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Review article

Chalcogenide-based materials for batteries: state of the art and research perspectives

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Abstract. In the context of the energy transition and the growing demand for electrochemical energy storage, the development of efficient and sustainable battery materials is a major scientific and technological challenge. Chalcogenide-based materials, including sulfides, selenides, and tellurides, have attracted increasing attention due to their versatile structural and electronic properties.

This article provides a concise overview of the role of chalcogenides in battery technologies, from their historical contribution to the emergence of lithium-ion batteries to their current applications as intercalation and conversion electrodes, nanostructured negative electrodes, solid electrolytes, and lithium-rich positive electrodes in solid-state batteries. Particular emphasis is placed on the relationships between composition, structure, electrochemical mechanisms, and performance. Finally, the potential of chalcogenide materials for post-lithium battery technologies, such as sodium-, potassium-, and magnesium-ion systems, is discussed, highlighting remaining challenges and future research perspectives.

Keywords. Chalcogenide materials, Lithium-ion batteries, Solid-state batteries, Solid electrolytes, Electrochemical energy storage, Post-lithium batteries.

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1. Introduction

In the current context of the energy transition and the sustained growth in demand for electrochemical energy storage devices, battery materials represent a strategic field of research and innovation [1,2]. This dynamic is driven by the simultaneous rise of renewable energies, electromobility, and portable technologies, which impose ever more stringent requirements in terms of energy density, lifetime, and environmental sustainability.

Today, various battery technologies are available, each one addressing specific needs depending on the field of application [3]. Lead-acid accumulators, a historical technology still widely used, are notably employed in automotive ignition systems and uninterruptible power supplies (UPS). Nickel-metal hydride (Ni–MH) batteries maintain a significant presence in small-power

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electronic devices such as electric shavers, cameras, pagers, and portable medical equipment. Lithium-ion accumulators, in turn, dominate almost all markets, ranging from smartwatches and mobile phones to laptops, drones, and electric vehicles. Nickel-cadmium (Ni–Cd) batteries, although in decline due to their toxicity and environmental regulations, are still found in certain portable power tools, model-making applications, and specialized photographic equipment.

Market projections for the 2015–2030 period, based on industrial data and sectoral analyses, indicate that lead- and lithium-based technologies are expected to remain predominant at least until 2030. The most dynamic sectors include lithium for electric vehicles, lithium for consumer electronics, and lead-acid for stationary and automotive applications. However, this scenario raises several critical issues. On one hand, the rising price of lithium is exacerbated by the progressive depletion of exploitable deposits and by the increasing costs of extraction, which requires substantial water resources and can generate significant environmental impacts. On the other hand, the growing global demand calls for the development of more efficient batteries, capable of supporting a higher number of charge–discharge cycles, while incorporating more abundant, less expensive, and more environmentally friendly materials.

In response to these challenges, the search for alternatives to conventional lithium-ion accumulators has turned toward emerging chemistries. Among them, materials derived from group 16 of the periodic table—sulfur, selenium, and tellurium—are attracting increasing attention due to their remarkable structural and electronic properties. Chalcogenides, in particular, stand out for their ability to form flexible covalent networks, their tunable electrical conductivity, and their chemical stability, all favorable characteristics for electrochemical energy storage. Several recent studies, such as those reported by Pruthvija [4], demonstrate their potential in advanced battery architectures, including solid-state and hybrid configurations, aiming to combine high energy density, enhanced safety, and extended operational lifetime.

These preliminary works open new research directions, where the selection and optimization of chalcogenide-based materials could simultaneously address the requirements of performance, durability, and resource availability, while remaining consistent with the economic and environmental constraints of the global battery market. In this article, we aim to assess the potential of selected chalcogenide materials for applications in electrochemical energy storage, through an approach combining structural and physicochemical characterization, analysis of electrochemical performance, and investigation of their behavior during charge–discharge cycling. The objective is to highlight the relationships between composition, structure, and functional properties, in order to identify the key parameters likely to optimize performance and stability. Through this approach, we seek to contribute to the definition of new battery design strategies based on more abundant and sustainable resources, while maintaining performance comparable to-or even superior to-that of current lithium-ion technologies.

2. Chalcogenide materials and the emergence of lithium-ion batteries: a historical perspective

The award of the 2019 Nobel Prize in Chemistry to Stanley Whittingham, John B. Goodenough, and Akira Yoshino recognized a series of discoveries that led to the development of lithium-ion batteries.

The development of electrochemical devices began in the 19th century with the voltaic pile (Cu/Zn, 1801), followed by the first fuel cells (1839) and lead-acid batteries (1859) as illustrated in Figure 1. The latter played a decisive role in the early industrial electrification. The 20th century saw the emergence of new chemistries: Ni–Zn (1901), Ni–Cd (1930), Ni–H_2 (1970), and Ni–MH (1975) systems. Although robust and well-suited for certain specific applications (notably space, in the case of Ni–H_2), these technologies were limited by their intrinsic energy density.

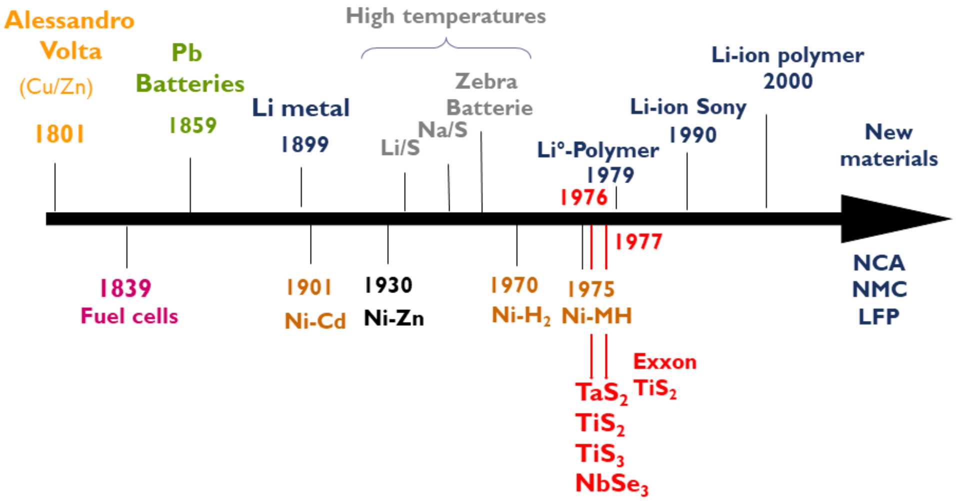

Figure 1. Timeline of the development history for batteries.

Lithium, owing to its low atomic mass (M = 6.94 g·mol^{-1}) and very negative electrochemical potential, emerged as an ideal candidate for energy storage systems. The fundamental reaction $\mathrm{Li} \leftrightharpoons \mathrm{Li}^+ + \mathrm{e}^-$ confers a theoretical specific capacity of 3860 Ah·kg^{-1}. As early as 1899, attempts were made to use metallic lithium as negative electrode. However, the formation of dendrites during charge–discharge cycles led to internal short circuits, raising major safety concerns.

In 1976, Stanley Whittingham (Exxon) [5,6] demonstrated the potential of layered transition-metal dichalcogenides (TiS_2, TaS_2, TiS_3, $NbSe_3$) as positive electrode materials. These compounds allow the reversible intercalation of lithium ions between their layers, thus realizing the first functional lithium battery. This discovery marked a foundational milestone, introducing the concept of host materials for ion insertion—the cornerstone of lithium-ion chemistry.

From 1978 onward, Don Murphy (Bell Laboratories) and other researchers initiated the transition from metallic lithium systems to lithium-ion systems, in which lithium ions shuttle between intercalation-type positive and negative electrodes without metallic deposition. In 1979, Michel Armand proposed the concept of a lithium-polymer battery [7,8], which was later explored by Hydro-Québec and eventually developed industrially several decades later.

In 1980, John B. Goodenough identified $LiCoO_2$ as a layered positive electrode material [9]. This compound doubled the operating potential compared with chalcogenide-based positive electrodes and significantly enhanced energy density. Finally, in 1985, Akira Yoshino introduced graphite as negative electrode material [10].

An initial industrial attempt at lithium-metal batteries was made in 1985 by Moly-Energy (250 Wh·kg^{-1}). However, problems associated with dendrite formation and safety concerns limited their widespread use. In 1990, Sony launched the first commercial lithium-ion battery ($LiCoO_2$/graphite), which quickly outperformed competing technologies (Ni–Cd, Ni–MH, Pb) in terms of energy density, lifetime, and safety. This milestone marked the turning point toward the massive adoption of Li-ion systems.

In the early 2000s, lithium-polymer batteries reached the market, extending the pioneering research initiated by Armand more than twenty years earlier. For further details, see Yoshino's retrospective and the comprehensive reviews discussing the challenges, recent advances, and positive electrode materials in lithium-ion batteries [1,11–13].

3. Conventional lithium batteries with liquid electrolytes

3.1. *The role of layered chalcogenide materials in the evolution of intercalation positive electrodes*

Transition-metal dichalcogenides and trichalcogenides such as TiS_2, TiS_3, $NbSe_3$, and VSe_2 were the first positive electrode materials investigated during the development of lithium batteries. Owing to their layered structure, which facilitates lithium-ion intercalation, these compounds paved the way for modern lithium-ion battery technology.

The development of lithium-ion batteries is inseparable from the search for host materials capable of reversibly accommodating lithium ions. As early as the 1970s, attention turned to layered dichalcogenides with the general formula MX_2, where M is a transition metal and X a chalcogen (sulfur or selenium). Their lamellar structure provided an ideal framework for reversible lithium insertion and extraction without significant disruption of the crystal lattice. These properties placed them at the center of the research carried out at Stanford and Exxon between 1973 and 1976, which led to the identification of TiS_2 as a reference positive electrode material and to the exploration of trichalcogenides such as TiS_3 and $NbSe_3$ [5,14–17].

The electrochemical behavior of TiS_3 has been studied in detail. This compound can be described as TiS(S–S), highlighting the presence of a polysulfide group that can react with lithium. During intercalation, the first step corresponds to the cleavage of the S–S bond, leading to the formation of Li_2TiS_3 through an irreversible process. In a second step, titanium is reduced from oxidation state +4 to +3, producing a reaction similar to the one observed in TiS_2. Unlike the first, this second step is reversible. However, TiS_3 exhibits only partial reversibility, due to a change in titanium coordination from trigonal prismatic to octahedral upon lithiation. This structural change represents a major limitation for practical use.

$NbSe_3$, on the other hand, exhibits reversible electrochemical behavior. Upon reaction with lithium, it can accommodate up to three lithium ions per formula unit, corresponding to a fully reversible global reaction. Compared with TiS_3, $NbSe_3$ thus showed greater potential as a positive electrode material. However, the structural complexity of this trichalcogenide, together with limitations in its electrical conductivity, hindered its industrial development [18].

Among chalcogenide materials, TiS_2 remains the most emblematic. In 1976, Stanley Whittingham proposed TiS_2 as an intercalation positive electrode. The first Li/TiS_2 battery prototypes, developed by Exxon in the late 1970s, used a liquid electrolyte consisting of lithium perchlorate dissolved in dioxolane and metallic lithium as the negative electrode. The latter was soon replaced by a Li–Al alloy to limit dendrite growth and improve safety [19].

These cells exhibited an average voltage of about 2 V and a theoretical specific capacity of 239 $mAh\cdot g^{-1}$. Most notably, they offered exceptional longevity, with more than one thousand cycles achievable—a major advance over previous systems. The excellent performance of TiS_2 stemmed from its compact hexagonal layered structure, in which Ti^{4+} ions occupy octahedral sites between sulfur layers. Lithium intercalates continuously into these interlayer spaces without requiring the nucleation of new phases. This single-phase mechanism results in a characteristic sloping voltage-capacity curve, indicative of reversible intercalation across the full composition range from TiS_2 to $LiTiS_2$, as illustrated in Figure 2 [19].

The efficiency of TiS_2, however, strongly depended on synthesis conditions. Below 600 °C, a stoichiometric compound favorable to lithium intercalation was obtained. Above this temperature, non-stoichiometric sulfides of the $Ti_{1+y}S_2$ type formed, with excess titanium atoms occupying van der Waals gaps. This structural disorder reduced ionic mobility and hindered lithium intercalation, thereby degrading electrochemical performance [19].

Most transition-metal dichalcogenides exhibit electrochemical behavior similar to that of TiS_2, characterized by single-phase and reversible lithium intercalation. A notable exception

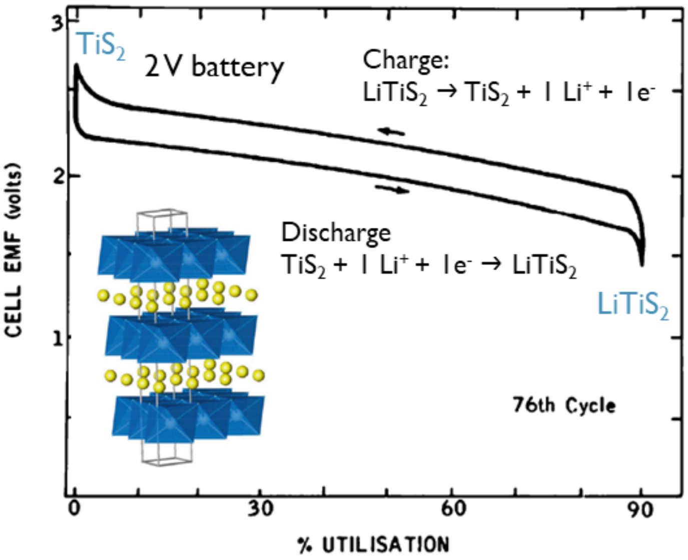

Figure 2. Layered structure of $LiTiS_2$ showing hexagonal close-packed S lattice with Ti ions in octahedral sites between alternating sulfur sheets. Discharge/charge curve of TiS_2 in lithium cells (76th cycle at 10 mA·cm^{-2}).

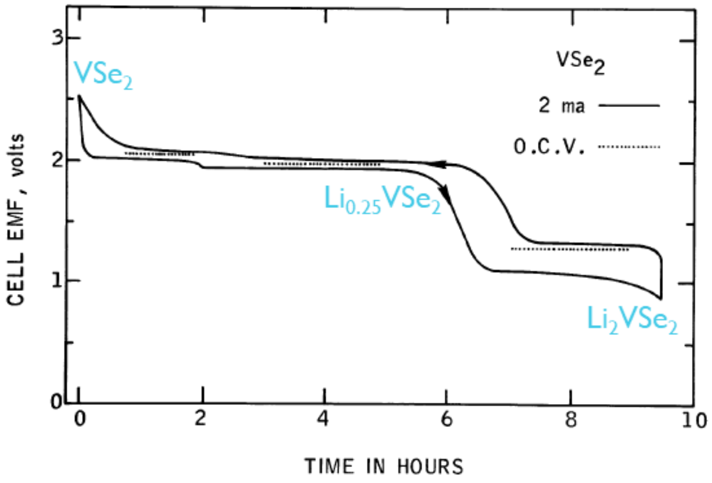

Figure 3. Electrochemical insertion of lithium into vanadium diselenide, showing reaction of two lithium (behavior on cycling at 2 mA·cm^{-2}).

is VSe_2. Unlike TiS_2, this compound exhibits a biphasic behavior during lithiation. The reaction proceeds through successive steps: first the formation of $Li_{0.25}VSe_2$, followed by $LiVSe_2$, and finally Li_2VSe_2, as illustrated in Figure 3. This sequence of transitions leads to distinct voltage plateaus during charge and discharge. This atypical behavior is related to a particular crystallographic c/a ratio and to the unusual coordination of vanadium. Whereas group V elements generally adopt trigonal prismatic coordination with sulfur or selenium, vanadium assumes octahedral coordination in VSe_2, resulting in distinct electrochemical behavior [20].

In parallel with lithium-based systems, research from 1978 also explored sodium-ion batteries, with Whittingham proposing transition-metal disulfides such as TiS_2 and TaS_2 as positive electrode materials. However, sodium chemistry introduced additional complexity. In Na_xTiS_2 and Na_xTaS_2 compounds, structural transitions occur as a function of sodium content. At low sodium concentrations, trigonal prismatic coordination is favored, while at higher contents ($x \rightarrow 1$), octahedral coordination becomes predominant. These successive structural transitions severely hindered electrochemical reversibility and limited the durability of these systems, preventing their adoption as viable alternatives to lithium-ion batteries.

Nevertheless, these studies laid the foundations to the development of layered transition-metal oxides, which enabled the commercialization of the first safe and high-performance lithium-ion batteries. Among the main intercalation positive electrode materials are $LiCoO_2$ (LCO), developed by Sony and commercialized in 1991; $LiTiS_2$ (LTS), studied at Exxon; mixed oxides of the NMC type ($LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ or NMC111), widely used in today's battery market; and NCA ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$), notably employed by Panasonic in Tesla vehicle batteries. Other examples include the spinel $LiMn_2O_4$ (LMO) and the olivine $LiFePO_4$ (LFP), which offer more stable and cost-effective alternatives. These layered transition-metal oxides exhibit higher operating voltages, while polyanionic compounds such as LFP provide additional advantages in terms of thermal stability and safety.

Thus, although progressively replaced by these newer families of materials, chalcogenides played a decisive role in the emergence of a technology that today dominates the landscape of electrochemical energy storage. The optimization of intercalation positive electrodes remains a major scientific and industrial challenge, particularly in view of the growing demands associated with electric mobility and the integration of renewable energy sources.

3.2. *Chalcogenide materials as conversion electrodes*

In addition to intercalation-type electrodes, which enabled the development of lithium-ion batteries, so-called *conversion electrodes* have attracted increasing attention, particularly in lithium-metal systems. Unlike intercalation materials—where lithium ions are inserted into a preserved host lattice—conversion electrode undergo a solid-state redox reaction involving significant structural rearrangement and the breaking and recombination of chemical bonds. This mechanism enables much higher specific capacities but also introduces major challenges in terms of cyclability, conductivity, and stability.

Conversion-type materials include a variety of chalcogenides and halides for transition metals. The general principle of these electrodes relies on a complete redox reaction, such as: $CoS + 2Li^+ + 2e^- \leftrightharpoons Co_2 + Li_2S$ for cobalt sulfide, or $FeF_3 + 3Li^+ + 3e^- \leftrightharpoons Fe_2 + 3LiF$ for iron fluoride [21]. Conversion reactions can also involve the elemental chalcogens themselves: sulfur, selenium, and tellurium can form Li_2S, Li_2Se, and Li_2Te during discharge, respectively. In all cases, these reactions are accompanied by profound structural reorganization, distinguishing these electrodes from conventional intercalation hosts. Figure 4 shows the approximate range of average discharge potentials and specific capacity of some of the most common conversion-type cathodes [21].

Among conversion materials, sulfur has been the most extensively studied due to its exceptionally high theoretical specific capacity of 1671 $mAh \cdot g^{-1}$, its natural abundance in the Earth's crust, and its low cost. The fundamental electrochemical reaction corresponds to the reduction of elemental sulfur to Li_2S, according to the equation $1/8\ S_8 + 2Li^+ + 2e^- \leftrightharpoons Li_2S$. The discharge profile exhibits long, nearly flat voltage plateaus, characteristic of favorable solid-solid reaction kinetics. However, the use of sulfur poses several challenges. First, sulfur is an electronic insulator with an extremely low intrinsic conductivity ($\approx 5 \times 10^{-27}$ $mS \cdot cm^{-1}$ at 25 °C), requiring the formation of composites with conductive carbon and polymeric binders. Second, both sulfur and its reaction product Li_2S undergo a large volume change (~80%), which destabilizes conventional

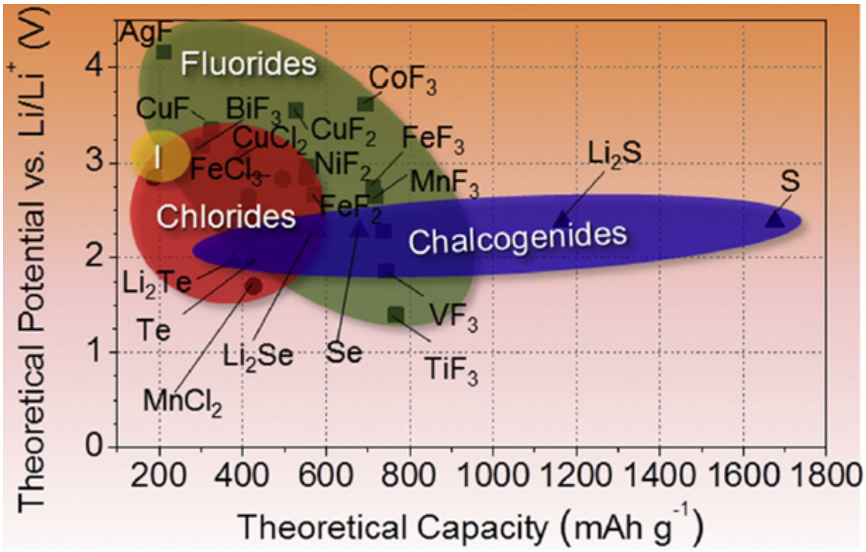

Figure 4. Approximate range of average discharge potentials and specific capacity of some of the most common conversion-type cathodes (theoretical).

composite electrodes. Finally, a major issue arises from the dissolution of soluble lithium polysulfide intermediates into the electrolyte, leading to rapid capacity fading and poor coulombic efficiency [21].

Until around 2009, these limitations resulted in very poor capacity retention. Since then, numerous strategies have been explored to address them. Encapsulating sulfur within hollow structures with internal void volume—such as TiO_2, carbon, or reduced graphene oxide shells—has proven effective in accommodating volume changes. Polymer hosts such as polyvinylpyrrolidone have also been employed. These architectures have enabled cycle lifetimes exceeding 1000 cycles in half-cell configurations [22].

In parallel, electrolyte engineering approaches have been developed, including the use of additives such as $LiNO_3$ or P_2S_5 to promote the formation of a protective solid-electrolyte interphase (SEI) on the lithium negative electrode. The use of high-molarity or solid-state electrolytes has also been investigated to suppress polysulfide dissolution.

From 2015 onwards, selenium and tellurium have received growing attention. Selenium exhibits a theoretical specific capacity of 678 $mAh{\cdot}g^{-1}$ and tellurium 420 $mAh{\cdot}g^{-1}$. Although these values are lower than that of sulfur, their volumetric energy densities are considerably higher, reaching 3254 $mAh{\cdot}cm^{-3}$ for selenium and 2621 $mAh{\cdot}cm^{-3}$ for tellurium in the fully lithiated state (3467 $mAh{\cdot}cm^{-3}$ for sulfur) [21]. Another key advantage of these materials lies in their much higher electronic conductivity compared to sulfur, resulting in better active material utilization and faster reaction kinetics.

Nevertheless, selenium suffers from the dissolution of lithium polyselenide intermediates, leading to rapid capacity fading and low coulombic efficiency, similar to sulfur. Tellurium, on the other hand, does not appear to suffer from this issue but presents other drawbacks. While its volume change upon lithiation is lower (35–40%), its high cost and relative scarcity in the Earth's crust make its large-scale application unrealistic. Consequently, selenium and tellurium have mainly been investigated as model materials or for niche applications. To enhance their stability, both elements have been incorporated into conductive matrices—especially porous carbons or doped graphene–to limit dissolution effects and maintain electrical contact.

3.3. *Chalcogenides as active material for negative electodes: nanostructures and composites*

The development of lithium-ion batteries (LIBs) has been strongly driven by the search for electrode materials offering both high specific capacity and satisfactory electrochemical stability. Conventional graphite negative electrode, which operate via lithium intercalation, exhibit a theoretical capacity of 372 mAh·g^{-1}, while positive electrode materials such as $LiCoO_2$ reach about 135 mAh·g^{-1}, as established in the earliest studies on commercialized batteries [23]. Despite their technological success, these materials remain limited in terms of energy density and stability under high-rate cycling, which has stimulated the exploration of alternative compounds among which transition-metal chalcogenides are gaining increasing attention [21].

When synthesized as electrode materials, chalcogenides exhibit remarkable electrochemical properties, particularly their ability to promote redox reactions while minimizing self-discharge [4]. Their structural versatility-often achieved through nanostructuring techniques-confers high porosity and good ionic conductivity, both of which are essential for fast charge–discharge processes. Their performance can be further enhanced by doping with metals such as copper, aluminum, or cobalt, which improve electronic conductivity. Complementarily, doping with semiconductors such as germanium or silicon promotes the formation of polycrystalline structures that are particularly active as electrodes [4].

A wide variety of metal sulfides have been investigated as negative electrode materials. For example, Bi_2S_3 obtained by mechanical milling exhibits an initial charge capacity of 1146 mAh·g^{-1} and a discharge capacity of 746 mAh·g^{-1} after 50 cycles, whereas a one-step synthesized CuS–$Cu_{1.8}S$ system retains a more modest capacity of 320 mAh·g^{-1} after 500 cycles. Other sulfides, such as WS_2 and MoS_2-graphene composites prepared via hydrothermal routes, reach initial capacities of 900 and 1157 mAh·g^{-1}, respectively, with the MoS_2-graphene composite maintaining 1066 mAh·g^{-1} after 100 cycles. These results highlight the potential of sulfide-based nanostructures-especially when combined with conductive additives such as graphene-to overcome the intrinsic limitations of conventional graphite negative electrode [4].

Metal selenides have also attracted growing attention as they overcome some of the limitations associated with sulfur-based electrodes. Their superior electronic conductivity, shorter ionic diffusion lengths, and additional properties such as hydrophilicity, photoconductivity, and photovoltaic response make them attractive for electrochemical energy storage. For instance, solvothermally synthesized SnSe-C composites exhibit an initial capacity of about 1098 mAh·g^{-1} and retain approximately 707 mAh·g^{-1} after 50 cycles, while $CoSe_2$-CNT composites show excellent stability, maintaining 1405 mAh·g^{-1} after 300 cycles. Other systems, such as Sb_2Se_3 thin films prepared by pulsed laser deposition, retain around 605 mAh·g^{-1} after 100 cycles, confirming the potential of selenides as high-performance negative electrode materials [4].

Although less explored, metal tellurides have emerged as particularly promising candidates owing to their intrinsic electronic conductivity, high volumetric energy density, and large volumetric specific capacity. For example, CuTe obtained by solvothermal synthesis has shown remarkable stability up to 5000 cycles, albeit with moderate capacity, while Te–C composites prepared by various methods—including melt-diffusion and high-energy ball milling (or high energy mechanical milling—HEMM)—have demonstrated initial capacities exceeding 1000 mAh·g^{-1}, with retention depending on synthesis conditions [4]. These findings underline the advantages of tellurium for potential use as both negative and positive electrode materials in advanced LIB systems. Table 1 tabulates metal sulfides, selenides, and tellurides characterized as negative electrode materials with their performance metrics.

Table 1. Metal-sulfide, metal-selenide, metal-telluride used as negative electrodes [4]

Composition	Synthesis technique	Initial charge capacity (mAh·g^{-1})	Current density	Discharge capacity (mAh·g^{-1})	Cycle number
Bi_2S_3–C	Ball milling	1146	100 mA·g^{-1}	746	50
CuS–$Cu_{1.8}S$	One-pot	620	4C	320	500
WS_2	Hydrothermal	900	47.5 mA·g^{-1}	–	20
MoS_2–S_2-graphene	Hydrothermal	1157	100 mA·g^{-1}	1066	100
SnSe-C	Grinding and solvothermal	1097.6	50 mA·g^{-1}	707	50
Sb_2Se_3	Pulsed laser deposition	624	500 mA·g^{-1}	605.1	100
$CoSe_2$-CNT	Hydrothermal	845	200 mA·g^{-1}	1405	300
FeSe–C	One-pot	390	40 mA·g^{-1}	340	40
$MoSe_2$-rGO	Hydrothermal	550	0.1 C	523	5
Se–Mo with CNT	Hydrothermal	1008.7	7000 mA·g^{-1}	607	40
CuTe	Solvothermal	229	400 mA·g^{-1}	180	5000
Te–C	Melting diffusion	–	0.1 C	429.6	100
Te–C	HEMM	1088	10 mA·g^{-1}	740	100

4. Solid-state batteries

Among the various battery chemistries currently available, solid-state batteries (SSBs) have emerged as a promising alternative to conventional lithium-ion batteries (LIBs) employing liquid electrolytes. The latter are intrinsically limited by several factors, notably by use of flammable organic liquid electrolytes and graphite negative electrode with a restricted specific capacity of 372 mAh·g^{-1}. By contrast, metallic lithium-with its very low density (0.59 g·cm^{-3}), high theoretical capacity (3860 mAh·g^{-1}), and extremely negative electrochemical potential-represents an ideal negative electrode material for achieving significantly higher gravimetric and volumetric energy densities [23].

Positive electrodes used in conventional batteries, such as $LiCoPO_4$ (4.8 V vs. Li/Li$^+$, 801 Wh·kg^{-1}) or $LiNi_{0.5}Mn_{1.5}O_4$ (4.7 V vs. Li/Li$^+$, 690 Wh·kg^{-1}), already offer high electrochemical potentials. However, their performances are inherently constrained by the chemical and electrochemical stability of the liquid electrolyte. Linear organic solvents (diethyl carbonate, dimethyl carbonate, ethyl methyl carbonate) or cyclic ones (ethylene carbonate, propylene carbonate, butylene carbonate, γ-butyrolactone), combined with conducting salts such as $LiPF_6$ or $LiClO_4$, present significant risks of leakage, evaporation, and particularly flammability [24]. Notable incidents, including failures in laptop batteries (Sony, Dell, Apple) and in the Boeing 787 Dreamliner, illustrate these safety limitations [25].

The transition to solid-state batteries aims to overcome these constraints. By replacing the liquid electrolyte with a nonflammable solid electrolyte and substituting graphite with metallic lithium, it becomes possible to simultaneously enhance safety and energy density while reducing system volume and weight [23], as illustrated in Figure 5. This development also opens the door to the use of new families of materials, including chalcogenides, whose electronic and ionic properties are particularly attractive for high-performance solid electrolytes.

The expected benefits of SSBs include enhanced safety due to the absence of organic solvents, improved thermal stability, and suitability for extreme environments, such as deserts or drilling sites. The reduction in module weight and the elimination of components, notably the separator, further facilitate integration into electric vehicles and other embedded applications [26].

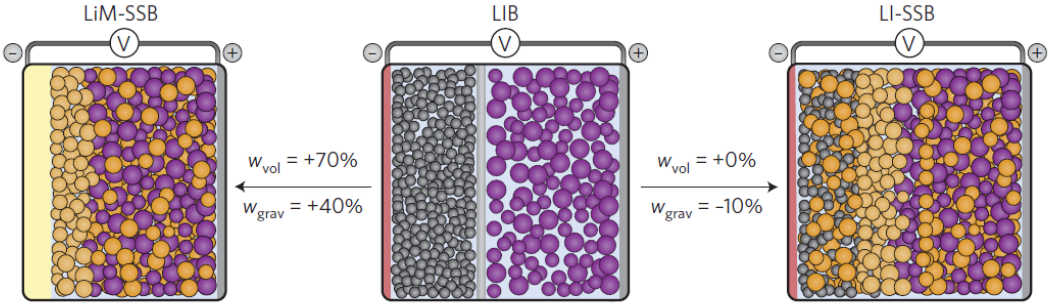

Figure 5. Comparative diagrams of a conventional lithium-ion battery (LIB in the center) and a solid-state battery with lithium metal (LiM-SSB on the left) or a composite negative electrode (Li-SSB on the right). W_{vol} and W_{grav} are the volumetric and gravimetric energy densities, respectively [23].

Chalcogenide materials—mainly sulfides, selenides, and tellurides—play an increasingly important role in solid-electrolyte research. Their appeal lies in a combination of structural and electronic properties favorable to ionic conduction. Unlike oxides, which generally offer high chemical stability but limited ionic conductivity, chalcogenides provide high ionic conductivities (up to 10 $mS{\cdot}cm^{-1}$ at room temperature for certain sulfides such as $Li_{10}GeP_2S_{12}$), comparable to or exceeding those of liquid electrolytes [27,28].

Sulfides are the most extensively studied in this context. Their relatively open crystal frameworks facilitate lithium-ion diffusion, enabling conductivities approaching 10 $mS{\cdot}cm^{-1}$, making them excellent candidates for solid electrolytes. Compounds such as amorphous or crystalline Li_2S–P_2S_5 offer a good balance between conductivity and mechanical flexibility, accommodating volumetric changes during cycling. However, their sensitivity to moisture and the formation of toxic H_2S upon degradation pose challenges for industrial-scale implementation [28].

Selenides and tellurides, less studied than sulfides, are gaining attention due to their higher electronic conductivity and improved chemical stability at electrode interfaces. Selenides, for instance, can enhance the interface with nickel-rich positive electrodes by reducing interfacial resistance, a key technological bottleneck in SSBs. Nevertheless, their higher cost and greater atomic mass limit competitiveness compared to sulfides, especially in applications where gravimetric energy density is critical.

A major remaining challenge is interfacial instability between electrodes and solid electrolytes. Chalcogenides, despite their promising conductivity, often undergo electrochemical degradation at the high potentials of positive electrodes (>4 V vs. Li/Li^+). Strategies to mitigate these issues include protective electrode coatings, the design of stabilized chalcogenide compositions, and optimized sintering and shaping processes for solid electrolytes [27].

Finally, lithium dendrite growth remains a critical obstacle in lithium-metal SSBs. Chalcogenide materials, owing to their superior plasticity relative to oxides, could potentially suppress dendrite propagation through more uniform mechanical stress distribution. However, a comprehensive understanding of lithium/chalcogenide electrolyte interactions is essential to ensure long-term device durability [28].

4.1. *Chalcogenide materials as solid electrolytes*

Inorganic solid electrolytes are at the core of solid-state battery (SSB) development, which aims to overcome the safety and performance limitations of liquid electrolytes. Among the various material families investigated, chalcogenides occupy a prominent position. In practice, the

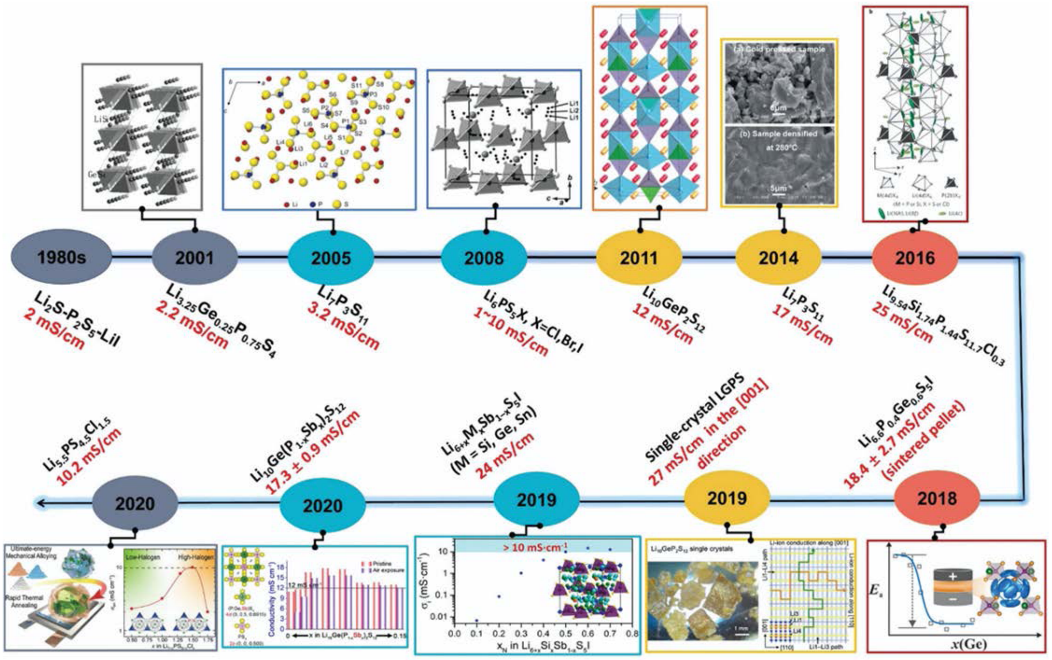

Figure 6. Developing trend of solid-state sulfide electrolytes [31].

literature shows that sulfides are almost exclusively used as solid electrolytes, both for lithium-ion and sodium-ion batteries [29,30], as illustrated in Figure 6 [31]. These materials exhibit high ionic conductivity on the order of 1 mS·cm^{-1}, favoring ductility for cold-press assembly, and interesting mechanical compatibility [32]. However, they suffer from moisture sensitivity, a limited electrochemical stability window, and parasitic reactions with electrode materials and metallic lithium.

Among sulfides, several families stand out. Solid electrolytes based on $Li_{10}GeP_2S_{12}$ (LGPS), argyrodites of the type Li_6PS_5X (X = Cl, Br, I), and glassy or crystalline derivatives of Li_3PS_4 have been extensively studied [33,34]. Li_3PS_4 exists in amorphous, glass-ceramic, or crystalline forms and has been the subject of numerous fundamental studies and recent patents [35–39].

Another important family is the argyrodites. Initially discovered in 1886 with the compound Ag_8GeS_6, these materials have attracted renewed attention since 2008 with the identification of Li-rich phases of the type Li_6PS_5X, exhibiting remarkable ionic conductivity [40]. These argyrodites adopt orthorhombic or cubic crystal structures depending on composition and temperature, with ionic conductivities ranging from 10^{-3} mS·cm^{-1} in the orthorhombic phase to ~1 mS·cm^{-1} in the cubic phase at room temperature [41]. Their high chemical flexibility allows aliovalent substitutions at various crystallographic sites to increase charge carrier concentration and expand diffusion pathways. For instance, tetravalent cations such as Si^{4+}, Sn^{4+}, or Ge^{4+} can partially replace phosphorus, while halides (Cl^-, Br^-, I^-, F^-), O^{2-}, or Se^{2-} can substitute for sulfur, yielding a softer and more polarizable lattice. This chemical engineering strategy has led to compositions with significantly enhanced conductivities, reaching up to 10 mS·cm^{-1} at 25 °C, such as the recently developed $Li_{5.4}PS_{4.4}BrCl_{0.6}$ electrolyte, surpassing commercial Li_6PS_5Cl (~1.5 mS·cm^{-1}) [42].

These advances translate into remarkable electrochemical performance. Cells using Li_6PS_5Cl or its derivatives exhibit low irreversible capacity, low polarization, and stable reversible capacity even after several hundred cycles at high current density, highlighting their potential for industrial-scale integration [42,43].

4.2. *Lithium-rich sulfides as positive electrode materials*

Beyond their well-established role as solid electrolytes, sulfides can also be considered as active positive electrode materials in solid-state batteries. This strategy relies on the use of lithiated sulfides, either alone or in combination with oxide-based lithium-active materials, to exploit their chemical richness and ionic conductivity. However, the direct integration of these materials faces significant interfacial challenges. Indeed, the difference in lithium electrochemical potential between oxides based positive electrode and sulfide solid electrolytes leads, upon contact, to undesired chemical reactions or the formation of a lithium-depleted interfacial layer, a phenomenon known as the "space-charge layer effect." A widely adopted solution to mitigate this issue is the insertion of an interlayer between the positive electrode material and the solid electrolyte. The coatings used must possess dual functionality: electronic insulation while maintaining ionic conductivity. Compounds identified as suitable coatings include $LiNbO_3$, ZrO_2, $Li_4Ti_5O_{12}$, Al_2O_3, and $LiTaO_3$, which ensure chemical compatibility and enhanced interfacial stability.

A particularly promising example of a sulfide positive electrode material is the lithium-rich compound $Li_{1.13}Ti_{0.57}Fe_{0.3}S_2$ (LTFS), recently studied by Marchini et al. [44]. Its synthesis is carried out via a solid-state reaction from a mixture of Li_2S, TiS_2, and FeS_2, sealed in a quartz tube under inert atmosphere, and annealed at 750 °C for 36 h, followed by rapid quenching in water. The resulting product consists of pseudo-spherical monolithic particles of 5–20 μm, forming a single phase crystallizing in the $R\bar{3}m$ space group, with lattice parameters $a = 3.53$ Å and $c = 18.09$ Å. This hexagonal structure is analogous to lithium-rich layered oxide phases of the type $Li_{1+y}M_{1-y}O_2$ but possesses a larger lattice capable of accommodating the bulkier sulfide ligands (S^{2-}). The structure is cation-disordered, with iron atoms sharing sites with titanium and lithium in the metal layers.

LTFS has a theoretical capacity of 261 $mAh{\cdot}g^{-1}$, attributable to mixed redox activity combining both cationic Fe^{2+}/Fe^{3+} and anionic S^{2-}/S^{n-} ($n < 2$) couples. Integrated into a solid-state cell of the type LTFS $+\beta$-$Li_3PS_4|\beta$-$Li_3PS_4|$InLi, this material exhibited promising electrochemical properties. The assembly of the cell is facilitated by the low mechanical rigidity of sulfides, whose reduced Young's modulus allows good densification under pressure. Scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) mapping reveal a continuous and homogeneous interface between the composite positive electrode and electrolyte, with uniform distribution of titanium and phosphorus, indicating good mixing between LTFS and β-Li_3PS_4 and effective electronic percolation.

Galvanostatic measurements at C/25 show an initial charge with a long redox plateau of around 2.1 V (2.7 V vs. Li/Li^+), accompanied by significant irreversible capacity loss, with an initial coulombic efficiency of 69% and a loss of ~50 $mAh{\cdot}g^{-1}$. In the second cycle, a reversible capacity of 120 $mAh{\cdot}g^{-1}$ is obtained at room temperature, increasing to 140 $mAh{\cdot}g^{-1}$ at 100 °C. However, using lithium alloys as negative electrodes, although functional, is impractical due to their high cost, weight, and the lower cell voltage compared to metallic lithium.

Experiments with LTFS $+\beta$-$Li_3PS_4|\beta$-$Li_3PS_4|$ Li cells yielded better results, with dense, continuous electrode structures, no visible cracks, and satisfactory interfacial contact. Galvanostatic charge–discharge cycles at C/50 exhibited low polarization (85 mV at 120 $mAh{\cdot}g^{-1}$) and excellent coulombic efficiency above of 99% as illustrated in Figure 7. After 10 cycles, the reversible capacity reached 214 $mAh{\cdot}g^{-1}$, corresponding to 83% of the theoretical capacity, or nearly one lithium ion per formula unit of LTFS. These performances demonstrate improved capacity retention and

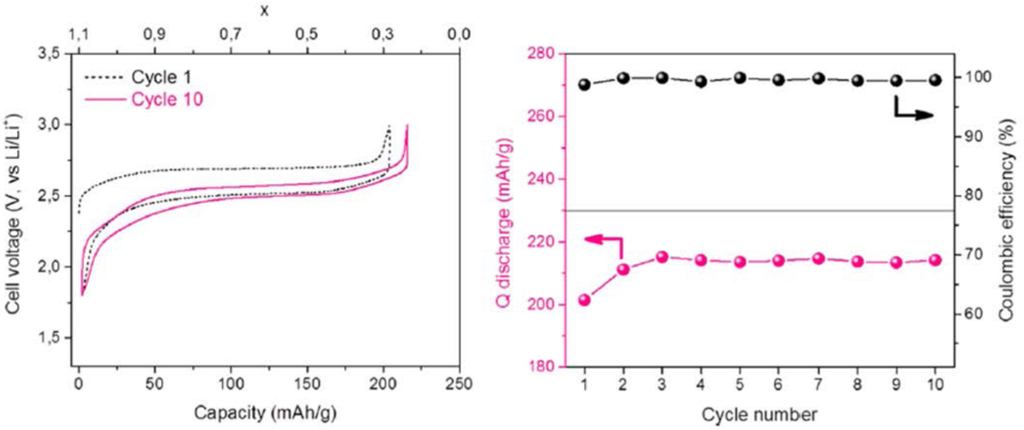

Figure 7. First and tenth galvanostatic charge/discharge cycles and discharge capacity and Coulombic efficiency obtained at C/50 and room temperature of LTFS $+\beta$-Li_3PS_4 (70–30 wt%) $|\beta$-$Li_3PS_4|$ Li battery [44].

enhanced stability in cells using metallic lithium negative electrodes compared to InLi alloy-based cells.

In summary, the use of lithium-rich sulfides as active positive electrode materials represents a highly promising approach for solid-state batteries. The LTFS compound illustrates this strategy by combining a crystal structure suited to sulfide ligands, mixed redox activity, and favorable integration with Li_3PS_4-type solid electrolytes. While challenges remain, particularly regarding interface optimization and reduction of initial irreversible losses, these results pave the way for a new generation of high-capacity positive electrodes capable of competing with the best current oxide-based solutions.

5. Chalcogenide materials as alternatives to Li-ion batteries

The growing demand for energy storage solutions has driven intensive research into alternatives to lithium-ion batteries (LIBs), particularly due to the limited availability of lithium and the need for more sustainable and cost-effective systems. Among the explored options, sodium-ion (SIBs), potassium-ion (PIBs), and magnesium-ion batteries (MIBs) emerge as promising technologies due to the abundance and favorable geographic distribution of these elements.

For sodium-ion batteries, sodium offers the advantage of being more abundant and less expensive than lithium while sharing a similar operating mechanism. However, the larger ionic radius of Na^+ (1.02 Å vs. 0.76 Å for Li^+) slows ion transport and electrochemical kinetics, which can reduce overall performance and introduce safety issues such as explosion or corrosion [45]. To compensate these limitations, chalcogenide materials have been extensively investigated as negative electrode materials. Their high storage capacity is, however, counterbalanced by low electrical conductivity and significant volumetric expansion during sodiation/desodiation cycles. Various modification strategies, including carbon doping, metal substitution, and the synthesis of hybrid nanostructured architectures, have been developed to enhance their performance [46,47]. Reducing particle size to the nanoscale significantly increases the electrode–electrolyte interfacial area and accommodates better mechanical stresses associated with volume changes. Two-dimensional layered dichalcogenides (TMDs) such as MoS_2, VS_2, or CoS_2, with their expanded interlayer spacing and high theoretical capacities, provide an ideal platform for rapid and reversible Na^+ intercalation [45]. Their electrochemical mechanism occurs in two steps: an initial intercalation at relatively high potential followed by a lower-potential conversion reaction, leading to the formation of sodium sulfides and elemental metals [46,47]. Beyond MoS_2 and VS_2, SnS_x-based materials stand out due to their high capacity, abundance, and low toxicity, making them an attractive option for SIBs. Nanoscale architectures, such as VS_2 "flower-like" morphologies or MoS_2 nanosheets, highlight the importance of surface engineering strategies [45].

Among the various configurations of sodium-based batteries (SBs), solid-state ones have also emerged as a particularly attractive option. A wide variety of inorganic solid electrolytes for sodium-ion solid-state batteries includes chalcogenide-based compounds such as the Na_3MS_4 series [48–51], the Na_3MSe_4 (M = P, Sb) family, [52,53] and the $Na_7P_3X_{11}$ (X = O, S, Se) series [54]. Recent studies also explore the development of glassy, glass-ceramic, and ceramic sulfide electrolytes, notably in Na_2S–GeS_2 [55] and Na_2S–SiS_2 systems [56,57]. Na_3PS_4 is the most studied representative. This material has recently undergone a reevaluation of its thermodynamic properties, revealing a high-temperature polymorph (γ-Na_3PS_4) characterized by plastic and mesomorphic behavior, along with a local tetragonal structure within a cubic phase [58,59]. Under pressure, its structural and conductive properties further evolve, providing insight into its stability and potential as a solid electrolyte for sodium-ion batteries [60].

Chalcogenide electrolytes represent attractive and cost-effective alternatives to oxide electrolytes, as they can be synthesized at relatively low temperatures. Nevertheless, they often suffer from poor air stability and the presence of voids, which can adversely affect ionic conductivity. To address these limitations, several modification strategies have been investigated, including cation doping at the P site, halogen substitution at the S site, the formation of hybrid organic–inorganic composites such as polyethylene oxide-based Na_3PS_4, high-temperature thermal treatments to induce favorable crystal phase transformations, as well as ceramization and vitrification processes. These approaches have proven effective in enhancing the stability, electrochemical performance, and mechanical properties of chalcogenide-based solid electrolytes for next-generation solid-state batteries [61–67].

Potassium-ion batteries represent another promising alternative. With a redox potential for K^+/K (−2.93 V vs. SHE) close to that of Li^+/Li (−3.04 V vs. SHE), PIBs can achieve operating voltages comparable to or even higher than those of LIBs and SIBs. Potassium, being a weaker Lewis acid and exhibiting higher ionic conductivity, facilitates reversible intercalation into graphite, unlike sodium, which forms irreversible intercalation [45]. Transition metal dichalcogenides such as MoS_2, SnS_2, and Sb_2S_3, with low energy barriers and high specific capacity, are considered prime candidates for PIB negative electrode materials. Their mechanisms involve either a simple intercalation or a combination of conversion/alloying, particularly for chalcogenides containing group 14 and 15 metals (Sb_2S_3, SnS_2, GeSe).

Magnesium-ion batteries have also attracted growing interest, mainly due to the intrinsic safety and abundance of magnesium. However, the divalent nature of Mg^{2+} ions presents challenges in terms of diffusion and reversibility. Innovative approaches include dual-electrolyte systems, combining co-intercalation of Mg^{2+} with monovalent cations (Li^+ or Na^+) to improve kinetics. TiS_2- and WS_2-based materials have shown promising potential as electrodes due to their ability to accommodate Mg^{2+} ions within their lattice [68,69].

In conclusion, transition metal chalcogenides represent a strategic family of materials for the development of "post-lithium" energy storage technologies. Current research focuses on optimizing their structural and electronic properties, particularly via nanostructuring and multi-metal approaches, to address challenges related to conductivity, cycling stability, and energy density. These advances highlight the potential of chalcogenides to play a key role in the energy transition and in the development of more sustainable, large-scale energy storage systems.

6. Conclusion

Research on chalcogenide materials has demonstrated their significant potential in the development of next-generation electrochemical energy storage systems, particularly as electrodes in rechargeable batteries. The history of these materials dates back to the early work on titanium disulfide (TiS_2), which was first used in 1970 and commercialized by Exxon in 1977 as an intercalation material for lithium batteries. This pioneering breakthrough paved the way for systematic exploration of chalcogenide materials across various configurations, ranging from liquid electrolyte systems to solid-state architectures. Titanium disulfide exemplifies the key role of layered materials capable of reversible intercalation of alkali ions, delivering a cell voltage of approximately 2 V in lithium-based systems.

Subsequently, research expanded to systems based on sulfur and its analogues, selenium and tellurium, which enable conversion reactions involving S_2, Li_2S, Se, or Te. These reactions provide high specific capacities, but their integration requires substantial optimization of electrode and electrolyte formulations. In the field of solid electrolytes, sulfides have become benchmark materials, with families such as $Li_{10}SnP_2S_{12}$ argyrodites, Li_3PS_4, and mixed phases $Li_4PS_4X_{1-y}X'_y$ (X = Cl, Br, I), while for sodium-ion batteries, Na_3PS_4 represents a promising option. These sulfide-based solid electrolytes are distinguished by high ionic conductivity and compatibility with chalcogenide electrodes, paving the way for the development of solid-state batteries (SSBs).

Metal-chalcogen compounds, including sulfides, selenides, and tellurides, are also proving to be relevant as positive electrode materials. Lithium-rich compositions such as $Li_{1.13}Ti_{0.57}Fe_{0.3}S_2$ (LTFS) illustrate the potential of high-energy-density sulfide positive electrodes. At the same time, the emergence of two-dimensional layered structures has reinforced interest in these materials, particularly for lithium alternatives such as sodium-ion, potassium-ion, and magnesium-ion systems, where chalcogenides provide stable and reversible reaction pathways.

Future perspectives in this field include optimizing synthesis routes and characterization techniques (XRD, Raman spectroscopy, SEM, as well as operando studies), improving solid-state battery assembly methods through cold or hot pressing (Spark Plasma Sintering—SPS—or Pulsed Electric Current Sintering—PECS), and developing prototypes incorporating multiscale models linking structure, kinetics, and performance. Significant efforts are still required in composite positive electrode formulation, the selection of conductive additives, negative electrode protection, and material recycling. The diversity of possible approaches, from liquid-electrolyte systems to lithium-metal- or composite-electrode-based solid-state architectures, highlights the considerable room for improvement. Optimizing chalcogenide materials, while considering environmental impact and recyclability, opens the path toward a new generation of energy storage systems that are more efficient, safer, and sustainable.

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Declaration of interests

The authors do not work for, advise, own shares in, or receive funds from any organization that could benefit from this article, and have declared no affiliations other than their research organizations.

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