Data-Driven Viewpoint for Developing Next-Generation Mg-Ion Solid-State Electrolytes

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VIEWPOINT

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Data-Driven Viewpoint for Developing Next-Generation Mg-Ion Solid-State Electrolytes

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Abstract

Magnesium (Mg) is a promising alternative to lithium (Li) as an anode material in solid-state batteries due to its abundance and high theoretical volumetric capacity. However, the sluggish Mg-ion conduction in the lattice of solid-state electrolytes (SSEs) is one of the key challenges that hamper the development of Mg-ion solid-state batteries. Though various Mg-ion SSEs have been reported in recent years, key insights are hard to be derived from a single literature report. Besides, the structure-performance relationships of Mg-ion SSEs need to be further unraveled to provide a more precise design guideline for SSEs. In this viewpoint article, we analyze the structural characteristics of the Mg-based SSEs with high ionic conductivity reported in the last four decades based upon data mining - we provide big-data-derived insights into the challenges and opportunities in developing next-generation Mg-ion SSEs.

Keywords: Data mining; Magnesium-ion solid-state electrolytes; All-solid-state batteries; Magnesium-ion conductivity

1. Introduction

Battery is a critical device in energy storage and conversion, which has been widely used in portable electronic devices, electric vehicles, and power grids [1,2]. All-solid-state batteries have attracted significant interest due to their higher safety and larger energy density than conventional liquid-state batteries. In recent decades, there has been substantial advancement in the field of all-solid-state Li-ion batteries (ASSLIBs). This progress is primarily attributed to the discovery of superionic conductivity in a variety of solid materials [3−5]. So far, an ionic conductivity with the order of magnitude of 10^{-2} S·cm^{-1} at room temperature has been achieved in solid-state electrolytes (SSEs), which can match that of liquid electrolytes [6−9]. However, the Li resources

within Earth's crust are limited, and the associated costs of extraction and processing are considerable [10−14]. Therefore, seeking a cheaper alternative is one possible solution. Compared to Li, Mg has a higher elemental abundance (the 8th most abundant element in the Earth's crust) [15], and is more environmentally friendly and safer (non-inflammability and non-corrosivity) [16,17]. In addition, Mg^{2+} ions can contribute nearly twice the theoretical volumetric capacity of Li-ion due to the double charge-per-ion (3832 mAh·cm^{-3} for Mg and 2062 mAh·cm^{-3} for Li). Therefore, Mg-based solid-state batteries may have a favorable potential in energy storage application.

Unfortunately, the development of all-solid-state Mg-ion batteries (ASSMIB) has been hampered by the low mobility of Mg^{2+} within the lattice of solid electrolytes, owing to the strong electrostatic

interactions between Mg^{2+} and anions [18−20]. The sluggish ionic migration would significantly decrease the overall performance of the rechargeable ASSMIB. The ionic conductivity is one of the key indicators for ionic diffusion in SSE, which can be described by Eq. (1) [21]:

$$\sigma = C_n Ze\mu = \frac{A}{T}C_n \exp\left(-\frac{E_a}{k_B T}\right) \qquad (1)$$

where σ is the ionic conductivity, A is the constant depending on the crystal structure, T is the temperature, C_n is the concentration of mobility-ion site (interstitials or vacancies) in materials, E_a is the activation energy, and k_B is the Boltzmann constant.

The first Mg^{2+} conducting solid (*i.e.*, the Mg-Zr-PO_4 system) was reported by Ikeda et al. in 1987. The composition $Mg_{0.5}Zr_2(PO_4)_3$ has an optimal ionic conductivity of 2.9×10^{-5} S·cm^{-1} at 400 °C [22,23]. Their results indicated that Mg-ion SSE has significant potential in solid-state batteries. Based on this pioneering work, more and more attention has been paid to exploring SSEs by optimizing experimental conditions and material structures in the past few decades. Kazakos-Kijowski et al. found that Mg^{2+} presented better ionic conductivity in the single-phase $Mg_{0.5}Zr_2(PO_4)_3$ synthesized by the sol-gel method [24]. The ionic conductivity of Mg^{2+} was further increased by Halim et al., by substituting Zr with Si in this structure [25]. Liang et al. obtained a composition of $Mg_{0.5}Ge_{0.2}Zr_{1.8}(PO_4)_3$ by liquid-feed flame spray pyrolysis, which had an ionic conductivity of 3×10^{-6} S·cm^{-1} at 280 °C [26]. Other types of materials were developed by using different counter-ions, such as $Mg(BH_4)_2$, $Mg_3(BH_4)_4(NH_2)_2$, $MgBH_4NH_2$, $MgSc_2Se_4$, and MgY_2Se_2 [27−31]. The ionic conductivity of Mg^{2+} in these SSEs was significantly improved. However, the low mobility of Mg^{2+} at room temperature continues to be a bottleneck that hampers the wide applications of Mg-ion batteries. It is necessary to explore novel electrolyte materials that further increase the ionic conductivity of Mg^{2+} in SSEs. Nevertheless, conventional trial-and-error-based experimental methods are costly and time-consuming to search for new materials in the complicated component and composition space.

Theoretical computations, such as density functional theory (DFT) calculations and molecular dynamics (MD) simulations, are splendid tools for investigating material properties due to the rapid development of computational science and supercomputer facilities to date, which can contribute to understanding the intricate characteristics and ion transport mechanisms from an atomic scale. Preliminary assessments of material properties can be made by computing simple physical quantities. For instance, electronic energy calculations can provide early insights into a material's relative stability, significantly reducing the cost associated with experiments. Specifically, advancements in computation technology have further facilitated the screening process. Revealing the relationship between structure and properties is meaningful to guide the optimization and design of SSEs. However, the substantial time investment remains a formidable challenge when dealing with extensive structures and conducting high-throughput searches. In recent years, machine learning (ML) modeling driven by a high volume of data has attracted attention due to its effectiveness in screening novel materials from complex high-dimensional data [32].

Motivated by the current stages, we recently developed a dynamic database of solid-state electrolytes (DDSE) by large-scale data mining and the subsequent data analysis [33,34]. As of April 2024, this database contains the ionic conductivity and material information of >1400 SSEs (including >10,000 performance data under different temperatures) reported during the past 40 years, with a variety of cations (*i.e.*, Li^+, Na^+, K^+, Ag^+, Ca^{2+}, Mg^{2+}, and Zn^{2+}). Relevant conductivity or diffusion kinetics information can be derived based on Eq. (1). According to the statistics from the DDSE, many divalent cation-conducting SSEs with high ionic conductivity have been reported recently, providing a distinct opportunity to derive new viewpoints that can drive the development of Mg-ion SSEs. Based upon a big-data-driven analysis, in this viewpoint, we discuss the challenges and opportunities of developing next-generation Mg-ion SSEs in terms of the materials' properties and operating mechanisms. We expect that these viewpoints can provide essential insights and design guidelines for developing next-generation divalent ion SSEs in batteries.

2. Discussion

2.1. Overview based on big data

Divalent ion SSEs have received wide attention due to their higher theoretical volumetric capacity than monovalent ion SSEs. However, the low ionic conductivity in divalent ion SSEs has hindered the development of solid-state batteries. Some divalent ions (*i.e.*, Ca^{2+}, Mg^{2+}, and Zn^{2+}) SSEs with high ionic conductivities have been found during the data mining for the DDSE database construction, as summarized in Fig. 1a. It can be clearly seen that during the past decades, Mg has attracted more attention than Zn and Ca as the SSE cation element, which was in part due to the larger gravimetric capacity and smaller volume of Mg^{2+}
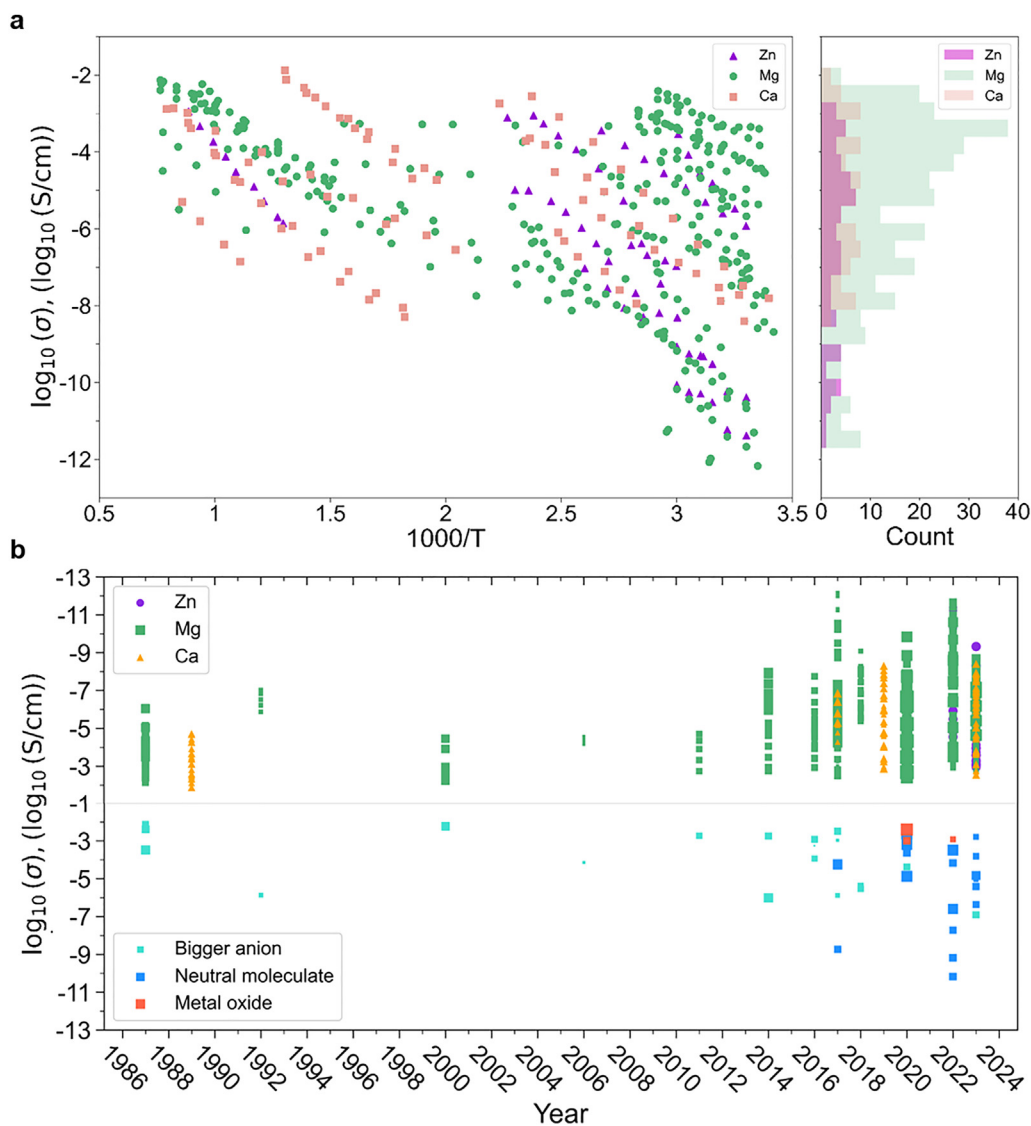
Fig. 1. Statistics of divalent-ion-conducting materials published during the past 40 years. (a) Distribution of divalent-ion-conducting SSEs as a function of temperature. The right frame shows the counts of SSEs in a diverse range of ionic conductivity. (b) Reports of Mg-, Zn-, and Ca-ion SSEs, where the diverse colors present different SSEs in the upper picture, and the lower picture shows the optimized strategies in Mg-based SSEs.

[35]. Therefore, the subsequent discussion will focus on Mg-based SSEs. To investigate the reason why some divalent SSEs have relatively higher ionic conductivities, the relationship between the structure and performance of SSEs can be analyzed in the DDSE [33,34]. Particularly, the processes of Mg^{2+} migration in SSEs were studied both experimentally and theoretically as reported in literature, providing understandings of how to improve the ionic conductivity. Interestingly, from big data, we can directly observe that SSEs with high ionic conductivity have one or more of the following characteristics (Fig. 1b), including i) having neutral molecules (*e.g.*, NH_3, H_2O, and NH_3BH_3) inside the SSE lattice, ii) having metal oxide in a mixture phase, and/or iii) having large-volume anions,

which account for around 46.9%, 4.0%, and 44.9% of the Mg-ion SSE publications, respectively.

To reveal the mechanism behind the enhancement of ionic conductivity, we first conducted an analysis of various Mg-based SSEs according to the DDSE database. It is noted that $Mg(BH_4)_2$ has a negligible Mg^{2+} mobility (~10^{-12} S·cm^{-1} at room temperature) [28]. In $Mg(BH_4)_2$, Mg^{2+} was confined in the tetrahedral center composed of four $[BH_4]^-$ anions (Fig. 2a), which could lead to slow Mg^{2+} migration due to the strong coulombic interactions [36]. Higashi et al. synthesized $Mg(BH_4)_2$ and achieved an ionic conductivity with the order of magnitudes of 10^{-9} S·cm^{-1} at 150 °C [29]. Pristine $Mg(BH_4)_2$ presents relatively limited ionic conductivity. However, they found that $Mg(BH_4)$

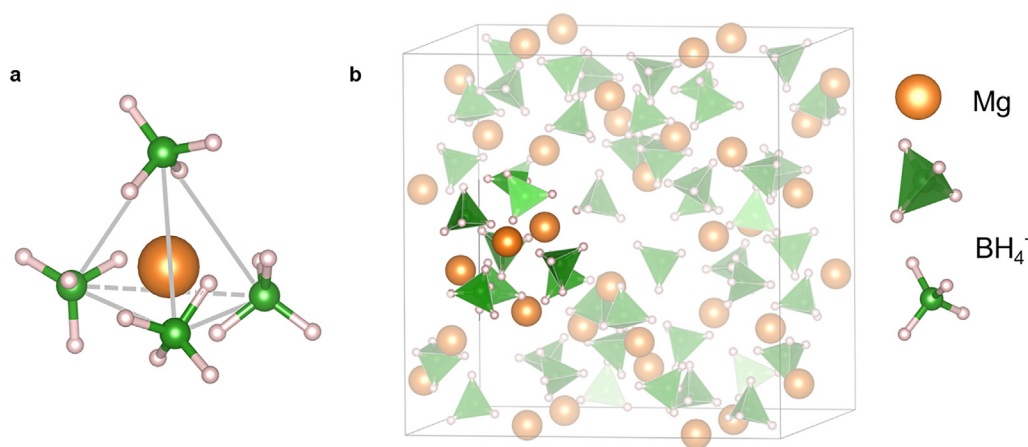*Fig. 2. The structure framework of Mg(BH₄)₂. (a) Coordination configuration of Mg²⁺ and four [BH₄]⁻. (b) Structure of a cubic Mg(BH₄)₂. Mg²⁺ is located at the center of a regular tetrahedron constructed by four [BH₄]⁻ anions.*

(NH$_2$) owns an ionic conductivity of 10^{-6} S·cm^{-1} at 150 °C by replacing the [BH$_4$]$^-$ in Mg(BH$_4$)$_2$ with NH$_2^-$ [29]. Ruyet et al. manifested that ionic conductivity of Mg(BH$_4$) (NH$_2$) can be significantly increased to 3 × 10^{-6} S·cm^{-1} at 100 °C by optimizing the synthetic conditions (*i.e.*, with ball milling and heat treatment) [37]. In addition, numerous Mg(BH$_4$)$_2$ derived materials with promising ionic conductivity were found, suggesting that Mg(BH$_4$)$_2$ could be a class of potentially promising SSEs. Matsuo et al. investigated the ionic conductivity of Mg^{2+} in high-temperature phase of Mg(BH$_4$)$_2$ using first principles MD simulations [38]. It was suggested that the mobility of Mg^{2+} could be improved by replacing [BH$_4$]$^-$ with a bigger size [AlH$_4$]$^-$. Ikeshoji et al. found that no Mg movement was observed by substituting [BH$_4$]$^-$ with Cl$^-$ and I$^-$, but Mg^{2+} would move outside the cage by introducing 20% larger-volume [AlH$_4$]$^-$ [39]. All these results provide clear evidence that improving the ionic conductivity of Mg(BH$_4$)$_2$ is achievable by employing targeted synthetic conditions or replacing [BH$_4$]$^-$ with other anions.

2.2. Strategy one to improve ionic conductivity: adding neutral molecules

Based on the Mg(BH$_4$)$_2$ structure, plenty of materials were designed to accelerate ionic migration by various strategies, such as adding neutral molecules (*e.g.*, NH$_3$, NH$_2$CH$_2$CH$_2$NH$_2$, CH$_3$NH$_2$, and NH$_3$BH$_3$) to the system [28,40−42]. The ionic conductivities of Mg^{2+} in Mg(NH$_2$CH$_2$CH$_2$NH$_2$) (BH$_4$)$_2$ and Mg(NH$_3$BH$_3$)$_2$(BH$_4$)$_2$ were reported to be 6.1 × 10^{-5} and 1.3 × 10^{-5} S·cm^{-1} at 70 and 30 °C, respectively [28]. The Mg-ion conductivity in Mg(BH$_4$)$_2$·2NH$_3$ was increased to 5 × 10^{-4} S·cm^{-1} at 75 °C [41,] which is dramatically improved compared to the performance of an original Mg(BH$_4$)$_2$ [28]. Amdisen et al. synthesized various methylamine magnesium borohydride compounds (β-Mg(BH$_4$)$_2$·CH$_3$NH$_2$), which achieved an ionic conductivity of 1.5 × 10^{-4} S·cm^{-1} at room temperature [40]. Experiments and theoretical calculations both revealed the mechanism that neutral molecules can enhance the ionic conductivity of Mg^{2+} in SSEs. The neutral molecules coordinating with Mg^{2+} can induce the asymmetrical distribution of cation charge, consequently weakening the Mg-coordination shell and leading to the fast mobility of Mg^{2+} [23,28,43]. Meanwhile, exchange of neutral molecules among lattice and interstitial Mg ions could accelerate Mg^{2+} migration in solid materials [44]. In addition, the neutral molecules could lead to an expanded structure framework in the system to promote Mg^{2+} migration [41,44]. It is noted that formation and migration of Mg vacancy could be a vital factor in affecting Mg^{2+} migration [41,45]. According to the above discussion, the performance of Mg(BH$_4$)$_2$ can be effectively optimized by adding neutral molecules. However, the Mg(BH$_4$)$_2$ derivatives developed by adding neutral molecules generally possess the electrochemical stability window <1.5 V, which could lead to low oxidative stability [28,41,42,46,47].

2.3. Strategy two to improve ionic conductivity: mixing with metal oxide

Plenty of experiments indicated that the number of neutral molecules will significantly affect the ionic conductivity of materials [48]. However, the stability of SSEs with a different ratio of neutral molecules remains a challenge. Yan et al. reported that Mg(BH$_4$)$_2$·1.6NH$_3$ stabilized by adding MgO nanoparticles exhibit excellent Mg^{2+} conductivity of the order of magnitude 10^{-5} S·cm^{-1} at room

temperature and 10^{-3} S·cm^{-1} at around 70 °C [49]. Additionally, they found that adding 67wt% Al$_2$O$_3$ to Mg(BH$_4$)$_2$·1.6NH$_3$ can significantly promote the Mg^{2+} mobility to 2.5×10^{-5} S·cm^{-1} at 22 °C, which could account for the favorable interface between MgO and amorphous state Mg(BH$_4$)$_2$·1.6NH$_3$ [50]. Oxygen vacancies in metal oxides can promote cation conduction in SSEs [51−54]. Wang et al. demonstrated that Mg^{2+} migration in a Mg(BH$_4$)$_2$·1.5NH$_3$ system can be substantially improved by adding 60wt% TiO$_2$, resulting in a conductivity of 2.96×10^{-4} S·cm^{-1} at room temperature. Their theoretical calculations revealed that the high ionic conductivity can be attributed to the "coordination-unlock" phenomenon [20], *i.e.*, Mg(BH$_4$)$_2$·1.5NH$_3$ can be broken and [BH$_4$]$^-$ can be captured by the oxygen vacancies on the surface of metal oxide. Subsequently, Mg^{2+} in the segment can migrate into the oxygen vacancy sites. However, their results indicated that this approach does not considerably affect Mg^{2+} migration in the compounds of Mg(BH$_4$)$_2$ and Mg(BH$_4$)$_2$·6NH$_3$ due to the strong Mg-coordination shells. Mixing with metal oxide could be an effective strategy to improve the stability of SSEs and increase Mg^{2+} ionic conductivity. Unfortunately, there is no apparent change in the electrochemical stability window (<1.5 V) by adding metal oxide into Mg(BH$_4$)$_2$ derivatives. Therefore, the utilization of new anions is essential for improving the performance of SSEs.

2.4. Strategy three to improve ionic conductivity: using large-volume anions

Ceder and co-workers reported a spinel structure (MgSc$_2$Se$_4$) with a high ionic conductivity of 10^{-4} S·cm^{-1} at room temperature. As illustrated in Fig. 3, one Mg^{2+} is arranged within a tetrahedron structure composed of four Se^{2-}, which can be transfered between two adjacent tetrahedrons (tet) through an octahedron (oct) (*i.e.*, a "tet-oct-tet" pathway). They suggested that the migration barriers of Mg^{2+} would be decreased by using a large volume anion, which could offer a larger triangular face for Mg^{2+} migration [30]. However, MgSc$_2$Se$_4$ exhibits a high electron conductivity due to the intrinsic defects or secondary non-Mg-containing phases, which makes it less desirable for battery applications. Fichtner et al. attempted to decrease the electron conductivity by synthesizing the MgSc$_2$Se$_4$ phase with excess Se, and by doping Ti^{4+} and Ce^{4+} into the materials [55]. Nevertheless, neither approach can effectively achieve the target.

Besides, the DDSE database found that a class of SSEs used *closo*-boranes or carboranes (*e.g.*, [B$_{12}$H$_{12}$]$^{2-}$, [CB$_{11}$H$_{12}$]$^-$, [B$_{10}$H$_{10}$]$^{2-}$ and [CB$_9$H$_{10}$]$^-$, as illustrated in Fig. 4) as the anions, which can exhibit high ionic conductivities (even at room temperature) and wide electrochemical stability windows [56,57]. These *closo*-type (or cage-like) anions generally have large volumes that can lead to a wide cation diffusion channel for Mg^{2+} migration. Moreover, the *closo*-structures with electronic deficiency can reduce the electrostatic interaction between the cation and anions [30,47,58], which may further decrease the migration barrier because electrons can be delocalized to the whole anion to disperse charge density. Using *closo*-boranes and carboranes can produce new SSEs by substituting hydrogen atoms or mixing various *closo*-materials, which can be an effective strategy to generate large-volume species [59−61]. Noted that in some studies, the hydrogen atoms were replaced by halogen (*i.e.*, Cl, Br, and I), which would decrease the ionic conductivity due to the stronger directional bonding and larger anion mass than hydrogen [62]. However, these
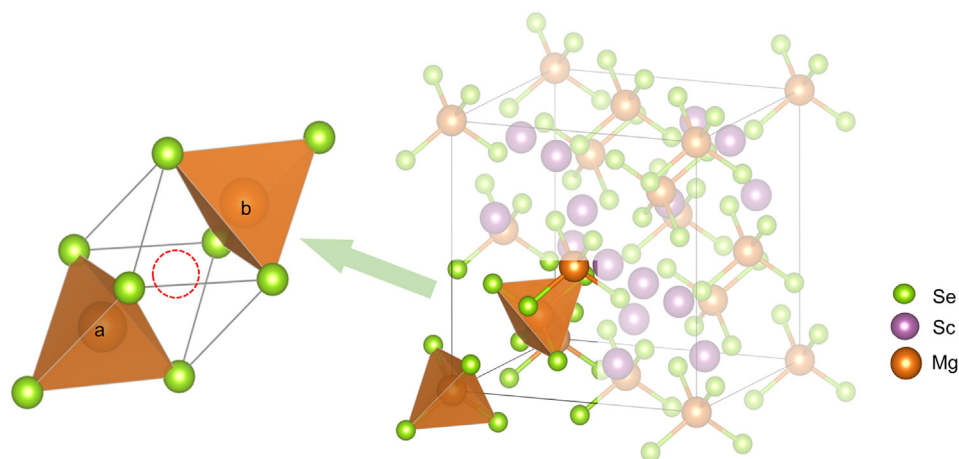

*Fig. 3. Illustration of Mg^{2+} migration in ternary spinel MgSc$_2$Se$_4$. Mg^{2+} will overcome an energy barrier to migrate from **a** to **b** (i.e., the "tet-oct-tet" pathway). A larger atomic volume is expected to result in a larger triangle plane for a more facile ionic migration.*
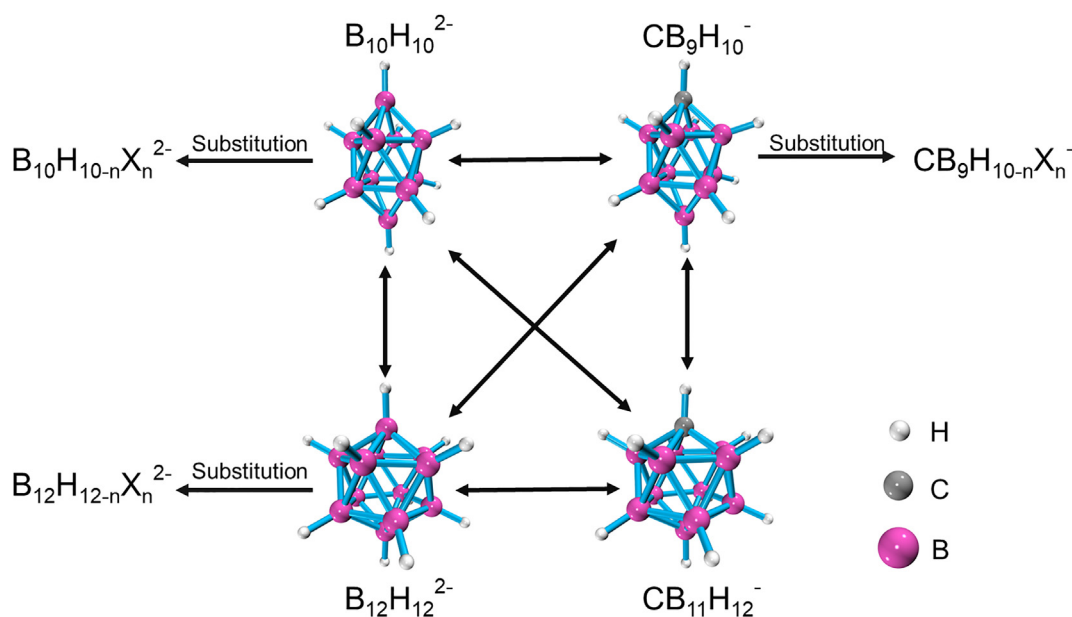
Fig. 4. *Different anion structures of closo-type materials and halogen analogs. X represents different halogen atoms (F, Cl, Br, and I) [58]. Note that halogens' atomic volumes are larger than the hydrogen atom, and electrostatic potential distribution is more heterogeneous, which could lead to a higher cation ion migration barrier [60].*

halogen analogs have higher thermal stability and phase transition temperature than the corresponding parent compounds [60], endowing an optimized approach for the thermal stability of *closo*-materials. Neutral molecules can further optimize the Mg^{2+} conductivity in the *closo*-type SSEs and could be attributed to the paddle wheel effect [47,63,64]. The mobility of Mg^{2+} within *closo*-boranes and carboranes is intricate and variable. Shen et al. summarized the ionic migration mechanisms in different *closo*-boranes and carboranes SSEs [58]. Orimo and colleagues reported that the rotation of anions can facilitate the fast diffusion of Mg-ions in *closo*-type materials [47]. The *closo*-boranes and carboranes combined with other divalent conducting cations, such as Ca- and Zn-ions, have been reported in recent years and shown dramatic performance [47,64,65]. Additionally, *closo*-type materials have high oxidation potential in wide temperatures and low density [58,66], making them promising as divalent-ion SSEs.

2.5. What we really need is an integrated workflow for comprehensive analysis

Based on the current stages of development, it is crucial to understand the internal mechanism of ionic mobility for optimizing and designing high-performance SSEs. What we really need is an integrated workflow for analysis, by combining the strengths and eliminating the weaknesses of current available techniques.

2.5.1. Pros and cons of current available techniques

Experiments and theoretical calculations are crucial to identify potential SSEs with high ionic conductivity from a complex materials space. Compared with conventional trial-and-error experiments, theoretical calculations (*e.g.*, *ab initio* calculations, which are primarily based on DFT and empirical force fields) can provide new insights to explore high-performance SSEs with lower cost and less time consumption. We can identify stable and promising materials for a specific class of materials, which can be used for further analysis to obtain high-performance materials. However, the high-throughput screening and nanoseconds timescales' dynamical simulation still require tremendous computational resources and time. In addition, there remain challenges in using theoretical computations to simulate a synthetic process (*e.g.*, the ball milling and molding, which could be crucial factors for improving the performance of SSEs).

Alternatively, machine learning (ML) is a promising method to screen and predict novel materials based on datasets, which has been used to successfully obtain high-performance SSEs in monovalent materials [67—70]. It is known that features and the quality of dataset play a crucial role in ML-based modeling and prediction. However, plenty of common inorganic compound databases (*e.g.*, the Materials Project and Inorganic Crystal Structure Database) lack properties to describe SSEs' performance, which would restrict the accuracy of a ML model. Based on the >1000 SSE materials in

the DDSE database (with >8000 performance data under various temperatures), we attempted to employ >50 chemical composition features (with diverse regression algorithms) to describe the experimentally acquired activation energies of divalent ion SSEs. However, the attainment of a precise ML model for SSEs still remains as a big challenge with a relatively poor extrapolation capacity [33], which is in part due to the limited number of reported SSE materials and meanwhile, most of the reports to date mainly published their materials with the highest performance and discarded the details of low-performance SSEs. Therefore, data scarcity remains a tremendous challenge in ML-related applications.

In the DDSE database, divalent ion SSEs with high ionic conductivity have attracted our attention, and they can be classified into different anion species. Interestingly, the movement of divalent cations is sluggish in some of the original SSE structures, but the ion migration would be improved by adding neutral molecules or metal oxides into the material lattice. Ionic mobility is crucial in evaluating the ion-conducting performance of materials, in which experiment techniques and theoretical calculations play a pivotal role in understanding the ion migration mechanism in various SSEs. High-resolution experimental methods (*e.g.*, quasielastic neutron scattering (QNES) and solid-state nuclear magnetic resonance (ssNMR)) could provide a straightforward certification for an unknown phenomenon. And theoretical calculations can determine the material properties at an atomic level. Various theoretical methods would help provide insights into the mechanism of ionic mobility in SSEs. For example, the climbing-image nudged elastic band (CI-NEB) is a powerful approach to search cation migration pathway and activation energy in SSEs based on transition state theory (TST) [71,72]. In addition, molecular dynamics (MD) has been widely applied to study the ionic diffusion and conductivity in SSEs. Additionally, Chen et al. developed the bond-valence-site-energy (BVSE) method to obtain the conduction pathway and estimate the approximate energy barrier [73]. These characteristics are helpful for understanding the microstructure and designing novel high ionic conductivity SSEs. However, many key challenges remain. For example, when using CI-NEB for cation migration analysis, it can only locate one transition state (TS) at a time based on one pair of selected initial and final state structures, while MD sometimes fails to do a broad sampling on an energy landscape with high activation energy (in particular, divalent ion

SSEs). To address these challenges, Campos dos Santos et al. recently developed a new framework combining genetic algorithm (GA) and meta-dynamics (MetaD) simulations [74] to investigate cation migration in complex SSEs. Through this method, the most stable structure can be identified from numerous potential compounds without depending on prior experimental information, and the theoretically acquired activation energies can be close to the experimental observations in divalent-ion-conducting SSEs. Notably, GA can search stable structures by global optimization, providing structural information without depending on experimental data. MetaD could be a more effective tool to sample the free energy surface of ionic migration and identify the activation energies when the ionic diffusion is too sluggish to be analyzed by conventional MD methods.

2.5.2. Combining the advantages of each technique via an integrated workflow

Each method itself has both pros and cons - it would be essential to develop an integrated analytical framework to combine the strengths and eliminate the shortcomings of each strategy. Herein, as summarized in Fig. 5, we propose a
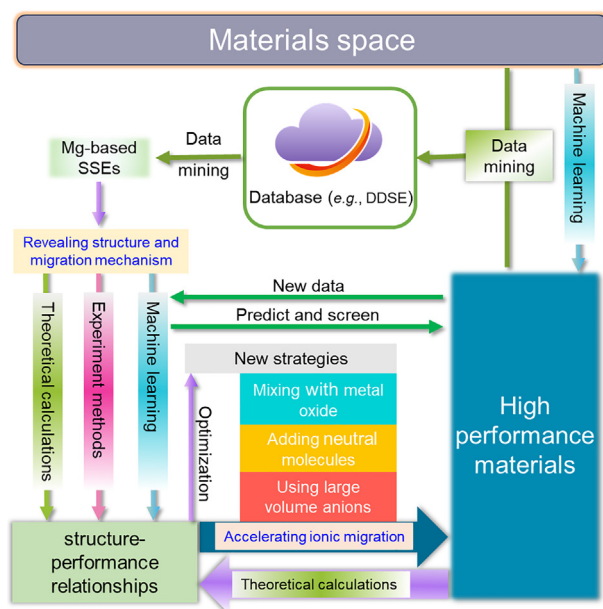
Fig. 5. A proposed scheme for obtaining high-performance SSEs from a complex material space of divalent ion SSEs. Data mining will play a key role in capturing promising divalent ion SSE materials as the basis, and an integrated strategy across subsequent data mining, theoretical calculations and modeling, and experiments will be used to reveal the ionic migration mechanism and structure-performance relationships of the potential SSEs. Finally, the ionic migration of these SSEs will be accelerated by considering various optimization strategies.

workflow to comprehensively analyze SSEs and make precise designs. First, data mining is a key strategy to analyze the SSE materials reported to date to acquire a comprehensive understanding on the features of high-performance SSEs, *e.g.*, the types of materials that possess high performance and their corresponding characteristics. Next, to understand the structure-performance relationships of high-performance SSEs, further data mining (on mechanistic research), theoretical calculations and modeling (including simulations and ML), and experiments are essential to elucidate the ionic migration mechanisms. Once the structure-performance relationships are established, modification strategies can be applied to further accelerate the ionic migration of the SSEs. Strategies from Sections 2.2−2.4 are the key guidelines to improve ionic conductivity. If we can develop new materials, theoretical calculations can further assist in understanding the complex migration mechanism, resulting in obtaining novel approaches or optimizing current strategies. These new experimental data and new insights from theoretical simulations can help further improve the accuracy of ML modeling.

3. Summary and prospects

In this viewpoint, we have summarized the structural characteristics of diverse Mg-ion SSEs with measurable ionic conductivity drawing from big-data analysis, and the advantages and challenges of Mg-ion SSEs have been analyzed. In the following parts, we highlight the key opportunities and challenges in developing next-generation Mg-ion SSEs.

3.1. Opportunities

3.1.1. New technique brings new hopes

Advanced experimental techniques can help provide new insights into better understanding of SSEs. ssNMR, QNES, and synchrotron powder X-ray diffraction (PXRD) techniques can reveal the complex mobility of ions, including their relaxation time [75−78], which could provide a more insightful understanding of ionic motion mechanisms and structural information. In addition, theoretical calculations can determine the structure-performance relationship of materials at an atomic level. The structural information and electronic distribution can evaluate the material stability and ion transport dynamics in the SSEs, which can hold a significant advantage in revealing material characteristics. Meanwhile, multiscale simulations can provide powerful support for

understanding the whole mass transfer processes (*e.g.*, the complex electrode/electrolyte interface) and internal mechanisms.

It is noted that ML techniques have been widely applied in screening and predicting novel monovalent ion SSEs, which could rapidly identify potential candidates from a complex material space. Feature explanation tools have been developed in recent decades [79−81], making ML no longer a "black box". These tools facilitate the interpretation of connections among features, offering a wealth of descriptors to reveal the structure-performance relationships of materials. More importantly, the combination of ML techniques, and theoretical computations and experiments could generate novel perspectives and solutions to research new SSE materials [82,83]. The results of ML and theoretical calculations can reduce experimental cost and improve material discovery efficiency [84]. Min and colleagues employed ML to screen potential Garnet-type SSEs with high ionic conductivity at room temperature [67]. Meanwhile, the experimental data could serve back to ML to provide new features and/or new training samples, and then optimize the generalization capacity of the ML model. Sendek et al. presented a classification model for screening promising SSEs by training a dataset of 40 crystal structures [85]. These innovative approaches could accelerate the search for high ionic conductivity SSEs and offer solutions in the future.

3.1.2. Some Mg-based SSEs applied at room temperature are promising

Further efforts have been made to optimize the material preparations (*e.g.*, ball milling and heat treatment) [37,86] and synthetic strategies (*e.g.*, adding neutral molecules or metal oxide) [40,49,64]. Various Mg-ion SSEs with their ionic conductivities reaching 10^{-4} S·cm^{-1} at room temperature were reported in recent years, which gradually narrows the performance gap between the Mg-ion and monovalent ion SSEs (and also, the traditional liquid electrolytes). Currently, various inorganic materials databases (*e.g.*, Materials Project and Inorganic Crystal Structure Database) include plentiful Mg-based compounds, which could provide potential high-performance materials. In addition, the different ionic migration mechanisms have been illustrated, and mature strategies of monovalent ion SSEs can provide lessons to optimize Mg-ion SSEs. These studies will contribute to understanding the microstructures and transport mechanisms of divalent ion-conducting materials, and pave the way for screening materials from a complex materials space.

3.2. Challenges

3.2.1. Limited data of Mg-ion SSEs

The number of reported Mg-ion SSEs is limited compared to monovalent ion SSEs (*i.e.,* Na- or Li-ion SSEs). In the most up-to-date version of the DDSE, we have compiled data related to Mg-ion SSEs reported over the past 40 years. However, the number of reported Mg-ion materials was found to be far less than monovalent ion materials, and only ~52 species (mainly focusing on oxide and hydroboron) were found so far (as of April 2024). The limited number of data would easily lead to overfitting and poor extrapolation in predictions using ML. In addition, the absence of experimental data describing battery properties hinders the exploration of novel high-performance materials. It indicates that a comprehensive database describing SSEs' features and timely data sharing is necessary.

3.2.2. Time consumption in material screening and simulations

DFT calculations can help understand material properties and mechanisms at the atomic scale, while MD simulations can provide atomic trajectory data, which is meaningful in exploring dynamic processes. They play a crucial role in understanding the ion migration mechanisms and screening high-performance materials. However, the significant time consumption remains a criticism in complex systems, significantly limiting the screening efficiency of high-performance Mg-ion SSEs from the material space. ML-accelerated theoretical calculations (*e.g.,* ML force field by fitting the potential energy surface) can be an effective approach, which can achieve similar accuracy with less time consumption to the first principle calculations. In addition, the computational results can provide ample data to train the ML model. Meanwhile, different ensemble algorithms should be developed to optimize the ML model. The ML-accelerated methods could tackle more challenges and problems in ASSBs, such as electrode/electrolyte interface, chemical compatibility, and mechanical property, which could help better understand the whole electrochemical process of SSE.

3.3. Summary

In summary, this viewpoint has summarized the optimization strategies for developing high-performance Mg-ion SSEs, including i) adding neutral molecules inside the SSE materials; ii) having metallic oxide as the mixture, and iii) adding large-volume anions inside the SSE lattice. Data mining shows significant advantages in SEE search

and understanding, which can achieve more comprehensive information by analyzing the big picture of SSEs, compared to the limited insights from a single literature report. Some Mg-ion SSEs with high ionic conductivities are available in the literature, which certificates the feasibility of divalent cations migration under room-temperature operating conditions. However, exploring new high-performance Mg-ion SSEs poses a challenge for data-driven ML due to the limited number of currently reported data. Combining theoretical calculations with ML could be a prominent approach to overcome this predicament. Theoretical calculations can introduce new features and structural properties into ML to enhance the model precision. Meanwhile, ML can rapidly screen potential candidates from a complicated material space, and followed by theoretical calculations to unveil the internal mechanisms governing the ionic conduction of SSEs. Upon the current stage, we propose a framework to comprehensively analyze the structure-performance relationship of Mg-ion SSEs (Fig. 5), which could accelerate the search for next-generation Mg-ion SSEs and offer innovative solutions in the future. All in all, though developing Mg-ion SSEs for next-generation batteries has remained a challenging topic, we are optimistic that many key bottlenecks will be solved by embracing new analytical technologies such as data science.

Acknowledgements

Conflict of interest

The authors decline no competing interest.

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数据驱动发展下一代镁离子固态电解质

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摘要

　　镁（Mg）在地壳中的储量丰富且理论体积容量高，这使得其在储能领域备受关注，特别是在固态电池中，它极具发展潜力，可作为锂（Li）的替代品。然而，镁离子在固态电解质（SSE）中传导缓慢，这是阻碍镁离子固态电池发展的关键挑战之一。近年来，各种传导镁离子的 SSE 被广泛报道，但很难从单一的文献报告中得出关键的信息。此外，进一步阐明镁离子 SSE 的结构与性能关系是有必要的，这将为 SSE 提供更精确的设计指南。在这篇文章中，我们基于数据挖掘分析了过去四十年报道的具有高离子电导率的镁基 SSE 的结构特征，总结了三个优化镁离子固态电解质的策略。基于实验和理论计算技术的发展，讨论了现阶段开发镁固态电解质的机遇和挑战，论述了实验、理论计算和机器学习在开发新型高性能镁离子 SSE 过程中的协作过程。我们为优化和开发下一代镁离子固态电解质提供了大数据见解。

关键字：数据挖掘；镁离子固态电解质；全固态电池；镁离子传导