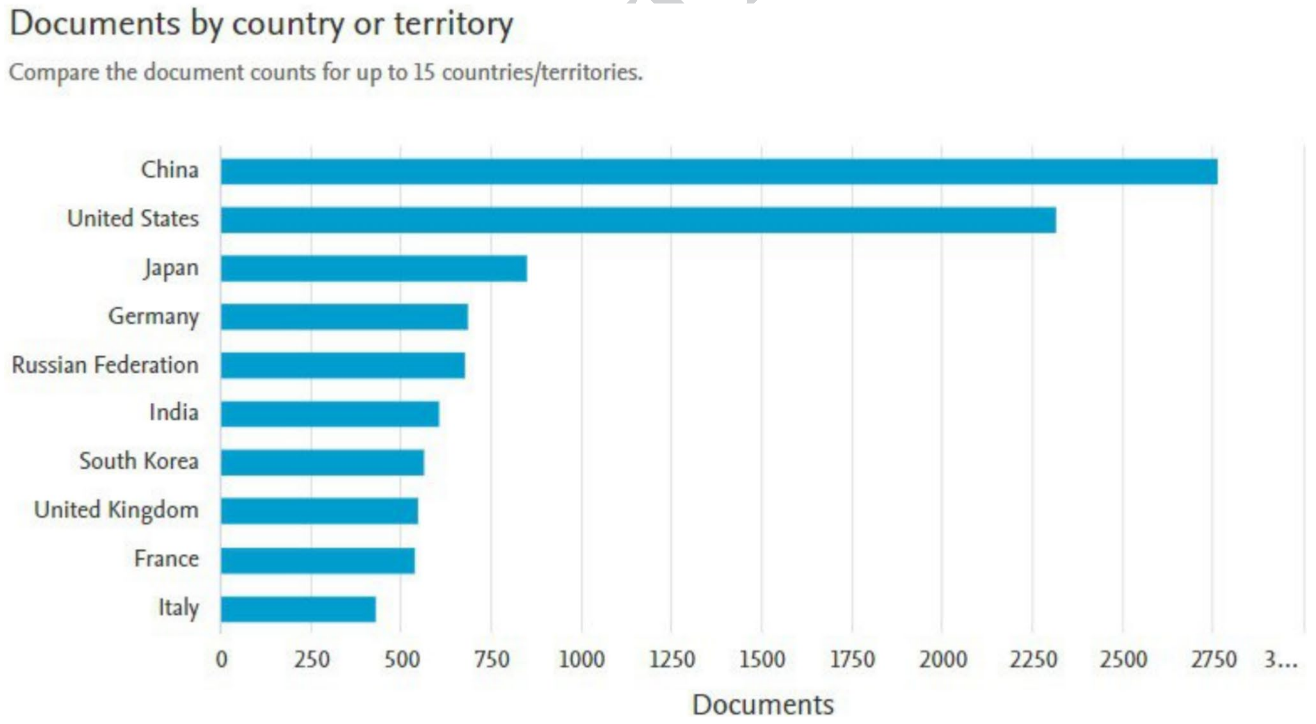


Fig. 10 Number of publications, by country, over the entire period of time devoted to the study of LiF crystals

(17.6%), collectively accounting for about 55% of all publications. This highlights the significance of LiF in both fundamental and applied research across materials, physics, and chemistry. Engineering applications (12.1%) and chemical engineering (6.9%) also show a substantial number of publications. The proportion dedicated to

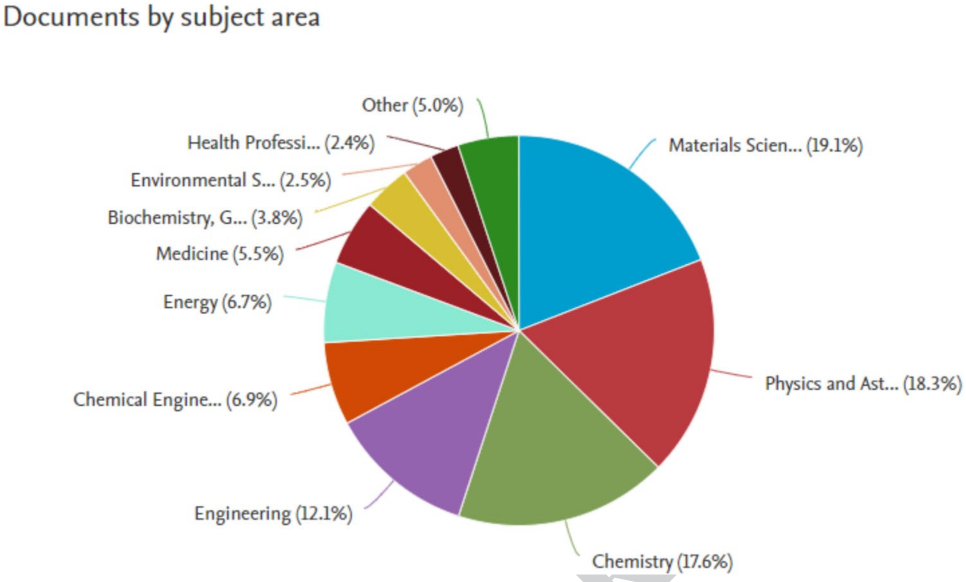


Fig. 11 Number of publications by scientific field for the entire time devoted to the study of LiF crystals

energy applications (6.7%) underscores LiF's importance in fields like batteries [79, 80] and nuclear technologies [81, 82], aligning with contemporary trends in renewable energy sources and energy storage.

The remaining publications cover biomedical and environmental research, including medicine (5.5%), biochemistry, genetics, and molecular biology (3.8%), environmental sciences (2.5%), and health professions (2.4%). This diversity illustrates the wide-ranging applications of LiF beyond the fields mentioned above.

From Figs. 2 and 11, it is evident that lithium fluoride has been actively utilized in recent years for electrochemistry and energy applications as an electrolyte in solid-state lithium-ion batteries [83]. The development of lithium-ion batteries has enabled significant progress in porTable electronic devices and facilitated the integration of electric vehicles. However, the low potential of anode reactivity necessitates the formation of a solid electrolyte interface (SEI) to passivate the electrode surface and ensure long-term cycling stability. Despite decades of research on SEI, a comprehensive understanding of its formation mechanisms and evolution remains elusive. The instability of SEI components leads to their decomposition, resulting in gas formation [84] and solute species in the electrolyte. This evolution increases SEI porosity, further electrolyte reduction, and thickening of SEI layers. Developing more stable SEI components is crucial for enhancing battery performance. Additionally, a better understanding of the nanostructure of SEI components and ion transport along grain boundaries is critically important for advancing in this direction. Of course, LiF has not been left out in this regard. In Fig. 12A, you can observe the mechanism and composition of the initial SEI [85]. As you can see, LiF is utilized as part of the SEI.

Based on these initial results, an approximately 50 nm thick SEI composed of lithium ethylene dicarbonate and LiF is generated, which can function as an effective passivation layer, thereby preventing further electrolyte decomposition and graphite peeling, as shown in Figs. 12B and 13.

As it can be seen, at this stage of development, LiF is actively used as SEI. While not a primary material in traditional lithium-ion batteries, it finds application in various auxiliary and innovative contexts related to lithium-ion technologies [87]. Lithium fluoride is sometimes used as a component in electrolytes to stabilize and enhance their characteristics [35, 88]. It can help mitigate electrolyte decomposition [37] and improve battery performance at high voltages [89, 90]. Introducing LiF into the electrolyte can also enhance thermal stability and safety [36, 91]. In solid-state lithium-ion battery research and development, LiF can be used as part of composite materials for solid electrolytes. Solid electrolytes have the potential to significantly increase safety and energy density compared to traditional liquid electrolytes [92, 93]. Lithium fluoride may be present in the SEI layer on the anode surface. The SEI layer forms during initial charge/discharge cycles and plays a crucial role in protecting the anode and ensuring battery stability. LiF can contribute to improving the stability of the SEI layer, thereby enhancing battery durability and performance.

Lithium fluoride can also be used as an additive in cathode materials to improve their structural stability and cyclic longevity. This is particularly important for cathodes operating at high voltages, where material stability is critical to prevent degradation [94–96]. Recent studies have shown [97] that adding LiF to various components of lithium-ion batteries can significantly enhance their performance. For instance, research indicates that a small amount of LiF [98] added to the electrolyte can

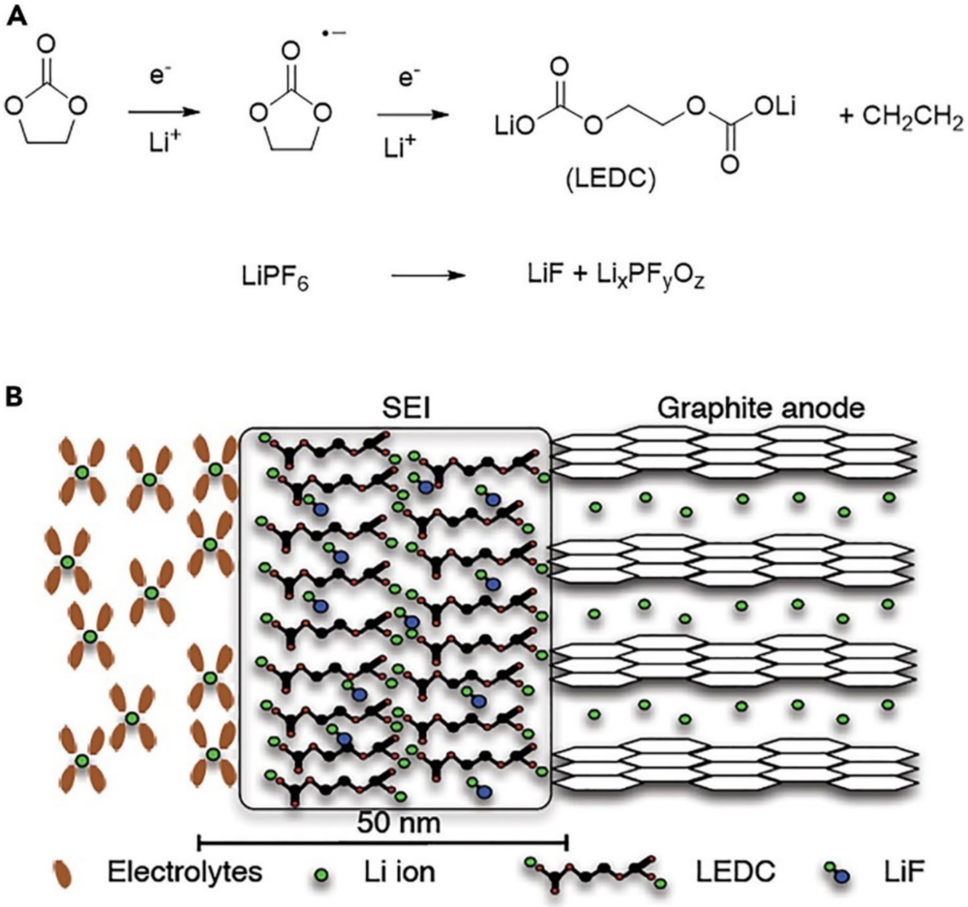


Fig. 12 Formation mechanism and composition of initial SEI (**A**) Initial ethylene carbonate reduction reactions at the interface of graphite electrodes. **B** Schematic representation of the initial SEI formed on the graphite surface during the first cycle of operation of a Li-ion battery. Reproduced from [85] with permission

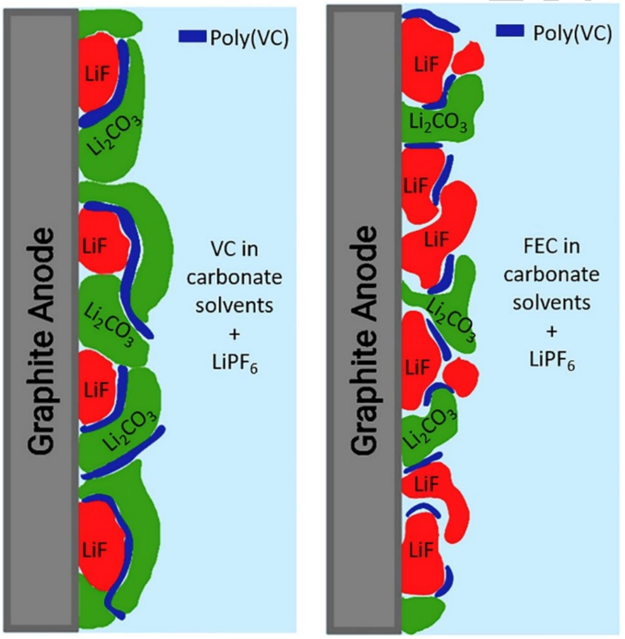


Fig. 13 Schematic representations of the initial SEI generated on graphite anodes for electrolytes containing vinylene carbonate (left) or fluoroethylene carbonate (right). Reproduced from [86] with permission

enhance cathode stability and reduce degradation rates over multiple charge–discharge cycles. For example, in study [99], the authors used LiF in phosphorus-based batteries. The research showed that LiF plays a key role in addressing the issue of soluble potassium polyphosphates encountered when using phosphorus as an anode material for potassium-ion batteries. LiF prevents the penetration of polyphosphates into the electrolyte before and after the formation of the SEI and, in combination with replacing the electrolyte KPF6 with KFSI, promotes the formation of a thin, stable, and homogeneous SEI layer on the electrode particle surface. Thanks to LiF, the initial coulombic efficiency increases to 73.7%, and the reversible specific capacity reaches 507.6 mAh•g-1 after 100 cycles at a current of 50 mA•g-1. Overall, LiF helps address the issue of soluble potassium polyphosphates, leading to improved initial efficiency, capacity, and cyclic stability of phosphorus-based potassium-ion battery systems.

In this [97] study, the authors propose using a composite protective layer LiF-Li$_3$N, which forms in situ on the surface of the lithium anode. LiF-Li$_3$N possesses high interfacial energy and adhesion, allowing it to effectively suppress side reactions and inhibit lithium dendrite growth. Figure 14 from this study demonstrates the impact of the LiF-Li$_3$N

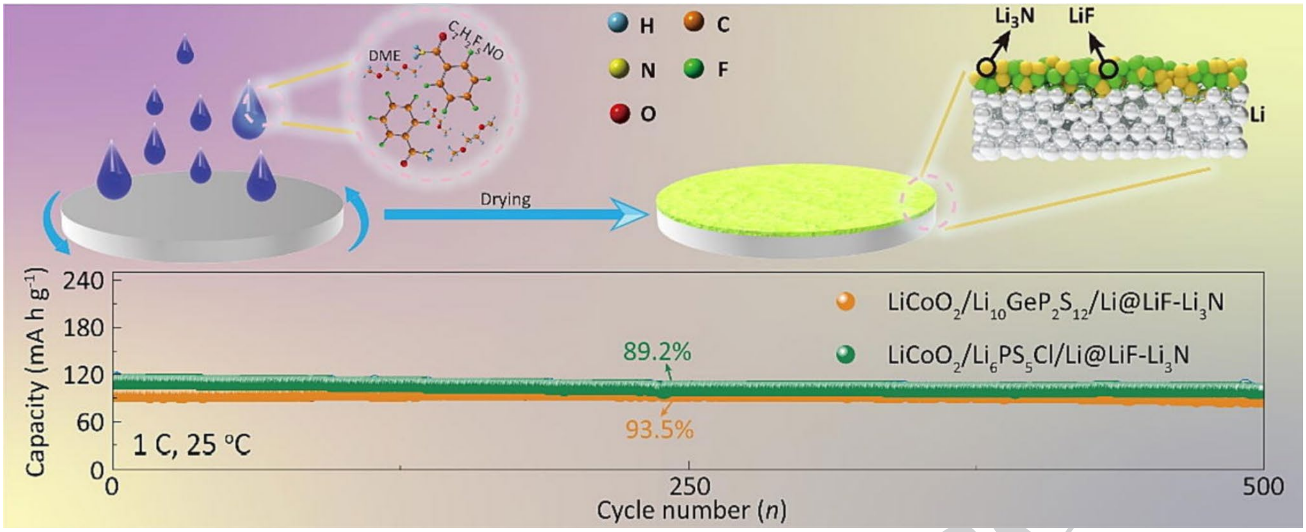


Fig. 14 Effect of LiF-Li_3N protective layer on the cycling capacity and stability of solid-state lithium batteries with $LiCoO_2$ cathode. Reproduced from [97] with permission

protective layer on the cyclic capacity and stability of solid-state lithium batteries with a $LiCoO_2$ cathode.

From Fig. 14, it can be seen that the fabricated LiF-Li_3N protective layer in solid-state lithium batteries prevents side reactions between lithium and the sulfide solid electrolyte, improves the reversibility of lithium stripping/plating, thereby suppressing lithium dendrite formation. Thanks to the LiF-Li_3N protective layer, the critical current densities of Li@LiF-Li_3N cells with $Li_{10}GeP_2S_{12}$ and Li_6PS_5Cl electrolytes can reach high values of 3.25 and 1.25 mA·cm^{-2}, respectively. As a result, the batteries demonstrate excellent cyclic stability over 500 cycles with capacity retention of 93.5% and 89.2% at 1 C charge or discharge rate, respectively.

Comparing these studies, in both cases LiF enhances battery performance, but through different mechanisms. In the first study, LiF acts as a barrier, preventing the negative impact of soluble components on the electrolyte, whereas in the second study, LiF is part of a protective layer that directly interacts with the lithium anode, stabilizing its surface.

Overall, LiF demonstrates its versatility and effectiveness in addressing various challenges in solid-state batteries. Its use contributes to the development of solid-state batteries, enhancing their safety, performance, and longevity. Below, we will delve into some studies that feature existing and new technologies, ultimately leading to the transition to solid-state batteries.

In the study [98] the use of mesoporous $La_xCoO_{3\text{-}\delta}$ nanofibers with controlled cationic defects as a composite polymer-oxide electrolyte for all-solid-state lithium batteries is investigated. The goal of the work was to address the difficulty of managing the interaction of components in composite polymer-oxide electrolytes to ensure efficient Li^+ ion transport and stable interfacial contact between the CPE and the electrode. To achieve this, the authors propose using mesoporous $La_xCoO_{3\text{-}\delta}$ nanofibers with a controlled level of cationic defects (cation deficiency) at the A-site (La). By adjusting the number of defects (x in $La_xCoO_{3\text{-}\delta}$ varies from 1.0 to 0.8), the interaction of the nanofibers with the PEO/LiTFSI polymer electrolyte can be enhanced.

The study demonstrated that this approach shows promise, with mesoporous $La_xCoO_{3\text{-}\delta}$ nanofibers with controlled cationic defects emerging as a potential material for creating composite polymer-oxide electrolytes. By regulating the defectiveness of the material, high lithium-ion conductivity and stable interfacial contact can be achieved, leading to the development of highly efficient and durable all-solid-state lithium batteries.

The problem of an unstable electrolyte/electrode interface, with dendrite growth and increased resistance, significantly reduces the safety and efficiency of all-solid-state lithium-metal batteries. In the study [100] an"in situ LiF nanodecoration"method is proposed to address this issue. The approach involves the uniform distribution of ultrathin LiF nanoparticles in an amorphous $Li_2B_{12}H_{12}$ matrix, which is formed in situ through a solid-phase reaction.

Characteristics of the new composite electrolyte:

- Li-ion conductivity: 5×10^{-4} S/cm at 75 °C.
- Low electronic conductivity: 9×10^{-10} S/cm at 75 °C.
- High compatibility with the electrode due to the formation of stable electrolyte/electrode interfaces.

- Dendrite suppression capability: critical current density of 3.6 mA/cm^2.
- Low interfacial resistance: 746 Ω·cm^2 after 10 cycles at 75 °C.

The new composite electrolyte contributes to the stable cycling of Li-LiFePO$_4$ ASSB, paving the way for the use of in situ nanodecoration chemistry to develop safe and highly efficient batteries.

The issue of low lithium-ion conductivity at room temperature is a significant challenge for polymer electrolytes, although polymer solid electrolytes possess flexibility and high safety.

In the study [101], polymer-ceramic composite electrolytes were developed for high-energy solid-state lithium-sulfur (Li–S) batteries. Specifically, the use of a flexible composite polymer-ceramic electrolyte, consisting of polyvinylidene fluoride and garnet-type $Li_{6.5}La_{2.5}Ba_{0.5}ZrTaO_{12}$, is discussed for operation at room temperature, demonstrating high lithium-ion conductivity (0.34 mS/cm at 20 °C). For the first time, polyvinylidene fluoride-garnet polymer-ceramic composite electrolytes were modified with the addition of LiF, which was confirmed by stable galvanostatic cycling at 0.2 mA/cm^2 for over 800 h. The addition of LiF improves the stability of polyvinylidene fluoride-based polymer-ceramic composite electrolytes, as confirmed by X-ray photoelectron spectroscopy and electrochemical measurements. The solid-state lithium-sulfur battery created with the modified polymer-ceramic composite electrolyte demonstrates a high specific capacity (936 mAh/g at 0.1C and 20 °C) and stable operation for over 80 cycles, as well as excellent rate capability and high efficiency. As can be seen, LiF improves the stability of these electrolytes by preventing dehydrofluorination and ensuring stable galvanostatic cycling. This significantly enhances the lifespan and efficiency of solid-state lithium-sulfur batteries at room temperature.

As seen, LiF is not only used in modern lithium-ion batteries, but its potential in next-generation battery technologies, such as lithium-sulfur (LSBs) and lithium-air (LABs) batteries, remains largely unexplored.

The incorporation of LiF in LSBs enhances cathode stabilization by reducing the solubility of lithium polysulfides, thereby mitigating the shuttle effect, extending battery lifespan, and suppressing lithium dendrite growth [102]. Additionally, LiF improves ion transport (conductivity) in sulfur-containing cathodes, increasing battery efficiency [103].

Furthermore, LABs hold significant potential for achieving much higher energy densities compared to conventional lithium-ion batteries and are currently in the active research phase. Although there are no specific studies on LiF's application in LABs, its key properties, including relatively high ionic conductivity, thermal stability, and electrochemical inertness, make it a promising candidate for future research. Given these characteristics, LiF is likely to find its place in next-generation lithium-air batteries [104].

By 2024, a process for creating an ultrathin (200 nm) lithium fluoride coating on the surface of lithium metal using vacuum evaporation has been developed. The study [88] investigated a simple and controlled surface fluorination method to create a dense and uniform ultrathin protective LiF coating on the surface of lithium metal via vacuum evaporation. As a result, dendrite-free deposition was achieved at a high current density of 3 mA/cm^2. Full cells, LiF@Li|LiFePO$_4$, with a LiF-coated anode (200 nm thick), demonstrated up to 85.31% capacity retention over 600 cycles. Stable lithium deposition was achieved for 1200 h under limited electrolyte conditions.

The conclusion was made that the protective lithium fluoride coating is a promising approach for enhancing the stability and safety of lithium-metal anodes. This method allows for the creation of stable interfaces and improved lithium-ion conductivity, leading to improved cycling stability and overall battery performance.

The primary function of the SEI is to protect the anode by acting as a barrier that allows the passage of lithium ions (Li^+) while blocking the movement of electrons. The SEI prevents further electrolyte decomposition on the anode surface by forming a protective layer.

Thanks to the SEI, the battery can operate for many charge/discharge cycles, thereby extending its lifespan. Additionally, the SEI helps prevent lithium dendrite growth, which could otherwise cause short circuits and reduce battery safety. Table 8 presents a comparative analysis of LiF-based solid electrolytes in contrast to conventional electrolytes.

As seen in Table 8, the percentage composition of SEI components in LIBs varies depending on the electrolyte composition and the anode type (graphite, silicon, lithium metal). It is evident that LiF and Li_2CO_3 remain the most commonly used SEI components due to their stability and protective properties [109]. Organic compounds are more frequently found in the outer SEI layer, which is in direct contact with the electrolyte.

A better understanding of the nanostructure of SEI components and ion transport along grain boundaries is crucial for further advancements in this field. LiF plays a key role in SEI formation due to its high thermal stability, extended battery lifespan, and improved safety. Despite its low ionic conductivity, it effectively protects the anode and reduces flammability risks, making it an essential component for long-lasting and safe lithium-ion batteries. Compared to other SEI components, LiF enhances battery safety, which can be attributed to the following mechanisms:

Table 8 Comparison of LiF to other components of SEI in Li-ion batteries

Compound	Characteristics	Percentage in LIB/Ionic Conductivity	Thermal Stability	Battery Lifespan	Safety Enhancement
Lithium Fluoride (LiF) [36, 105–108]	High chemical stability. Low ionic conductivity	20–30%/Low, but enhances SEI durability	Above 850 °C	Extends lifespan by stabilizing SEI	Reduces short-circuit and fire risks
Lithium Carbonate (Li_2CO_3) [109, 110]	Provides mechanical stability. Prevents dendrite growth	30–40%/Medium	Decomposes above 700 °C	Reduces anode degradation, increases lifespan	Moderately reduces risks, prevents dendrite formation
Lithium Oxide (Li_2O) [110]	Forms a dense layer. Protects anode from electrolyte reactions	10–15%/Low	Above 900 °C	Improves SEI stability but decomposes over cycles	Medium protection level
Lithium Nitride (Li_3N) [97]	High ionic conductivity. Stabilizes the anode	< 5%/High	Decomposes above 500 °C	Improves charge–discharge performance	May cause side reactions with the electrolyte
Lithium Hydroxide (LiOH) [105]	Less stable. May contribute to SEI degradation	< 5%/Low	Decomposes at 450–500 °C	May reduce SEI lifespan	Increases SEI degradation risk
Polycarbonates and Carbonates [111]	Form a porous outer layer. May be less stable	20–25%/Medium	Decomposes above 300 °C	Provides SEI flexibility	Medium protection level
Lithium Alkyl Carbonates [110]	Provide SEI flexibility. Reduce side reactions	5–10%/Medium	Decomposes above 400 °C	Improves lifespan by reducing side reactions	Moderately enhances safety
Polymers [112]	Increase SEI stability. Reduce ionic conductivity	< 5%/Low	Decomposes at 200–400 °C	Enhances SEI mechanical strength	May reduce short-circuit risk
Lithium Silicate (LixSiOy) [113, 114]	Forms on silicon anodes. Stabilizes SEI on Si	Up to 30% (on Si)/Medium	Above 700 °C	Improves silicon anode lifespan	Moderately reduces SEI degradation risk

- LiF facilitates the formation of a stable ion-conducting SEI layer, preventing electrolyte decomposition and lithium dendrite growth [115].
- Compared to organic electrolyte components, LiF has a high decomposition temperature (> 800 °C), reducing the risk of thermal runaway [116].
- Low solubility of LiF in liquid electrolytes minimizes side reactions, extending battery lifespan and improving safety. Comparative studies indicate that the presence of LiF in SEI reduces gas release under overheating conditions [116].
- X-ray photoelectron spectroscopy (XPS) studies confirm that LiF-modified electrolytes provide more stable performance over multiple charge–discharge cycles [106, 117].
- LiF, as an excellent electronic insulator, prevents electron tunneling, thereby suppressing side reactions between the electrolyte and lithium metal anode [118].
- Due to its interfacial properties, LiF induces lateral lithium-ion dispersion, promotes vertical transport, and facilitates uniform lithium deposition [119].

Ultimately, many studies [120–124] indicate that the transition to solid-state batteries is ineviTable, with LiF playing a significant role.

In recent years, with the advancement of nanoscience, nanostructured LiF coatings have been increasingly utilized in lithium-ion battery (LIB) designs. The application of nanostructured LiF coatings for enhancing battery quality and longevity is a promising direction, particularly in terms of electrode protection [125, 126] and electrolyte–electrode interface stabilization [127–129].

A nanostructured protective LiF layer reduces side reactions with the electrolyte, thereby extending battery lifespan [130]. In cathodes, thin LiF layers help mitigate structural changes during charge/discharge cycles, reducing material degradation [129, 131]. Furthermore, nanostructured coatings offer high thermal stability and prevent electrode cracking during cycling [126, 132].

The integration of nanostructured LiF coatings in lithium-ion batteries could significantly extend their lifespan, improve efficiency, and enhance safety, particularly in next-generation batteries. This is especially relevant for energy storage systems, mobile devices, and electric vehicles.

Machine learning (ML) is being increasingly applied in the development of next-generation batteries, including lithium-sulfur, metal-air, and multivalent metal batteries [133]. The key advantages of ML in battery research include:

- Discovery of new promising materials [134].
- Prediction of material properties, such as chemical, thermodynamic, and electrochemical characteristics [135, 136].
- Performance forecasting, including cycle stability, specific capacity, and degradation rates.

The use of ML significantly accelerates the discovery and optimization of novel battery materials, reducing costs and improving energy storage performance [137].

Additionally, additive manufacturing (3D printing) allows for the precise fabrication of battery components, ensuring better control over material properties [138]. This technology facilitates wider and more efficient use of LiF in modern batteries and advances energy storage technology development [139, 140].

The review makes it clear that due to the high demand for LiF, its industrial production plays a crucial role in various industries, including optics, nuclear energy, and battery technologies. The production of lithium fluoride involves several key stages aimed at obtaining a high-purity product. Lithium fluoride is found in nature as an extremely rare mineral called griceite. It forms in pegmatites and alkaline intrusions where lithium and fluorine are present. Due to its rarity and specific formation conditions, griceite is found in only a limited number of deposits.

The industrial production of LiF involves several key stages aimed at obtaining a high-purity product.

Raw Materials

- Lithium hydroxide (LiOH) or lithium carbonate (Li_2CO_3): These compounds serve as lithium sources.
- Hydrofluoric acid (HF): Used as a fluorine source.

Chemical Reaction

The production of lithium fluoride is based on the reaction between lithium compounds and hydrofluoric acid:

- Using lithium hydroxide: $LiOH + HF \rightarrow LiF + H_2O$
- Using lithium carbonate: $Li_2CO_3 + 2HF \rightarrow 2LiF + H_2O + CO_2$

These reactions are carried out in reactors made from corrosion-resistant materials due to the aggressive nature of HF. Temperature and reagent concentration are carefully controlled to ensure complete reaction and high product purity. The industrial production of lithium fluoride requires strict quality control at all stages to meet industry standards and application requirements. Producing each ton of LiF crystal generates approximately 5 tons of wastewater, containing about 0.3–1 g/L of lithium and ~1.10 g/L of fluorine. Due to the increasing demand for lithium, new methods for recovering lithium and fluorine from wastewater are being developed. The entire synthesis process is efficient, environmentally friendly, and holds great potential for industrialization [141].

Conclusion and future prospective

The review describes in detail a number of unique characteristics of LiF crystals, which are formed due to the creation of defects on the surface, and their impact on technological progress in various fields to this day.

LiF is a unique compound among all known materials due to its largest band gap, which results in high optical transparency and chemical stability. These aspects comprehensively influence the use of this material across a wide range of science and technology Since the 1950 s, lithium fluoride has been used in various applications. Table 9 lists some of the main areas of application.

Thus, studying the subsurface region of LiF is a promising research direction that can lead to the creation of new materials and devices, as well as solving current societal challenges. A sharp increase in the number of publications (threefold by 2025) related to experimental and theoretical studies on the surface of LiF is expected, driven by its growing potential in lithium-ion batteries, especially as a key component of solid electrolytes. Its relatively high ionic conductivity, chemical stability, and compatibility with other materials make it an ideal candidate for this role. Research in this area is ongoing, and undoubtedly, LiF will be increasingly used in advanced lithium-ion technologies and future generations of batteries.

For clarity, we have created Table 10, which provides a structured overview of the key research directions related to LiF, including its applications, challenges, and future prospects. The Table examines the role of LiF in solid-state electrolytes, optoelectronics, and other critical scientific areas. It also highlights potential challenges, such as high synthesis costs, difficulties in material integration, and recycling complexities, while proposing possible solutions, forming a roadmap for further research and industrial applications of LiF.

As seen in Table 10, the main challenges associated with LiF are:

1. High production costs of LiF.
2. Difficulties in recycling and reprocessing.
3. Corrosive effects in nuclear energy applications.
4. Compatibility of LiF with other materials.
5. Effects of space environment exposure.

These challenges require further research and technological advancements for the successful industrial implementation of LiF. By prioritizing research in these key

Table 9 Applications of lithium fluoride from the 1950 s to the present

Application Area	Examples of Use	Description
Optical and Laser Technologies	Use of LiF in UV optics for telescopes and laser systems (e.g., in the Hubble Space Telescope and laser engraving systems) [142]	Used in laser systems, UV, and IR optics due to its high transparency and resistance to laser radiation
Nuclear Technologies	Application of LiF-based molten fluoride salts in nuclear reactors with liquid-fuel salt technology (e.g., in the MSRE – Molten-Salt Reactor Experiment) [143–145]	Component of flux salts in molten salt reactors, valued for chemical inertness and high melting point
Electronics and Microelectronics	Dielectric layers for electron injection in organic light-emitting devices (OLEDs) [146]	Used in thin-film technologies as a dielectric material due to its wide bandgap and excellent insulating properties
Lithium-Ion Batteries	Application of LiF in interphase electrolyte layers to improve stability and extend battery lifespan (e.g., in Tesla batteries and other manufacturers) [147]	Forms protective coatings on lithium-metal anodes, preventing dendrite formation and improving battery stability
Space Research	Use of LiF for radiation shielding in satellite systems and spacecraft, as well as thermal protection coatings [148]	Applied in thermal protective coatings of spacecraft due to resistance to extreme temperatures and radiation
Chemical Industry	Catalysts and reagents for metallurgy [149]	Used in chemical processes as a catalyst and reagent due to its high chemical stability
Medical Applications	Radiation dosimeters for medical personnel and workers in radiation-exposed environments [150, 151]	Applied in luminescent dosimeters for radiation measurement, leveraging its luminescent response to exposure

Table 10 Key research directions, challenges, and prospects of LiF

Research Area	Rationale	Potential Impact	Challenges	Solutions
High-Performance Solid-State Electrolytes	LiF's relatively high ionic conductivity and wide electrochemical stability range make it a promising material for next-generation solid-state electrolytes	Enhances battery safety and energy density	Developing cost-effective and scalable synthesis methods for high-purity LiF	Exploring alternative synthesis routes and optimizing existing processes to reduce costs and improve yield
Optoelectronic Materials	LiF's unique optical properties, such as a wide bandgap, are beneficial for optoelectronic applications	Improving performance in devices such as UV lasers and radiation detectors	Ensuring compatibility of LiF with other materials in composite structures, especially in battery systems	Investigating interface engineering techniques and conducting comprehensive material compatibility studies
Nanostructured Coatings	LiF-based coatings can enhance surface properties, including corrosion resistance and optical clarity	Extending the lifespan and efficiency of optical components and protective coatings	Assessing the environmental impact and economic feasibility of large-scale LiF production and recycling	Implementing sustainable extraction methods, developing efficient recycling processes, and conducting life-cycle analyses
LiF Production	LiF is obtained from lithium-containing compounds using fluorine-based reagents	Providing a raw material base for battery, optical, and nuclear applications	High extraction and processing costs, potential environmental contamination	Optimizing synthesis methods and developing eco-friendly production technologies
LiF Recycling and Reprocessing	The need for reusing LiF from spent batteries and optical devices	Reducing costs of new LiF extraction and minimizing waste	High recycling costs, difficulty in purifying recovered material to the required standard	Advancing selective extraction and LiF recovery techniques, implementing closed-loop production cycles
Space Technology	LiF is used in thermal shields, radiation detectors, and optical systems of spacecraft	Protecting equipment from extreme temperatures and space radiation	High production and integration costs, impact of space conditions on material longevity	Developing new LiF-based composites with improved thermal resistance and radiation stability
Nuclear Energy	LiF is used as a component of molten salt reactors in nuclear energy applications	Improving the safety and efficiency of nuclear reactors	Corrosive effects on structural materials, challenges in processing spent nuclear salts	Developing advanced alloys for reactor components and improving recycling and safe storage methods for spent nuclear materials

areas and addressing the related issues, a clearer roadmap for future studies can be established, facilitating the practical integration of LiF into advanced technologies.

Based on current trends and conclusions, several promising research directions in the field of LiF can be predicted:

- In-depth studies of the mechanism of ionic conductivity in LiF on solid electrolytes will lead to improved and optimized ionic conductivity and reduced resistance. This will also enhance the stability and compatibility of LiF in contact with other materials, preventing degradation and increasing lifespan. LiF could become a key component in the development of new solid electrolytes for solid-state batteries. Solid electrolytes with LiF additives can provide relatively high ionic conductivity and stability at high temperatures. Lithium fluoride has significant potential for improving lithium-ion battery performance, especially in the context of high-voltage and fast-charging systems. Its use as a coating and electrolyte component can significantly enhance the stability, efficiency, and durability of batteries, making LiF an important material for future energy storage developments.
- Analyzing various types of defects (vacancies, interstitial atoms, dislocations) on the LiF surface will change mechanical and electrochemical properties, which can be manipulated and used in developing new processing methods, nanostructuring, and surface modification of LiF to improve its characteristics, including creating protective layers. In the future, structural defects could become a trigger and key factor in solid-state batteries'failure. Proper management of defects in LiF will lead to the stabilization of high-voltage cathodes, such as LCO, by reducing oxidative reactions at high voltages. This will allow for higher operating voltages and increased energy density of batteries.
- Researching the possibilities of using LiF in composite materials, such as polymers, ceramics, and metals, to enhance their strength, stability, and conductivity, will lead to the creation of new materials with unique properties.
- Using advanced molecular dynamics methods and theoretical modeling to predict defect behaviors, such as ion diffusion and interaction with other substances, and their impact on LiF properties.
- Studying LiF's behavior under high temperatures and radiation exposure, its resistance to various types of stresses and deformations, which is important for applications in space technology and nuclear energy.
- Developing methods for recycling and reprocessing LiF after use in devices to minimize environmental impact and reduce production costs, improving LiF's availability for widespread use.
- In the future, the results of these studies are mainly important for new types of commercial tomographs using fast electrons [152], for biological, space, and nuclear research.

These research directions can lead to significant improvements in lithium-ion battery technology and the creation of new materials with unique properties, which will have a wide range of applications in various industries and technologies.

In addition to traditional methods, the use of 3D printers, integration with composite materials, the assistance of artificial intelligence, various simulation programs, and advanced interdisciplinary sciences and technologies will lead to more widespread use of LiF in science and technology.

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