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REVIEW PAPER

Ionic diffusion in post-lithium batteries

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Abstract
Although lithium-ion batteries are the mainstream choice for batteries, they raise sustainability, safety, and economic concerns that need to be addressed. Lithium resources might be inadequate for the ever-increasing demand, so alternative, relatively abundant and sustainable materials for battery applications are sought. Alternative ionic species, such as sodium-ion, magnesium-ion, and calcium-ion oxides are being explored as next-generation electrode and electrolyte materials beyond lithium-ion technology. Sodium, magnesium, and calcium are far more abundant than lithium, they are cheaper and more sustainable. However, the replacement of lithium with these larger cations does not come without challenges. A major limitation that must be overcome is that they exhibit reduced diffusion kinetics in comparison to lithium. This is of critical importance for the cathode and electrolyte and, hence, the overall performance of the battery. To facilitate faster diffusion coefficients for these larger cations, it is important to accommodate them in appropriate crystal lattices. Furthermore, kinetics can be accelerated using defect engineering strategies. Atomistic simulation is an efficient way to accelerate progress in the quest for efficient post-lithium battery materials. In this review, we discuss recent advances, including the deployment of artificial intelligence (AI) techniques, in the investigation of sodium-ion, magnesium-ion, and calcium-ion oxides for energy storage applications.

Keywords Batteries · Diffusion · Defect engineering · Doping · Sodium · Magnesium · Calcium

Introduction

The intermittency of electricity generation from renewable energy sources has necessitated the development of energy storage technology so that electricity can be delivered on demand and reach remote rural areas that may be off-grid or have unreliable access to the power grid. The urgency for the advancement of frontier technologies in energy storage is further emphasized by the profound shift in operating norms driven by the rapid adoption of electric vehicles [1–25].

The energy market has been dominated by lithium storage technology, powering a huge array of devices with their high energy density and efficiency. Lithium compounds such as lithium carbonate (Li_2CO_3), lithium oxide (Li_2O), and lithium hydroxide (LiOH) offer favorable electrochemical fundamentals and cost-effective manufacturing options for the fabrication of rechargeable batteries, which utilize approximately three-quarters of the present global production of lithium. Despite its noticeably clear advantages in electrochemical energy storage and its dominant position in the energy market, lithium technology raises significant concerns for long-term sustainability. Lithium is a finite resource with geographically constrained reserves, and the increasing global demand is projected to surpass supply in coming decades, potentially driving up costs and creating supply chain vulnerabilities. Additionally, current production of lithium-ion batteries depends on critical materials, such as cobalt and nickel, which pose significant environmental and ethical issues due to mining practices and geopolitical limitations. These factors highlight the need to explore alternative battery

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chemistries that are more sustainable, cost-effective, and abundant.

In the quest for high-performance energy storage, some researchers have explored novel materials involving exotic crystallographic structures that pose a significant obstacle to large-scale factory production and, consequently, widespread adoption in daily life. There are materials that offer remarkable theoretical energy densities and unique electrochemical properties, which have attracted the attention of the research community, but some of them involve rare, costly, or environmentally challenging to extract and refine elements [26–49]. This makes the case for considering more abundant, environmentally benign, and cost-effective elements such as sodium (Na), magnesium (Mg), and calcium (Ca) even stronger. These materials not only align with the principles of sustainable development but also promise to enable battery technologies that can be manufactured at scale, without exacerbating resource scarcity or geopolitical tensions.

Sodium, a chemical sibling of lithium, is the sixth most abundant element in the Earth's crust and is widely distributed in seawater and minerals, ensuring a virtually unlimited and cost-effective supply [42]. Its abundance and accessibility render it an attractive alternative, particularly for applications where the higher energy density of lithium-ion batteries is not a strict requirement, such as stationary energy storage for renewable grids. Na is very similar to lithium and, as such, sodium-based batteries benefit from shared manufacturing methodologies and knowledge with lithium technology, facilitating (in theory) an easy and smooth transition [42]. The biggest drawback of sodium batteries that hampers their widespread adoption is the larger size of the sodium ion which causes slow insertion/extraction kinetics and low theoretical capacity for many Na-ion battery materials. The focus of study for many researchers is the assessment of crystal structures that can provide the necessary kinetics that will compensate for the larger size of Na.

Magnesium-based batteries are another type of storage technology that is currently being considered as a replacement for lithium ones. These batteries are attracting much of the scientific community's attention due to their high gravimetric and volumetric capacity, non-toxicity, higher melting point, and large and widely distributed reserves across the world [43, 44]. Additionally, magnesium metal is more stable in air and safer to handle, reducing concerns related to dendrite formation and flammability, which plague other battery materials. But the most noteworthy attribute is the fact that Mg ions are of comparable size to Li ions, thus Mg batteries can have, theoretically, the same, good, kinetics as Li batteries. Despite this advantage, the stronger ionic interaction of Mg ions in the lattice renders intercalation harder [43, 44], so it is imperative that the research focus on the reduction of the size of the cathode ions and the shielding increase of Mg^{+2} [32, 33].

Potentially, calcium is, also, an attractive alternative to lithium. As is the case with the aforementioned materials, calcium is very abundant on the Earth's crust, even more so than sodium and magnesium; hence, batteries made of calcium metal (or, generally, calcium-based batteries) can be easier and cheaper to produce and to supply the market. Its divalent nature allows calcium ions (Ca^{2+}) to carry more charge and thus achieve better energy densities compared to monovalent ions like Li^{+} or Na^{+}, potentially leading to higher energy densities [50–53]. Additionally, Ca can potentially exhibit better reaction kinetics than Mg (which is the other divalent ion discussed), due to its lower polarizing character. Nonetheless, the practical realization of calcium battery technology faces considerable obstacles, primarily the lack of compatible electrolytes and cathode materials capable of accommodating the larger ionic radius and higher charge density of Ca^{2+} ions. Despite these technical challenges, the potential for calcium batteries to deliver scalable, sustainable, and environmentally friendly energy storage solutions underscores their importance in ongoing research efforts.

In this review, we explore research on post-lithium battery technologies, focusing on sodium-ion, magnesium-ion, and calcium-ion batteries. We discuss recent advancements in electrode materials, ranging from polyanion-type to oxide-type materials, focusing mostly on the former. We also discuss the fundamental challenges each system faces and strategies that are being developed to overcome these hurdles. Specifically, each technology is studied for its potentially favorable ionic diffusion properties, while we consider ways to tune them if necessary. Lastly, the paper considers the future development for these technologies and emphasizes the need for continued interdisciplinary efforts to realize their commercial viability.

Materials and methods

Molecular dynamics and density functional theory

Many researchers have conducted work on inorganic materials with the use of DFT (density functional theory) and MD (molecular dynamics). In this short section, we will briefly summarize key aspects of these methods that were useful in acquiring accurate results on the kinetics, but for more detailed descriptions, we refer to more comprehensive reviews [54, 55].

Quantum mechanics offer the most comprehensive framework for describing nature. The Schrödinger equation is the basis for describing every microscopic system that exists and thus finding its solution(s) is particularly important. However, solving the equation analytically for systems with

many electrons is computationally challenging due to the intricate interactions among electrons [56]. To address this complexity, the density functional theory (DFT) approach was introduced [57, 58]. In DFT, the exchange–correlation energy of electrons is approximated using methods such as the local density approximation (LDA), the generalized gradient approximation (GGA), or more sophisticated hybrid functionals that incorporate a fraction of exact exchange from Hartree–Fock theory. A key feature of DFT is the use of a plane-wave basis set and the pseudopotential method, which simplifies calculations by modeling core electrons with effective potentials, while treating valence electrons explicitly. DFT is commonly applied to predict activation energies for ionic diffusion by determining the minimum energy path, often using techniques like the nudged elastic band method [59]. Despite its ability to render complex problems computationally manageable, DFT simulations are typically limited to hundreds of atoms, restricting their application to larger-scale phenomena such as microstructures or extended defects.

Classical potential-based molecular dynamics is a popular approach for studying atomic diffusion in oxides, as well as extended defects such as grain boundaries and their effect on the kinetics and energy of the crystal. Classical MD represents the system by the positions and momenta of all particles, which are the most important type of information required by Newton's equations of motion, which are solved iteratively, in order to simulate the system's temporal evolution. Particle interactions are governed by potential energy functions, and for ionic systems specifically, these interactions typically follow the classical Born-like framework [60] and are often modeled using a combination of a long-range Coulombic term and a short-range parameterized pair potential [61–63]. The computational efficiency of MD enables the simulation of very large systems, encompassing millions of ions. However, this method does not account for the electronic structure of the system. Despite this limitation, classical MD remains a powerful tool for investigating diffusion and defect chemistry in ionic materials.

Post-lithium materials

Sodium-ion batteries

Sodium-based energy storage technology is emerging as a promising contender to lithium batteries. There is quite a broad selection of materials that have been considered recently by researchers as suitable for energy storage applications. The list of the most prominent materials includes $NaZr_2(PO_4)_3$, $Na_3V(PO_4)_3$, $Na_2Ti_3O_7$, $Na_3Fe_2(PO_4)_3$, $Na_2FeP_2O_7$, and $Na_2MnP_2O_7$. The diffusion of sodium atoms is crucial for the adaptation of sodium batteries, because it impacts the charge/discharge rates and energy density of the cells, and this is the reason why we are dedicating this section to it. Table 1 reports the activation energies of diffusion of Na atoms with the purpose of providing a clear comparison between the most prominent materials.

$NaZr_2(PO_4)_3$, also known as NZP, is a NASICON type material which showed a very low activation energy of diffusion ranging from 0.2 to 0.3 eV, with the research team of Zou et al. [19] presenting an energy of 0.23 eV and Chronaios et al. [46] an energy of 0.26 eV. Both research papers analyze the characteristic rhombohedral structure of the crystal, composed of corner-sharing ZrO_6 octahedra and PO_4 tetrahedra, which creates a three-dimensional framework with channels for a significant Na^+ ion concentration and a long-range migration profile. It is interesting to note that in the same paper [46], the researchers examined the efficacy of Na atom encapsulation with DFT and concluded that this exoergic incorporation of sodium results in the rise of electron density as the concentration of Na increases. Figure 1 illustrates the long-range Na-ion diffusion in $NaZr_2(PO_4)_3$.

$Na_2Ti_3O_7$ belongs to the $P2_1/m$ space group [67, 68] and there are three different pathways that sodium ions can follow as calculated by Irranious et al. [65]. The monoclinic unit cell of $Na_2Ti_3O_7$ has four Na atoms that are characterized by the same Wyckoff position of "2e," with each pair occupying two different crystallographic sites that hold the $(Ti_3O_7)^{2-}$ layers together [67, 68]. Regarding the activation energies of the three diffusion cases, undoped $Na_2Ti_3O_7$, due to the bulk structure that was described above, demonstrated very promising values: 0.23 eV, 0.38 eV, and 0.76 eV, with $E_a = 0.23$ eV being the lowest energy barrier of a long-range zig-zag pathway along the *ab*-plane consisting of 3.18 Å Na-Na hops [65]. Thus, $E_a = 0.23$ eV indicates that $Na_2Ti_3O_7$ has a high feasibility of ion migration in this direction, suggesting effective ion conduction properties, which are crucial for battery performance. Figure 2 illustrates the crystal structure of $Na_2Ti_3O_7$ and the three most promising ionic pathways for Na diffusion.

$Na_2FeP_2O_7$ is one of scientists' most favorable materials because of its similarities to $Li_2FeP_2O_7$, which is the

Table 1 The activation energies of diffusion of Na in candidate Na-ion battery materials

Material	Activation energy (eV)	Comments
$NaZr_2(PO_4)_3$	0.26	Ref. [46]
$Na_3V(PO_4)_2$	0.59	Ref. [64]
$Na_2Ti_3O_7$	0.23	Ref. [65]
$Na_3Fe_2(PO_4)_3$	0.45	Ref. [66]
$Na_2FeP_2O_7$	0.33	Ref. [65]
$Na_2MnP_2O_7$	0.58	Ref. [65]

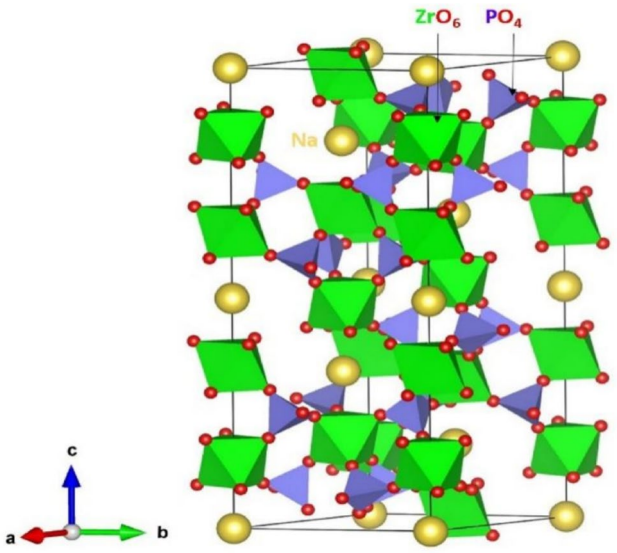

Fig. 1 Schematic representation of the long-range Na-ion diffusion in $NaZr_2(PO_4)_3$. The yellow spheres represent Na atoms, the green octahedrals are ZrO_6 and the blue tetrahedrals are PO_4 [47]

most common material for lithium-ion batteries, especially in large-scale storage applications. It has a triclinic structure (space group P1) consisting of three-dimensional frameworks formed by FeO_6 octahedra and P_2O_7 pyrophosphate units. These units are interconnected, creating large tunnels along the (011) direction within which the Na atoms are present. Clark et al. concluded that this structure can maintain long-range Na^+migration across the three axes and calculated three different migration energies: 0.33 eV along the a-axis, 0.42 eV along the b-axis, and 0.49 eV along the c-axis, indicating that the pathways of Na-ion diffusion are quasi-three-dimensional [65]. To further emphasize the promising characteristics of $Na_2FeP_2O_7$, the study also compares its energy barriers with the corresponding values of $Li_2FeP_2O_7$ and concludes that the two materials have many similarities. Figure 3 illustrates Na ion migration along the *a*-, *b*-, and *c*-axes of $Na_2FeP_2O_7$.

Magnesium-ion batteries

Magnesium-ion batteries are another good alternative to Li and many scientific papers discuss potential materials for electrodes that may bring this technology into the spotlight. Mg-based battery systems can theoretically provide higher energy densities because two electrons per ion are transferred compared to one electron in the case of Li. Nevertheless, Table 2 reports the activation energies of Mg diffusion in candidate Mg-ion battery materials and it is evident that, compared to Na-based materials, the energy values are bigger, which according to Li et al. can be attributed to the higher charge density of Mg^{2+} and consequently to the stronger Coulombic interactions with the polar groups of the host lattice [66].

The first material in the table is MgV_2O_4, which has the lowest activation energies among most of the electrode materials including the ones in Table 2. MgV_2O_4 forms a spinel structure (specifically a vanadium spinel structure) with Mg^{2+} ions occupying tetrahedral sites. Calculations about its activation energy have been thoroughly conducted. According to Hu et al. [69], in a MgV_2O_4 crystal, where vacancies are very sparse, Mg migration happens with an energy barrier of 0.45 eV, while Kuganathan et al. [44] reported a 3D diffusion pathway and a 0.52 eV barrier in a similar structural order. Despite these values appearing to be low, MgV_2O_4 cannot reach the low activation energies of Li and Na materials [44, 46]. Figure 4 illustrates Mg ion diffusion paths constructed by Mg-Mg hops in the crystal structure of spinel MgV_2O_4.

$MgFeSiO_4$ is a less popular counterpart to MgV_2O_4, especially with reference to Mg kinetics, due to its more

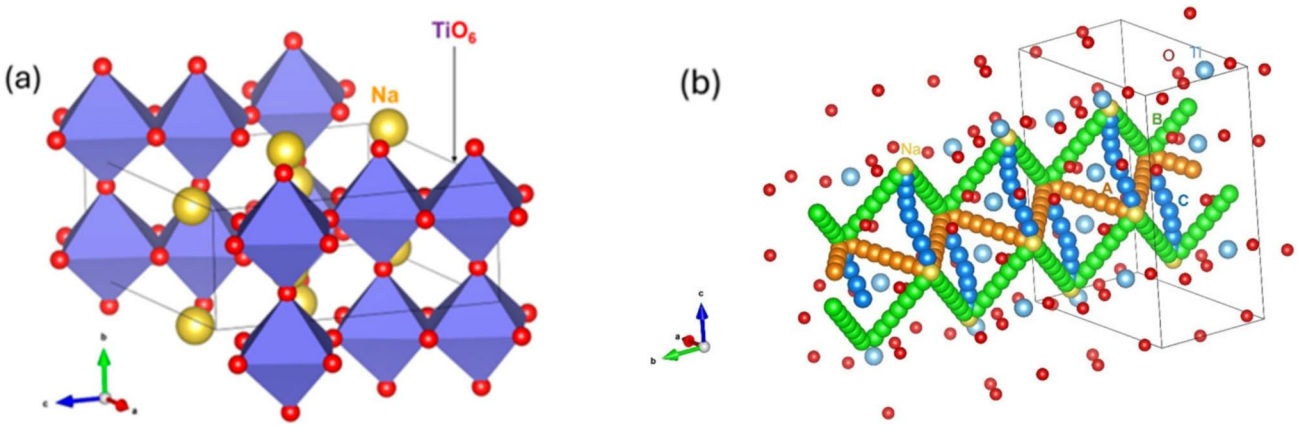

Fig. 2 **a** Crystal structure of $Na_2Ti_3O_7$ (the yellow spheres are Na atoms and the TiO_6 is pictured as the blue octahedral) and **b** the three most promising ionic pathways for Na diffusion (pathway A: orange, pathway B: green, and pathway C: blue) [65]

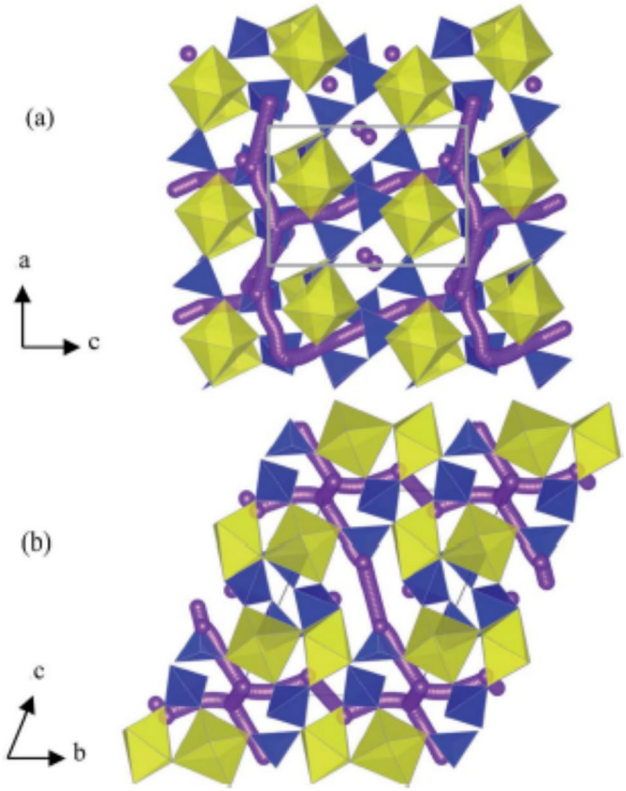

Fig. 3 Na-ion migration along the *a*-, *b*-, and *c*- axis axes of $Na_2FeP_2O_7$; **a** view of the *ac*-plane and (**b**) view of the *bc*-plane (Na-ions: purple and FeO_6 octahedral: yellow) [65]

Table 2 The activation energies of diffusion of Mg in candidate Mg-ion battery materials

Material	Activation energy (eV)	Comments
MgV_2O_4	0.45–0.56	Ref. [44, 69]
$MgTiO_3$	0.88	Ref. [70]
$MgFeSiO_4$	0.6	Ref. [71]

complicated olivine structure of octahedral sites and the potential changes in Fe oxidation states (Fe^{2+}-Fe^{3+}), but in a 2017 study [71], it was shown that $MgFeSiO_4$ can be interesting. Specifically, there is a pathway along the *bc*-plane, where Mg ions cover a distance of 3 Å in a small zig-zag pattern, with an activation energy of 0.6 eV. According to the study, there have been experiments in similar olivine structures [51] which give comparable energy values, suggesting favorable Mg^{2+} ion transport in this type of crystal structure. Figure 5 illustrates the olivine structure of $MgFeSiO_4$ and the lowest energy Mg-ion curved pathway parallel to *c*-axis.

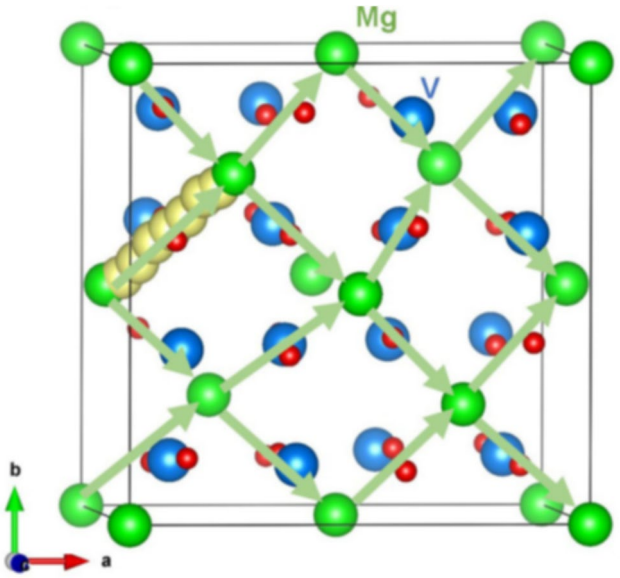

Fig. 4 Mg-ion diffusion paths constructed by Mg-Mg hops in the crystal structure of spinel MgV_2O_4, showing Mg in green, V in blue and O in red [44]

Calcium-ion batteries

Calcium-based materials have attracted a lot of attention lately. Ca is another divalent ion, which, just like Mg, can be, theoretically, the basis for higher capacity batteries compared to Li. The biggest difference with Mg is the size, with Ca^{2+} being bigger than Mg^{2+}, indicating harder ion migration in contrast to materials mentioned in "Magnesium-ion batteries." Additionally, despite its similar radius to Na^+, the kinetics in host lattices are considered worse [50] due to the stronger electrostatic forces that are exerted on the divalent Ca^{2+}. Regardless of the challenges that come with designing advanced electrode materials, many researchers are convinced that Ca-ion batteries can have smaller scale commercial use, but it is very difficult to replace Li-ion batteries completely. Table 3 presents the activation energies of diffusion of Mg in candidate Ca-ion battery materials.

The activation energy for Ca^{2+} migration in $Ca_3Fe_2Si_3O_{12}$, also known as andradite garnet, has been calculated at 2.63 eV using classical pair potential method [52]. This energy indicates a substantial barrier to ion mobility within the material's crystal lattice, which is probably attributed to the rigid garnet structure, where ions face strong coulombic interactions with oxygen. In addition, Torres et al. [53] examined many Ca-based minerals, which included $Ca_3Mn_2Si_3O_{12}$ and $Ca_3Cr_2Si_3O_{12}$, two very similar materials both to each other and to $Ca_3Fe_2Si_3O_{12}$ and reported, specifically for these two, that the activation energies were 2.09 eV and 2.07 eV, respectively. The lower energy level (by ~ 0.5 eV) is expected since the researchers used different

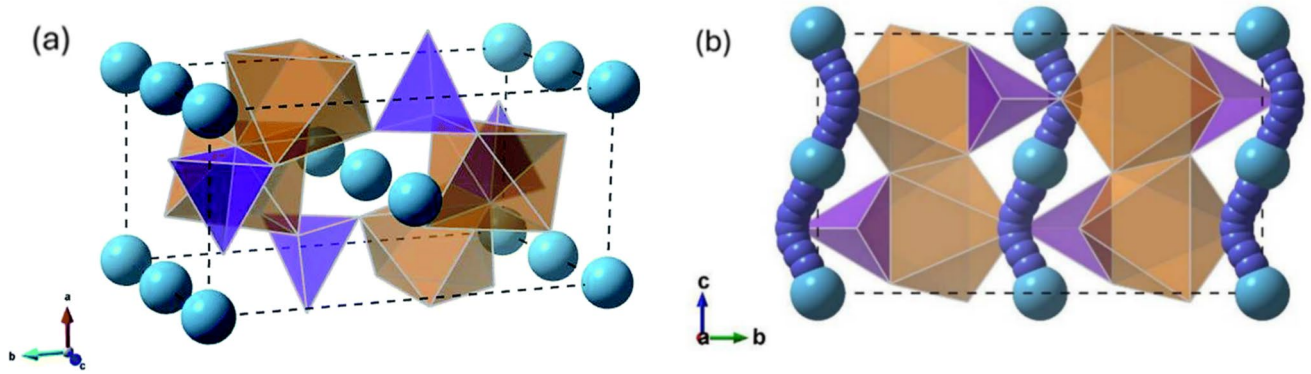

Fig. 5 **a** Olivine structure of $MgFeSiO_4$ (brown octahedra: FeO_6; purple tetrahedra: SiO_4; blue spheres: Mg^{2+} ions) and **b** the lowest energy Mg-ion curved pathway parallel to *c*-axis [71]

Table 3 The activation energies of diffusion of Mg in candidate Ca-ion battery materials

Material	Activation energy (eV)	Comments
$Ca_3Fe_2Si_3O_{12}$	2.63	Ref. [52]
$Ca_3Mn_2Si_3O_{12}$	2.09	Ref. [52, 53]
$Ca_3Cr_2Si_3O_{12}$	2.07	Ref. [52, 53]
$CaMn_2O_4$	1.3, 1.8	Ref. [72]
$CaFeSi_2O_6$	4.36, 4.49	Ref. [73]

computational methods, and the transition elements are also different. Figure 6 illustrates the crystal structure of $Ca_3Fe_2Si_3O_{12}$ and the long-range Ca ion migration pathway along the *ab*-plane.

The $CaMn_2O_4$ is a calcium-manganese oxide that is characterized by its MnO_6 octahedra that form double rutile chains. Dompablo et al. [72] noted that this mineral, theoretically, has a structure that exists in nature called marokite or postspinel, and two polymorphs, the virtual spinel, that has yet to be created in a lab and $CaFe_2O_4$, which can be produced under high-pressure treatment. They applied DFT to investigate the energy barrier of these three compounds and concluded that the marokite and $CaFe_2O_4$ activation energy is above 1 eV. Specifically, the former exhibited 1.8 eV and 1.3 eV, while the virtual spinel showed a 0.5 eV barrier, though, as previously stated this cannot be verified by an experiment [72]. Despite these values appearing low, lower compared to the other Ca-based minerals, they are still quite high to expect good Ca mobility along the most probable

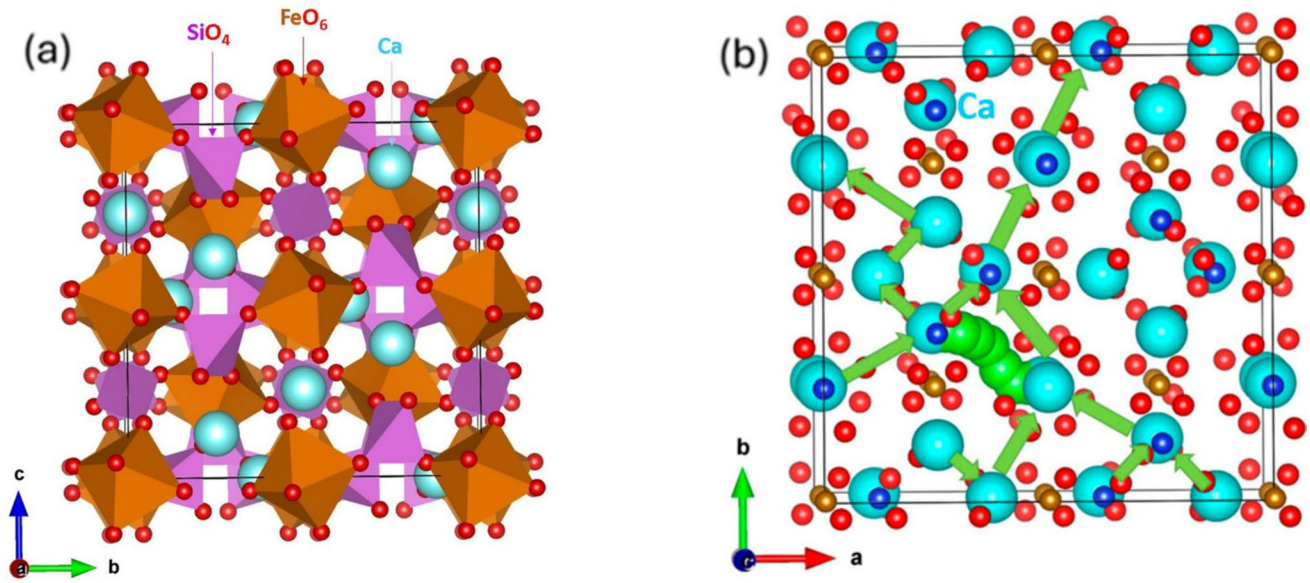

Fig. 6 **a** The crystal structure of $Ca_3Fe_2Si_3O_{12}$ and **b** the long-range Ca-ion migration pathway along the *ab*-plane (SiO_4: pink; FeO_6: orange; Ca: light blue; and O: red) [52]

pathway, which is the tunnel built up by the interconnected Ca sites. The significant activation energies of all the materials that were reviewed in this paper suggest that assistance is needed for ion diffusion improvement, such as doping with atoms that could potentially lower the barrier and expand the material's utility in electrochemical applications. Figure 7 illustrates the crystal structures of the investigated $CaMn_2O_4$ polymorphs.

Improving the ionic diffusion by doping

The previous discussion highlights that Na-, Mg-, and Ca-based materials have potential for the creation of sustainable battery cells capable of fulfilling the ever-growing needs of modern societies, with Na-ion batteries being the most prominent. To compete with lithium technology and even surpass it, scientists have been trying their best to tune the electronic and structural properties of the electrode materials by introducing extrinsic atoms. This method is known as doping and has become essential in the world of material science for enhancing functionality [6, 7, 9]. In the context of diffusion in batteries, doping is an efficient way to increase electron density (i.e., the number of electrons), thus tuning the number of intrinsic defects required for diffusion, and to decrease the migration energy barrier. Vacancies are considered the most favorable type of defect that facilitates the movement of ions through a material [45, 50–53, 64, 69–75] and doping introduces foreign atoms into a material's lattice that usually differ in valence (charge), leading to charge compensation. Charge compensation happens when the overall charge balance of the crystal is disrupted due to different oxidation states of extrinsic atoms and, to restore neutrality, the material often forms vacancies that compensate for the excess or deficient charge introduced. These vacancies also act as additional active sites or "holes" for ion adsorption or intercalation, thus extending the pathways in which the ions can move. It should be stressed that the activation energy and the migration energy barrier are not quantitatively equal, since the activation energy is the sum of the migration energy barrier and the formation energy of the vacancies of the migration path, but the terms "activation energy" and "energy barrier" have been used interchangeably.

Of the three types of electrode materials, sodium minerals are the most studied, due to the many similarities of Na with Li. Therefore, there is a volume of scientific papers discussing how detailed doping procedures can alter and improve sodium minerals. Kuganathan et al. [74] considered iron isovalent dopants, such as Sc, La, Gd, and Y and inserted them in Fe sites of $Na_3Fe_2(PO_4)_3$ to form $Na_3(Fe_xM_{1-x})_2(PO_4)_3$ observing an increase in conductivity. Importantly, they focused their research on the creation of vacancies and concluded that doping on Fe sites with Zr increases Na vacancy concentration, which is beneficial for Na ion migration and generally for the charging/discharging process of the battery. Lastly, the researchers observed that Si doping on P sites results in the formation of Na interstitials that are the key factor for capacity enhancement. As regards $Na_3V(PO_4)_2$, the lowest energy intrinsic defect process is not the Na Frenkel mechanism, which is important for the formation of a Na vacancy and interstitial pair. This indicates that very few Na vacancies are likely to form naturally in the material and any doping will be more challenging [64]. Regardless, it is possible (and necessary) to insert Ge^{4+}, a tetravalent ion, on the V site to solve this problem, and, in addition, it is possible to increase the Na interstitial concentration that is required for higher capacity by using the same ion as a replacement for P in the respective sites [64]. $Na_2Ti_3O_7$ already has low activation energy, but

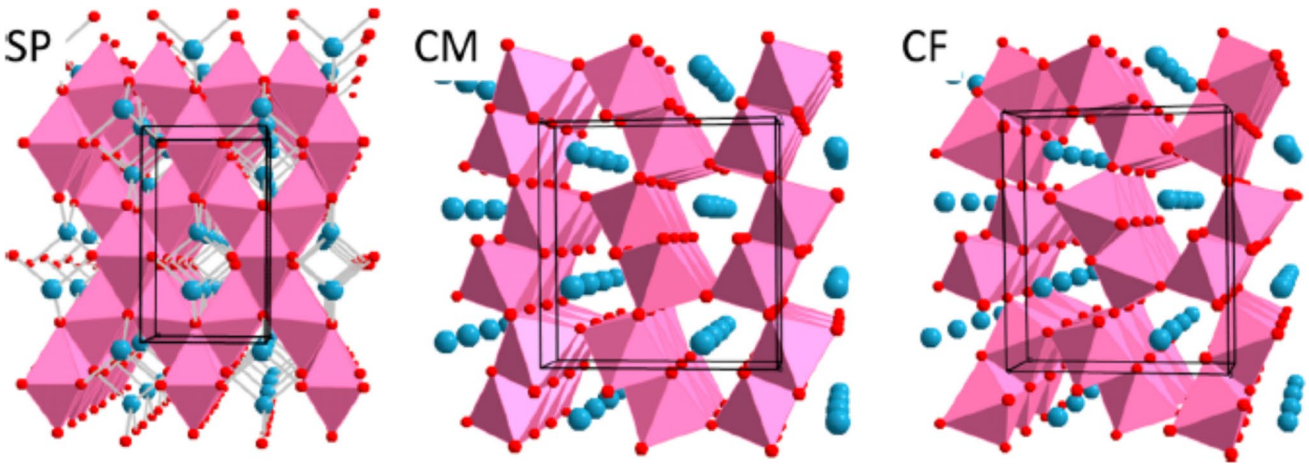

Fig. 7 Crystal structures of the investigated $CaMn_2O_4$ polymorphs: the virtual spinel (SP), the post-spinel $CaMn_2O_4$ (CM), and the post-spinel $CaFe_2O_4$ (CF). The blue spheres symbolize Ca and the pink octahedra are MnO_6 [72]

it has shown slow rate capability [75], leading researchers to experiment with doping its crystal structure. Chen et al. introduced F atoms replacing O atoms in the lattice and concluded that this doping mechanism created additional active sites for Na^+ diffusion and increased both the specific capacity and the rate capability (i.e., the ability to maintain high capacity during charge and discharge cycles performed at low current densities), which are very important characteristics for a battery material [75]. Tackling the same problem, Chen et al. doped $Na_2Ti_3O_7$ with Nb, partially substituting Ti ions. Since Nb^{5+} has more valence electrons than Ti^{4+}, the result is increased electron density, which in turn improves the capacity, conductivity, and rate performance of the material significantly [76].

Conversely to Na materials, papers discussing doping and its advantages on Mg-based minerals are scarcer. Regardless, the same study that reported the activation energy of 0.56 eV for MgV_2O_4, also investigated the impact of substituting vanadium (V) sites with cobalt (Co^{2+}) [44]. The findings suggest that Co^{2+} doping facilitates the formation of magnesium interstitials and oxygen vacancies, which are theoretically beneficial for Mg migration. Despite there being scientific material for $MgTiO_3$ and $MgFeSiO_4$, the effects of doping on the diffusion pathways and energy are not explicitly stated, necessitating further research and experiments. It should be mentioned that Kuganathan et al. introduced Mn^{2+}, Fe^{2+}, Co^{2+}, Ca^{2+}, Zn^{2+}, and Al^{3+} onto Mg sites of the $MgTiO_3$ crystal and Ge^{4+} and Si^{4+} onto the Ti sites, assessing their solution energies [70]. Islam et al. investigated the substitution of dopants such as Al^{3+}, Ga^{3+}, and V^{3+} at the Si sites, theorizing that this could lead to the introduction of Mg interstitials that could enhance diffusion [71].

The difficulty that Ca-based materials exhibit in Ca^{2+} ion diffusion is good enough reason for the scientific community to focus on mechanisms that facilitate ion kinetics. Unfortunately, this type of materials suffer from the scarcity of relevant scientific literature, as is the case for the Mg-based ones, but there are some important works. Doping $Ca_3Fe_2Si_3O_{12}$ has yielded some positive results for ion migration in the lattice. Specifically, there is a reduction in the activation energy in the presence of Mn^{2+} on the Fe site by 0.45 eV (2.18 eV), which might seem good but leaves much to be desired, since the overall value does not drop below 2 eV, a significantly large number [52]. In the case of Al^{3+} on the Si site, the reduction is very small, only by 0.09 eV, smaller than Mn^{2+} doping, and as such it is unhelpful in the goal of migration improvement [52]. It is important to mention that in both cases Ca–Ca distances have been slightly elongated due to the charge and ionic radius mismatch between the extrinsic and intrinsic atoms. In [73], a range of dopants in $CaFeSi_2O_6$ were tested in order to find the most favorable. $CaFeSi_2O_6$ has two pathways for Ca migration, on the *bc*-plane (pathway A) and one on the *ab*-plane (pathway B), with slightly different activation energies of 4.36 eV and 4.49 eV, respectively. Kuganathan et al. substituted the Si^{4+} ions with Al^{3+}, resulting in the reduction of both activation energies, with lower energy of pathway A by 0.02 eV and of pathway B by 0.48 eV, which is currently the lowest one in the crystal [73]. Also, the introduction of Al^{3+} moderately enlarges the distance of Ca-Ca and increases the concentration of Ca^{2+}. Again, as in the case of $Ca_3Fe_2Si_3O_{12}$, another calcium-silicate compound, the activation energy of $CaFeSi_2O_6$ is absurdly high and doping is not very effective in bringing it to levels comparable to current Li-based minerals.

The kinetics of Na ions and to a lesser extent Mg and Ca show that some minerals have a lot of potential to be used in battery cells that could be practical for household and commercial use, especially in light of the fact that these three ions are far more abundant, more environmentally friendly, sustainable, and economical, compared to Li. Therefore, should the engineering requirements be met, they will make a significant contribution to energy storage from renewable production sites.

Perspectives for tailoring ionic diffusion

The typical method in efforts to drive the energetics of ionic diffusion to appropriate levels for technological applications (i.e., in fuel cells or batteries) is to use appropriate dopants as discussed in the previous section. Additionally, geometrical ways (i.e., form interfaces) and mechanical strain can have a very important impact on the diffusion energetics in oxide materials [6, 77–87]. These unorthodox ways to pump solid state diffusion can add to the complexity of manufacturing. Atomic scale modeling can provide complementary information to experiment to identify the key parameters that need to be determined for material selection and device optimization. Considering ionic diffusion, this is typically governed by the Arrhenius relation, where key to kinetics is the activation energy of diffusion. The activation energy of diffusion needs to be lowered. It is in essence dependent upon the migration energy of the ions (i.e., the energy barrier towards the next position) and the formation energy (i.e., how much energy is required to form the defects required to facilitate the diffusion of the ions). Strain is an efficient way to lower the migration energy in energy-related materials as it has been demonstrated in previous studies [8, 77]. The formation of interfaces is another fruitful way to pump ionic diffusion as it was previously determined by Lee et al. [87] who considered the heterointerface between a fluorite material (CeO_2) and bixbyite (Y_2O_3). In this study, they achieved very high concentration of interfacial oxygen vacancies that in turn act as vehicles for ionic diffusion [87]. This paradigm that is potentially important for memristive and ionotronic

devices [87] could also serve as a way to increase the diffusivity in post-lithium batteries. Both Mg and Na ions would benefit from heterointerface geometries as there is technological need to enhance their diffusion energetics. It was also recently demonstrated that designed interfaces is not the only way to pump the concentration of the defects required for ionic diffusion. In particular, Chiabrera et al. [17] showed that the tuning of the non-stoichiometry in grain boundaries is also an effective path towards the amplification of diffusion properties. This approach is anticipated to lead to designed interfacial architectures for energy materials so that expensive and unsustainable materials (i.e., lithium) will be substituted by more ordinary and abundant materials.

What has been now systematically demonstrated by the community is that the kinetics alternative to Li ions and in particular Na ions [88–94]. The analysis of the results and the intricacies of the crystal structures and diffusion can benefit from the use of thermodynamic models such as the cBΩ model [95–97]. This model links the microscopic properties (i.e., activation energy of diffusion) to macroscopic properties (i.e., bulk modulus), and as such, it may lead to a higher-level understanding of the structural/compositional details that govern the kinetics of ions in battery as it has been demonstrated in other energy-related materials [98–105].

The investigation into alternatives to Li for batteries has recently been the domain of application for artificial intelligence (AI) and machine learning (ML), in the hope that the discovery of advanced oxides can be accelerated, and predictions about material performance can be utilized for the optimization of material design. For example, ML assisted in understanding phase transitions (e.g., P_2-to-O_2 transitions) in layered oxides, to design more stable materials [106]. Machine learning algorithms trained on an extensive dataset of experimental results and predicted the performance of various metal combinations in sodium-based layered oxides, focusing on transition metals such as manganese, nickel, titanium, and iron. In another example, the work described in [107] employed a machine learning model to optimize the energy density of sodium-ion batteries by identifying the optimal composition of sodium-containing transition-metal layered oxides ($NaMeO_{22}$). The researchers created a comprehensive database of experimental data spanning 11 years, and including sixty-eight distinct $NaMeO_{22}$ compositions, and experimented with several machine learning algorithms, including Bayesian optimization, to study how different elemental ratios affect properties such as operating voltage, capacity retention, and energy density. Their findings led to the identification of $Na[Mn_{0.36}Ni_{0.44}Ti_{0.15}Fe_{0.05}]O_{22}$ as the optimal composition for achieving high energy density in sodium-ion batteries, with subsequent experimental synthesis and testing of battery cells. In [108], machine learning is combined with DFT and experimental approaches to develop low-cost, high-energy NASICON cathodes for sodium-ion batteries. The research focused on materials like $Na_{3.5}MnV_{0.5}Ti_{0.5}(PO_4)_3$, which exhibited excellent electrochemical performance, including a specific capacity of 133.14 mAh/g and impressive cycling stability. Finally, in [109], ML provided critical insights into which variables need to be controlled during material synthesis to optimize performance. The study focused on predicting the performance of functionalized hard carbon anodes derived from grapefruit peels using a three-layer feed-forward artificial neural network (ANN). The model utilized physicochemical characteristics, such as porosity and surface chemistry, to establish correlations with energy storage capacity.

The role of machine learning interatomic potentials (MLIPs) is increasingly crucial in battery research, offering a balance of accuracy and efficiency that surpasses traditional methods like density functional theory (DFT) and empirical force fields. The Heenen Group at the Fritz Haber Institute is developing MLIPs for energy materials, focusing on complex interfaces in battery systems and catalysis, where traditional methods are limited by computational costs and accuracy [110]. These MLIPs are designed to capture complex chemical spaces and reactive chemistry, making them ideal for simulating systems like Li-sulfur battery chemistry and solid-state electrolytes. For instance, the moment tensor potential (MTP) has been used to predict the ionic conductivity of Li-ion solid-state electrolytes with high accuracy, significantly reducing computational time compared to *ab initio* molecular dynamics (AIMD) [111].

The application of MLIPs extends to the development of cathode materials, where they are used to predict material properties with accuracy comparable to DFT but at much faster speeds [112]. Recent studies have evaluated advanced MLIP models such as CHGNet and M3GNet for their engineering applications, demonstrating their ability to replicate thermodynamic phase stability and ionic configurations in materials like $LiFePO_4$. Furthermore, universal MLIPs (uMLIPs) are emerging as powerful tools for solid-state electrolytes, with models like MatterSim showing superior performance in complex material systems [113]. These advancements highlight the potential of MLIPs to accelerate the discovery of novel battery materials by efficiently screening candidates and simulating material behavior under various conditions [114, 115]. However, some uMLIPs exhibit a consistent potential energy surface softening effect, which needs to be addressed for optimal performance [116].

As the community progresses in the quest for advanced post-lithium battery materials and the implications that these introduce, the use of advanced computational techniques become necessary [117–121].

Summary and conclusions

The present demand for lithium batteries, particularly for transportation applications, but also for the purpose of grid energy storage of excess renewable energy production, is a technological challenge. This is because of several issues including limited reserves, concentrated in certain regions which may not be accessible, environmental cost of mining and significant environmental concerns. To address these issues, the community investigates alternative ions for the post-lithium battery era. This is the main subject of this review that focuses on Na, Mg, and Ca ions, which are the key alternatives to Li in batteries. Here, we focus on more recent computational modeling results mainly based on classical approaches (MD or atomistic simulations) and DFT. The focus of this review is the defect chemistry and the kinetics of ions. These will have a significant impact upon the realization or not of post-lithium ion energy storage technologies. As it is demonstrated throughout this review, theoretical techniques can play a significant role to identify the pathways of diffusion in the most promising materials and doping strategies. These in turn accelerate progress as they guide experimental work to the most important systems. Typically, the most fruitful systems have rather complicated crystal structures, stoichiometry, and composition. The continuously increasing computational power allows time consuming but more accurate quantum MD simulations to become a more standard tool and this will add to our appreciation of electronic properties of more extended systems. The use of advanced techniques such as AI and ML will eventually gain ground and lead to the discovery of compositions with optimum diffusion and other battery related properties. This will accelerate progress as the most appropriate systems for more detailed theoretical and experimental work will be identified earlier.

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