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Design and Optimization of Alkali Superionic Conductors for Solid-State Batteries using First-Principles Calculations

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Design and Optimization of Alkali Superionic Conductors for Solid-State Batteries

using First-Principles Calculations

A dissertation submitted in partial satisfaction of the

requirements for the degree Doctor of Philosophy

in

NanoEngineering

by

Zhuoying Zhu

Committee in charge:

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Professor Jian Luo
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Professor Oleg Shpyrko

2019
The Dissertation of Zhuoying Zhu is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

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Chair

University of California San Diego

2019
DEDICATION

To My Parents

Mr. Canping Zhu and Mrs. Guiqin Qi
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Zhu, Sunny Hy, Zhi Deng, Ying Shirley Meng and Shyue Ping Ong, 2016, 6, 33733. The dissertation author contributed AIMD simulations and was the coauthor of this paper. Chapter 4.3, in full, is a reprint of the material, “Studies of Functional Defects for Fast Na-Ion Conduction in Na$_{3-y}$PS$_{4-x}$Cl$_x$ with a Combined Experimental and Computational Approach”, as it appears in Advanced Functional Materials, Xuyong Feng, Po-Hsiu Chien, Zhuoying Zhu, Iek-Heng Chu, Pengbo Wang, Marcello Immediato-Scuotto, Hesam Arabzadeh, Shyue Ping Ong and Yan-Yan Hu, 2019, 29, pp.1807951(1-9). The dissertation author was the coauthor and primary investigator for the computational part of this paper. The DFT calculations and analyses were done by the author.

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PUBLICATIONS


ABSTRACT OF THE DISSERTATION

Design and Optimization of Alkali Superionic Conductors for Solid-State Batteries

using First-Principles Calculations

by

Zhuoying Zhu

Doctor of Philosophy in NanoEngineering

University of California San Diego, 2019

Professor Shyue Ping Ong, Chair

All-solid-state alkali-ion batteries (ASSABs) utilizing alkali superionic conductor (ASIC) solid electrolytes (SEs) are an efficient solution to address safety issues from flammable organic solvent-based liquid electrolytes and tend to be more energy-dense. In this dissertation, we illustrate the application of density functional theory (DFT) methods to gain profound insights into the key properties of ASIC solid electrolytes and accelerate their optimization and discovery. This dissertation is divided into three projects.
In the first project, we developed a high-throughput (HT) first-principles screening workflow and applied it to Li–P–S ternary and Li–M–P–S chemical spaces, where M is a non-redox-active element. Given the extraordinary superionic conductors in the silver composition space such as α–AgI and the structural similarity between Ag and Li compounds, we substituted Li for Ag in Ag–P–S and Ag–M–P–S chemical spaces and predicted two novel superionic conductors Li₃Y(PS₄)₂ and Li₃PS₄Cl₂. An efficient tiered screening strategy combining quick topological analysis and short ab initio molecular dynamics (AIMD) simulations was developed to rapidly exclude candidates which are unlikely to exhibit satisfying conductivity.

In the second project, we investigated the influence of Na defects and cation/anion dopants in Na₃PS₄ and evaluated the phase stability, dopant formation energy as well as Na⁺ conductivity. Aliovalent M⁴⁺ (M = Si, Ge, Sn) for P⁵⁺ substitution in c-Na₃PS₄ introduces Na⁺ excess, which is shown to significantly enhance ionic conductivity. AIMD simulations predict that 6.25% Si-doped c-Na₃PS₄ has a conductivity of 1.66 mS/cm, which is very close to the experimental value of 0.74 mS/cm at a 6% Si-doping ratio. Further analysis using topological methods and the van Hove correlation function explains how dopants affect the channel volume and how correlation motions of Na⁺ enhance Na diffusion in this material. Besides cation doping, we showed that anion doping, e.g., Cl⁻ substitution for S²⁻, is an alternative strategy for introducing vacancy defects in t-Na₃PS₄ to improve both electrochemical stability and Na⁺ conductivity, with a conductivity of ~1.14 mS/cm demonstrated experimentally. In collaboration with NMR experiments, we show via AIMD simulations that maximizing the concentration of Cl dopants while maintaining relatively low Na deficiency can further enhance Na conductivity to 2 mS/cm.

In the third project, we systematically assessed cation mixing effects on Na₃Ptₓ₃Pn"₁₋ₓS₄ and Na₄₋ₓTt₁₋ₓPn₃S₄ (Pn = P, As, Sb; Tt = Si, Ge, Sn) in terms of thermodynamic/
electrochemical/moisture stability and conductivity. Isovalent and aliovalent cation mixing in prototype structures including Na\textsubscript{3}PnS\textsubscript{4} and Na\textsubscript{11}Sn\textsubscript{2}PS\textsubscript{12} as a subset, gives the lever of tuning Na concentration and cation types/ratio simultaneously to achieve the twin goals of better stability and larger diffusion channel. We demonstrated that Na\textsubscript{3}Pn\textsuperscript{′}\textsubscript{x}Pn\textsuperscript{″}\textsubscript{1-x}S\textsubscript{4} exhibits negative or very small positive mixing enthalpies, including these cation-mixed compositions are likely to form solid solutions. The newly experimental Na\textsubscript{11}Sn\textsubscript{2}PS\textsubscript{12} prototype with I\textsubscript{4}a\textsubscript{1} space group is an excellent model to study and holds the promise to perform even better as a solid electrolyte after substituting with other Tt\textsuperscript{4+} and Pn\textsuperscript{5+} elements. We proposed a new compound of Na\textsubscript{11}Sn\textsubscript{2}AsS\textsubscript{12} which can potentially achieve higher conductivity and chemical stability than already experimentally reported compounds.
Chapter 1. Introduction

1.1 Alkali-Ion Battery

The rechargeable Li-ion battery (LIB) is the dominant energy storage solution today, with applications from portable electronics to electric vehicles to large-scale grid energy storage. Despite its ubiquity, there remains much room for advancement in rechargeable energy storage.

The typical LIB today comprises of a transition metal oxide cathode (e.g., LiCoO$_2$ or LCO) and a graphitic anode separated by an ionically conducting, electronically insulating electrolyte, as shown in Figure 1.1. The graphitic anode was a necessary development in the 1990s$^1$ to address potential short circuits caused by dendrite formation during the deposition of Li metal$^2$, an issue that remains unsolved to the present day. The most common electrolyte today is a solution of a Li salt such as LiPF$_6$ in a mixed organic solvent such as 1:1 ethylene carbonate(EC)/dimethyl carbonate (DMC).$^3$ However, the flammability of the organic solvent has given rise to significant safety concerns in recent years, especially as LIBs move beyond portable electronics to transportation and large-scale grid storage applications.

All-solid-state alkali-ion batteries (ASSABs) are a promising solution to address several shortcomings in today’s LIBs. By utilizing an alkali superionic conductor solid electrolyte (SE), ASSABs mitigates the safety risk of flammable liquid electrolytes. At the same time, ASSABs can potentially enable higher energy densities either through new stacking architectures or by enabling higher voltage cathodes or dendrite-free lithium anodes. Beyond Li-ion chemistry, other alkali ions,
particularly Na\(^+\), can also provide alternative cathode and SE chemistries that are potentially more abundant and lower cost.

The key component in ASSABs is the alkali superionic conductor solid electrolyte (SE), which must satisfy a stringent set of properties. A high room-temperature ionic conductivity, with 0.1 mS/cm as a typical minimum threshold, is key. Chemical and mechanical compatibility must also be maintained between the SE and the high voltage cathode and the low voltage anode, either intrinsically or via passivation.

1.2 Fast Alkali Conductors

1.2.1 Lithium Superionic Conductors

Tremendous efforts have been made on inorganic lithium superionic conductors. Figure 1.2 shows the conductivity evolution of different types/generations of lithium conductors. The early-stage research on Li solid electrolytes such as Li\(_3\)N, lithium phosphorus oxynitride (LIPON)\(^4\) and LISICON Li\(_{14}\)Zn(PO\(_4\))\(_4\)\(^5\) either suffer severe chemical instability (Li\(_3\)N)\(^6\) or show the room-temperature conductivities several orders of magnitude lower than those of organic electrolytes (LIPON, LISICON). NASICON-type AM\(_2\)(PO\(_4\))\(_3\) (A = Li, Na, K; M = Ge, Zr, Ti) was also widely investigated since 1976\(^7\) with a series of trials to improve the conduction properties. Substitutions in all possible sites prove Al could benefit mostly in the composition of Li\(_{1+x}\)M\(_x\)Ti\(_{2-x}\)(PO\(_4\))\(_3\) (M = Al, Cr, Ga, Fe, Sc, In, Lu, Y or La)\(^8,9\) for conductivity enhancements whereas another composition of Li\(_{1+x}\)Al\(_x\)Ge\(_{2-x}\)(PO\(_4\))\(_3\) attracts the attention with a relatively wide electrochemical window.\(^10\)
The Li$_{3x}$La$_{2/3-x}$TiO$_3$ (LLTO)\textsuperscript{11} perovskite exhibits Li$^+$ ionic conductivity exceeding 1 mS/cm. However, the reduction of Ti$^{4+}$ against Li metal hinders its application in LIBs. Garnet-type cubic Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO),\textsuperscript{12} which is stable against Li metal, shows the conductivity as high as 1 mS/cm though it is two orders of magnitude lower of conductivity in the thermodynamically stable tetragonal phase.\textsuperscript{13}

The exciting discovery of Li$_{10}$GeP$_2$S$_{12}$ (LGPS)\textsuperscript{14} indicates the start of a new generation of thiophosphate solid electrolyte materials. First reported by Kamaya and co-workers in 2011, LGPS possesses an ionic conductivity of 12 mS/cm, which is comparable with organic liquid electrolytes. With improved synthesis techniques that minimize the grain boundary resistance, the conductivity of another thiophosphate, the Li$_7$P$_3$S$_{11}$ glass-ceramic conductor, has also been pushed to 17 mS/cm with a low activation energy of 176 meV.\textsuperscript{15,16} More recently, Kato reported two new members in LGPS family with the highest conductivity so far (25 mS/cm for Li$_{9.54}$Si$_{1.74}$P$_{1.44}$S$_{11.7}$Cl$_{0.3}$)\textsuperscript{17} and high stability with Li metal (Li$_{9.6}$P$_3$S$_{12}$).\textsuperscript{17}

Moreover, the exploration of new classes of Li superionic conductors is getting ahead. Recently, a computation-guided family of fast Li-ion conductor, LiTaSiO$_5$ (LTSO) with sphere structure,\textsuperscript{18} has been identified and synthesized. Zr-doping to Ta sites can lead to high-energy sites partially occupied by Li and promote the concerted motions with conductivity enhanced by three orders of magnitude compared to pristine LTSO.\textsuperscript{19} Another freshly baked work by Kato and Hautier reported that LiTi$_2$(PS$_4$)$_3$ (LTPS)\textsuperscript{20} has the unusual structure lack of regular tetrahedral or octahedral Li sites. Super high pre-factor and relatively low activation energy coming from frustrated energy landscape exist simultaneously, which is rare, in this material and it opens the future searching for this exceptional type of frameworks. Besides oxides and sulfides, researchers
also extend the view to the unexplored hydride and halide lithium superionic conductors and exciting findings like $0.7\text{Li(CB}_9\text{H}_{10})-0.3(\text{CB}_{11}\text{H}_{12})$ $^{21}$ and $\text{Li}_3\text{YCl}_6$ $^{22,23}$ imply the great potential of those areas.

Comparing the two main categories of alkali superionic conductors, oxide and sulfide, Figure 1.3 illustrated the advantages and disadvantages from ten aspects including ion selectivity, chemical stability, mechanical properties and so on. Conductivity is not the only pursuit for a promising solid electrolyte candidate, electrochemical/chemical stability and mechanical property are also important. For example, LLZO garnet deserved much attention because of its excellent electrochemical stability even against Li metal. On contact with strained electrodes during charge/discharge, the solid electrolytes should have the ability of deformation to achieve excellent interface compatibility without crack forming. Although softer than oxide-based SEs $^{24}$, sulfide-based SEs should overcome the mismatch due to the volumetric expansion of cathode and Li dendrite formation towards Li anode to develop the full potential for future large-scale energy storage and conversion applications.

### 1.2.2 Sodium Superionic Conductors

The initial study on Na-ion battery (NIB) arose in parallel with the Li-ion battery in the 1970s. $^{25,26}$ With the rapid development of commercialized LIBs since the 1990s, the exploration in NIBs was shelved for several decades. The resurgent interest of NIBs in recent years $^{27-29}$ can be attributed to the fact that Na source is more abundant and much cheaper than Li.

Well-studied sodium solid electrolytes such as β-alumina and NASICON exhibit reasonable ionic conductivities only at higher temperatures and are typically implemented in Na-
S batteries for large-scale storage.\textsuperscript{30,31} In 2012, the cubic Na$_3$PS$_4$ superionic conductor was firstly reported by Hayashi et al.,\textsuperscript{32} achieving a relatively high conductivity of 0.74 mS/cm via doping strategies.\textsuperscript{33} This finding initialized the plentiful and fruitful discoveries on this novel family of sodium conductors, including the works reported in this dissertation.

Besides the property enhancements in Na$_3$PS$_4$ and its analogs, another mainstream thought is substituting Na for Li in some famous and extraordinary Li conductors. The current number of sodium conductors substituted from lithium thiophosphate is relatively few. The potentially existing Na$_{10}$MP$_2$S$_{12}$ (M = Si, Ge, Sn)\textsuperscript{34} materials predicted by first-principles calculations were only verified experimentally in Na$_{10}$SnP$_2$S$_{12}$. Na$_7$P$_3$S$_{11}$,\textsuperscript{35} derived from Li$_7$P$_3$S$_{11}$ with super high conductivity over 10 mS/cm, is not trivial to synthesize through the thermodynamic calculations. Later, researchers extend the synthesis protocol to the entire Na–Sn–P–S chemical space and gained the harvest of a novel single crystal Na$_{11}$Sn$_2$PS$_{12}$.\textsuperscript{36}

1.3 Objectives and Overview

Despite the fruitful progress on novel alkali superionic conductors made in recent years, the ideal candidates that satisfy major requirements and are qualified for commercialized solid electrolytes have not appeared. The features that determine fast ion diffusion in typical frameworks remain unclear. In this dissertation, we apply DFT methods to investigate crucial issues of alkali superionic conductors for solid electrolytes. Over three projects, we demonstrate how DFT methods can be used to design and optimize the SE materials.

In the first project, we develop a high-throughput workflow for screening solid electrolytes with a novel tiered diffusivity evaluation scheme. We screened the Li–P–S ternary and Li–M–P–S
quaternary from silver chemical space and identified two promising lithium conductors, Li$_3$Y(PS$_4$)$_2$ and Li$_5$PS$_4$Cl$_2$, with excellent conductivity and electrochemical stability predicted from our calculations. The significance of this work is not only the discovery of two novel lithium superionic conductors. The workflow presented is transferable for any conductors with adjustment of mobile species radius and targeting diffusivity range.

In the second project, we present a complete study on the Na$_3$PS$_4$ superionic conductor via cation and halide doping. We used multiple methods including probability function density and van Hove function to visualize the fast Na$^+$ diffusion in cubic Na$_3$PS$_4$ and target to find the key factor that leads to its orders of magnitude higher conductivity than the tetragonal phase which is more thermodynamically stable. A series of M$^{4+}$ dopants is tested for P$^{5+}$ site substitution. The conductivity of Si-doped Na$_3$PS$_4$ is in excellent agreement with experimentally-reported value at a similar doping ratio. We predict the Sn dopant should further improve the conductivity than Si, a result that was independently confirmed by a subsequent experimental work.$^{37}$ The reason for the improvement in conductivity is due to Na interstitial defects introduced by aliovalent doping. Subsequently, we also explored halide doping (Cl$^-$ for S$^{2-}$) in collaboration with the Meng group. For the latter one (halide doping), we study how tunable vacancy defect/Cl dopant concentration contributes to the Na$^+$ diffusion and indeed which factor leads to the high conductivity. Functional defects are captured by solid-state nuclear magnetic resonance (NMR) and it confirms the rationality of unequal amounts of Cl substitutions and Na vacancy resulting from the change of P oxidation state from 5+ to 4+. The tracer-exchange NMR method was utilized to determine the ion transport pathways. Functional defects are maximized to promote Na conduction and a full cell of Na/Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$/Na$_3$V$_2$(PO$_4$)$_3$ is demonstrated with a reversible room-temperature capacity of 100 mAh/g.
In the third project, we give a complete comparison of Na$_3$Pn’$_x$Pn”$_{1-x}$S$_4$ and Na$_4$TtS$_4$–Na$_3$PnS$_4$ (where Pn = P, As, Sb and Tt = Si, Ge, Sn) cation mixing systems from prototypes of Na$_3$PS$_4$, Na$_4$SnS$_4$ and newly reported Na$_{11}$Sn$_2$PS$_{12}$ structures, in terms of phase stability, electrochemical stability, moisture tolerance and conductivity. In isovalent Pn’-Pn” mixing for Na$_3$Pn’$_x$Pn”$_{1-x}$S$_4$, high miscibility is observed in this system, especially for P-As mixtures. Arsenic also results in better moisture stability than pure Na$_3$PS$_4$ phase. For aliovalent mixed Na$_{4-x}$Tt$_{1-x}$Pn$_x$S$_4$, we found that the newly reported Na$_{11}$Sn$_2$PS$_{12}$ prototype is the most energetically favorable. Through a comprehensive screening of Tt–Pn combinations, we identified Na$_{11}$Sn$_2$AsS$_{12}$ as a potential SE candidate exhibiting better moisture stability and higher conductivity.

The dissertation is divided into the following chapters. A brief description for each subsequent chapter is listed as below:

- Chapter 2 gives an introduction of DFT methods which are usually utilized in solid electrolyte materials, especially ab initio molecular dynamics for fast alkali conductor application.
- Chapter 3 presents our work on how the efficiently tiered ab initio molecular dynamics workflow contributes to discovering the novel lithium superionic conductors from silver thiophosphates.
- Chapter 4 discusses the role of Na$^+$ interstitials and dopant effects in enhancing Na$^+$ ionic conductivity in cubic Na$_3$PS$_4$ and use DFT methods to guide halide dopant selection. With the experimental collaboration with the Meng group, we synthesized Cl-doped t-Na$_3$PS$_4$. 
And we further investigate how functional defects (Cl and Na vacancy) can individually promote Na diffusion and what is the transport mechanism in Na\textsubscript{3-x}PS\textsubscript{4-x}Cl\textsubscript{x} material.

- Chapter 5 presents a comprehensive investigation of cation mixing for stable and high ionic conductivity sodium solid electrolytes in Na\textsubscript{3}Pn\textsubscript{3}Pn''\textsubscript{1-x}S\textsubscript{4} and Na\textsubscript{4-x}Tt\textsubscript{1-x}Pn\textsubscript{x}S\textsubscript{4} (Pn = P, As, Sb; Tt = Si, Ge, Sn).

- Chapter 6 summarizes the significant findings of this dissertation and provides an outlook for future research in this field.
Figure 1.1 Schematic of an alkali-ion battery.\textsuperscript{38} (Reprinted with permission from Ref 38. Copyright 2016 Nature Research.)

Figure 1.2 Thermal evolution of ionic conductivity of the new Li\textsubscript{10}GeP\textsubscript{2}S\textsubscript{12} phase, together with those of other lithium solid electrolytes, organic liquid electrolytes, polymer electrolytes, ionic liquids and gel electrolytes.\textsuperscript{14} (Reprinted with permission from Ref 14. Copyright 2011 Springer Nature.)
Figure 1.3 Radar plots of the performance properties of (a) oxide solid electrolytes; (b) sulfide solid electrolytes.\textsuperscript{39} (Reprinted with permission from Ref 39. Copyright 2017 Springer Nature.)
First-principles method is a quantum-mechanical based method that does not require any other assumptions such as the empirical model or fitting parameters.\textsuperscript{40} Quantum mechanics is a robust tool to simulate electrons and atomic nuclei motions, in which we can gain many material properties reflected through electrons behaviors.\textsuperscript{41–43} As predicted by Dirac in 1929, \textit{The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.}

As one of the most widely used first-principles approaches, DFT has enjoyed its success in predicting various physical properties of materials.\textsuperscript{44} Today, standard DFT calculations are performed by solving Kohn-Sham equation,\textsuperscript{45} which provides a tractable solution to the Schrödinger equation\textsuperscript{46} for practical materials. First proposed by Hohenberg and Kohn in 1964,\textsuperscript{47} this theory stresses that electron density is the unique quantity that entirely determines the ground-state properties of a given system.\textsuperscript{44} The Nobel prize for chemistry in 1998 to Kohn indicated the highest recognition for DFT and its wide application. DFT is built upon two major principles:

\begin{itemize}
    \item The total energy of a system of electrons and nuclei is a unique functional of the electron density
    \item The variational minimum of the energy is exactly equivalent to the true ground-state energy
\end{itemize}

The core strength of Kohn-Sham DFT is that one can use electron density rather than complicated many-body wavefunction, which requires more efforts on good parametric description to solve many-body problems.
2.1 General Considerations

Owing to the rapid advances of computational resources in recent years, first principles methods based on density functional theory become an invaluable complementary toolkit to experiments in the understanding and design of battery materials, including Alkali SuperIonic Conductors (ASICs). Pioneer work was carried out by Ceder and co-workers to gain insights to understanding the battery performance, especially cathode materials.\textsuperscript{48–50} Later, this framework was applied to ASICs to understand their multi-properties such as phase and electrochemical stability, and diffusion mechanism,\textsuperscript{28,51,52} which are all equally important to the actual performance of all-solid-state AIBs.

Phase stability is a prerequisite for almost any materials design consideration. Usually, the phase stability can be estimated through a multi-component phase diagram constructed by first-principles methods at 0K. To construct a phase diagram, one need to get the energy of all compounds within this chemical space and compare their thermodynamic stability. The ground-state energies are usually calculated using the generalized gradient approximation (GGA) or GGA+U extension depending on if transition metal existing in the phase diagram.\textsuperscript{53}

Another crucial property of an ASIC is its electrochemical stability against the electrodes, (1) the ASIC has a sufficiently wide electrochemical window such that it becomes inert with respect to the electrodes throughout the operating voltage range. In other words, the ASIC will get neither oxidized nor reduced to the electrodes. (2) the ASIC reacts with the electrodes, forming secondary products at the ASIC/electrode interfaces. Numerous studies on solid electrolyte-electrode interface diagnose using DFT methods are recommended for interested readers.\textsuperscript{54–56}
There are in general two broad classes of ab initio techniques for the study of ionic diffusion and conduction in materials in the scientific literatures: transition state methods\textsuperscript{57} (e.g., nudged elastic band\textsuperscript{58} and kinetic Monte Carlo\textsuperscript{59}) and molecular dynamics simulations\textsuperscript{41,60,61}. In the following subsections, we will focus on the latter, i.e., ab initio molecular dynamics (AIMD) simulation.

\textbf{2.2 Ab Initio Molecular Dynamics}

Molecular dynamics (MD) simulations model the motion of atoms at finite temperatures by integrating Newtonian equations of motion. A critical input that enables all MD simulations is the description of the interatomic interactions. In the more commonly used classical MD simulations, these interactions are predefined by empirical potentials, which are based on analytical formula and parameters fitted from experiments or first principles calculations\textsuperscript{62–64}. Despite the significant lower computational costs, classical MD simulations do suffer from several serious drawbacks that arise from empirical potentials, such as the lack of transferability across chemistries and the difficulty in handling complex interatomic interactions using simple functional forms.

In ab initio MD simulations, on the other hand, interatomic interactions are directly derived from solving the Schrödinger equation, albeit using various approximations. The minimal parameterization in ab initio methods means that AIMD can be generally applied across broad chemical spaces, and the accuracy of the interatomic interactions are limited only by the underlying approximations of ab initio method. There are two main variants of AIMD today:
• In the Born-Oppenheimer (BO) variant, the motions of the ions and electrons are treated separately. The electronic structure part is reduced to solving the time-independent, stationary Schrödinger equation, while the ions are propagated according to classical mechanics with ionic forces obtained from electronic structure calculations.

• In the Car-Parrinello (CP) variant, the ionic and electronic degrees of freedom are coupled via fictitious dynamics variables. Unlike BO-AIMD, minimization of the electronic energy is not required at each time step. However, a sufficiently small fictitious mass must be chosen for the electrons to maintain adiabaticity, and, correspondingly, the time step for integrating the equations of motions is typically smaller than that required for BO-AIMD.

The theoretical underpinnings and implementation of AIMD techniques are beyond the scope of this work but are extensively covered by many excellent reviews and books. The main disadvantage of AIMD methods is their significantly higher computational cost relative to classical MD, which places constraints on the accessible system sizes and simulation timeframes. Nevertheless, these disadvantages can be mitigated by continued computational power growth, as well as the features of the materials of interest, as discussed in the introduction.

The main output from AIMD simulations is the trajectories of the ions, from which transport properties such as the diffusivity and conductivity can be derived. Currently, most AIMD studies of superionic conductors only simulate the self-diffusion of ions at equilibrium conditions (instead of under driving forces) under the assumption that the ionic displacements between ions are uncorrelated. From an AIMD simulation, the self-diffusion coefficient $D^*$ in a 3D crystal
structure with N mobile ions can be calculated from the velocity autocorrelation function through the Green-Kubo relation:

$$D^* = \frac{1}{3N} \int_0^\infty dt \sum_{i=1}^N \langle \mathbf{v}_i(t_0) \cdot \mathbf{v}_i(t + t_0) \rangle_{t_0}$$  \hspace{1cm} (2.1)$$

where $\mathbf{v}_i(t)$ is the velocity of ion $i$ at time $t$ and angular bracket $\langle \cdot \rangle_{t_0}$ stands for ensemble average over time argument $t_0$.

More commonly, the diffusivity is computed from ionic displacements via the Einstein relation:

$$D^* = \frac{1}{6N} \lim_{t \to \infty} \frac{\partial \Delta \mathbf{r}(t)^2}{\partial t} = \frac{1}{6N} \lim_{t \to \infty} \frac{\partial}{\partial t} \langle \sum_{i=1}^N [\mathbf{r}_i(t + t_0) - \mathbf{r}_i(t_0)]^2 \rangle_{t_0}$$  \hspace{1cm} (2.2)$$

$$\Delta \mathbf{r}(t)^2 \equiv \frac{1}{N} \langle \sum_{i=1}^N [\mathbf{r}_i(t + t_0) - \mathbf{r}_i(t_0)]^2 \rangle_{t_0}$$  \hspace{1cm} (2.3)$$

where $\mathbf{r}_i(t)$ is the position of mobile ion $I$ and $\Delta \mathbf{r}(t)^2$ is the mean square displacement (MSD) of the mobile ions over time $t$ as an ensemble average (over time argument $t_0$).

It should be noted that $D^*$ from the Green-Kubo relation (Eq. (2.1)) and the Einstein relation (Eq. (2.2)) are strictly equivalent. However, there are practical considerations to prefer one method over the other, especially given the relatively short accessible time scale of AIMD simulations (up to a few hundreds of ps in most cases). For example, the long-time tail of the integral in Eq. (2.1) may cause numerical inaccuracy in the estimate of diffusivity in short
simulation time scales; as such, Eq. (2.2) is more reliable and commonly used for computing the diffusivity.

The ionic conductivity can be calculated from the self-diffusion coefficient $D^*$ using the Nernst-Einstein equation:

$$\sigma = \frac{\rho z^2 F^2}{RT} D^*$$ \hspace{1cm} (2.4)

where $\rho$ and $z$ are the molar density and the charge of the mobile ions in the unit cell, respectively. $F$ is the Faraday constant and $R$ is gas constant. It should be noted that the self-diffusion coefficient obtained from any computer simulations is essentially the tracer diffusivity in experiments, and the ionic conductivity from Eq. (2.4) assumes no ionic correlation. The ionic correlation can be reflected by the so-called Haven ratio, which is defined as the ratio of tracer diffusivity to charge diffusivity ($D_\sigma$)\textsuperscript{70}:

$$H_R \equiv \frac{D^*}{D_\sigma}$$ \hspace{1cm} (2.5)

$$D_\sigma = \frac{1}{6N} \lim_{t \to \infty} \frac{\partial}{\partial t} \left[ \sum_{i=1}^{N} [\Delta \mathbf{r}_i(t)]^2 \right]$$ \hspace{1cm} (2.6)

$H_R = 1$ for uncorrelated ionic diffusion, whereas $H_R < 1$ when concerted motions exist. Typical values of $H_R$ for highly correlated superionic conductors are between 0.3 and 0.6\textsuperscript{71–73}. Given that the convergence of $D_\sigma$ using Eq. (2.6) is often slow, only a few studies have attempted to estimate $H_R$ within the time scales accessible via AIMD simulations\textsuperscript{34}.
Under the assumption of no phase transitions and an abundance of defect carriers, the diffusivity $D$ generally follows an Arrhenius relationship:

$$D = D_0 \exp \left( -\frac{E_a}{kT} \right)$$  \hspace{1cm} (2.7)

where $E_a$ is the activation energy of ionic diffusion and $k$ and $T$ are Boltzmann constant and temperature, respectively. $D_0$ is the diffusivity at $T \to \infty$. By calculating the diffusivities from AIMD simulations at multiple temperatures, $E_a$ can be estimated from a linear fitting of the log of $D$ versus $1/T$. As AIMD simulations are usually performed at elevated temperatures to increase the number of diffusion events, Eq. (2.7) is also used to obtain diffusivities at room or lower temperatures. Care must be taken in the interpretation of these extrapolated values as the core assumption is that the fundamental mechanisms of diffusion remain unchanged between the lower and higher temperatures.

In addition to diffusivity and conductivity estimates, the ionic trajectory data provide a treasure trove of information about the energy landscape in the material and the mechanisms of ionic diffusion. The information can be extracted via several analyses:

- The probability density function $P(r)$ plot can provide useful message on high occupancy positions which are corresponding to low-energy sites in a superionic conductor, as well as the migration pathways in the crystal structure. $P$ is normalized such that with $\int_{\Omega} P d\mathbf{r} = 1$ with $\Omega$ being the volume of the unit cell. Site occupancies of geometrically distinct sites also can be acquired to further investigate the diffusion of dynamic process through AIMD simulations.
• The van Hove correlation function can provide useful information about the correlation in the motion of ions. The van Hove correlation can be split into the self-part $G_s$ and the distinct-part $G_d$, defined as follows:

$$G_s = \frac{1}{4\pi r^2 N_d} \sum_{i=1}^{N_d} \delta(r - |r_i(t_0) - r_i(t + t_0)|) > t_0$$

(2.8)

$$G_d = \frac{1}{4\pi r^2 \rho N_d} \sum_{i \neq j}^{N_d} \delta(r - |r_i(t_0) - r_i(t + t_0)|) > t_0$$

(2.9)

Here, $\delta(\cdot)$ is the one-dimensional Dirac delta function. $N_d$ and $r$ represent for the number of mobile ions in the unit cell and radial distance, respectively. $\rho$ is the average number density which serves as the “normalization factor” in $G_d$ to ensure $G_d \to 1$ when $r \gg 1$. The self-part $G_s(r, t)$ may be interpreted as the probability density that a particle diffuses away from its initial position by a distance of $r$ after time $t$, while the distinct-part $G_d(r, t)$ describes the radial distribution of $N - 1$ particles at time $t$ with respect to the initial reference particle. A peak near $r = 0$ is an indication of collective motions. Besides, $G_d$ is reduced to the static pair distribution function when $t = 0$, which is often adopted to study the dynamics of structural changes.

For practical AIMD simulations of fast ion conductors, decisions need to be made about several key parameters as outlined below. In general, the trade-off is between more realistic models (whether in a spatial or temporal sense) and computational cost, and such decisions have to be made based on the system in question:

1. **Simulation cell size.** Simulation supercell sizes should be large enough to avoid introducing artificial correlated motion due to periodic boundary conditions. However, due
to the high cost of AIMD methods, only a moderate-sized supercell of 10 Å in each lattice direction is usually used today. Depending on the number of mobile ions and the correlation between their motion, larger or smaller cells may be appropriate, and proper convergence tests should be performed for high-accuracy studies. For comparative/qualitative studies evaluating similar topologies and/or chemistries, strict convergence with respect to cell sizes may not be necessary.

2. **Spin.** Non-spin-polarized calculations can significantly speed up electronic convergence. The decision of whether to exclude spin has to be made based on the chemistry in question. For nonmagnetic s/p systems, excluding the effect of spin is usually a reasonable approximation.

3. **Time step.** For BO-AIMD simulations of fast ion conductors, a time step of 1–2 fs is typically sufficient, though smaller values may be required for fast proton conductors. For CP-AIMD, the simulation time step usually has to be considerably smaller (~ 0.02–0.2 fs).

4. **Total simulation time.** The total simulation time necessary to achieve converged diffusion statistics depends on the diffusivity of the system and the simulation temperature. Fortunately, the generally high diffusivities of fast ion conductors mean a higher number of diffusion events per unit time, and good results for superionic conductors have been obtained with AIMD simulations of 100–200 ps at temperatures as low as 600–1200 K.

5. **Simulation temperatures.** Most AIMD simulations are performed at higher temperatures to increase the number of diffusion events for faster convergence of diffusion statistics. Typical temperatures range from 600–2000 K, depending on the chemistry. AIMD simulations of oxides, which usually have much higher melting points, can be performed
at much higher temperatures. AIMD simulations of sulfides, on the other hand, are usually performed at lower temperatures.

6. **Ensemble.** Though the \( NpT \) (constant number of particles, pressure and temperature) ensemble is more representative of real-world environments, many AIMD studies of fast ion conductors are performed using the \( NVT \) ensemble (constant number of particles, volume and temperature) due to the smaller energy cutoff requirement\(^{75,76} \). Furthermore, the use of the \( NVT \) ensemble allows simulations to be performed at higher temperatures without melting. In using the \( NVT \) ensemble, care should be taken to ensure that the initial volume is representative of the material. This initial volume is either obtained via experimental input or from ab initio structure optimization.

### 2.3 Dopability

Diffusion is defect-driven process. As such, tuning the concentration of defects, either intrinsically or via extrinsic doping, is a common strategy to enhancing ionic conductivity\(^{17,77,77,78} \). Indeed, AIMD simulations of fast ionic conductors based on reported stoichiometric compositions frequently result in diffusivity and conductivity estimates that are much lower than the reported experimental values\(^{43,79,80} \). Doping can also be a means to introducing desired phase transitions (e.g., to a higher conductivity phase)\(^{81,82} \) or to optimizing other properties such as cost or stability\(^{83,84} \).

The feasibility of introducing a dopant into a crystal structure depends on many factors, including the ionic radius and oxidation state of the dopant relative to existing species in the crystal. One measure of dopability is the neutral dopant formation energy, which is defined as follows\(^{85} \):
$$E_f[doped] = E[doped] - E[pristine] - \sum_{i=1}^{N} n_i \mu_i$$  \hspace{1cm} (2.10)

Here, $E[doped]$ and $E[pristine]$ are the total energies of the structure with and without the neutral dopant, respectively; $\mu_i$ is the atomic chemical potential of species $i$ that varies based on different experimental conditions; $N$ is the total number of species in the doped structure; $n_i$ indicates the number of atoms of species $i$ being added ($n_i > 0$) or removed ($n_i < 0$) from the pristine structure. $\mu_i$ can further be decomposed as $\mu_i = E_i + \Delta \mu_i$, where $\Delta \mu_i$ is the chemical potential of species $i$ referenced to the elemental solid/gas with energy $E_i$. Eq. (2.10) can be rearranged as

$$E_f[doped] = E_f^0[doped] - \sum_{i=1}^{N} n_i \Delta \mu_i$$ \hspace{1cm} (2.11)

$$E_f^0[doped] = E[doped] - E[pristine] - \sum_{i=1}^{N} n_i E_i$$ \hspace{1cm} (2.12)

The neutral dopant formation energy is thus a function of $\{\Delta \mu_i\}$ whose values depend on the synthesis conditions. The achievable values of $\{\Delta \mu_i\}$ should be constrained under equilibrium growth conditions. First, precipitation of all single elements should be avoided. Second, the doped structure should remain stable during synthesis. In other words, the decomposed products of the doped structure are not allowed to form. Third, $\{\Delta \mu_i\}$ should be selected such that the pristine structure remains stable.

Chapter 2, in part, is a reprint of the material “Ab Initio Molecular Dynamics Studies of Fast Ion Conductors” as it appears in Computational Materials System Design, Zhuoying Zhu, Zhi
Deng, Iek-Heng Chu, Balachandran Radhakrishnan and Shyue Ping Ong, 2018, Springer, Cham, pp. 147-168. The dissertation author was the primary investigator and author of this book chapter.
Chapter 3. Discovery of Novel Lithium Conductors from Silver Thiophosphates

Ab initio molecular dynamics simulation is a specialized tool with the strength of extraordinary predictive power and accuracy but much more computational costing than classical MD. In this chapter, we develop a scheme using tiered AIMD which costs acceptable computational resources and gives reliable prediction whether a material is likely to exhibit as a superionic conductor. The investigated chemical space is ternary Li–P–S and quaternary Li–M–P–S substituted from silver compounds. The comprehensive evaluations on phase stability, electrochemical stability and ionic conductivity are provided.

3.1 Introduction

All-solid-state rechargeable lithium-ion batteries (ss-LIBs) are a revolutionary architecture for energy storage that holds the promise to be both more energy dense as well as safer than traditional organic-liquid-electrolyte-based lithium-ion batteries. The crucial enabling component in ss-LIBs is the nonflammable lithium superionic conductor solid electrolyte, which must possess a challenging suite of properties, including high Li\(^+\) conductivity, excellent phase stability, electrochemical and mechanical compatibility with the electrodes, and ideally, stability under ambient air.

Thiophosphate lithium superionic conductors have emerged as one of the leading contenders for ss-LIB solid electrolyte applications. For instance, the Li\(_{10}\)GeP\(_2\)S\(_{12}\) (LGPS) family of materials and the Li\(_7\)P\(_3\)S\(_{11}\) glass-ceramic have ionic conductivities exceeding 10
mS/cm, on par or even exceeding that of organic solvent electrolytes. More recently, Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}, which also has the LGPS structure, was reported to have an ionic conductivity as high as 25 mS/cm at room temperature. Besides typically higher ionic conductivities, sulfides have the advantage of being softer than oxides, allowing low porosity and intimate electrode-electrolyte contact to be achieved via cold-pressing techniques.

Despite these advances, the number of known lithium superionic conductors remains relatively few, and existing materials all suffer from various limitations. For instance, Li_{10}GeP_{2}S_{12} is expensive due to the use of Ge, whereas the Sn^{71} and Si^{83,92} substituted analogues tend to form conducting, nonpassivating phases upon contact with the Li anode. Other candidates, such as Li_{7}P_{3}S_{11}, are metastable and tend to form nonpassivating layers with the typical LiCoO_{2} cathode used in today’s LIBs. There is thus an urgent need for the development of novel lithium superionic conductors that can potentially mitigate some of these limitations.

When surveying the space of known lithium thiophosphates, an interesting observation is that many of them have analogues in Ag thiophosphates. For example, Li_{7}P_{3}S_{1} and Li_{3}PS_{4} bear remarkable structural similarity to Ag_{7}P_{3}S_{11} and Ag_{3}PS_{4}, respectively. The highly interesting Li argyrodite superionic conductors with formula Li_{6}PS_{5}X (X = Cl, Br, I) derive their name from the mineral argyrodite (Ag_{8}GeS_{6}), and show promising Li^{+} conductivities of > 1 mS/cm for X = Cl and Br. Many Ag compounds are also known to exhibit extraordinarily high ionic conductivities; for example, α-AgI is perhaps the best known, and one of the first superionic conductors ever discovered.

Inspired by this observation, we have performed a comprehensive screening of the ternary Li–P–S and quaternary Li–M–P–S (where M is a non-redox-active element) chemical spaces for
new lithium superionic conductors using an efficient screening approach based on high-throughput density functional theory (DFT) calculations. The scope of this chapter extends beyond the known Li thiophosphates and includes novel candidates obtained from Li for Ag substitution of Ag thiophosphates. The screening yielded two highly promising candidates, Li$_3$Y(PS$_4$)$_2$ and Li$_5$PS$_4$Cl$_2$, which are predicted to satisfy the necessary combination of excellent phase and electrochemical stability, high Li$^+$ conductivity, and low electronic conductivity. We also show that the conductivity of the more promising Li$_3$Y(PS$_4$)$_2$ material can be further enhanced multifold via aliovalent doping. Finally, we will discuss the relative merits of this new superionic conductor compared to current state-of-the-art superionic conductors.

3.2 Methods

3.2.1 Initial Candidate Selection

The initial pool of candidate lithium superionic conductors was constructed from the following:

1. All known ordered Li–P–S and Li–M–P–S structures from the 2015 version of the Inorganic Crystal Structure Database (ICSD). Only non-redox-active elements were allowed for M.

2. Substitution of Ag with Li on all known ordered Ag–P–S and Ag–M–P–S structures from the ICSD.
Unique structures were identified from the pooled candidates using an in-house structure matching algorithm implemented in the Python Materials Genomics (pymatgen) materials analysis library.\textsuperscript{105}

### 3.2.2 DFT Calculations

All DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP)\textsuperscript{106} within the projector augmented-wave approach.\textsuperscript{107} The exchange-correlation functional and calculation parameters were carefully selected to achieve a balance between computational accuracy and cost for the different types of calculations.

- **Structure Relaxation.** Spin-polarized calculations using the Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation (GGA)\textsuperscript{108} functional were used for all structural relaxations. The convergence parameters, e.g., $k$-point density of at least 1000/(number of atoms in the unit cell) and energy cutoff of 520 eV, were similar to those used in the Materials Project (MP), which have been tested extensively over a broad range of chemistries.\textsuperscript{109}

- **Phase Stability.** The phase stability of a compound was estimated by determining its energy above the convex hull $E_{\text{hull}}$ in the relevant Li–P–S and Li–M–P–S phase diagrams.\textsuperscript{51} Stable compounds have an $E_{\text{hull}}$ of 0, and the higher the value, the more unstable the compound is at 0 K. Apart from the compounds of primary interest in this work, the energies of existing compounds were extracted from MP database\textsuperscript{109} using the Materials Application Programming Interface (API).\textsuperscript{110} To account for overbinding of sulfur in DFT calculations, an energy correction of $-0.66$ eV per S atom for sulfides was applied.\textsuperscript{73}
• **Electrochemical Stability.** The electrochemical stability was assessed using the lithium grand potential phase diagram approach.\(^\text{15}\) In this approximation, Li is treated as the main mobile species and the solid electrolyte/electrode interface can be modeled as an open system with respect to Li. The relevant thermodynamic potential is therefore the grand potential, which can be approximated as \(\phi \approx E - \mu_{Li} N_{Li} \) in which \(E\), \(N_{Li}\) and \(\mu_{Li}\) are DFT total energy, number of lithium atoms in the open system, and lithium chemical potential, respectively. The phase equilibria at the anode and charged cathode can be approximated as the lithium superionic conductor composition at high \(\mu_{Li} = \mu_{Li}^0\) and low \(\mu_{Li} = \mu_{Li}^0 - 5\) eV (\(\mu_{Li}^0\) is the chemical potential of metallic Li), respectively. The limiting value of 5 V is chosen based on typical cutoff voltages (\(> 4.2\) V) in the current LiCoO\(_2\) and other next generation cathodes used in today’s lithium-ion batteries.

• **Ab Initio Molecular Dynamics (AIMD) Simulations.** Automated non-spin-polarized AIMD simulations were performed in an \(NVT\) ensemble at elevated temperatures with a Nose–Hoover thermostat.\(^\text{75,76}\) A smaller plane-wave energy cutoff of 280 eV, a minimal \(\Gamma\)-centered \(1 \times 1 \times 1\) \(k\)-point mesh, and a time step of 2 fs were adopted. The simulation supercell sizes were at least 9 Å along each lattice direction. In line with previous studies,\(^\text{111}\) the simulation cell parameters were fixed at the fully relaxed cell parameters at 0 K. The Li\(^+\) diffusivity was obtained via a linear fit of the mean square displacement (MSD) with time, and Arrhenius plots were constructed from simulations at multiple temperatures to obtain the activation energy \(E_a\) and extrapolated room-temperature self-diffusivity \(D_{300 K}\) and conductivity \(\sigma_{300 K}\).

• **Climbing Image Nudged Elastic Band (CI-NEB) Calculations.** CI-NEB calculations were performed to determine the vacancy migration barriers for the most promising
candidates. Overall charge neutrality was achieved via adding a positive background charge. The forces were converged to within 0.05 eV/Å.

- **Electronic Structure.** Band gap calculations were performed using the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional\textsuperscript{112,113} due to the well-known underestimation of band gaps by semilocal functionals\textsuperscript{114}.

### 3.2.3 Derivation for Short AIMD Estimation

Short AIMD simulations of 60 ps were performed for the quick screening step. The first 10 ps (\(\sim 5,000 \) time steps) was used for heating up as well as for equilibration, and the trajectories from 10 ps to 60 ps were used to estimate the MSD. Based on our previous AIMD calculations, the diffusivities for most known superionic conductors at 800 K are at least 10\textsuperscript{−6} cm\textsuperscript{2}/s. Li\textsuperscript{+} self-diffusivity can be obtained via the following expression:

\[
D = \frac{MSD}{2dt}
\]  

(3.1)

Where \(d\) is the dimensionality factor that equals 3 for 3D crystal structure and MSD is the mean square displacement over a time duration \(t\).

By combining Eq. (3.1) and benchmarking results shown in Figure 3.2, we have set set MSD\textsubscript{800K} > 5 Å\textsuperscript{2} as the baseline diffusivity criterion. Assuming that the diffusivity follows an Arrhenius relationship as Eq. (2.7), combing combining Eq. (3.1) and Eq. (2.7), we can write:

\[
MSD = 2D_0 dt e^{-\frac{E_a}{kT}}
\]  

(3.2)
Let us consider the ratio of MSD at 1200 K and 800 K for the same simulation time period $t$.

\[
\frac{MSD_{1200\text{K}}}{MSD_{800\text{K}}} = e^{-\frac{E_a}{1200\text{K}} - \frac{E_a}{800\text{K}}}
\]

(3.3)

\[
E_a = 2400k \ln \left( \frac{MSD_{1200\text{K}}}{MSD_{800\text{K}}} \right)
\]

(3.4)

For \(\frac{MSD_{1200\text{K}}}{MSD_{800\text{K}}} < 7\), \(E_a < 402\) meV.

### 3.3 Results

#### 3.3.1 Parameterization of Screening Criteria

Figure 3.1 shows a schematic of the high-throughput (HT) screening framework used in this work, which is tiered based on considerations of the relative importance of each property for lithium solid electrolyte applications and the computational cost required to calculate it.

First and foremost, all technologically relevant materials must be synthesizable, i.e., exhibit good phase stability. In this work, we have adopted a cutoff of \(E_{\text{hull}} < 30\) meV/atom, which is based on similar cutoffs adopted in previous HT computational materials screening efforts\(^{115, 116}\) as well as the fact that \(\text{Li}_7\text{P}_3\text{S}_{11}\) and \(\text{Li}_{10}\text{GeP}_2\text{S}_{12}\), both well-known superionic conductors, have been predicted to have an \(E_{\text{hull}}\) of 21–25 meV/atom. Second, a lithium superionic conductor must have a high \(\text{Li}^+\) conductivity at room temperature \(\sigma_{300\text{K}}\). Because of the near unity transference number of lithium superionic conductors, \(\sigma_{300\text{K}}\) exceeding 0.1 mS/cm should suffice for
comparable performance with organic liquid electrolytes, though $\sigma_{300 \text{ K}} > 1 \text{ mS/cm}$ is preferred. However, obtaining converged diffusivity and conductivity numbers from AIMD simulations is a highly computationally demanding process, usually requiring at least hundreds of picoseconds of simulation time ($\sim 50000–100000$ time steps) at multiple temperatures. Because we are interested only in superionic conductors with extremely high diffusivity, we have adopted the following three-step diffusivity screening approach in this work.

**Topological Screening Step.** The first screening step is based purely on topological considerations.\textsuperscript{117,118} Only materials exhibiting >1D diffusion networks with a minimum bottleneck size $r_c$ of 1.75 Å, are considered as suitable candidates for lithium superionic conductors. This cutoff is slightly smaller than the channel size for the Li$_{10}$GeP$_2$S$_{12}$ superionic conductor (1.84 Å). A looser cutoff is used to avoid screening out too many candidates in the first screening step. The topological evaluation was carried out using the open source software Zeo++\textsuperscript{119,120}

**Quick Estimation Step.** Quick estimates of the diffusivity and activation energy were obtained using the mean square displacements (MSDs) obtained from short AIMD simulations of 50 ps at 800 K (MSD$_{800 \text{ K}}$) and 1200 K (MSD$_{1200 \text{ K}}$). Figure 3.2 shows a log–log plot of the MSD$_{1200 \text{ K}}$ versus MSD$_{800 \text{ K}}$ for a wide range of known compounds as well as the materials screened in this work. The known superionic conductors evaluated include an approximate ordered model (Li$_{10}$Si$_{1.5}$P$_{1.5}$S$_{11.5}$Cl$_{0.5}$) for the recently reported Li$_{9.54}$Si$_{1.74}$P$_{1.44}$S$_{11.7}$Cl$_{0.3}$ superionic conductor, which has the LGPS structure and an extraordinarily high conductivity of 25 mS/cm.\textsuperscript{17}

We may observe that all known superionic conductors fall within the white region bounded by MSD$_{800 \text{ K}} > 5$ Å$^2$ and MSD$_{1200 \text{ K}}$/MSD$_{800 \text{ K}} < 7$, and have therefore used these criteria in our screening process. The former criterion ensures a minimum baseline diffusivity, whereas the
second criterion ensures that the activation energy is below $\sim 400$ meV. The relative trends are consistent with the known properties of the conductors, with faster conductors such as $\text{Li}_{10}\text{Si}_{1.5}\text{P}_{1.5}\text{S}_{11.5}\text{Cl}_{0.5}$ exhibiting larger $\text{MSD}_{800 \text{ K}}$ (higher diffusivity at 800 K) and lower $\text{MSD}_{1200 \text{ K}} / \text{MSD}_{800 \text{ K}}$ (lower activation barriers) than slightly poorer conductors such as $\text{Li}_{10}\text{GeP}_{2}\text{S}_{12}$. It should be noted that though $\text{Li}_{7}\text{P}_{3}\text{S}_{11}$ was experimentally reported to have an ionic conductivity of 17 mS/cm,$^{16}$ recent computational work by the authors of this work suggests that the intrinsic conductivity of this material may be as high as 60 mS/cm,$^{15}$ which accounts for its high $\text{MSD}_{800 \text{ K}}$. Also, though $\text{Li}_{3}\text{OCl}_x\text{Br}_{1-x}$ and $\text{Na}_3\text{PS}_4$ were initially reported to be superionic conductors,$^{32,121}$ the pristine crystalline phases have been shown to have low room-temperature conductivities, and higher ionic conductivities are obtained only with the introduction of a large number of defects/dopants (e.g., doped-$\text{Na}_3\text{PS}_4$) and/or via amorphization.$^{80,122,123}$

*Converged Screening Step.* Finally, longer AIMD simulations at six temperatures were performed on the materials that pass the first two screening steps to obtain converged diffusivities (and conductivities) and activation barriers. The above three-step screening process allows us to eliminate rapidly poor candidates with a minimum amount of computational resources, and devote expensive AIMD simulations to obtain converged diffusivity statistics on the most promising materials.

Besides excellent $\text{Li}^+$ conductivity, a solid electrolyte for all-solid-state rechargeable lithium-ion batteries must also be electronically insulating and exhibit good electrochemical stability against the electrodes. An assessment of these properties was carried out for the most promising candidates.

### 3.3.2 Identification of Potential Candidates
Table 3.1 summarizes the phase stability, topological parameters and rapid AIMD screening results of all new Li–P–S and Li–M–P–S candidates. The rapid AIMD screening results are also presented in Figure 3.2 for comparison with known superionic conductors. We note that though we did perform Li for Ag substitution of Ag–P–S compounds, the derived compounds are all well-known compounds such as Li$_7$P$_3$S$_{11}$ and Li$_3$PS$_4$ that have already been extensively explored as lithium superionic conductors, and thus will not be considered further here.

Among the new quaternary compounds, only Li$_3$Y(PS$_4$)$_2$ (LYPS) and Li$_3$PS$_4$Cl$_2$ (LPSCl) satisfy all the initial screening criteria: low $E_{\text{hull}}$, $r_c > 1.75$ Å, MSD$_{800\, \text{K}} > 5$Å$^2$ and MSD$_{1200\, \text{K}}$/MSD$_{800\, \text{K}} < 7$. Their MSD$_{800\, \text{K}}$ are on par with that of the leading LGPS-based candidate, Li$_{10}$Si$_{1.5}$P$_{1.5}$S$_{11.5}$Cl$_{0.5}$, but their MSD$_{1200\, \text{K}}$/MSD$_{800\, \text{K}}$ ratios are slightly higher. Though Li$_{15}$P$_4$S$_{16}$Cl$_3$, LiZnPS$_4$ and LiAl(PS$_3$)$_2$ are also predicted to have fairly low $E_{\text{hull}}$ and reasonably high MSD$_{800\, \text{K}}$, their MSD$_{1200\, \text{K}}$/MSD$_{800\, \text{K}}$ are far too high, indicating high activation barriers. The remaining candidates do not pass either the phase stability criterion or the topological screening. During the preparation of this paper, it has come to our attention that the LiZnPS$_4$ candidate in Table 3.1 has been investigated as a superionic conductor. Our screening calculations show that the stoichiometric LiZnPS$_4$ compound fails the MSD ratio cutoff by a factor of 2, which is consistent with the high activation barriers reported for the stoichiometric compound reported in Richards et al.’s work. A more in-depth comparison of our proposed candidates with known superionic conductors is provided in the Discussion section.

The crystal structures of LYPS and LPSCl are shown in Figure 3.3, and the relaxed lattice parameters are given in Table 3.2. LYPS and LPSCl belong to the monoclinic C2/c and
orthorhombic C2mm space groups, respectively. Both LYPS and LPSCI structures have two symmetrically distinct Li sites, which are labeled as Li1 and Li2 in Figure 3.6 and Figure 3.7.

### 3.3.3 Li⁺ Conductivities and Mechanisms

Long AIMD simulations of at least 200 ps at multiple temperatures were performed on the promising LYPS and LPSCI candidates. Figure 3.4 shows the Arrhenius plot of the diffusivity versus 1000/temperature for the two candidates, and Table 3.3 summarizes the key conductivity properties extracted. The estimated activation energies $E_a$ for LYPS and LPSCI are 278 and 304 meV, respectively. The extrapolated room-temperature conductivities are 2.16 mS/cm for LYPS and 1.85 mS/cm for LPSCI, i.e., both candidates are indeed verified to be lithium superionic conductors.

To understand further the atomistic diffusion mechanisms and pathways, we calculated the Li⁺ probability density function (PDF) and the distinct part of van Hove correlation function from the AIMD simulations of the two candidates at 800 K. CI-NEB calculations were then performed to calculate the vacancy migration barriers in the identified pathways. From Figure 3.5, we observe that both candidates have 3D diffusion networks. Schematics of the identified diffusion pathways and the corresponding calculated CI-NEB migration barriers are given in Figure 3.6 and Figure 3.7 for LYPS and LPSCI, respectively. The plots of the distinct part of van Hove correlation function (see Figure 3.8) indicate that a diffusing Li⁺ is replaced by another Li⁺ within 10 ps, which suggests that the Li⁺ motions are highly concerted in both materials, similar to other well-known lithium superionic conductors such as Li$_7$P$_3$S$_{11}$ and Li$_{10}$GeP$_2$S$_{12}$. 
For LYPS, there are five symmetrically distinct hops between neighboring Li sites, namely, 
A→B, B→F, B→C, C→E and C→H (see Figure 3.6). We may observe that the lowest barrier
percolating pathway in LYPS is A→B→C→D (Li1→Li1→Li2→Li1) with a barrier of 210 meV.
To enable >1D diffusion, the next lowest barrier pathway is G→C→H (all Li2) along the c
direction with an overall barrier of 268 meV. The E→B→F (all Li1) pathway has a much higher
overall barrier of 406 meV, which suggests it is more likely for a vacancy at E to diffuse to B via
the lower barrier E→G→C→B path. The estimated effective 3D vacancy migration barrier
(268 meV) is therefore in good agreement with the activation energy from AIMD simulations (278
meV).

For LPSCl, we may observe that the crystal structure comprises layers of Li1 and Li2 (see
Figure 3.7) in the b-c plane stacked along the a direction. Within each Li1 plane, the vacancy
migration barriers are relatively low (A→B→C→D with overall barrier of 168 meV, and B→
E with barrier of 217 meV). For 3D diffusion, the H→G→F Li1-only path connecting different
Li1 layers has the lowest overall barrier of 321 meV. This is again in reasonably good agreement
with the AIMD activation energy of 304 meV. All other paths involving vacancy hops between
Li1 and Li2 sites have significantly higher barriers (>380 meV).

3.3.4 Electronic Band Gap

Figure 3.9 shows the calculated HSE densities of states for LYPS and LPSCl. Both
candidates are large band gap (>3 eV) insulators. In both candidates, the valence band maximum
is dominated by anion S-p character, whereas the conduction band minimum has contributions
from the framework cations (Y and P) as well as anion S.
The band gap is also an upper limit for the intrinsic stability of the material against reduction (acceptance of an electron) and oxidation (loss of an electron). Similar to other sulfide-based solid-electrolytes, the intrinsic electrochemical stability of the two candidates are limited to \( \sim 3.5 \) eV.

### 3.3.5 Electrochemical Stability

Better estimates of the electrochemical stabilities of LYPS and LPSCl were obtained using the lithium grand potential approach.\(^{54}\) Table 3.4 summarizes the predicted phase equilibria at the solid electrolyte/anode (metallic Li) interface and solid electrolyte/charged 5 V cathode interface. The dominant product at the anode is Li\(_2\)S in all cases, which is a good electronic insulator and reasonable Li conductor, especially as an amorphous interphase. The other products at the anode are YP, a semiconductor with band gap of \( \sim 1 \) eV,\(^{125}\) and Li\(_3\)P. On the solid electrolyte/charged cathode, P\(_2\)S\(_5\) is always predicted to be one of the products. However, the presence of S\(_2\)Cl\(_2\) and PCl\(_5\) at the LPSCl/cathode interface may prove problematic in real-world applications as they undergo hydrolysis readily to form HCl. For reference, the predicted interfacial equilibria in the 0–5 V vs Li/Li\(^+\) for both candidates are given in Figure 3.10, and we note that the observations made above apply for typical cutoff voltages in rechargeable lithium-ion batteries.

For comparison, Table 3.4 also presents the predicted phase equilibria for the Li\(_{10}\)Si\(_{1.5}\)P\(_{1.5}\)S\(_{11.5}\)Cl\(_{0.5}\) model of the recently reported Li\(_{9.54}\)Si\(_{1.74}\)P\(_{1.44}\)S\(_{11.7}\)Cl\(_{0.3}\) superionic conductor as well as Li\(_{10}\)GeP\(_2\)S\(_{12}\) and Li\(_7\)P\(_3\)S\(_{11}\). Similar to the candidates identified in this work, Li\(_2\)S is predicted to be the dominant product at the anode/electrolyte interface in all instances, with the small band gap Li\(_3\)P comprising a relatively small fraction. For Li\(_{10}\)Si\(_{1.5}\)P\(_{1.5}\)S\(_{11.5}\)Cl\(_{0.5}\) and Li\(_{10}\)GeP\(_2\)S\(_{12}\), there is an additional Li\(_{2}\)Si\(_5\) or Li\(_{15}\)Ge\(_4\) phase, which also have a small band gap,
consistent with previous experimental studies.\textsuperscript{94,95} At the cathode/Li\textsubscript{10}Si\textsubscript{1.5}P\textsubscript{1.5}S\textsubscript{11.5}Cl\textsubscript{0.5} interface, S\textsubscript{2}Cl\textsubscript{2} is predicted to be one of the products, though the proportion is much less in comparison to LPSCl due to the much lower content of Cl.

3.4 Discussion

From the results in the preceding sections, Li\textsubscript{3}Y(PS\textsubscript{4})\textsubscript{2} (LYPS) and Li\textsubscript{5}PS\textsubscript{4}Cl\textsubscript{2} (LPSCl) have emerged as promising novel lithium superionic conductors based on a comprehensive screening of the Li–P–S and Li–M–P–S chemical spaces. Both candidates exhibit good phase stability (low $E_{\text{hull}}$) and excellent topological characteristics (>1D large conduction channels) and are predicted to be electronic insulators with high Li\textsuperscript{+} conductivities (exceeding 1 mS/cm). The Li\textsuperscript{+} conduction mechanisms and migration barriers were elucidated using CI-NEB calculations, and the results further confirm the predictions from the AIMD simulations. In addition, both candidates comprise entirely of earth-abundant elements, making them practical from a cost perspective.

Both candidates are derived from the replacement of Ag with Li in known quaternary Ag thiophosphates in the ICSD. We see this as a further positive attribute of the two candidates as ion exchange from the known Ag-based compounds is therefore a potential initial synthesis route that can be explored. For example, ion exchange has similarly been used to synthesize the well-known Li\textsubscript{7}P\textsubscript{3}S\textsubscript{11} superionic conductor from Ag\textsubscript{7}P\textsubscript{3}S\textsubscript{11}.\textsuperscript{98} We speculate that due to the significantly larger ionic radii of Ag (129 pm) compared to Li (90 pm), Li-substituted Ag compounds may present large percolating voids conducive to fast 3D Li mobility. Such a strategy can certainly be expanded beyond just the thiophosphate chemistries that are the focus of this work. However, we would point out that the large ionic radii difference between Ag\textsuperscript{+} and Li\textsuperscript{+} can potentially lead to incompatibility of Li with the Ag-based host framework, which is why a computational assessment
of phase stability is a critical first step to determine the likelihood of synthesis. Also, not all Ag compounds have percolating 3D diffusion networks of sufficient channel size. Here again, the efficient tiered screening approach outlined in this work based on inexpensive topological analysis followed by more computationally intensive first-principles calculations can provide useful guidelines.

Between the two candidates, it is our belief that LYPS is the more promising one. Not only is LYPS predicted to have a marginally higher Li$^+$ conductivity than LPSCl in AIMD simulations, it is also predicted to be significantly more stable ($E_{\text{hull}} = 2$ meV/atom) and its lack of Cl means that there is likely to be fewer issues with reaction products at higher voltages. We will note that like all sulfide-based materials, air and moisture stability may be a potential area of concern, though this limitation has not prevented the development of prototype all-solid-state rechargeable lithium-ion batteries utilizing other sulfide solid electrolytes. Like other sulfides, both materials are predicted to be relatively soft (elastic constants shown in Table 3.6), which should make it easier to achieve low porosity using cold-pressing methods.

### 3.4.1 Further Optimization of LYPS

To explore if further enhancement of the conductivity of LYPS is possible, we performed isolvalent substitutions and aliovalent doping of LYPS. La$^{3+}$ was examined as a potential substitute for Y$^{3+}$ due to its slightly larger ionic radii (117 pm compared to 104 pm for Y$^{3+}$). The computed $E_{\text{hull}}$ for Li$_3$La(PS$_4$)$_2$ is 20 meV, significantly higher than LYPS, and its ionic conductivity is only slightly higher at 3.27 mS/cm with a slightly lower activation energy of 263 meV (see Figure 3.4), which can be attributed to the ∼5% volume expansion and increase in channel size (1.92 Å).
Unlike isovalent substitutions, aliovalent doping can have the additional effect of introducing Li$^+$ vacancies or interstitials. Both Ca$^{2+}$ or Zr$^{4+}$ dopants that have comparable ionic radii to Y$^{3+}$ were explored using a 1 × 1 × 2 supercell of LYPS, with the introduction of Li$^+$ interstitials and vacancies, respectively. Table 3.5 summarizes the dopant formation energies and room-temperature Li$^+$ conductivities for the doped structures. Both Ca$^{2+}$ and Zr$^{4+}$ were found to have reasonably low dopant formation energies of 0.63 and 0.26 eV, respectively. From AIMD simulations, we find that aliovalent doping of LYPS with the introduction of either vacancies or interstitials can lead to multifold increases in its ionic conductivity. Substitution of 12.5% of Y$^{3+}$ with Ca$^{2+}$ and Zr$^{4+}$ leads to extrapolated room temperature conductivities of 7.14 and 5.25 mS/cm, respectively, with corresponding decreases in activation energies to 231 and 241 meV, respectively (see Figure 3.4).

Due to computational cost considerations, our explorations of dopant optimization is limited by the size of the supercell accessible within AIMD simulations. Nevertheless, the doping results are a proof of concept that there is significant scope for further fine-tuning of dopant and Li concentration in LYPS to achieve even higher conductivities, a claim that we hope will be verified by experimental efforts at synthesizing undoped and doped LYPS.

### 3.4.2 Comparison with Other State-of-the-Art Superionic Conductors

In comparison with state-of-the-art sulfide superionic conductors such as Li$_7$P$_3$S$_{11}$, the LGPS family (Li$_{10}$GeP$_2$S$_{12}$ and Li$_{9.54}$Si$_{1.74}$P$_{1.44}$S$_{11.7}$Cl$_{0.3}$), LYPS (undoped or doped) has slightly lower Li$^+$ conductivity. However, bulk ionic conductivity is no longer the critical factor in all-solid-state battery performance beyond 1 mS/cm. Indeed, other properties such as interfacial stability play a far more critical role. For instance, though the Li$_{9.54}$Si$_{1.74}$P$_{1.44}$S$_{11.7}$Cl$_{0.3}$ superionic
conductor recently reported by Kato et al.\textsuperscript{17} has an extraordinarily high room temperature ionic conductivity of 25 mS/cm, its interfacial stability is much poorer than the Li\textsubscript{9.6}P\textsubscript{3}S\textsubscript{12} composition in the same structure, which has a lower conductivity of \(\sim\) 1 mS/cm.\textsuperscript{16} The result is that Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}, which has a voltage of 1.5 V against Li/Li\textsuperscript{+}, had to be used as the anode with Li\textsubscript{9.54}Si\textsubscript{1.74}P\textsubscript{1.44}S\textsubscript{11.7}Cl\textsubscript{0.3}, lowering achievable energy densities due to the low overall operating voltage of \(\sim\) 2.5 V. In contrast, full cell performance at a relatively high operating voltage of up to 4.2 V was demonstrated for Li\textsubscript{9.6}P\textsubscript{3}S\textsubscript{12} with standard graphitic anodes.

LYPS compares favorably to these known superionic conductors in terms of both phase and electrochemical stability. The calculated \(E_{\text{hull}}\) of LYPS is only 2 meV/atom, substantially lower than that of Li\textsubscript{7}P\textsubscript{3}S\textsubscript{11} (21 meV/atom),\textsuperscript{15} Li\textsubscript{10}GeP\textsubscript{2}S\textsubscript{12} (25 meV/atom)\textsuperscript{111} and Li\textsubscript{10}Si\textsubscript{1.5}P\textsubscript{1.5}S\textsubscript{11.5}Cl\textsubscript{0.5} (30 meV/atom). Recently, Richards et al. also reported computational evidence of extraordinarily high Li\textsuperscript{+} conductivities exceeding 50 mS/cm in the Li\textsubscript{1+2x}Zn\textsubscript{1−x}PS\textsubscript{4} solid solution,\textsuperscript{124} a compound that was also considered in our screening. However, these high conductivities were obtained only with the introduction of a large number of defects, requiring high predicted synthesis temperatures exceeding 950 K. In comparison, doped LYPS with conductivities of up to 7 mS/cm still maintains a relatively low \(E_{\text{hull}}\) and small dopant formation energies.

In terms of interfacial stability, there are no reaction products of major concern at the cathode/LYPS interface, unlike Li\textsubscript{10}Si\textsubscript{1.5}P\textsubscript{1.5}S\textsubscript{11.5}Cl\textsubscript{0.5} where the presence of Cl is predicted to result in the formation of S\textsubscript{2}Cl\textsubscript{2}. On the anode/LYPS interface, the presence of the semiconducting YP phase may be of potential concern, though its band gap (\(\sim\) 1 eV)\textsuperscript{125} is still higher than the Li−Si alloys (e.g., band gaps of 0.6 eV for Li\textsubscript{12}Si\textsubscript{7} and 0.08 eV for Li\textsubscript{7}Si\textsubscript{3} ) predicted to form at the anode/Li\textsubscript{10}Si\textsubscript{1.5}P\textsubscript{1.5}S\textsubscript{11.5}Cl\textsubscript{0.5} interface. An electrically insulating interface is desired for passivation to
avoid further propagation of the reaction front. Furthermore, Li–Si alloys are also well-known to undergo significant volume expansion (in excess of 300%) at high lithiation, which may be detrimental to maintaining intimate electrode/electrolyte contact.  

In summary, we speculate that LYPS may present an overall better balance of properties as a lithium superionic conductor solid electrolyte for all-solid-state battery applications. It has clearly better predicted phase stability, and likely better interfacial stability based on the predicted phase equilibria at the electrode/electrolyte interface. Its conductivity, though somewhat lower than some of the state-of-the-art candidates, is sufficiently high that it is not likely to be a limiting factor, and can potentially be further improved with the demonstrated doping strategies.

3.5 Conclusions

To conclude, we have performed a comprehensive screening of the Li–P–S and Li–M–P–S chemical spaces for novel lithium superionic conductors, including candidates obtained by replacing Ag with Li in Ag–P–S and Ag–M–P–S compounds. By combining rapid topological evaluation with a short AIMD screening, a large number of candidates that are unlikely to satisfy the stringent Li+ conductivity requirements are excluded using a minimum amount of computational resources. Li$_3$Y(PS$_4$)$_2$ (LYPS) and Li$_3$PS$_4$Cl$_2$ (LPSCl) emerged as the most promising candidates with good phase and electro-chemical stability, high 3D ionic conductivity and low electronic conductivity. We performed further optimization on LYPS, the more promising of the two candidates, and demonstrate that the Li$^+$ conductivity can be further increased from 2.16 mS/cm to 7.14 and 5.25 mS/cm via 12.5% doping of Y$^{3+}$ with Ca$^{2+}$ and Zr$^{4+}$, respectively. The LYPS framework therefore presents an intriguing candidate ripe for further optimization as a
lithium superionic conductor solid electrolyte for next-generation all-solid-state rechargeable lithium-ion batteries.

Chapter 3, in full, is a reprint of the material “Li$_3$Y(PS$_4$)$_2$ and Li$_5$PS$_4$Cl$_2$: New Lithium Superionic Conductors Predicted from Silver Thiophosphates using Efficiently Tiered \textit{Ab Initio} Molecular Dynamics Simulations” as it appears in Chemistry of Materials, Zhuoying Zhu, Iek-Heng Chu and Shyu Ping Ong, 2017, 2017, 29(6), pp. 2474-2484. The dissertation author was the primary investigator and author of this paper. All calculations and corresponding data analyses were done by the author.
Figure 3.1 Flowchart of the screening procedure for new lithium superionic conductors. M refers to non-redox-active elements. The relative sizes of the arrows indicate the number of candidates remaining after the current screening step.
Figure 3.2 Plot of MSD\textsubscript{1200 K} versus MSD\textsubscript{800 K} for a wide range of known alkali conductors and the new candidates in this work. A log–log scale is used for better resolution across orders of magnitude differences in diffusivity/conductivity. Square markers indicate known materials, which include well-established superionic conductors such as Li\textsubscript{7}P\textsubscript{3}S\textsubscript{11},\textsuperscript{16} the LGPS family\textsuperscript{14,17} (Li\textsubscript{10}SnP\textsubscript{2}S\textsubscript{12},Li\textsubscript{10}GeP\textsubscript{2}S\textsubscript{12},Li\textsubscript{10}SiP\textsubscript{2}S\textsubscript{12},Li\textsubscript{10}Si\textsubscript{1.5}P\textsubscript{1.5}S\textsubscript{11.5}Cl\textsubscript{0.5}), and doped Na\textsubscript{3}PS\textsubscript{4}\textsuperscript{73,123} as well as relatively poorer conductors such as pristine Na\textsubscript{3}PS\textsubscript{4}\textsuperscript{32,73} and Li\textsubscript{3}OCl\textsubscript{x}Br\textsubscript{1-x}\textsuperscript{80,121} Circle markers indicate new candidates screened, with predicted superionic conductors in green and predicted poor conductors in yellow. All superionic conductors fall into the white trapezoid zone, which is bounded by the lines MSD\textsubscript{800 K}=5Å\textsuperscript{2} and MSD\textsubscript{1200 K}/MSD\textsubscript{800 K}=7.
Table 3.1 Energy above Hull \( (E_{\text{hull}}) \), >1D channel size \( (r_c) \), and short AIMD (50 ps) results \( \text{MSD}_{800K} \), \( \text{MSD}_{1200K}/\text{MSD}_{800K} \) of Li thiophosphates studied in the initial screening. \(^a\)

<table>
<thead>
<tr>
<th>Compound ((\text{space group}))</th>
<th>Source ((\text{ICSD number}))</th>
<th>( E_{\text{hull}} ) ((\text{meV/atom}))</th>
<th>( r_c ) ((\text{Å}))</th>
<th>( \text{MSD}_{800K} )</th>
<th>( \text{MSD}<em>{1200K}/\text{MSD}</em>{800K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Promising candidates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Li}_3\text{Y(PS}_4\text{)}_2 ) ((C2/c))</td>
<td>Ag(_3\text{Y(PS}_4\text{)}_2 ) ((417658))</td>
<td>2</td>
<td>1.88</td>
<td>65.1</td>
<td>4.5</td>
</tr>
<tr>
<td>( \text{Li}_3\text{PS}_4\text{Cl}_2 ) ((C2mm))</td>
<td>Ag(_3\text{PS}_3\text{Cl}_2 ) ((416587))</td>
<td>17</td>
<td>1.76</td>
<td>77.9</td>
<td>3.1</td>
</tr>
<tr>
<td><strong>Candidates failing at least one screening criteria</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Li}_{15}\text{P}<em>4\text{S}</em>{16}\text{Cl}_3 ) ((I\bar{4}3d))</td>
<td>Ag(_{15}\text{P}<em>4\text{S}</em>{16}\text{Cl}_3 ) ((416586))</td>
<td>8</td>
<td>1.76</td>
<td><strong>2.2</strong></td>
<td><strong>145.1</strong></td>
</tr>
<tr>
<td>( \text{LiZnPS}_4 ) ((I\bar{4}))</td>
<td>ICSD ((95785))</td>
<td>0</td>
<td>1.83</td>
<td>24.7</td>
<td>13.9</td>
</tr>
<tr>
<td>( \text{LiAl(PS}_3\text{)}_2 ) ((C2/c))</td>
<td>ICSD ((425979))</td>
<td>0</td>
<td>1.82</td>
<td>27.8</td>
<td><strong>16.5</strong></td>
</tr>
<tr>
<td>( \text{Li}_2\text{Zn(PS}_3\text{)}_2 ) ((C2/c))</td>
<td>Ag(_2\text{Zn(PS}_3\text{)}_2 ) ((72719))</td>
<td>33</td>
<td>1.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{LiIn(PS}_3\text{)}_2 ) ((P\bar{3}1c))</td>
<td>Ag(_\text{In(PS}_3\text{)}_2 ) ((202185))</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{LiZnPS}_4 ) ((Pna2_1))</td>
<td>Ag(_\text{ZnPS}_4 ) ((48197))</td>
<td>16</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Measures in which various candidates fail one of the screening criteria are bolded.
Figure 3.3 Crystal structures (conventional cell) of the identified Li superionic conductor candidates, (a) Li₃Y(PS₄)₂ and (b) Li₅PS₄Cl₂. Purple tetrahedra, PS₄; dark green octahedra, YS₆; green spheres, Li; yellow spheres, S; red spheres, Cl.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atoms/cell</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (deg)</th>
<th>β (deg)</th>
<th>γ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₃Y(PS₄)₂</td>
<td>56</td>
<td>17.122</td>
<td>9.290</td>
<td>9.137</td>
<td>90.0</td>
<td>122.3</td>
<td>90.0</td>
</tr>
<tr>
<td>Li₅PS₄Cl₂</td>
<td>24</td>
<td>7.212</td>
<td>10.494</td>
<td>6.024</td>
<td>90.0</td>
<td>90.0</td>
<td>90.0</td>
</tr>
</tbody>
</table>
Figure 3.4 Arrhenius plots of promising lithium superionic conductor candidates from AIMD simulations.

Solid lines indicate the initial Li$_3$Y(PS$_4$)$_2$ and Li$_5$PS$_4$Cl$_2$ candidates. Dashed lines indicate the further optimized candidates obtained via aliovalent doping or substitution of Li$_3$Y(PS$_4$)$_2$ (Li$_3$La(PS$_4$)$_2$, Li$_3$.125Y$_{0.875}$Ca$_{0.125}$(PS$_4$)$_2$ and Li$_2$.875Y$_{0.875}$Zr$_{0.125}$(PS$_4$)$_2$).

Table 3.3 Li$^+$ ionic conductivity ($\sigma_{300K}$) and diffusivity ($D_{300K}$) at 300 K, error Range of $\sigma_{300K}$ and activation energy ($E_a$) for Li$_3$Y(PS$_4$)$_2$ and Li$_5$PS$_4$Cl$_2$ from AIMD simulations.

<table>
<thead>
<tr>
<th>Formula</th>
<th>$\sigma_{300K}$ (mS/cm)</th>
<th>Error range of $\sigma_{300K}$</th>
<th>$E_a$ (meV)</th>
<th>$D_{300K}$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_3$Y(PS$_4$)$_2$</td>
<td>2.16</td>
<td>[1.46, 3.19]</td>
<td>278</td>
<td>3.56×10$^{-8}$</td>
</tr>
<tr>
<td>Li$_5$PS$_4$Cl$_2$</td>
<td>1.85</td>
<td>[1.38, 2.47]</td>
<td>304</td>
<td>1.36×10$^{-8}$</td>
</tr>
</tbody>
</table>
Figure 3.5 Isosurfaces of Li$^+$ probability density distribution $P$ (light blue) for Li$_3$Y(PS$_4$)$_2$ and Li$_5$PS$_4$Cl$_2$ from AIMD simulations at 800K with $P = 0.0001$ a$_0^{-3}$ (a$_0$ is the Bohr radius).
Figure 3.6 Investigated Li vacancy diffusion paths in Li₃Y(PS₄)₂ viewed along b direction. Symmetrically distinct Li1 and Li2 are represented by green and blue spheres, respectively. Celadon polyhedra and gray tetrahedra indicate YS₆ and PS₄. (b–d) Calculated CI-NEB migration barriers for selected percolating paths.
Figure 3.7 Investigated Li vacancy diffusion paths in Li₅PS₄Cl₂ viewed along (a) \( a \) direction; (b) \( b \) direction. Green, blue, red spheres represent Li₁, Li₂ and Cl atoms, respectively. Gray tetrahedra are PS₄ tetrahedra. (c−e) Calculated CI-NEB migration barriers for selected paths.
Figure 3.8 Plots of distinct part of the van Hove correlation function (Gd) for (a) Li$_3$Y(PS$_4$)$_2$ and (b) Li$_5$PS$_4$Cl$_2$ at 800 K. The emergence of the pronounced peak near $r = 0$ within 10 ps provides an estimate of the time scale at which a diffusing atom is replaced by another.
Figure 3.9 Calculated element-projected density of states for (a) Li$_3$Y(PS$_4$)$_2$ (band gap $E_g = 3.41$ eV) and (b) Li$_5$PS$_4$Cl$_2$ ($E_g = 3.57$ eV) using the HSE screened hybrid functional.
Figure 3.10 Li grand potential phase stability plots for Li$_3$Y(PS$_4$)$_2$ and Li$_5$PS$_4$Cl$_2$ solid electrolytes. At low voltage, Li$_3$Y(PS$_4$)$_2$ and Li$_5$PS$_4$Cl$_2$ undergo reduction process and uptake Li whereas at high voltage, they are oxidized and lose Li. Text in the plot indicates predicted phase equilibria at corresponding regions.
Table 3.4 Phase equilibria for the Li$_3$Y(PS$_4$)$_2$ and Li$_3$PS$_4$Cl$_2$ candidates as well as other known superionic conductors at 5 V cathode and metallic Li anode.$^a$

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Phase equilibria at 5 V cathode</th>
<th>Phase equilibria at anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_3$Y(PS$_4$)$_2$</td>
<td>YPS$_4$ + 0.5 P$_2$S$_5$ + 1.5 S</td>
<td>YP + Li$_3$P + 8 Li$_2$S</td>
</tr>
<tr>
<td>Li$_3$PS$_4$Cl$_2$</td>
<td>0.067 PCl$_5$ + 0.833 S$_2$Cl$_2$ + 0.467</td>
<td>Li$_3$P + 4 Li$_2$S + 2 LiCl</td>
</tr>
</tbody>
</table>

Promising candidates

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Phase equilibria at 5 V cathode</th>
<th>Phase equilibria at anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>{10}$Si$</em>{1.5}$P$<em>{1.5}$S$</em>{11.5}$Cl$_{0.5}$</td>
<td>0.75 P$_2$S$_7$ + 0.25 S$_2$Cl$_2$ + 1.5 SiS$_2$ + 2.75 S</td>
<td>1.5 Li$_3$P + 0.3 Li$_2$Si$_5$ + 0.5 LiCl + 11.5 Li$_2$S</td>
</tr>
<tr>
<td>Li$_{10}$GeP$<em>2$S$</em>{12}$</td>
<td>P$_2$S$_5$ + GeS$_2$ + 5 S</td>
<td>2 Li$<em>3$P + 0.25 Li$</em>{15}$Ge$_4$ + 12</td>
</tr>
<tr>
<td>Li$_7$P$<em>3$S$</em>{11}$</td>
<td>1.5 P$_2$S$_5$ + 3.5 S</td>
<td>3 Li$_3$P + 11 Li$_2$S</td>
</tr>
</tbody>
</table>

Known superionic conductors

$^a$Coefficients given per formula unit of solid electrolyte.
Table 3.5 Calculated dopant formation energy ($E_f$), energy above hull ($E_{\text{hull}}$), and room-temperature Li$^+$ ionic conductivity ($\sigma_{300\text{K}}$) and activation energy ($E_a$) for aliovalent doped Li$_3$Y(PS$_4$)$_2$.

<table>
<thead>
<tr>
<th>Dopa</th>
<th>Formula</th>
<th>$E_f$ (eV)</th>
<th>$E_{\text{hull}}$ (meV/atom)</th>
<th>$\sigma_{300\text{K}}$ (mS/cm)</th>
<th>Error range of $\sigma_{300\text{K}}$ (mS/cm)</th>
<th>$E_a$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>Li$<em>{3.125}$Y$</em>{0.875}$Ca$_{0.125}$(PS$_4$)$_2$</td>
<td>0.63</td>
<td>6</td>
<td>7.14</td>
<td>[4.67, 10.92]</td>
<td>231</td>
</tr>
<tr>
<td>Zr</td>
<td>Li$<em>{2.875}$Y$</em>{0.875}$Zr$_{0.125}$(PS$_4$)$_2$</td>
<td>0.26</td>
<td>4</td>
<td>5.25</td>
<td>[3.77, 7.31]</td>
<td>241</td>
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</tbody>
</table>

Table 3.6 Elastic constants for Li$_3$Y(PS$_4$)$_2$ and Li$_5$PS$_4$Cl$_2$ using PBE functional.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Bulk modulus (GPa)</th>
<th>Shear modulus (GPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_3$Y(PS$_4$)$_2$</td>
<td>27.0</td>
<td>9.7</td>
<td>26.0</td>
<td>0.34</td>
</tr>
<tr>
<td>Li$_5$PS$_4$Cl$_2$</td>
<td>30.1</td>
<td>13.6</td>
<td>35.4</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Chapter 4. Dopants and Functional Defects for Fast Na$^+$ Conduction in Na$_3$PS$_4$ Superionic Conductor

In this chapter, we present our investigations of dopants and defects on Na$_3$PS$_4$ material. We design the optimization strategy from two sides: M$^{4+}$ cation doping (introducing Na$^+$ interstitials) and Cl$^-$ doping (introducing Na vacancy). We firstly discuss how Na$^+$ excess enhances the Na$^+$ conductivity in c-Na$_3$PS$_4$ by several orders of magnitude higher than tetragonal phase and provide an evaluation of M$^{4+}$ dopant effect. Then we present our work on DFT-guided halide doping in t-Na$_3$PS$_4$ to improve both conductivity and electrochemical stability. Our prediction is successfully verified by experimental results and Cl-doped t-Na$_3$PS$_4$ is implemented into the full cell to deliver 80 mAhg$^{-1}$ at the current density of C/10. Finally, we tune functional defects in Cl-doped t-Na$_3$PS$_4$ and use tracer-exchange NMR method to determine the ion transport pathways. A joint experimental and computational study is given to elucidate how functional defects (Cl, Na vacancy) promote Na-ion transport.

4.1 Role of Na$^+$ Interstitials and M$^{4+}$ Cation Dopants in Cubic Na$_3$PS$_4$

4.1.1 Introduction

Rechargeable Na-ion batteries have enjoyed a resurgence of interest in recent years, propelled in part by concerns about the global availability of lithium, and also by the exciting possibility of novel chemistries. Though significant advances have been made in the development
of Na-ion cathodes and anodes, a major impediment to the commercial viability of rechargeable Na-ion batteries is the lack of an effective electrolyte. Current Na-ion electrolytes are mostly based on the same fundamental chemistry as Li-ion electrolytes, a mixture of cyclic and linear organic carbonates with a Na-salt. Such organic solvent-based liquid electrolytes are flammable and have limited electrochemical windows.

A promising alternative architecture is all-solid-state Na-ion battery utilizing nonflammable ceramic Na superionic conductor electrolytes. Na solid electrolytes such as β-alumina and NAtrium Superionic CONductors (NASICON) are wellstudied, but they typically exhibit reasonable ionic conductivities only at higher temperatures.

An exciting recent development is the discovery of the cubic phase of Na$_3$PS$_4$ (c-Na$_3$PS$_4$, space group: $I\bar{4}3m$) in 2012. Initially reported to have a Na$^+$ conductivity of 0.2 mS/cm, Hayashi and co-workers were able to subsequently enhance the conductivity of c- Na$_3$PS$_4$ to 0.46 mS/cm using crystalline Na$_2$S with high purity of over 99% followed by heat treatment. Further efforts at optimizing the conductivity within the $(1-x)$Na$_3$PS$_4$:xNa$_4$SiS$_4$ pseudobinary system yield a maximum ionic conductivity as high as 0.74 mS/cm at x around 0.06. Recent first-principles work also shows that Na$_3$PS$_4$ is likely to have favorable elastic properties that allow good electrode contact to be achieved with cold-press sintering.

c-Na$_3$PS$_4$ is therefore a promising solid electrolyte candidate, particularly if its ionic conductivity is further improved with proper doping strategies. Using first-principles computational methods, one can rapidly investigate the microscopic mechanisms of diffusion in c-Na$_3$PS$_4$ and the effect of doping on its overall conductivity. The insights gained from such an
exercise would not only guide further optimization, but also provide important insights for design of other novel Na superionic conductors.

In this work, we performed a first-principles investigation of the phase stability and Na\textsuperscript{+} ionic transport in undoped and M\textsuperscript{4+}-doped (M = Si, Ge, and Sn) c-Na\textsubscript{3}PS\textsubscript{4}. We demonstrate that pristine c-Na\textsubscript{3}PS\textsubscript{4} is in fact an extremely poor ionic conductor, but with the introduction of Na\textsuperscript{+} interstitials, a reasonably high conductivity can be achieved. We further demonstrate that 6.25% doping of Si\textsuperscript{4+} for P\textsuperscript{5+} with the concomitant introduction of compensating Na\textsuperscript{+} interstitials result in Na\textsubscript{3+x}Si\textsubscript{x}P\textsubscript{1−x}S\textsubscript{4} with predicted Na\textsuperscript{+} conductivities that are in excellent agreement with previous experimental results. Furthermore, we show that increased Si\textsuperscript{4+} doping (from x = 0.0625 to 0.125) and Sn\textsuperscript{4+} doping can potentially achieve even higher conductivities.

4.1.2 Methods

All calculations were performed with the Vienna Ab initio Simulation Package (VASP),\textsuperscript{106} within the projector augmented wave (PAW) approach.\textsuperscript{107} The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA)\textsuperscript{108} was adopted for the exchange correlation functional. Other parameters such as kinetic energy cutoff, \textit{k}-mesh were carefully chosen under different situations to ensure the convergence of energies while keeping the computational cost reasonable, as detailed in the subsections below. The Python Materials Genomics (pymatgen) materials analysis library\textsuperscript{105} was used for all analyses.

**Phase Stability.** Cubic Na\textsubscript{3}PS\textsubscript{4} (\textit{I}\textsubscript{4}3\textit{m}) has two symmetrically distinct Na sites: the 6\textit{b} site (Na\textsubscript{1}) with a partial occupancy of 0.8, and the 12\textit{d} site (Na\textsubscript{2}) with a partial occupancy of 0.1 (Figure 4.1a).\textsuperscript{136} Structural optimizations were carried out on all symmetrically distinct orderings
of the primitive cell enumerated using the algorithm of Hart et al.\textsuperscript{137} We then selected the lowest energy configuration in subsequent calculations.

We also studied Na\textsubscript{3+x}M\textsubscript{x}P\textsubscript{1−x}S\textsubscript{4} with M = Si, Ge, and Sn. Since the maximum ionic conductivity reported by Hayashi et al.\textsuperscript{33,136} was achieved with Si/P ratio equal to 6:94, an initial value of x = 0.0625 was chosen to mimic the reported dopant concentration. The doped systems were constructed using a 2×2×2 supercell of the conventional unit cell of c-Na\textsubscript{3}PS\textsubscript{4}, in which one P\textsuperscript{5+} is replaced by M\textsuperscript{4+} (Si, Ge, or Sn) and a Na\textsuperscript{+} added to maintain overall charge neutrality. For M = Si, we also studied the effect of dopant concentration by doubling x to 0.125 with corresponding increase in Na\textsuperscript{+} concentration.

The calculation parameters used (spin-polarized, kinetic energy cutoff of 520 eV and k-point density of 1000 per atom) are consistent with those used in the Materials Project (MP).\textsuperscript{109} The phase stabilities of c-Na\textsubscript{3}PS\textsubscript{4} and Na\textsubscript{3+x}M\textsubscript{x}P\textsubscript{1−x}S\textsubscript{4} were investigated by constructing the Na–M–P–S phase diagrams\textsuperscript{51} using precomputed energies of existing Na\textsubscript{x}P\textsubscript{y}S\textsubscript{z} and Na\textsubscript{w}M\textsubscript{x}P\textsubscript{y}S\textsubscript{z} compounds in the MP database extracted via the Materials Application Programming Interface.\textsuperscript{110} To ensure a good coverage of the Na–P–S chemical space, we also performed S for O substitution of all Na–P–O and Na for Li substitution of all Li–P–S compounds and included the Na\textsubscript{4}P\textsubscript{2}S\textsubscript{6} and Na\textsubscript{2}P\textsubscript{2}S\textsubscript{6} structures that were reported recently.\textsuperscript{104,138}

For all materials of interest, we computed the decomposition energy (also known as the energy above hull), \( E_{\text{decomp}} \), of each phase of interest to the most stable linear combination of equilibrium phases in the Na–P–S or Na–M–P–S phase diagram. Stable phases would have an \( E_{\text{decomp}} \) of 0, while the higher the \( E_{\text{decomp}} \), the more unstable a phase is.
Correction for Sulfur. In our investigations, we found that the binding energy of ground state sulfur (monoclinic S$_8$) is significantly overestimated by the PBE functional, similar to the well-known overbinding observed for the O$_2$ molecule.$^{139}$ Following a similar methodology as that proposed by Wang et al., we have fitted a correction for sulfur using the formation energies of main group sulfides (see Figure 4.2). This correction, which corrects for both the overbinding as well as the incomplete self-interaction error cancellation in going from S$_8$ to S$^{2-}$, is estimated to be -0.66 eV per S atom and is applied to all subsequent analyses. This correction will be incorporated into the Materials Project to improve predicted sulfide formation energies.

Dopant Formation Energy. Neutral dopant formation energies were calculated using the formalism presented by Wei et al.$^{85}$

$$E_f[M] = E_{tot}[M] - E_{tot}[bulk] - \sum_{i=1}^{N} n_i \mu_i$$

(4.1)

where $E_{tot}[M]$ and $E_{tot}[bulk]$ are the total energies of the structure with and without the neutral dopant M, respectively; $\mu_i$ is the atomic chemical potential of species i that varies based on different experimental conditions; $n_i$ indicates the number of atoms of species i being added ($n_i > 0$) or removed ($n_i < 0$) from the pristine structure. $\mu_i$ can further be decomposed as $\mu_i = E_i + \Delta \mu_i$, where $\Delta \mu_i$ is the chemical potential of species i referenced to the elemental solid/gas with energy $E_i$. In the case of Na$_{3+x}$M$_x$P$_{1-x}$S$_4$ with M = Si, Ge, and Sn, and x = 0.0625, the formation of the defect structure involves an addition of the dopant M$^{4+}$ and a Na$^+$ interstitial, together with the removal of a host P$^{5+}$ ion. The corresponding formation energy $E_f$ can be expressed as follows:
\[ E_f[M] = E_f^0[M] - \Delta \mu_M - \Delta \mu_{Na} + \Delta \mu_P \] (4.2)

\[ E_f^0[M] = E_{tot}[M] - E_{tot}[\text{bulk}] - E_M - E_{Na} + E_P \] (4.3)

Additional constraints can be applied to the atomic chemical potentials \( \mu_i \) under equilibrium growth conditions. First, to avoid precipitation of the elemental M, Na, P, and S, \( \Delta \mu_i \leq 0 \). Second, to maintain a stable c-Na\(_3\)PS\(_4\) framework structure during synthesis

\[ E_f[Na_3PS_4] = 3\Delta \mu_{Na} + \Delta \mu_P + 4\Delta \mu_S \] (4.4)

where \( E_f[Na_3PS_4] \) is the formation energy of the pristine c-Na\(_3\)PS\(_4\) per formula unit (f.u.). Third, possible secondary phases formed between the dopant M and the framework structure are to be avoided as well. In the case of Na\(_{3+x}\)Si\(_x\)P\(_{1-x}\)S\(_4\) with \( x = 0.0625 \), for example, the formation of the possible secondary phase Na\(_4\)SiS\(_4\), as indicated in Table 4.1, should be avoided. This leads to the following inequality:

\[ 4\Delta \mu_{Na} + \Delta \mu_{Si} + 4\Delta \mu_S \leq E_f[Na_4SiS_4] \] (4.5)

where \( E_f[Na_4SiS_4] \) is the formation energy of Na\(_4\)SiS\(_4\).

The lower bound of the dopant formation energy can be directly estimated using the above formalism and is equal to \( E_{\text{decomp}}[M] - E_{\text{decomp}}[\text{bulk}] \) where \( E_{\text{decomp}}[M] \) and \( E_{\text{decomp}}[\text{bulk}] \) are, respectively, the decomposition energies of the M-doped and pristine c-Na\(_3\)PS\(_4\). Unless
mentioned explicitly, the calculated dopant energies presented in the next section refer to this lower bound.

**Ab Initio Molecular Dynamics Simulations.** The diffusivities and conductivities of the pristine and doped c-Na$_3$PS$_4$ structures were calculated using ab initio molecular dynamics (AIMD) simulations. Apart from the aforementioned doped structures, defect structure where a single Na$^+$ excess is introduced was also studied by removing an electron with a compensating background charge. In all simulations, the lowest energy configurations with a unit cell size equivalent to that of the $2 \times 2 \times 2$ c-Na$_3$PS$_4$ were selected.

Similar AIMD simulation parameters were used as per previous work by the authors. Non-spin-polarized AIMD simulations were conducted in the $NVT$ ensemble at 800–1400 K with a Nose–Hoover thermostat. A smaller plane-wave energy cutoff of 280 eV and a minimal Γ-centered $1 \times 1 \times 1$ $k$-point mesh were adopted. The time step of the simulations was 2 fs. The initial structure was fully relaxed at 0 K, and the volume was fixed for AIMD simulations at elevated temperatures until the diffusivity is converged. No framework melting was observed in all simulations. All calculations were automated using an in-house AIMD workflow. The central quantity obtained from each AIMD simulation is the Na ion diffusivity that can be expressed as

\[
D = \frac{1}{2d t} < [\Delta r(t)]^2 > \tag{4.6}
\]

where $d$ is the dimensionality factor and equals 3 for 3-D crystal structures, and $< [\Delta r(t)]^2 >$ is the average mean square displacement (MSD) over a time duration $t$. 
The diffusivity was obtained by performing a linear fitting of the MSD vs $2dt$. The Arrhenius plots were constructed to determine the activation energies and obtain extrapolated room-temperature diffusivities $D_{300\,K}$. The room-temperature Na ion conductivity $\sigma_{300\,K}$ can then be derived from the Nernst–Einstein equation as follows:

$$\sigma_{300\,K} = \frac{\rho z^2 F^2}{RT} D_{300\,K}$$  \hspace{1cm} (4.7)

where $\rho$ is the molar density of diffusing Na in the unit cell; $z = +1$ is the charge of Na ions; and $F$ and $R$ are the Faraday constant and $R$ is gas constant, respectively. $T = 300\,K$ was used in the above equation. It should be noted that the Nernst–Einstein relation applies only for uncorrelated species diffusion. The implication of correlated motion will be discussed in the Discussion section (4.1.4).

**van Hove Correlation Function Analysis.** To investigate the correlations in the Na ionic motions, we calculated and plotted the van Hove correlation function using trajectories from our AIMD simulations, which can be split into the self-part $G_s$ and the distinct part $G_d$ as Eq.(2.8) and Eq.(2.9).

### 4.1.3 Results

**Phase Stability Analysis.** c-Na$_3$PS$_4$ belongs to the $I\bar{4}3m$ space group with a lattice parameter of $6.9965(9)\,\text{Å}$.\textsuperscript{136} It is the high-temperature phase of the tetragonal Na$_3$PS$_4$ (t-Na$_3$PS$_4$). The lattice parameters for t- and c-Na$_3$PS$_4$ differ only by around $0.1\,\text{Å}$, and the experimental transition temperature from t-Na$_3$PS$_4$ to c-Na$_3$PS$_4$ is around $540\,K$.\textsuperscript{142} The major difference is that the tetragonal phase is an ordered structure, whereas the cubic phase is disordered with two distinct sodium sites.
The $E_{\text{decomp}}$ and the corresponding equilibrium phases for the undoped and doped c-Na$_3$PS$_4$ phases are listed in Table 4.1. For the undoped c-Na$_3$PS$_4$, our calculation predicts its $E_{\text{decomp}}$ to be only 5 meV/atom, with t-Na$_3$PS$_4$ being the stable phase. This result is consistent with previous experimental data that the cubic phase is the metastable phase that is likely entropically stabilized. With the introduction of a Na$^+$ interstitial, we find that the Na sites redistribute to maintain an approximately even distribution within a chain, leading to Na atoms that are slightly displaced from the Na1 and Na2 positions (Figure 4.1b).

Our results show that at $x = 0.0625$, the E decomp of the M$^{4+}$ doped structures are 13 meV/atom for M = Si and Ge, and 15 meV/atom for Sn, respectively. The relatively low decomposition energies indicate that though these doped structures are metastable at 0 K, they can potentially be stabilized at room temperature by entropic effects. This is in qualitative agreement with the synthesizibility of Si-doped Na$_3$PS$_4$ with similar dopant concentration in experiments. At a higher Si dopant concentration with $x = 0.125$, the resulting E decomp increases to 30 meV/atom, indicating that the structure is more unstable. For Si, Sn-doped structures, the predicted equilibrium phases are t-Na$_3$PS$_4$ and Na$_4$MS$_4$ (M = Si, Sn), while the Ge-doped structure has the equilibrium phases of Na$_6$Ge$_2$S$_7$, Na$_2$S, and t-Na$_3$PS$_4$. Note that the sulfur energy correction does not affect the decomposition products in the systems studied in this work. This is because the t-Na$_3$PS$_4$ and Na$_4$SiS$_4$ remain stable before and after the sulfide correction.

**Dopant Formation Energies.** The dopant formation energy is an important quantity that measures the synthesizibility of the materials with dopants. The dopant formation energies of all dopants studied are tabulated in Table 4.1. At $x = 0.0625$, we find relatively low doping energies of 1.04 eV for both 6.25% Ge and Si doping compared to 6.25% Sn doping (1.32 eV) or 12.5% Si.
doping (1.65 eV). We note that Si doping in c-Na$_3$PS$_4$ was experimentally achieved for x up to 0.1. Since the dopant formation energy of 6.25% Sn lies between the dopant formation energies of 6.25% and 12.5% Si doping, we expect that 6.25% Sn-doping of c-Na$_3$PS$_4$ to be achievable experimentally.

**Probability Density and Site Occupancy.** The probability density distribution defined on a uniform 3D grid, namely, $P(r)$, is a powerful tool for investigating the ion diffusion of a given species. Two important pieces of information can be obtained from the distribution: (1) high probability sites where the ions tend to reside, which correspond to the low-energy sites in the structure, (2) the pathways of the ions among the low-energy sites. In this work, $P$ is obtained by first counting the number of Na ions at each point in the spatial uniform grid within a given time scale. A time averaging is then performed for $P$. Also, $P$ is normalized such that $\int P d\Omega = 1$ with $\Omega$ being the volume of the unit cell. We define the maximum of $P(r)$ as $P_{\text{max}}$.

Figure 4.3 shows the isosurfaces of probability density distributions for Na ions in Na$_{3+x}$Si$_x$P$_{1-x}$S$_4$ (x = 0.0625) at 800 K (the lowest temperature at which the AIMD simulations were performed) at various cutoffs. In general, the $P(r)$ are fairly similar across all systems investigated. As expected, we find that the high probability density positions correspond to the high occupancy (low energy) Na1 sites. As the cutoff is decreased, the isosurfaces show that the Na1 sites are connected to one another via the lower occupancy Na2 sites. We may therefore surmise that the Na2 sites are local minima sites with non-negligible occupation probability that help mediate Na$^+$ transport in this structure.

We also calculated the average site occupancies of the different Na sites at 800 K. The site occupancies for the Na1 and Na2 sites for the Na$_{3+x}$Si$_x$P$_{1-x}$S$_4$ (x = 0.0625) are 0.76 and 0.13,
respectively, which are fairly close to the reported site occupancies of 0.8 and 0.11, respectively. The deviations between the calculated occupancies and experiments are likely due to the fact that the AIMD simulations are carried out at higher temperatures (800 K) compared to experiments (300 K). Similar trends are observed for Ge-doped, Sn-doped, and Na-excess c-Na$_3$PS$_4$ (see Table 4.2). For the pristine c- Na$_3$PS$_4$, the average site occupancy for Na2 is less than 0.1 even at 800 K.

**Na$^+$ Conductivity.** Figure 4.4 shows the Arrhenius plots of the log of the diffusivity, $D$, versus the reciprocal of the temperature, 1000/$T$, for the systems of interest. Diffusivities at six temperatures (800, 900, 1000, 1100, 1200, and 1400K) are plotted for all systems except for pristine c-Na$_3$PS$_4$ where simulations at only four temperatures were run. Table 4.3 summarizes the extrapolated diffusivities $D_{300K}$ and ionic conductivities $\sigma_{300K}$, including the error range for $\sigma_{300K}$.

From Figure 4.4a, we may observe that the calculated Na$^+$ conductivity is extremely low ($1.1 \times 10^{-4}$ mS/cm) and the activation barrier is extremely high (537 meV) in the pristine c-Na$_3$PS$_4$ material. The introduction of a Na$^+$ interstitial increases the conductivity by 4 orders of magnitude to 1.06 mS/cm, while the activation energy decreases to 256 meV.

In practical materials, aliovalent doping is a common approach to modifying the Na concentration. In c-Na$_3$PS$_4$, Na$^+$ interstitials can be created by doping the P$^{5+}$ sites with M$^{4+}$ cations such as Sn$^{4+}$, Ge$^{4+}$, and Si$^{4+}$. The Arrhenius plots for doped Na$_{3+x}$M$_x$P$_{1-x}$S$_4$ with different values of M and x are given in Figure 4.4b, and the corresponding room-temperature conductivities and activation energies are reported in Table 4.3 as well. In general, we observe that similar Na$^+$ concentrations tend to result in similar conductivities (e.g., for $x = 0.0625$ in the Na-excess, Si-doped, and Ge-doped cases), indicating that this is the dominant factor influencing the overall ionic conductivity. The predicted room-temperature Na$^+$ conductivity for Na$_{3.0625}$Si$_{0.0625}$P$_{0.9375}$S$_4$ is 1.66
mS/cm, in excellent agreement with the previously measured experimental value of 0.74 mS/cm for 0.94 Na₃PS₄·0.06Na₄SiS₄.³³,¹³⁶

Remarkably, the Sn-doped c-Na₃PS₄ is predicted to have a significantly higher Na⁺ conductivity of 10.7 mS/cm compared to the other doped structures. The activation energy for diffusion in this material is also the smallest at 171 meV. We also investigated the effect of different dopant concentrations in the case of the Si-doped structure. From Figure 4.4b and Table 4.3 we may observe that higher doping concentrations can potentially enhance the Na⁺ conductivity further to 2.99 mS/cm, though at the cost of increased dopant formation energy and decreased phase stability (see Table 4.1).

**Channel Size, Channel Volume, and van Hove Function.** Using the open source Zeo++ software,¹¹⁹,¹⁴³ we performed a topological analysis of all systems of interest. In all these materials, Na ions were removed from the relaxed structures to compute the largest radius of the free sphere that can pass through the remaining structure formed by framework cations and anions (P⁵⁺, S²⁻, and M⁴⁺), which is defined as “channel size” and shown in Table 4.3. In general, the channel sizes for all cases are very similar to the difference of no more than 0.03 Å. At a dopant concentration of x = 6.25%, both Ge and Sn-doped structures have the largest channel sizes.

Using the ionic trajectories from AIMD simulations at 800 K, we also calculated the average channel volumes of all systems investigated. This quantity is defined as the unit cell volume minus the volume of the framework polyhedrons (PS₄ or MS₄), and it describes the “free volume” for Na ions during the diffusion. The results are given in Table 4.3. We find that the channel volumes in all doped structures are very similar to each other, with the exception of Sn-
doped structure where the channel volume is more than 4% higher than those in the rest of the cases.

Figure 4.5 presents the distinct part of the van Hove correlation function $G_d$ for each doped structure at 800 K. Our calculations show that $G_d$ of all the doped structures always exhibit a pronounced peak at the proximity of $r = 0$, indicating that the Na ion motions in these materials are highly correlated. The correlated motion in the Sn$^{4+}$ doped structure (see Figure 4.5c) takes place sooner than the other doped structures with the same dopant concentration. This is in accordance with the higher diffusion coefficient found in this structure. In fact, we observe a large amount of single Na$^+$ hops between neighboring Na1 and Na2 sites within a 1 ps time scale as well as correlated hops between adjacent Na ions in our AIMD trajectories.

4.1.4 Discussion

c-Na$_3$PS$_4$ is a highly promising sodium superionic conductor whose ionic conductivity can be further enhanced by aliovalent doping. In this work, we conducted a comprehensive investigation of the phase stability, dopant formation energies, and Na$^+$ conductivities of pristine and doped c-Na$_3$PS$_4$, with the aim of understanding the reasons for its high conductivity and elucidating potential strategies to further push its conductivity beyond 1 mS/cm.

Our work shows that Na disorder induced by Na excess is key to the high ionic conductivity in c-Na$_3$PS$_4$. We find that stoichiometric c-Na$_3$PS$_4$ has a very low ionic conductivity, which is similar to reported value of t-Na$_3$PS$_4$. Stoichiometric c-Na$_3$PS$_4$ also has relatively low occupancy on the Na2 site (<0.1 at 800 K), similar to t-Na$_3$PS$_4$. Both these observations are not surprising, given the small differences in lattice parameters between t- and c-Na$_3$PS$_4$. It is only
when the Na\(^+\) interstitials are introduced to c-Na\(_3\)PS\(_4\) that the Na2 site occupancy increases and the Na\(^+\) conductivity increases appreciably to the 0.1−1 mS/cm levels observed experimentally.

With these results in mind, it is therefore somewhat surprising that the initially reported ionic conductivity of pristine c-Na\(_3\)PS\(_4\) by Hayashi et al. is as high as 0.2 mS/cm. We speculate that there may have been doped impurities in the original sample, e.g., from the carbon electrodes or Zr, resulting in Na excess. It should be noted that Hayashi et al. specifically excluded Zr as a possible contaminant, and the calculated dopant formation energy of 6.25% Zr doping is estimated to be 1.45 eV/f.u., substantially higher than that for 6.25% Si doping (1.04 eV/f.u.). The fact that the same authors were subsequently able to obtain a significant increase in conductivity to 0.46 mS/cm using a Na\(_2\)S precursor with high purity further supports the hypothesis that Na\(^+\) interstitial defects are crucial to achieving high Na\(^+\) conductivity in this structure. Though a purer Na\(_2\)S does not necessarily mean Na\(^+\) interstitials will be formed, a less pure Na\(_2\)S precursor can potentially result in Na deficiency and reduce the likelihood of forming Na\(^+\) interstitials.

The increase in conductivity with the introduction of Na\(^+\) interstitials is likely caused by the increased Coulombic repulsion between Na\(^+\), leading to a redistribution that causes Na to be slightly displaced from the Na1 and Na2 positions. We speculate that this redistribution leads to a shallow energy landscape that promotes the cooperative motion of Na, leading to lower activation barriers and increased conductivity. The van Hove correlation function analysis, which indicates that correlated Na motion happens within a relatively short time scale, supports this hypothesis. Indeed, the higher the conductivity (e.g., in Sn-doped c-Na\(_3\)PS\(_4\)), the shorter the time scale in which correlated motion occurs.
A typical strategy to introduce Na\(^+\) interstitials is through aliovalent substitution of M\(^{4+}\) for P\(^{5+}\) in c-Na\(_3\)PS\(_4\). At a Si doping concentration of 6.25\%, the predicted room-temperature Na\(^+\) conductivity of 1.66 mS/cm is in excellent agreement with the reported experimental conductivity of 0.74 mS/cm for 0.94 Na\(_3\)PS\(_4\)·0.06 Na\(_4\)SiS\(_4\) reported by Tanibata et al.\(^{77,136}\) At a higher Si doping concentration of 12.5\%, the predicted Na\(^+\) conductivity further increases to 2.99 mS/cm, but the dopant formation energy increases substantially. This increased dopant formation energy is a possible reason why Tanibata et al. reported “unknown secondary phases” at doping concentrations beyond 10\%.\(^{77,136}\)

Among the M\(^{4+}\) dopants that we investigate, our calculations indicate that a particularly promising candidate for further investigation is Sn-doped structure. Na\(_{3.0625}\)Sn\(_{0.0625}\)P\(_{0.9375}\)S\(_4\) is predicted to have a much higher Na\(^+\) conductivity of 10.7 mS/cm, while the dopant formation energy is only slightly higher than Si doping at a similar concentration. Given that Si doping in c-Na\(_3\)PS\(_4\) as high as 10\% have been achieved experimentally, 6.25\% Sn doping should be achievable. As of now, we can only speculate on the reasons why there is such a significant difference in conductivity between Sn versus Si doping. Topological analyses find that the Sn-doped structure has a slightly larger channel size and free channel volume for Na\(^+\) diffusion than the Si-doped structure. However, a similar relative difference in channel size and volume in the Li\(_{10}\)MP\(_2\)S\(_{12}\) (M = Si, Ge, and Sn) superionic conductor\(^{91}\) leads to the opposite trend in Na\(^+\) conductivity of Si > Sn.

It may be that such different trends are the result of (a) the different dimensionality of diffusion in Li\(_{10}\)MP\(_2\)S\(_{12}\) systems (quasi 1D) and doped Na\(_3\)PS\(_4\) systems (3D), and (b) the different diffusing species, i.e., Li\(^+\) in Li\(_{10}\)MP\(_2\)S\(_{12}\) and Na\(^+\) in c-Na\(_3\)PS\(_4\). It is our hope that future experiments will verify if the Sn-doped structure can be synthesized, and if it does indeed exhibit higher conductivities than the Si and Ge-doped structures.
It should be noted that Eq. (4.6) provides a good estimate of the diffusivity only in the case of uncorrelated diffusion. The degree to which ionic motion is correlated is frequently described using the Haven ratio, $H_R$, which is defined as the ratio of the tracer diffusivity to the charge or dc diffusivity.\textsuperscript{70,72} We have not attempted to determine this ratio from AIMD due to the extremely slow convergence of the charge diffusivity. Nevertheless, typical $H_R$ values for similar highly correlated diffusion systems are in the range of $0.3−0.6$ (e.g., $H_R[\text{Li}_{10}\text{SnP}_2\text{S}_{12}] \approx 0.3$).\textsuperscript{71} We therefore expect that the computed diffusivities and conductivities in this work to be lower bound estimates that are off by no more than a factor of 3 and that the qualitative trends should remain valid.

### 4.1.5 Conclusions

To conclude, we have performed a comprehensive investigation of the phase stability, dopant formation energy, and Na$^+$ conductivity of c-$\text{Na}_3\text{PS}_4$ and $\text{Na}_{3+x}\text{M}_{x}\text{P}_{1-x}\text{S}_4$ ($M = \text{Si}$ with $x = 0.0625$ and 0.125; $M = \text{Ge, Sn}$ with $x = 0.0625$). Our results show that Na disorder induced by Na$^+$ excess is a key factor to enhancing the Na$^+$ conductivity in c-$\text{Na}_3\text{PS}_4$. Si$^{4+}$, Ge$^{4+}$, and Sn$^{4+}$ are all viable dopants to introduce Na$^+$ excess in c-$\text{Na}_3\text{PS}_4$ for this purpose due to their relatively low dopant formation energies. Our calculated Na$^+$ conductivity of 1.66 mS/cm for 6.25% Si-doped c-$\text{Na}_3\text{PS}_4$ is in an excellent agreement with experiments. We also find that the Na$^+$ conductivity can be further enhanced by increasing Si dopant concentration from 6.25% to 12.5%, but at the cost of much higher dopant formation energy. Finally, we predict that 6.25% Sn-doped c-$\text{Na}_3\text{PS}_4$ is a potentially promising Na superionic conductor with a significantly higher Na$^+$ conductivity than 6.25% Si-doped c-$\text{Na}_3\text{PS}_4$. 


4.2 Halide Doping Strategy into Tetragonal Na$_3$PS$_4$

4.2.1 Introduction

In Chapter 4.1, we proposed that Na-excess-induced Na disorder is the reason for the high conductivity observed in c-Na$_3$PS$_4$, and that Sn$^{4+}$ cation doping (for P$^{5+}$) may yield greater improvement in conductivity than Si$^{4+}$ doping but at the expense of higher dopant formation energy. The introduction of defects via aliovalent doping is a common strategy to improve the ionic conductivity of materials.

For Na$_3$PS$_4$, previous efforts have mainly focused on the cubic phase and the introduction of Na excess interstitials via substitution of P$^{5+}$. An alternative strategy of aliovalent doping is to introduce Na$^+$ vacancies in Na$_3$PS$_4$. Halide (X$^-$) anion doping (for S$^{2-}$) is a potential strategy for Na$^+$ vacancy creation. However, previous experimental efforts with (1-x)c-Na$_3$PS$_4$-xNaI glass-ceramics achieved a Na$^+$ conductivity of ~0.1 mS cm$^{-1}$, which is lower than that of the undoped and Si-doped c-Na$_3$PS$_4$. Furthermore, an unknown phase was found as the major precipitant when NaI was introduced at $x \geq 0.1$, suggesting an intrinsic incompatibility of I$^-$ ions with the S$^{2-}$ host at such high doping levels.

Besides, we demonstrate the stable cycling of a TiS$_2$/t-Na$_{3-x}$PS$_4$-xCl$_y$/Na ss-SIB at room temperature, with a capacity of about 80 mAh g$^{-1}$ at a rate of C/10 over 10 cycles for the first time. The key enabler to this outstanding cell performance is a novel Cl-doped t-Na$_3$PS$_4$ solid electrolyte with formula Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$, which was developed using a tightly integrated combination of density functional theory (DFT) calculations, synthesis and characterization. From DFT calculations, we show that Cl$^-$ exhibits good chemical compatibility with the S$^{2-}$ host, with low
dopant formation energy and similar ionic radius. The concomitant introduction of Na vacancies results in a predicted room-temperature Na\(^+\) conductivity exceeding 1 mS cm\(^{-1}\). These predictions are confirmed through experimental synthesis of tetragonal Na\(_{2.9375}\)PS\(_{3.9375}\)Cl\(_{0.0625}\), and its demonstration in a ss-SIB architecture. We will also present evidence from DFT computations that suggest the superior performance achieved in this cell is not only the result of the high Na\(^+\) conductivity of the solid electrolyte, but also the formation of electronically-insulating, ionically-conducting passivation layers at the electrode-solid electrolyte interface due to the presence of the Cl\(^-\) anion.

**4.2.2 Results**

The computational methods are elaborated in Chapter 4.1. Similar experimental methods including synthesis, characterization will be provided in Chapter 4.3. To avoid repetition, we will not talk about the methods part here.

Using DFT calculations, we first performed a systematic investigation of the dopability of potential halide X\(^-\) (X=F, Cl, Br and I) into both the tetragonal and cubic phases of Na\(_3\)PS\(_4\). As the DFT predictions for both phases are extremely similar, we will henceforth present only the results of the more stable tetragonal phase for brevity as follows.

**Dopability of Na\(_3\)PS\(_4\).** Figure 4.6a shows the crystal structure of t-Na\(_3\)PS\(_4\). There are two symmetrically distinct Na sites in t-Na\(_3\)PS\(_4\), Na1 (4d) and Na2 (2a), and the PS\(_4\) tetrahedra are centered at the 2b positions.\(^{142}\) It is worth pointing out that the symmetrically distinct Na sites in c-Na\(_3\)PS\(_4\) are labeled similarly as cubic Na1 (6b) and Na2 (12d). The Na1 (4d) and Na2 (2a) sites in t-Na\(_3\)PS\(_4\) essentially occupy the same positions as the Na1 (6b) sites in c-Na\(_3\)PS\(_4\).\(^{144}\)
A single halide dopant is introduced into a 2 × 2 × 2 supercell of t-Na$_3$PS$_4$ by replacing one of the S atoms with X, and simultaneously a Na vacancy is introduced to form Na$_{47}$P$_{16}$S$_{63}$X, or t-Na$_{3-x}$PS$_{4-x}$X$_x$ with $x = 0.0625$. All symmetrically distinct $V'_{Na} - X'_S$ configurations (Kröger–Vink notation is adopted) were evaluated, and the lowest energy configuration was used for subsequent analyses.

Table 4.4 summarizes the halide dopant formation energies. We find that all halides (F, Cl, Br and I) are predicted to have relatively low formation energies at a doping level of $x = 0.0625$. Fluoride doping is predicted to be the most favorable ($E_f = 0.76$ eV/F$^-$), followed by chloride ($E_f = 0.96$ eV/Cl$^-$) and iodide ($E_f = 0.99$ eV/I$^-$). Bromide doping is by far the least favorable with $E_f = 1.11$ eV/Br$. Higher doping levels result in a significantly higher dopant formation energy, e.g., $E_f = 1.77$ eV when doping Cl$^-$ in the same supercell size at $x = 0.125$. For all doped structures, the lowest energy structure has the X$^-$ anion substituted in the S$^{2-}$ (8e) site with a vacancy on the Na$_2$ site. Nevertheless, the energy differences between different $V'_{Na} - X'_S$ orderings are generally small (< 10 meV/atom), which suggest that the dopants and vacancies are likely to be disordered at room temperature.

Despite the fact that F$^-$ doping is predicted to be the most favorable, we have selected Cl$^-$ doping for further investigation due to several considerations. First, NaCl, aka table salt, is by far a more commonly available precursor than NaF. Second, with fluoride chemistry inherently comes the possibility of HF exposure. Finally, the Cl$^-$ anion has an ionic radius that is closest to S$^{2-}$, which would minimize the local structural distortion introduced at the substituted site. The doping concentration of Cl is fixed at $x = 0.0625$, given that previous work in doping I$^-$ (which has a
similar dopant formation energy at the same concentration) into c-Na$_3$PS$_4$ at $x > 0.1$ result in formation of unknown phases.$^{145}$

**Ionic conductivity of Cl-doped t-Na$_3$PS$_4$.** As demonstrated in recent work by some of the co-authors,$^{73}$ pristine c-Na$_3$PS$_4$, i.e., without interstitial or vacancy defects, is predicted to be an extremely poor ionic conductor in AIMD simulations. Using AIMD simulations (see Methods section), a similar result is obtained with t-Na$_3$PS$_4$ in this work, which is not surprising given that the small differences in lattice parameters and atomic positions between the cubic and tetragonal polymorphs.

Figure 4.7a shows the Arrhenius plot of the log of the conductivity-temperature product ($\sigma \cdot T$) versus $1/T$ for t-Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$ obtained from AIMD simulations. With the introduction of a $V_{Na}^\prime - Cl$ defect pair, the Na$^+$ conductivity at 300 K is predicted to be 1.38 mS cm$^{-1}$ with an activation barrier of 232 meV. During the preparation of this work, it has come to our attention that Klerk et al. has also performed AIMD simulations on halide doping in t- and c-Na$_3$PS$_4$.$^{144}$ Though the qualitative conclusions of vacancy-induced conductivity are similar, we note that Klerk et al. only performed relatively short AIMD simulations at a single temperature of 525 K; room-temperature Na$^+$ conductivities and activation energies were therefore not obtained.

From the Na$^+$ probability density distribution (Figure 2b), we may observe that t-Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$ is predicted to be a 3D diffuser comprising of chains of Na1 sites along the c direction interconnected via the Na2 sites, which form a body-centered cubic sublattice. Such a 3D diffusion network is expected to be highly robust against the potential introduction of blocking defects.$^{146}$
Electrochemical stability of t-Na$_{3-x}$PS$_{4-x}$Cl$_x$. Besides high ionic conductivity, an effective solid electrolyte candidate should also exhibit good electrochemical stability against the electrodes. Electrochemical stability may be achieved in two ways. First, the solid electrolyte can be intrinsically inert against any reaction with the electrodes. However, due to the high reactivity of Na metal and the highly oxidizing nature of the most charged high-voltage cathodes, it is difficult to find a material that is intrinsically stable over such a wide range of sodium chemical potential.

A second, more achievable option is to optimize the electrode-solid electrolyte chemistry as a whole such that good passivation layers are formed at the electrode-solid electrolyte interfaces that act as a barrier against further reaction. A good passivation layer should have a reasonable Na$^+$ conductivity, and low electronic conductivity.

Figure 4.8 shows the Na grand potential phase stability plot of the t-Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$ solid electrolyte as a function of Na chemical potential. We find that at the Na metal anode ($\mu_{\text{Na}} - \mu_{\text{Na}}^0 = 0$ eV), the predicted phase equilibria comprises Na$_2$S, NaCl and Na$_3$P in the ratio of 63:1:16. The dominant phase Na$_2$S is a good electronic insulator with PBE band gap of 2.4 eV, and NaCl has a PBE band gap of 5.0 eV. Na$_3$P has a small PBE band gap of 0.4 eV (the screened hybrid HSE functional gives a band gap of 0.76 eV), but is not expected to dominate the conductivity characteristics of the anode/electrolyte interface. The predicted phase equilibria are indeed very similar to those of the pristine t-Na$_3$PS$_4$ that consists of Na$_2$S and Na$_3$P in the ratio of 4:1. It should be noted that the PBE functional tends to severely underestimate band gaps, and the true band gaps are likely to be even higher. These phases are expected to exhibit moderate Na$^+$ conductivity, particularly in an amorphous solid-electrolyte interphase (SEI) layer.
At voltages above 2.4 V versus Na/Na\(^+\), we find that the t-Na\(_{2.9375}\)PS\(_{3.9375}\)Cl\(_{0.0625}\) solid electrolyte is predicted to be unstable against Na extraction to form NaPS\(_3\) + S + NaCl. However, if the operating voltage is kept below 2.4 V, the predicted phase equilibria at the charged cathode-solid electrolyte interface retains t-Na\(_3\)PS\(_4\) + NaCl as the primary component.

**Synthesis and characterization of t-Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_x\).** Pure t-Na\(_3\)PS\(_4\) was synthesized from Na\(_2\)S and P\(_2\)S\(_5\) precursors. The Cl\(^-\) dopant was introduced by adding NaCl following the chemical reaction (1.5-\(x\)) Na\(_2\)S + 0.5P\(_2\)S\(_5\) + \(x\) NaCl \(\rightarrow\) Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_x\). The resulting pellets were then densified via spark plasma sintering (SPS) to minimize porosity of the solid electrolyte.

Figure 4.9a shows the XRD data for the two compositions, t-Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_x\) with \(x = 0\)% and 6.25%. At \(x = 0\)%, we identify the crystalline phase formed to be t-Na\(_3\)PS\(_4\), and the XRD pattern is in excellent agreement with the previous study by Jansen et al.\(^{142}\) With the addition of chloride via NaCl at \(x = 6.25\)%, the tetragonal phase is retained with trace amounts of unreacted NaCl, and no reflections from unknown crystals in the spectra. Additionally, we observe a slight increase in the peak intensities of all the XRD reflections, with the most significant change occurring in the high index peaks, (112) and (211), at about 31°. This observation is the first indication that aliovalent substitution of S\(^2-\) by Cl\(^-\) was successful, because the halogen has a higher scattering factor than sulfur.

Rietveld refinement calculations were first conducted for t-Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_x\). To obtain a baseline of the crystal parameters, a refinement calculation was performed on the pristine (\(x = 0\)%) structure. The refined XRD pattern of the pristine structure is shown in Figure 4.9b. The refined lattice constants for the pristine structure are in excellent agreement with the previously reported values.\(^{142}\) These parameters were then used as an initial model to study the aliovalent substitution.
of $S^{2-}$ by $Cl^-$. Figure 4.9c shows the refined pattern of doped t-$Na_{2.9375}PS_{3.9375}Cl_{0.0625}$. No unknown phase was detected in the crystal, and no side reactions were observed during the synthesis. Although a trace amount of NaCl was detected in the spectrum, our refinement results show that it comprises less than 1 at%.

Table 4.6 summarizes the crystallographic parameters (lattice constants, thermal factors, and atomic occupancies) of the pristine and doped solid electrolyte from the Rietveld refinement and DFT calculations, which are in excellent agreement. From the refinement calculations, we estimated an increase in the lattice volume associated with the substitution of $S^{2-}$ by $Cl^-$. This volumetric change is very small and also agrees well with the DFT values. With the introduction of $Cl^-$, there is a corresponding decrease in sodium and sulfur occupancies and increases in their respective isotropic thermal factors ($B_{iso}$). These observations can be attributed to the formation of the Na$^+$ vacancy. In summary, the Rietveld refinement supports the successful incorporation of $Cl^-$ into the $S^{2-}$ sublattice, with the concomitant introduction of Na$^+$ vacancies. More advanced characterization techniques such as solid-state nuclear magnetic resonance (NMR) may be employed to confirm the success of the doping in future work.

Cross-sectional SEM images of the pristine t-$Na_3PS_4$ and doped t-$Na_{2.9375}PS_{3.9375}Cl_{0.0625}$ SPS samples under identical processing conditions are shown in Figure 4.9d and Figure 4.9e, respectively. We note that the $Cl^-$ doping does not lead to any significant morphology changes. The images show that the local morphology of the pellets is densely formed due to SPS processing in both compounds. An EDX measurement was collected from the doped sample (see Figure 4.11). From the EDX measurement, we determined that sulfur and chlorine are uniformly distributed throughout the sample, with no noticeable aggregation of element-rich domains. In conjunction
with the refinement results, the majority of the chloride dopant is found to be integrated into the host crystal lattice.

**Conductivity measurements of t-Na$_{3-x}$PS$_{4-x}$Cl.$x$.** The experimental measurement of pristine t-Na$_3$PS$_4$ shows a low ionic conductivity of 0.05 mS cm$^{-1}$ at 303 K, with an activation energy value of 317 meV (see Figure 2a and Table 4.5). The t-Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$ solid electrolyte, on the other hand, shows an extremely high conductivity of 1.14 mS cm$^{-1}$ at 303 K and a low activation barrier of 249 meV. The measured conductivity and activation barrier are in excellent agreement with the calculated values (Table 4.5). A significantly larger semi-circle is observed for the pristine t-Na$_3$PS$_4$ compared to doped t-Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$, indicating a much larger total resistance in the pristine t-Na$_3$PS$_4$.

**Electrochemical performance.** A full cell was constructed using a TiS$_2$ charged cathode and a Na metallic anode. The choice of the TiS$_2$ cathode is motivated by its suitable operating voltage (~1.7 V versus Na/Na$^+$), which is well within the limits of the DFT predicted stability window of the t-Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$ solid electrolyte, as well as its fast kinetics for Na$^+$ intercalation.$^{151}$ The cell was galvanostatically cycled from 1.2 V to 2.4 V. The cell was held for two minutes between switching from charging to discharging. A current density of 0.149 mA cm$^{-2}$ was applied, corresponding to a C/10 rate. The theoretical capacity of the NaTiS$_2$ active material is 198 mAh g$^{-1}$. The discharge and charge capacity of the first cycle were ~ 240 mAh g$^{-1}$ and 80 mAh g$^{-1}$, respectively. The source of the excess capacity as well as the large irreversible capacity of the first cycle is currently under investigation and will be the evaluated in a subsequent study of the interface stability and its effects on cyclability and longevity. Currently, impedance measurements during the first cycle clearly indicate the formation of stable interfacial phases at
the solid-electrolyte/electrode interfaces. The subsequent charge and discharge capacities of the cell over 10 cycles were \(~80 \text{ mAh g}^{-1}\), with a coulombic efficiency above 98% (see Figure 4.10). Such a stable performance is consistent with the cyclic voltammetry results in which Cl-doped t-\(\text{Na}_3\text{PS}_4\) is found electrochemically stable against the Na anode for up to 5 V. Strong polarization, common in Na-ion cells, was also observed at the point of switching from charging to discharging, and vice versa.

4.2.3 Discussion

The design of an all-solid-state rechargeable battery is a multi-component, multi-property optimization effort; it is therefore insufficient to merely focus on bulk ionic conductivity of the solid electrolyte as the only target parameter. In this work, we have demonstrated how an integrated computational and experimental effort can significantly accelerate such multi-component, multi-property optimization, resulting in a promising new t-\(\text{Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}\) solid electrolyte that has been demonstrated in a full ss-SIB cell with good cyclability and capacity.

Aliovalent doping is common strategy to introduce defects (vacancies or interstitials) into a solid electrolyte candidate to further enhance its conductivity. Surprisingly, we find halide doping in \(\text{Na}_3\text{PS}_4\) to be somewhat more favorable than cation (\(\text{Si}^{4+}\), \(\text{Ge}^{4+}\) and \(\text{Sn}^{4+}\)) doping, with slightly lower dopant formation energies of 0.76 – 1.11 eV vs 1.04 – 1.32 eV for cation. Though dopant formation energies of 0.76 – 1.11 eV might appear at first glance to be relatively high, it should be noted that these values depend strongly on the chemical potential references used. At the elevated temperatures during synthesis, \(\text{Na}_2\text{S}\) loss is likely to lower the chemical potentials of Na and S, significantly promoting \(V'_{\text{Na}} - X'_S\) formation.
Both the cation + interstitials and anion + vacancies doping strategies are predicted to be effective in enhancing the ionic conductivity of Na$_3$PS$_4$. In fact, we find no evidence of any significant difference in the predicted bulk Na$^+$ conductivities between the cubic and tetragonal Na$_3$PS$_4$, which is not surprising given the very small differences in lattice parameters between the two polymorphs.$^{152}$ We speculate that the nature of the defects present would promote the formation of one polymorph over another. Excess Na interstitials would need to occupy the cubic Na$_2$ (12$d$) sites, promoting the formation of the disordered cubic phase, while Na vacancies with halide substitution would result in slight lattice expansion (due to reduced electrostatic attraction) and promote the formation of the tetragonal phase. Indeed, our attempts at synthesizing a phase-pure Cl-doped c-Na$_3$PS$_4$ phase has been unsuccessful, while the Cl-doped t-Na$_3$PS$_4$ was readily obtained.

The fundamental difference between cation M$^{4+}$ and anion X$^-$ doping is in the interfacial products that are predicted to form at the Na anode. For Si or Sn-doped Na$_3$PS$_4$, small-gap compounds such as Na$_4$Si$_4$ (space group of C2/c; PBE band gap of ~1.2 eV) and Na$_{15}$Sn$_4$ (space group of I43d; PBE band gap of ~0 eV) as well as Na$_2$S and Na$_3$P are predicted to form at the anode/solid electrolyte interface. For Cl-doped Na$_3$PS$_4$, on the other hand, the anode/solid electrolyte interface comprises predominantly Na$_2$S with smaller amounts of NaCl and Na$_3$P.

Alkali halides are well-known components in the solid-electrolyte interphase (SEI) of rechargeable lithium-ion batteries, where LiF is formed from the reaction between the LiPF$_6$ salt and the electrodes. Indeed, the “salting” of the SEI is likely to improve its ionic conductivity as Cl$^-$ dopants will similarly be introduced to the amorphous Na$_3$P + Na$_2$S SEI. It should be noted that in all cases (undoped, cation-doped, and halide-doped), the small-gap compound Na$_3$P (PBE band gap of ~0.4 eV) is also predicted to form at the Na anode, though it is not the dominant phase. Based on the
achieved cycling performance in this work as well as in previous works on c-Na₃PS₄, we would surmise that the effect of Na₃P on the interfacial stability is small.

Ultimately, the total conductivity of a solid electrolyte depends not only on its bulk conductivity, but also the grain boundary contributions. In this respect, the specifics of the synthesis procedure are critically important. In this work, spark-plasma sintering was used to achieve a fully-dense solid electrolyte with reduced grain boundary resistance, and an overall conductivity exceeding 1 mS cm⁻¹ that is very close to the DFT predicted bulk conductivity (see Figure 4.7). This overall conductivity is higher than that of Si-doped c-Na₃PS₄ (0.74 mS cm⁻¹) and is the highest value for sodium thiophosphates achieved thus far. Although recently reported Na₃PSe₄ and Na₃SbS₄ have higher conductivities, the more expensive and less stable Se²⁻ anion is utilized in Na₃PSe₄, while Na₃SbS₄ requires a more complicated electrolyte bilayer approach using c-Na₃PS₄ to stabilize the interface at the Na anode.

We have demonstrated the potential of the t-Na₂.9375PS₃.9375Cl₀.0625 solid electrolyte by integrating it in a ss-SIB full cell. In a full cell, the choice of the cathode and anode must be given careful consideration, as well as their interactions with the solid electrolyte. From the DFT grand potential analysis, we find that the t-Na₂.9375PS₃.9375Cl₀.0625 electrolyte is predicted to be relatively stable up to ~2.4V vs Na/Na⁺, while passivation is predicted to occur at the Na anode. Therefore, TiS₂ was chosen as the cathode. At a rate of 0.149 mA cm⁻², a cell capacity of ~80 mAh g⁻¹ was achieved over 10 cycles of the TiS₂/t-Na₂.9375PS₃.9375Cl₀.0625/Na full cell. The increase in internal cell resistance, leading to capacity decay after subsequent cycling, is common when forming a SEI layer. Though the reversible capacity reported by Hayashi et al. for the c-Na₃PS₄ solid electrolyte is similar, that performance was achieved with a much lower current density (0.013 mA cm⁻²)
against a Na-Sn alloy as the anode. Though the Si-doped c-Na₃PS₄ and Na₃PSe₄ solid electrolytes have higher measured conductivities than c-Na₃PS₄, their room-temperature performance in a full ss-SIB cell has not yet been demonstrated.¹⁵³,¹⁵⁴ To our knowledge, this is the first time that cycling at a rate as high as C/10 has been demonstrated in a full ss-SIB with a Na metal anode at room temperature.

4.2.4 Conclusion

In conclusion, we have demonstrated the prediction and synthesis of a novel Cl-doped tetragonal Na₃PS₄ solid electrolyte, or t-Na₂.₉₃₇₅PS₃.₉₃₇₅Cl₀.₀₆₂₅, and its good cycling performance in a full all-solid-state rechargeable sodium-ion cell at a rate of C/10. The predicted bulk and measured total conductivities of the t-Na₂.₉₃₇₅PS₃.₉₃₇₅Cl₀.₀₆₂₅ solid electrolyte exceeding 1 mS cm⁻¹, which is one of the highest conductivities reported for any sodium superionic conductor thus far. More importantly, the “salting” of Na₃PS₄ is predicted to improve the characteristics of the interfacial phase equilibria at the anode/solid electrolyte interface, forming an electronically insulating and ionically conducting solid-electrolyte interphase. We also demonstrate the potential of spark-plasma sintering as a technique for achieving a dense sulfide electrolyte with reduced grain boundary resistance.

4.3 Functional Defects in Na₃₋ₓPS₄₋ₓClₓ

4.3.1 Introduction

The cubic phase of Na₃PS₄ (c-Na₃PS₄, an analogue of Li₃PS₄) from the Na₂S-P₂S₅ system was first reported by Hayashi et al. in 2012 with a measured Na⁺ conductivity of 0.2 mS/cm.³²
Further improvement in ionic conductivity has been achieved by Si doping (0.74 mS/cm).\textsuperscript{33,15673} Furthermore, substitution of S with larger Se ions increased the ionic conductivity to 1.16 mS/cm and replacement of P with As increased the conductivity to 1.46 mS/cm, though at the expense of reduced electrochemical stability.\textsuperscript{152,165, 167} The tetragonal-Na\textsubscript{3}PS\textsubscript{4} (t-Na\textsubscript{3}PS\textsubscript{4}) phase has a low ionic conductivity of 0.05 mS/cm,\textsuperscript{142} which can be significantly improved to reach ~ 1.1 mS/cm by creating structural defects with Cl doping.\textsuperscript{123} In addition, halogen doping promotes the formation of passivating solid-electrolyte interphases, which significantly improves the interfacial stability of thiophosphate-based solid electrolytes when used in all-solid-state batteries.\textsuperscript{123}

In the typical halogen-doped Na\textsubscript{3}PS\textsubscript{4} compounds, halide doping for S\textsuperscript{2−} is charge compensated by Na vacancies, i.e., Na\textsubscript{3−x}PS\textsubscript{4−x}Cl\textsubscript{x}, which facilitate Na conductivity. However, the resulting Na deficiency can decrease both the ionic charge carrier concentration and the volume of Na conduction channel, which contributes negatively to the improvement of ionic conductivity. Herein, we report a new synthesis strategy to enhance the ionic conductivity of modified t-Na\textsubscript{3}PS\textsubscript{4}. This new strategy is informed by the identification of the functional defects that promote fast ion conduction through understanding the ion transport mechanism. The synthesis approach is designed to maximize those functional defects and minimize detrimental ones to fast ion conduction.

In the following, we start by presenting the strategic synthesis of fast Na ion conductors with room-temperature ionic conductivities 1.96 mS/cm and activation energy of 0.19 eV (Na\textsubscript{3.0}PS\textsubscript{3.8}Cl\textsubscript{0.2}). Then the Na ion conduction mechanism is explained based on the results of tracer-exchange NMR with a discussion of the structure-ion conduction correlation and the rationale for the strategic synthesis. We provide evidence from DFT calculations that independent
tuning of Cl doping and Na deficiency helps boosting the Na\(^+\) conductivity. The conversion of P\(^{5+}\) to P\(^{4+}\) is also observed from both solid-state \(^{31}\)P NMR peak shifting and integrated polarized-spin charge density calculations. The manuscript concludes with a performance demonstration of the new Na solid electrolyte within a full solid-state rechargeable Na-ion battery.

4.3.2 Results and Discussions

Synthesis and Structural Characterizations of t-Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_x\). Two crystal structures of Na\(_3\)PS\(_4\) have been reported, tetragonal- and cubic-phase.\(^{32,123,142}\) c-Na\(_3\)PS\(_4\) adopts the space group of \(I\bar{4}3m\) with the lattice parameter \(a = 6.9965\ \text{Å}\), while t-Na\(_3\)PS\(_4\) crystallizes in \(P-42_1c\) with lattice parameters of \(a = 6.9520\ \text{Å}\) and \(c = 7.0757\ \text{Å}\). These two forms are significantly different in Na positions: in c-Na\(_3\)PS\(_4\), Na is reported to occupy the 12\(d\) site while in t-Na\(_3\)PS\(_4\), Na sits at both 2\(a\) and 4\(d\) sites. Na-ion conductivity is reported to be on the order of \(10^{-4}\) S/cm for glass-ceramic c-Na\(_3\)PS\(_4\),\(^{32}\) but this value is much smaller for glass-ceramic t-Na\(_3\)PS\(_4\), \(10^{-5}\) S/cm.\(^{123,142}\)

The goal of this study is to understand how different structural defects affect Na-ion conduction in usual Cl doped t-Na\(_3\)PS\(_4\) (Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_x\)) and to maximize functional defects for enhancing Na-ion conduction. The insights obtained will be useful for developing other fast-ion conductors. The structure of t-Na\(_3\)PS\(_4\) is shown in Figure 4.6a, in which P is tetrahedrally coordinated with four S. Na\(_1\) and Na\(_2\) occupy 4\(d\) and 2\(a\) sites, respectively. Defects in glass-ceramic t-Na\(_3\)PS\(_4\) compounds (t-Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_x\)) are created with partial Cl replacement of S in the structure and Na deficiency is generated for charge compensation. The X-ray diffraction (XRD) patterns of t-Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_x\) are shown in Figure 4.6b along with the simulated XRD patterns of t- and c-Na\(_3\)PS\(_4\). Most of the diffraction peaks in the XRD patterns collected on t-Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_x\) (\(x = 0, 0.0625, 0.1, \) and 0.2) come from t-Na\(_3\)PS\(_4\), except small and broad peaks at around 21° and 44° from the Kapton film
and the stainless-steel holder. The XRD patterns of t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ (x = 0, 0.0625, 0.1, and 0.2) only exhibit very slight difference, and the most visible one is the merging of the two diffraction peaks at $2\theta = 30.79^\circ$ and $31.09^\circ$. This may suggest the exchange of the two Na sites in t-Na$_3$PS$_4$, which makes the structure gradually converge to c-Na$_3$PS$_4$ with increasing x. In addition, some minor peaks from impurities appear in the sample of Na$_{2.8}$PS$_{3.8}$Cl$_{0.2}$, which is consistent with calculation results. The thermal stability is greatly compromised with increased x value in t-Na$_{3-x}$PS$_{4-x}$Cl$_x$.

**Na$^+$ Conduction in t-Na$_{3-x}$PS$_{4-x}$Cl$_x$.** The ionic conductivity of t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ (x = 0, 0.0625, 0.1, and 0.2) samples is determined with electrochemical impedance spectroscopy (EIS) and the results are shown in Figure 4.12a. The ionic conductivity of t-Na$_3$PS$_4$ is $\sim 10^{-5}$ S/cm at room temperature (Figure 4.12), compared with $\sim 10^{-4}$ S/cm for c-Na$_3$PS$_4$. Cl replacement of S in t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ leads to significantly improved Na-ion conduction. The highest conductivity of 0.3 mS/cm at room temperature is obtained when x equals to 0.1, i.e., t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$. Larger or smaller x values yield larger impedance and thus slower ion conduction (Figure 4.12).

The ionic conductivities of t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ are also measured at variable temperatures within the range of 21–120 °C (Figure 4.19) and the results are shown in Figure 4.12b. The activation energy, $E_a$, is determined based on the Arrhenius equation:

$$\sigma = A \times \exp \left( \frac{-E_a}{RT} \right)$$

where $A$ is a constant, $R$ is the universal gas constant with the value of $8.314 \times 10^{-3}$ kJmol$^{-1}$K$^{-1}$, and $T$ is temperature in Kelvin. The activation energy of t-Na$_3$PS$_4$ is determined to be 0.34 eV, and
it decreases with more Cl → S replacement (0.24 eV for Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$, 0.23 eV for Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$, and 0.19 eV for Na$_{2.8}$PS$_{3.8}$Cl$_{0.2}$). As a reference, the activation energy for most solid electrolytes is > 0.24 eV. The achieved small activation energy in t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ is beneficial for flexible adaption of these solid electrolytes to be used in different climates especially at low temperatures with no significant decrease in ionic conductivity.

**Solid-State $^{23}$Na NMR Characterizations of Structural Defects.** To identify structural features that contribute to Na-ion conduction in t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ (x = 0, 0.0625, 0.1, and 0.2), high-resolution solid-state magic-angle-spinning (MAS) $^{23}$Na NMR in a high magnetic field of 19.6 T is employed for identifying the local structural environments of Na ions and then tracer-exchange NMR is used to probe Na-ion transport pathways. As shown in Figure 4.13, a clear evolution of $^{23}$Na resonances is observed as x increases in t-Na$_{3-x}$PS$_{4-x}$Cl$_x$. The $^{23}$Na spectrum of t-Na$_3$PS$_4$ shows two main resonance peaks at 3.1 ppm and 3.4 ppm, and the corresponding quadrupolar coupling constants $C_Q$ are 1.7 MHz and 2.3 MHz. These are assigned to Na$_1$ and Na$_2$ sites in the t-Na$_3$PS$_4$ structure. Large $C_Q$ values for Na$_1$ and Na$_2$ resonances suggest an asymmetric structural environment with low Na mobility. In addition to Na$_1$ and Na$_2$ resonances, another NMR component appears at 12 ppm with a $C_Q$ value of 2.4 MHz (marked with #). This accounts for 4.5% of the total $^{23}$Na integral and may come from defective sites. Upon partial replacement of S by Cl in t-Na$_{3-x}$PS$_{4-x}$Cl$_x$, two new resonances labeled as Na$_3$ and Na$_4$ emerge at 9.6 ppm and 18 ppm with vanished quadrupolar coupling interactions, $C_Q = 0$. These two $^{23}$Na resonances arise from defective structural sites introduced by the Cl → S replacement, and the amount of these defects increases with the x values in t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ (Figure 4.13). In principle, the $C_Q$ values should increase for non-symmetric defective sites. The obtained small $C_Q$s for Na$_3$ and Na$_4$ suggest fast Na-ion motion, which significantly reduces quadrupolar coupling interactions of $^{23}$Na spins.
Another evidence of fast Na-ion motion is the significantly larger $T_1$ relaxation times for Na$_3$ sites ($\sim 10$ s) compared with those for Na$_1$ and Na$_2$ sites ($< \sim 0.2$ s) in t-Na$_3$PS$_4$. For Na$_1$ and Na$_2$, the $^{23}$Na NMR $T_1$ relaxation is driven by quadrupolar interactions and the relaxation time is typically on the order of milliseconds, while for Na$_3$ and Na$_4$, with the quadrupolar interactions minimized by fast Na motion, the NMR relaxation is driven by other interactions such as dipolar couplings and the typical $T_1$ relaxation time is on the order of seconds. Na$_3$ is assigned to Na sites close to Cl and Na$_4$ to Na sites in the vicinity of Na vacancies, based on the fact that Na$_4$ resonance is reduced as the Na vacancies are filled, as is discussed later in this work.

**Na-ion Transport Mechanism in t-Na$_{2.8}$PS$_{3.8}$Cl$_{0.2}$.** To understand how the structural defects generated by Cl $\rightarrow$ S replacement contributes to the significantly improved ionic conductivity in t-Na$_{3-x}$PS$_{4-x}$Cl$_x$, tracer-exchange NMR$^{162}$ is employed to probe Na-ion transport pathways in t-Na$_{3-x}$PS$_{4-x}$Cl$_x$. Ideally, these experiments should be carried out by monitoring the replacement of one Na isotope with another under relevant electrochemical condition. However, as Na has only one isotope, i.e., $^{23}$Na, an alternative strategy is adopted by using Li to replace Na driven by a biased electric potential. In the experimental setup, the t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ solid electrolyte pellet is sandwiched by two pieces of $^7$Li metal (Figure 4.14a). Driven by a biased potential, Li ions diffuse through the solid electrolyte and on the pathway, Li ions replace active Na ions. By identifying at which structural sites Na ions are replaced, the ion transport pathways can be identified. This tracer-exchange experiment is performed on t-Na$_{2.8}$PS$_{3.8}$Cl$_{0.2}$ and the results are shown in Figure 4.14b and Figure 4.14c. Significant decrease in the intensity of the Na$_3$ and Na$_4$ resonances after tracer-exchange and increase in Na$_1$ and Na$_2$ resonances are observed. The decrease in Na$_4$ resonance intensity and increase in Na$_1$ and Na$_2$ amount are correlated. Li fills Na vacancies in t-Na$_{2.8}$PS$_{3.8}$Cl$_{0.2}$, which leads to the conversion of Na sites next to Na vacancies, i.e.,
Na3, to Na1 and Na2. The decrease in Na3 amount is due to the replacement of 23Na by 7Li. The results suggest that Na3, which is Na next to Cl, is the active site for ion conduction. This is also confirmed by the positive correlation of enhanced ionic conductivity and the amount of Na3 in t-Na2.8PS3.8Cl0.2. On the other hand, the amount of Na vacancy concentration seems to correlate negatively with the increase in ionic conductivity at higher concentration.

Based on the understanding of ion transport mechanism in t-Na2.8PS3.8Cl0.2, to further enhance the ionic conductivity, the amount of Na3 needs to be increased while Na vacancies should be minimized, which means large x and small y in t-Na3-yPS4-xClx. New synthesis strategies are needed to maximize the Cl → S replacement while preventing significant Na vacancy formation. Following this guideline, we have designed the following reaction to synthesize t-Na3-yPS4-xClx with improved ionic conductivity.

\[
t-Na_{3-x}PS_{4-x}Cl_x + z \text{ NaCl} \rightarrow t-Na_{3-x+z}PS_{4-x-z}Cl_{x+z} + z \text{ S} \quad (0 < x - z = y)
\]  

(4.9)

Vacuum is applied to remove the product S during the synthesis, which drives the reaction to proceed to the right. With this method, several compounds are synthesized starting with t-Na2.9PS3.9Cl0.1 and t-Na2.8PS3.8Cl0.2.

The XRD patterns of the t-Na2.9PS3.9Cl0.1/zNaCl (z = 0.1, 0.3, and 0.5) series are shown in Figure 4.15a along with the reference patterns of t-Na3PS4 and NaCl. The incorporation of 0.1 NaCl to t-Na2.9PS3.9Cl0.1 is successful, manifested as no observed NaCl diffraction peaks. Also, the additional NaCl modifies the t-Na2.9PS3.9Cl0.1 structure to converge to the cubic structure, suggested by the merging of the diffraction peaks at 2θ = 30.79° and 31.09°. When 0.3 NaCl is
added to t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$, minor NaCl residues are seen from the XRD pattern and the NaCl peaks become obvious with 0.5 NaCl added. To further probe the structural changes induced by the added NaCl, high-resolution $^{23}$Na NMR spectra are acquired and presented in Figure 4.15b. As expected, the addition of 0.1 NaCl to t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$ fills the Na vacancies, thus the disappearance of the 18 ppm resonance (Na$_4$). When more NaCl is added, the resonance from NaCl at 6.6 ppm arises and increases. Summarizing the results from both PXRD and NMR, the z value in t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$/zNaCl should be less than 0.1 to achieve the goal of partially filling Na vacancies without introducing NaCl impurity. The real formula of t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$/0.1NaCl should be t-Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$, based on the XRD and NMR results. The optimal z value in t-Na$_{2.8}$PS$_{3.8}$Cl$_{0.2}$/zNaCl is determined to be 0.2 (Figure 4.20) and the formula for the best sample should be t-Na$_{3.0}$PS$_{3.6}$Cl$_{0.4}$.

**Enhanced Na-ion Conduction with Maximizing Functional Defects in t-Na$_{3-y}$PS$_{4-x}$Cl$_{y}$**.

As suggested by tracer-exchange NMR, Na$_3$ site is responsible for Na conduction. Therefore, Na ionic conductivity can be increased by maximizing Cl$\rightarrow$S replacement and minimizing Na vacancy formation (Na$_4$). Figure 4.16 presents the results of AC impedance measurements on several t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$/zNaCl ($z = 0.1, 0.3,$ and 0.5) compounds to validate the proposed strategy. By filling Na vacancies in t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$/zNaCl ($z = 0.1, 0.3,$ and 0.5), the ionic conductivity is increased. The highest ionic conductivity (1.77 mS/cm at 21°C and 1.96 mS/cm at 25 °C) is obtained for t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$/0.1NaCl, nominally t-Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$. For $z = 0.3$ and 0.5, an impurity of NaCl is produced and the observed ionic conductivity is slightly lowered. The activation energy for Na-ion conduction in t-Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$ is determined to be 0.19 eV with variable temperature EIS (Figure 4.16b).
AIMD simulations are performed to verify the doping effect of Cl and Na vacancy in t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ ($x = 0.0625$ and $0.125$; $y = 0$, $0.0625$, and $0.125$) on Na ionic conductivity. The calculated Arrhenius plots for structures with various Cl doping/Na vacancy ratio are shown in Figure 4.17. The conductivity of pristine t-Na$_3$PS$_4$ is poor (< 0.01 mS/cm) but can be increased to 1.38 mS/cm by introducing 2.1% Na vacancy, as reported in previous work.$^{123}$ When Cl concentration increases, we find that the conductivity of t-Na$_{2.875}$PS$_{3.875}$Cl$_{0.125}$ can be pushed to a higher value of 6.38 mS/cm, with low activation energy of 0.199 eV. When Na vacancies are partially filled while maintaining the Cl concentration (Na$_{2.9375}$PS$_{3.875}$Cl$_{0.125}$), the conductivity is further increased to 9.03 mS/cm and the activation energy is reduced to 0.174 eV, which is consistent with the experimental results. However, the conductivity decreases sharply to close to that of pristine t-Na$_3$PS$_4$ when all Na vacancies are filled (Na$_3$PS$_{4-x}$Cl$_x$, $x = 0.0625$ and $0.125$). It should be noted that $^{23}$Na NMR studies show no sign of Na vacancies for the Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$ nor Na$_{3.0}$PS$_{3.6}$Cl$_{0.4}$ which exhibit highest ionic conductivities of all the t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ compounds synthesized in this work. This discrepancy is likely due to amount of Na vacancies is too small to be detected. As shown in Figure 4.13, in Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$, Na$_4$ resonance which represents Na vacancies can be clearly observed. The estimated detection limit of Na vacancies should be much smaller than $0.0625/3 \approx 2\%$. Based on the signal/noise ratio (SNR) of $^{23}$Na NMR spectra, the detection limit is estimated to be $3 \times 14.21 = 42.63$.

Topological analyses using open source software$^{120}$ Zeo++ were conducted to assess the free channel volumes for structures with different Cl dopant/Na vacancy ratio. As shown in Table 4.7, when the Na vacancy was fixed, e.g. Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$ vs. Na$_{2.9375}$PS$_{3.875}$Cl$_{0.125}$, the introduction of Cl dopants leads to larger Na channel volumes. In contrast, Na vacancies leads to a decrease in channel volumes. For example, a 2.1% Na vacancy concentration decreases the
channel volume from 937 Å$^3$ to 924 Å$^3$. The diffusion pathways can be visualized from Na$^+$ probability density distribution (see Figure 4.7b). In t-Na$_{2.9375}$PS$_{3.875}$Cl$_{0.125}$, 3D diffusion tubes comprise chains of Na$_1$ sites along $c$ direction and Na$_1$-Na$_2$-Na$_1$ hopping within $ab$ plane, which finally form the cubic sub-lattice, similar to that observed in previous studies of Cl-doped Na$_3$PS$_4$.$^{14}$ From a series of AIMD results, we find that in the presence of small amount of Na vacancy, increase of Cl doping concentration significantly improves the Na$^+$ conductivity. The calculated channel volume and conductivity results indicates that independent tuning of Cl and Na vacancy amount can lead to optimized conduction performance. Without compensating Na vacancies, the introduction of the Cl$^-$ dopant is charge compensated by the reduction of P, as shown in the next section.

**Change of P Oxidation State in t-Na$_{3-y}$PS$_{4-x}$Cl$_x$.** Cl $\rightarrow$ S replacement also leads to changes in the local structural environment of P as seen in $^{31}$P NMR (Figure 4.21). In addition to $^{31}$P resonances from t-Na$_3$PS$_4$ at $\sim$ 87 ppm, additional $^{31}$P NMR peaks appear between $105-115$ ppm for t-Na$_{3-y}$PS$_{4-x}$Cl$_x$. P with an oxidation state of 4+ often resonate at a position $> 100$ ppm, for instance P in Li$_4$P$_2$S$_6$ (Li$_2$PS$_3$) shows multiple $^{31}$P NMR peaks $> 105$ ppm.$^{163}$ Therefore, these additional $^{31}$P resonances observed for t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ compounds suggest the conversion of P$^{5+}$ to P$^{4+}$ due to Cl $\rightarrow$ S replacement, and the amount of P$^{4+}$ increases with x in t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ (Figure 4.22). Multiple $^{31}$P NMR resonances at $> 105$ ppm suggest an inhomogeneous structural environment due to Cl $\rightarrow$ S replacement. Both $^{23}$Na and $^{31}$P NMR indicate that Cl$\rightarrow$S replacement in t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ does not necessarily lead to Na vacancies, instead the charge imbalance due to the replacement can at least be partially compensated by reduction of P$^{5+}$ to P$^{4+}$. Another evidence for the formation of P$^{4+}$ is the formation of elemental S. We collected the powder evaporated
during the synthesis of Na$_{2.8}$PS$_{3.8}$Cl$_{0.2}$, and characterized it using XRD. The XRD pattern of the evaporated powder highly resembles that of the standard S$_8$ (Figure 4.23). These experimental observations are supported by plotting the spherically integrated spin-polarized charge density of all P ions as a function of cutoff radius from our DFT calculations of Na$_3$PS$_{3.9375}$Cl$_{0.0625}$ (Figure 4.24). A non-zero integrated spin was observed (~1/2 $\mu_B$ at the radius of 2 Å) for the P in the center of PS$_3$Cl tetrahedra, indicating the reduction of P$^{5+}$ to P$^{4+}$. In contrast, all remaining P in PS$_4$ tetrahedra has negligible net spins, i.e., P$^{5+}$. Besides, previous reports have suggested based on empirical evidence$^{164}$ that P$^{4+}$ helps to improve the stability of thiophosphate solid electrolytes.

With the formation of P$^{4+}$, a concern arises that P$^{4+}$ can potentially serve as an electron donor, leading to enhanced electron conduction, while electron conduction is not desirable for solid electrolytes. We have measured the electronic conductivity of both t-Na$_3$PS$_4$ and t-Na$_3$PS$_{3.8}$Cl$_{0.2}$, and the electronic conductivity of t-Na$_3$PS$_{3.8}$Cl$_{0.2}$ is $1.2 \times 10^{-8}$ S cm$^{-1}$, which is only slightly higher than that for t-Na$_3$PS$_4$, that is, $0.8 \times 10^{-8}$ S cm$^{-1}$ (Figure 4.25). Both values are much lower than the measured ionic conductivity $\approx 2 \times 10^{-3}$ S cm$^{-1}$ for t-Na$_3$PS$_{3.8}$Cl$_{0.2}$.

**Full-Cell Performance.** The stability of t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ is tested using cyclic voltammetry within a Na|Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$|In cell. The scan rate is 0.2 mVs$^{-1}$ and the battery is cycled between −0.5 and 10 V (vs Na/Na$^+$). As seen in Figure 4.18a, only Na deposition and dissolution occur at around 0 V. No decomposition of Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$ is seen even at a high potential of 10 V, which is attributed to the low electronic conductivity of Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$, limiting the rate of side reactions. The all-solid-state Na-ion battery using Na as anode, Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$ as electrolyte, and Na$_3$V$_2$(PO$_4$)$_3$ as cathode achieves a capacity of 100 mAh g$^{-1}$ at room temperature (Figure 4.18b) in an initial test, with slight decay over further cycling being observed. The main cause to the
capacity decay is interfacial stability upon electrochemical cycling. The impedance of the Na|Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$ |Na$_3$V$_2$(PO$_4$)$_3$ full cell before and after cycling is measured and the results are shown in Figure 4.26. Before cycling, the total interfacial resistance is only 80 $\Omega$ and it increases to $\approx 1300 \Omega$ after cycling due to nonconductive products formed at electrode–electrolyte interfaces from undesirable side reactions of Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$ with the electrodes (Na anode and Na$_3$V$_2$(PO$_4$)$_3$ cathode). To improve the electrochemical performance of the full cell using Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$ as the electrolyte, Na-Sn alloy instead of Na should be employed and surface modification of cathode materials is necessary to minimize side reactions of Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$ with the cathode at high potentials.

4.3.3 Conclusions

A series of Cl-doped t-Na$_3$PS$_4$ solid electrolytes have been prepared for use in all-solid-state rechargeable Na-ion batteries. Structural analyses have been carried out with techniques including X-ray diffraction and solid-state NMR. In particular, solid-state $^{23}$Na MAS NMR identifies the functional defects that promote fast ion conduction. A new synthesis strategy is implemented to maximize the fraction of functional defects while preventing the formation of other defects that impede Na-ion conduction. As a result, the best ionic conductivity is achieved in the composition of Na$_{3.0}$PS$_{2.8}$Cl$_{0.2}$, which is about 170 times larger compared with t-Na$_3$PS$_4$, with a low activation energy of 0.19 eV. The P oxidation state changes from 5+ to 4+, which is observed from both NMR and spin moment calculations, allows the introduction of more Cl and less Na vacancy in stable structures of Na$_{3-y}$PS$_{4-x}$Cl$_x$. DFT calculations verify that high ionic conductivities can be achieved by independent turning of Na vacancy and Cl-doping. The
performance of Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$ is tested in a Na | Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$ | Na$_3$V$_2$(PO$_4$)$_3$ cell, which delivers a capacity of 100 mAh/g.

4.3.4 Experimental Section

**Synthesis of t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ (0 ≤ y ≤ x ≤ 0.2) solid electrolytes:** t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ (0 ≤ y ≤ x ≤ 0.2) solid electrolytes were prepared via solid-state reactions. All the chemicals (Na$_2$S, P$_2$S$_5$, and NaCl) were purchased from Sigma-Aldrich and dried under vacuum at 120 °C overnight before use. Na$_2$S, P$_2$S$_5$, and NaCl were weighed inside an Ar-filled glove box and the molar ratios were calculated based on the target compositions. The mixtures were manually ground first, then sealed in a 25-mL ZrO$_2$ jar under vacuum and ball-milled using a SPEX Sample Prep 8000M mixer for 2 h with two 10-mm ZrO$_2$ balls as the milling media. The mixtures were then cold pressed into pellets, which were sintered at 420 °C for 12 h under vacuum with a heating rate of 1 °C/min in a tube furnace (Carbolite MTF). The vacuum environment and temperature gradient generated within the tube furnace facilitate the extraction of S, which favors the replacement of S by Cl. Heating was then turned off to allow the sintered pellets to cool down to room temperature.

**Characterizations of t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ (0 ≤ y ≤ x ≤ 0.2):** The phase identity is examined by powder X-ray diffraction (PXRD). The as-sintered pellets were ground into fine powders and placed in a holder, which was covered by a thin Kapton film to ensure a moisture- and oxygen-free environment. The PXRD patterns were acquired on a Philips X’Pert powder X-ray diffractometer at 45 kV and 40 mA at room temperature by using a Cu-K$_\alpha$ radiation ($\lambda = 1.5406$ Å) with a fixed scanning speed of 2°/min from 15° to 60°. The morphologies of t-Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$
were checked by Scanning Electron Microscopy (SEM) on a NOVA NanoSEM 400 field-emission scanning electron microscope.

**Solid-state Nuclear Magnetic Resonance (NMR):** $^{23}\text{Na}$ solid-state NMR experiments were performed on a Bruker DRX-830 spectrometer (19.6T) with a home-built 3.2-mm low-E and high-sensitivity magic-angle spinning (MAS) probe. The Larmor frequency of $^{23}\text{Na}$ is 219.6 MHz. $^{23}\text{Na}$ spectra were acquired using a single pulse with a solid 90° pulse length of 4.95 μs, a recycle delay of 50 s, and a MAS rate of 16 kHz. $^{23}\text{Na}$ Spin-lattice relaxation time ($T_1$) measurements were carried out with a saturation recovery pulse sequence. $^{23}\text{Na}$ chemical shift was calibrated to a 0.1 M NaCl solution at 0 ppm. $^{31}\text{P}$ solid-state NMR spectra were obtained on a Bruker Avance III-500 spectrometer (11.75 T) with a 2.5-mm Bruker HXY MAS probe, operating at a Larmor frequency of 202.4 MHz. $^{31}\text{P}$ spectra were acquired using a rotor-synchronized Hahn-echo pulse sequence with a 90° pulse length of 4.2 μs, a recycle delay of 200 s, and a MAS rate of 25 KHz. $^{31}\text{P}$ chemical shift was calibrated to an 85% $\text{H}_3\text{PO}_4$ solution at 0 ppm.

**Electrochemical tests:** Ionic conductivities of t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ pellets at different temperatures were determined using AC impedance measurements. Indium (In) foils with a diameter of 5 mm were attached onto t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ pellets as blocking electrodes and current collectors. The sandwiched cell, In$|$t-Na$_{3-y}$PS$_{4-x}$Cl$_x$|In, was then sealed in a home-made cylindrical cell for tests. AC impedance measurements were performed on a Gamry Reference 600$^+$ potentiostatic with a perturbation of 50 mV and a scanning frequency from 5 MHz to 1 Hz. Variable-temperature impedance measurements were performed from room temperature to 120 °C. Cyclic voltammetry measurements were carried out on Na $|$ t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ $|$ In between −0.5V and 10 V at a scanning rate of 1 mV/s.
Fabrication and performance evaluation of all-solid-state sodium-ion batteries: A full cell was assembled using Na$_3$V$_2$(PO$_4$)$_3$/C as cathode, Na metal as anode, and t-Na$_3.0$PS$_{3.8}$Cl$_{0.2}$ as solid electrolyte. Na$_3$V$_2$(PO$_4$)$_3$/C was prepared via a sol-gel process using citric acid as both chelating agent and carbon source. V$_2$O$_5$, NH$_4$H$_2$PO$_4$, CH$_3$COONa, and citric acid (molar ratio 1:3:3.15:2) were dissolved in deionized water first, and then the solution was continuously stirred at 80 °C to obtain a uniform gel. The gel was then heated at 350 °C for 5 h and at 800 °C for another 6 h in an argon atmosphere to obtain the final Na$_3$V$_2$(PO$_4$)$_3$/C cathode. The solid electrolyte t-Na$_3.0$PS$_{3.8}$Cl$_{0.2}$ (50 mg) was cold-pressed using a 6-mm stainless steel die and then 5 mg composite cathode which contains 60% t-Na$_3.0$PS$_{3.8}$Cl$_{0.2}$ and 40% Na$_3$V$_2$(PO$_4$)$_3$/C was pressed on top of the t-Na$_3.0$PS$_{3.8}$Cl$_{0.2}$ electrolyte layer. Pure Na metal was pressed into a thin film which was attached to the opposite site of the t-Na$_3.0$PS$_{3.8}$Cl$_{0.2}$ anode. The whole battery was sealed in a home-made cylindrical cell and cycled at current density of 10 mA/g calculated based on the mass of Na$_3$V$_2$(PO$_4$)$_3$ within a voltage window of 2.5V–3.8V.

Density functional theory (DFT) calculations: All DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) within the projector augmented-wave approach. Similar parameters were used as previous works by the authors. Briefly, all calculations were performed using the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA) functional. For each composition (Na and Cl concentration), we carried out spin-polarized structure relaxation and total energy calculations of all symmetrically distinct configurations of $v'_{Na} - Cl$ in a 2×2×2 supercell of t-Na$_3$PS$_4$ (16 formula units) using parameters consistent with those in Materials Project (MP), i.e., an energy cutoff of 520 eV and a k-point mesh of at least 1000/atom. The lowest energy configuration was then selected for the subsequent calculations and analyses.
Non-spin-polarized AIMD simulations were performed for t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ at $x = 0.0625$ and 0.125 and $y = 0$, 0.0625, and 0.125 in an NVT ensemble at elevated temperatures with a Nose–Hoover thermostat. A smaller plane-wave energy cutoff of 280 eV, a minimal Γ-centered $1 \times 1 \times 1$ k-point mesh, and a time step of 2 fs were adopted. The simulation supercell sizes were around 14 Å ($2 \times 2 \times 2$ supercell) along each lattice direction. The structures were fully relaxed at 0 K and the volumes were fixed for AIMD at elevated temperatures (800 K–1400 K). No framework melting observed at the temperatures we adopted. The Na$^+$ diffusivity was calculated using the Einstein relation $D = \frac{1}{2dt} \langle [\Delta \vec{r}(t)]^2 \rangle$, where $d$ is the dimensionality of diffusion (=3 for 3D conductors here) and $[\Delta \vec{r}(t)]^2$ is the average Na$^+$ mean square displacement (MSD) over a time duration $t$. The diffusivity was obtained via a linear fitting of the MSD with time. Arrhenius plots were constructed to determine the activation energies and obtain extrapolated room-temperature diffusivities $D_{300K}$. We derived the room-temperature Na ion conductivity from the Nernst-Einstein equation, $\sigma_{300K} = \frac{\rho z^2 F^2}{RT} D_{300K}$ where $\rho$ is the molar density of diffusing Na ions in the unit cell; $z = 1$ is the charge of Na ions; and $F$ and $R$ are the Faraday's constant and the gas constant respectively. $T = 300$ K was used in the above equation. The Python Materials Genomics (pymatgen) materials analysis library was used for all analyses and structure generation.

Chapter 4.1, in full, is a reprint of the material “Role of Na$^+$ Interstitials and Dopants in Enhancing the Na$^+$ Conductivity of the Cubic Na$_3$PS$_4$ Superionic Conductor” as it appears in Chemistry of Materials, Zhuoying Zhu, Iek-Heng Chu, Zhi Deng and Shyue Ping Ong, 2015, 27(24), pp. 8318-8325. The dissertation author was the primary investigator and author of this paper. Most of the calculations and corresponding data analyses were done by the author. The van Hove function and site occupancy analysis were done by collaborator and coauthor of this paper,
Dr. Iek-Heng Chu. Chapter 4.2, in part, is a reprint of the material “Roo-Temperature All-Solid-State Rechargeable Sodium-Ion Batteries with a Cl-doped Na$_3$PS$_4$ Superionic Conductor” as it appears in Scientific Reports, Iek-Heng Chu, Christopher S. Kompella, Han Nguyen, Zhuoying Zhu, Sunny Hy, Zhi Deng, Ying Shirley Meng and Shyue Ping Ong, 2016, 6, 33733. The dissertation author contributed AIMD simulations and was the coauthor of this paper. Chapter 4.3, in full, is a reprint of the material, “Studies of Functional Defects for Fast Na-Ion Conduction in Na$_{3-y}$PS$_{4-x}$Cl$_x$ with a Combined Experimental and Computational Approach”, as it appears in Advanced Functional Materials, Xuyong Feng, Po-Hsiu Chien, Zhuoying Zhu, Iek-Heng Chu, Pengbo Wang, Marcello Immediato-Scuotto, Hesam Arabzadeh, Shyue Ping Ong and Yan-Yan Hu, 2019, 29, pp.1807951(1-9). The dissertation author was the coauthor and primary investigator for the computational part of this paper. The DFT calculations and analyses were done by the author.
Figure 4.1 (a) Crystal structure of c-Na₃PS₄ primitive cell with green-white spheres, which represent the partially occupied Na sites, whereas dark purple tetrahedrons are PS₄³⁻. (b) The lowest energy ordering of the 2×2×2 c-Na₃PS₄ supercell with an Na⁺ interstitial (located within the dashed rectangle).

Figure 4.2 Determination of energy difference constant (0.66 eV per S atom) between the DFT and experimental formation energies for sulfides.
Figure 4.3 Isosurfaces (blue) of Na ion probability density distribution \( P \) for \( \text{Na}_{3+x}\text{Si}_x\text{P}_{1-x}\text{S}_4 \) (\( x = 0.0625 \)) at 800 K.

Table 4.1 Decomposition energies \( E_{\text{decomp}} \), the corresponding decomposed products, and neutral dopant formation energies \( E_f \) of the doped \( c\)-NaPS\(_4\) compared with undoped case.

<table>
<thead>
<tr>
<th>Dopant M</th>
<th>( x )</th>
<th>( E_f ) (eV/f.u.)</th>
<th>( E_{\text{decomp}} ) (meV/atom)</th>
<th>Decomposed products</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped</td>
<td>N/A</td>
<td>N/A</td>
<td>5</td>
<td>t-NaPS(_4)</td>
</tr>
<tr>
<td>Si</td>
<td>0.125</td>
<td>1.65</td>
<td>30</td>
<td>t-NaPS(_4), Na(_4)SiS(_4)</td>
</tr>
<tr>
<td>Si</td>
<td>0.0625</td>
<td>1.04</td>
<td>13</td>
<td>t-NaPS(_4), Na(_4)SiS(_4)</td>
</tr>
<tr>
<td>Ge</td>
<td>0.0625</td>
<td>1.04</td>
<td>13</td>
<td>t-NaPS(_4), Na(_4)GeS(_4)</td>
</tr>
<tr>
<td>Sn</td>
<td>0.0625</td>
<td>1.32</td>
<td>15</td>
<td>t-NaPS(_4), Na(_4)SnS(_4)</td>
</tr>
</tbody>
</table>
Table 4.2 Average site occupancies for pristine t-Na$_3$PS$_4$, pristine and doped c-Na$_3$PS$_4$ compounds with different dopant concentrations $x$ at 800K. To compare with the case of c-Na$_3$PS$_4$, we artificially label the Na sites in t-Na$_3$PS$_4$ as Na1, whereas the middle points between any two neighboring Na sites are labeled as Na2.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structures</th>
<th>$x$</th>
<th>Na1 site occupancy</th>
<th>Na2 site occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Na$_3$PS$_4$</td>
<td>pristine</td>
<td>NA</td>
<td>0.88</td>
<td>0.06</td>
</tr>
<tr>
<td>c-Na$_3$PS$_4$</td>
<td>pristine</td>
<td>NA</td>
<td>0.84</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>Na$^+$ excess</td>
<td>NA</td>
<td>0.68</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Si-doped</td>
<td>0.0625</td>
<td>0.76</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>Ge-doped</td>
<td>0.0625</td>
<td>0.62</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>Sn-doped</td>
<td>0.0625</td>
<td>0.79</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Figure 4.4 Arrhenius plots for (a) c-Na₃PS₄ with Na⁺ excess and pristine structures; (b) doped structures Na₃₊ₓMₓP₁₋ₓS₄ (M = Si, Ge, or Sn).
Table 4.3 Channel size, channel volume, extrapolated Na\(^+\) conductivity, diffusivity at 300K, and activation energy.

<table>
<thead>
<tr>
<th>x</th>
<th>Channel size (Å)</th>
<th>Channel volume (Å(^3))</th>
<th>(\sigma_{300 \text{K}}) (mS/cm)</th>
<th>Error range of (\sigma_{300 \text{K}}) (mS/cm)</th>
<th>(D_{300 \text{K}}) (cm(^2)/s)</th>
<th>(E_a) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>N/A</td>
<td>2.15</td>
<td>863</td>
<td>1.1×10(^{-4})</td>
<td>0.68–1.1×10(^{-12})</td>
<td>537</td>
</tr>
<tr>
<td>Na(^+) excess</td>
<td>0.0625</td>
<td>2.15</td>
<td>874</td>
<td>1.06</td>
<td>0.79–1.40</td>
<td>9.8×10(^{-9})</td>
</tr>
<tr>
<td>Na(_{3+x})Si(<em>x)P(</em>{1-x})S(_4)</td>
<td>0.125</td>
<td>2.16</td>
<td>879</td>
<td>2.99</td>
<td>2.27–3.94</td>
<td>2.8×10(^{-8})</td>
</tr>
<tr>
<td>Na(_{3+x})Si(<em>x)P(</em>{1-x})S(_4)</td>
<td>0.0625</td>
<td>2.13</td>
<td>869</td>
<td>1.66</td>
<td>1.14–2.41</td>
<td>1.5×10(^{-8})</td>
</tr>
<tr>
<td>Na(_{3+x})Ge(<em>x)P(</em>{1-x})S(_4)</td>
<td>0.0625</td>
<td>2.16</td>
<td>873</td>
<td>0.54</td>
<td>0.38–0.78</td>
<td>5.1×10(^{-9})</td>
</tr>
<tr>
<td>Na(_{3+x})Sn(<em>x)P(</em>{1-x})S(_4)</td>
<td>0.0625</td>
<td>2.16</td>
<td>910</td>
<td>10.7</td>
<td>6.86–16.8</td>
<td>1.0×10(^{-7})</td>
</tr>
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</table>
Figure 4.5 Plots of the distinct-part of the van Hove correlation function ($G_d$) for Na$_{3+x}$M$_x$P$_{1-x}$S$_4$ at 800K. $G_d$ is a function of the Na–Na pair distance $r$ and time $t$. 
Figure 4.6 Structure and powder X-ray diffraction characterizations of t-Na$_{3-x}$PS$_4-x$Cl$_x$.

(a) Crystal structure of pristine tetragonal-Na$_3$PS$_4$ (space group = $P4_{2}1c$). Two crystallographically distinct sites Na$_1$ (4d) and Na$_2$ (2a), are shown in green and red, respectively. (b) Powder X-ray diffraction patterns of t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ ($x = 0, 0.0625, 0.1$, and $0.2$). Asterisk (*) indicates the background signals from sample holder and Kapton film.

Table 4.4 Formation energies of anion dopants in t-Na$_3$PS$_4$. Dopant formation energies $E_f$ and ratio of halide to sulfide ionic radii ($R_X/R_S$) of the t-Na$_{3-x}$PS$_{4-x}$X$_x$ (X=F, Cl, Br and I) at $x = 6.25\%$.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$R_X/R_S$</th>
<th>$x$ (%)</th>
<th>$E_f$ (eV/dopant)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.70</td>
<td>6.25</td>
<td>0.76</td>
</tr>
<tr>
<td>Cl</td>
<td>0.98</td>
<td>6.25</td>
<td>0.96</td>
</tr>
<tr>
<td>Br</td>
<td>1.07</td>
<td>6.25</td>
<td>1.11</td>
</tr>
<tr>
<td>I</td>
<td>1.21</td>
<td>6.25</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Figure 4.7 Ionic conductivity and Na\(^+\) probability density distribution of t-Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_{x}\). (a) Arrhenius plots of the t-Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_{x}\) with \(x = 0\) (blue) and 6.25% (red) obtained from SPS measurements, and \(x = 6.25\%\) (green) from AIMD simulations. The filled green triangle indicates the extrapolated ionic conductivity at 300K from AIMD simulations. (b) Isosurface of the Na\(^+\) probability density distribution \((P)\) in the t-Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_{x}\) \((x = 6.25\%)\) at 800K, with \(P = 0.0001\ a_0^{-3}\) \((a_0\) is the Bohr radius).

Table 4.5 Room temperature ionic conductivity and activation energy of t-Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_{x}\). Calculated AIMD and experimental Na\(^+\) conductivity and activation energy of the t-Na\(_{3-x}\)PS\(_{4-x}\)Cl\(_{x}\) superionic conductor. Values in the square brackets indicate the error range of the calculated ionic conductivity.

<table>
<thead>
<tr>
<th>(x) (%)</th>
<th>AIMD simulations</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\sigma_{300K}) (mS cm(^{-1}))</td>
<td>(E_a) (meV)</td>
</tr>
<tr>
<td>0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>6.25</td>
<td>1.38 [1.04, 1.82]</td>
<td>232</td>
</tr>
</tbody>
</table>
Figure 4.8 Electrochemical decomposition products of doped Na$_3$PS$_4$ compounds. Plots of Na uptake per formula unit (f.u.) of t-Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$ (red solid), c-Na$_{3.0625}$Sn$_{0.0625}$P$_{0.9375}$S$_4$ (blue dashed) and c-Na$_{3.0625}$Si$_{0.0625}$P$_{0.9375}$S$_4$ (green dashed) solid electrolytes against voltage vs Na/Na$^+$. At low voltage (high Na chemical potential), each solid electrolyte undergoes reduction and uptakes Na, while at high voltage (low Na chemical potential), each solid electrolyte is oxidized and loses Na. Text indicates the predicted phase equilibria at corresponding regions of the profile. Only selected regions are annotated for brevity.
Table 4.6 Rietveld refinement of t-Na$_{3-x}$PS$_{4-x}$Cl$_x$. Rietveld refinement results of t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ systems, where $a$, $b$ and $c$ are lattice constants, and $V$, Occ., and $B_{\text{iso}}$ are normalized cell volume, site occupation numbers, and isotropic atomic displacement parameters, respectively. Residual factors, $R_b$ and $R_{wp}$, for the pristine ($x = 0\%$) composition are 3.86% and 4.97%, respectively; and for the doped ($x = 6.25\%$) are 4.29% and 5.31%. For the pristine t-Na$_3$PS$_4$, the DFT calculated cell parameters are $a = b = 6.99$ Å, $c = 7.12$ Å, $V = 348$ Å$^3$, in excellent agreement with the refinement results as well as those by Jansen et al. (Ref. 27): $a = b = 6.952$ Å, $c = 7.076$ Å, $V = 341.97$ Å$^3$.

<p>| | | | | | |</p>
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<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>Pristine</strong> ($x = 0%$), Space Group $P42_1c$</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a = b = 6.956(5)$ Å, $c = 7.088(6)$ Å, $V = 342.9(5)$ Å$^3$</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$R_b = 3.86%$, $R_{wp} = 4.97%$</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na1 (4$d$)</td>
<td>0</td>
<td>0.5</td>
<td>0.426(4)</td>
<td>2.00</td>
<td>2.54(9)</td>
</tr>
<tr>
<td>Na2 (2$a$)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.00</td>
<td>3.2(1)</td>
</tr>
<tr>
<td>P (2$b$)</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>1.00</td>
<td>0.5(6)</td>
</tr>
<tr>
<td>S (8$e$)</td>
<td>0.315(3)</td>
<td>0.345(2)</td>
<td>0.167(2)</td>
<td>4.00</td>
<td>1.1(6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Doped</strong> ($x = 6.25%$), Space Group $P42_1c$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a = b = 6.970(4)$ Å, $c = 7.092(5)$ Å, $V = 344.5(4)$ Å$^3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_b = 4.29%$, $R_{wp} = 5.31%$</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Na1 (4$d$)</td>
<td>0</td>
<td>0.5</td>
<td>0.428(6)</td>
<td>1.99(4)</td>
<td>3.0(2)</td>
</tr>
<tr>
<td>Na2 (2$a$)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.99(4)</td>
<td>3.4(3)</td>
</tr>
<tr>
<td>P (2$b$)</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>1.00</td>
<td>0.1(1)</td>
</tr>
<tr>
<td>S (8$e$)</td>
<td>0.316(4)</td>
<td>0.344(3)</td>
<td>0.165(3)</td>
<td>3.94(4)</td>
<td>1.19(9)</td>
</tr>
<tr>
<td>Cl (8$e$)</td>
<td>0.316(4)</td>
<td>0.344(3)</td>
<td>0.165(3)</td>
<td>0.02(4)</td>
<td>1.19(9)</td>
</tr>
</tbody>
</table>
Figure 4.9 Characterization and morphology of t-Na$_{3-x}$PS$_{4-x}$Cl$_x$. (a) XRD patterns for t-Na$_3$PS$_4$.xCl$_x$ with x = 0% and 6.25%, and previous study in Ref. 27. (b) Refinement plot of the pristine t-Na$_3$PS$_4$. (c) Refinement plot of Cl-doped t-Na$_3$PS$_4$. Solid red and black lines denote the observed and calculated XRD patterns, while the green ticks mark the position of the reflections allowed by the space groups of t-Na$_3$PS$_4$ ($P4_2_1c$) and NaCl ($Fm\overline{3}m$). The difference between the observed and calculated patterns is signified by the blue line. (d) SEM image of pristine t-Na$_3$PS$_4$ SPS sample, and (e) SEM image of SPS sample of doped t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ (x = 6.25%). Scale bar is 10 µm.
Figure 4.10 Electrochemical performance of TiS$_2$/t-Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$/Na all-solid-state full-cell. Charge-discharge profile of TiS$_2$/t-Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$/Na full-cell at room-temperature. Cell was cycled under constant current conditions with a current density of 0.149 mA cm$^{-2}$ (C/10 rate) from 1.2 V to 2.4 V. The cell was able to routinely deliver 80 mAh g$^{-1}$ over 10 cycles. Red and black lines in the charge-discharge profile denote charging and discharging, respectively. Similarly, red and black markers signify charge and discharge capacities, while the green circles mark the coulombic efficiency by cycle.

Figure 4.11 EDX element maps of doped sample (x = 6.25%) for (a) S and (b) Cl. Maps correspond to SEM image (Figure 4e). Scale bar is 10 µm.
Figure 4.12 Electrochemical Impedance measurements at 21 °C and Nyquist plots of t-Na$_{3-x}$PS$_{4-x}$Cl$_x$. (a) Nyquist plots of t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ (x = 0, 0.0625, 0.1, and 0.2). (b) Arrhenius plot of t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ (x = 0, 0.0625, 0.1, and 0.2).
Figure 4.13 Evolution of structural defects in t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ (x = 0, 0.0625, 0.1, and 0.2) electrolytes probed by $^{23}$Na solid-state magic-angle-spinning (MAS) NMR. $^{23}$Na MAS NMR spectra together with simulation results of t-Na$_{3-x}$PS$_{4-x}$Cl$_x$ (x = 0, 0.0625, 0.1, and 0.2).
Figure 4.14 Identification of functional defects with tracer-exchange NMR and $^{23}\text{Na}$ solid-state magic-angle-spinning (MAS) NMR. (a) Schematic of electrochemically driven $^7\text{Li} \rightarrow ^{23}\text{Na}$ tracer-exchange method. $^{23}\text{Na}$ MAS NMR spectra (b) and quantification (c) of t-\text{Na$_{2.8}$PS$_{3.8}$Cl$_{0.2}$} before/after $^7\text{Li} \rightarrow ^{23}\text{Na}$ tracer-exchange.
Figure 4.15 Structure characterizations of synthesized t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$/zNaCl (z = 0, 0.1, 0.3, and 0.5). (a) Powder X-ray diffraction patterns and (b) $^{23}$Na MAS NMR spectra of t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$/zNaCl (z = 0, 0.1, 0.3, and 0.5). Asterisk (*) indicates the background signals from sample holder and polyimide film.

Figure 4.16 Enhanced ionic conductivities of t-Na$_{3-x}$PS$_{4+x}$Cl$_{x}$ (a) Nyquist plots of t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$/zNaCl (y = 0, 0.1, 0.3, and 0.5). (b) Variable-temperature impedance spectra of t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$/0.1NaCl. (c) Arrhenius plots of t-Na$_{3}$PS$_{4}$, t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$, and t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$/0.1NaCl.
Figure 4.17 Ionic conductivity of t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ from AIMD simulations. Arrhenius plots for Na$_3$PS$_{3.9375}$Cl$_{0.0625}$ (red), Na$_3$PS$_{3.875}$Cl$_{0.125}$ (orange); Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$ (yellow); Na$_{2.9375}$PS$_{3.875}$Cl$_{0.125}$ (green), and Na$_{2.875}$PS$_{3.875}$Cl$_{0.125}$ (blue) obtained from AIMD simulations. Squares and circles denote compositions with and without Na vacancies, respectively. Filled circles or squares indicate the extrapolated diffusivities at 300 K.

Table 4.7 Calculated Na ionic conductivity, activation energy and the channel volume of t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ (x = 0.0625 and 0.125; y = 0, 0.0625, and 0.125). Values in the square brackets indicate the error range of the calculated ionic conductivity. Channel volumes are the averaged Na$^+$ diffusion channels obtained from AIMD trajectories at 800K.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\sigma_{300K}$ (mS/cm)</th>
<th>$E_a$ (eV)</th>
<th>Error range of $\sigma_{300K}$ (mS/cm)</th>
<th>Channel volume ($\AA^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$<em>3$PS$</em>{3.9375}$Cl$_{0.0625}$</td>
<td>0.009</td>
<td>0.388</td>
<td>[0.005, 0.014]</td>
<td>937</td>
</tr>
<tr>
<td>Na$<em>3$PS$</em>{3.875}$Cl$_{0.125}$</td>
<td>0.002</td>
<td>0.447</td>
<td>[0.002,0.004]</td>
<td>947</td>
</tr>
<tr>
<td>Na$<em>{2.9375}$PS$</em>{3.9375}$Cl$_{0.0625}$</td>
<td>1.38</td>
<td>0.232</td>
<td>[1.04, 1.82]</td>
<td>924</td>
</tr>
<tr>
<td>Na$<em>{2.9375}$PS$</em>{3.875}$Cl$_{0.125}$</td>
<td>9.03</td>
<td>0.174</td>
<td>[5.74, 14.2]</td>
<td>948</td>
</tr>
<tr>
<td>Na$<em>{2.875}$PS$</em>{3.875}$Cl$_{0.125}$</td>
<td>6.38</td>
<td>0.199</td>
<td>[5.89, 6.91]</td>
<td>932</td>
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</table>
Figure 4.18 Cyclic Voltammetry and electrochemical performance of a full cell solid-state battery made of Na | t-Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$ | Na$_3$V$_2$(PO$_4$)$_3$. (a) CV of a Na | t-Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$ | In cell, (b) The charge and discharge profiles of Na | t-Na$_{3.0}$PS$_{3.8}$Cl$_{0.2}$ | Na$_3$V$_2$(PO$_4$)$_3$ performed at room temperature with a current density of 10 mA/g calculated based on the mass of Na$_3$V$_2$(PO$_4$)$_3$.

Figure 4.19 Variable-temperature Nyquist plots of (a) t-Na$_3$PS$_4$, (b) t-Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$, (c) t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$, and (d) t-Na$_{2.8}$PS$_{3.8}$Cl$_{0.2}$. 
Figure 4.20 (a) Nyquist plots of t-Na$_{2.8}$PS$_{3.8}$Cl$_{0.2}$/z NaCl (z = 0, 0.1, 0.2, and 0.5). (b) Summary of ionic conductivity in t-Na$_{2.9}$PS$_{3.9}$Cl$_{0.1}$/z NaCl (z = 0, 0.1, 0.3, and 0.5) and t-Na$_{2.8}$PS$_{3.8}$Cl$_{0.2}$/z NaCl (z = 0, 0.1, 0.2, and 0.5) at 21°C.

Figure 4.21 Changes in phosphorous local environment of t-Na$_{3-y}$PS$_{4-x}$Cl$_x$ detected by $^{31}$P MAS NMR. (a) $^{31}$P NMR spectra of five selected samples. (b) 6-fold magnification of (a) to show the changes in the spectral range of 90–120 ppm.
Figure 4.22 Summary of $^{31}$P MAS NMR spectra.
(a) FWHM of PS$_4^{3-}$ unit at 86.5 ppm in t-Na$_3$PS$_4$ structural framework. (b) Normalized $^{31}$P integral of P$^{4+}$ signals (108 to 116 ppm) induced by Cl$^{-}$ doping.

Figure 4.23 XRD patterns of the evaporated S from the synthesis of t-Na$_{2.8}$PS$_{3.8}$Cl$_{0.2}$ and standard S$_8$. 
Figure 4.24 Calculated integrated spin charge density as a function of radius cutoff around P in t-
Na$_3$PS$_{3.9375}$Cl$_{0.0625}$.

Figure 4.25 DC polarization curve of Na$_3$PS$_4$ and Na$_3$PS$_{3.8}$Cl$_{0.2}$ under 1 V (diameter of In current
collector is 5 mm, thickness is 1mm)
Figure 4.26 AC impedance of Na|Na\textsubscript{3.0}PS\textsubscript{3.8}Cl\textsubscript{0.2}|Na\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} full cell before and after cycling.
Chapter 5. Cation Mixing in Stable, High Conductivity Sodium Solid Electrolytes

In this chapter, we present our work on Na$_3$Pn'S$_4$–Na$_3$Pn'S$_4$ isovalent and Na$_4$TtS$_4$–Na$_3$PnS$_4$ aliovalent mixing (Pn = P, As, Sb; Tt = Si, Ge, Sn) in Na–Tt–Pn–S composition space to optimize and improve their properties using first principles method. The multiple dimensions to tune Na concentration and cation types in this composition space can significantly enhance the possibility to simultaneously achieve the twin goals of high ionic conductivity and good electrochemical and chemical stability.

5.1 Introduction

Rechargeable all-solid-state sodium-ion batteries (SSABs) utilizing a superionic conductor solid electrolyte (SE) have garnered substantial interest in recent years.$^{168-170}$ An all-solid-state architecture promises to be safer and potentially more energy dense, while the use of abundant and cheap sodium in place of lithium addresses potential concerns with regards to availability and cost, especially for larger scale applications. Furthermore, sodium-ion chemistry also opens up unexplored compositions and structural spaces that are not found in lithium-ion chemistry (e.g., P2 layered materials), which expands the scope for finding chemically and mechanically well-matched electrode-SE combinations.

Among known sodium superionic conductors, $^{168-170,34}$ Na$_3$PS$_4$$^{32,135}$ and its derivatives have stood out due to their especially high ionic conductivities. First reported by Hayashi et al.$^{32}$ with an ionic conductivity of 0.2 mS cm$^{-1}$ in 2012, intensive research has pushed its conductivity to
above 1 mS cm\(^{-1}\) via aliovalent cation (e.g., P\(^{5+}\) for Sn\(^{4+}\))\(^{37,73}\) and anion (e.g., S\(^{2-}\) for Cl\(^{-}\))\(^{123,172}\) doping as well as isovalent substitution of P for Sb/As.\(^{165,155,183}\) More recently, a new prototype has been discovered in the Na\(_3\)PnS\(_4\)-Na\(_4\)TtS\(_4\) system with composition Na\(_{11}\)Tt\(_2\)PnS\(_{12}\) (Pn = P/Sb, Tt = Sn) and a tetragonal \(I4_1/\text{acd}\) space group.\(^{36,161}\) Na\(_{11}\)Sn\(_2\)PS\(_{12}\) have independently been reported by Zhang et al.\(^{36}\) and Duchardt et al.\(^{169}\) with an ionic conductivity of 1.4-3.7 mS/cm, while Na\(_{11}\)Sn\(_2\)SbS\(_{12}\) has also been reported by Heo et al.\(^{176}\) and Ramos et al.\(^{177}\) with an ionic conductivity of 0.2-0.56 mS/cm. This unique prototype shows the superiority with isotropic 3D Na\(^+\) conduction and low grain boundary resistance.\(^{36,177}\)

In this work, we present a comprehensive study of the Na\(_3\)PnS\(_4\)-Na\(_4\)TtS\(_4\) (Pn = P/As/Sb, Tt = Si/Ge/Sn) phase space of superionic conductors using density functional theory (DFT) calculations. We quantify the enthalpy for isovalent mixing, i.e., P/Sb/As mixing, in tetragonal and cubic polymorphs of Na\(_3\)PnS\(_4\), as well as the effect of such mixing on relative polymorph stability, electrochemical and moisture stability. We further extend our study to mixed Na\(_4-x\)Tt\(_{1-x}\)Pn\(_x\)S\(_4\) phases, including the recently-reported Na\(_{11}\)Tt\(_2\)PnS\(_{12}\) prototype. We demonstrate that fundamental electrochemical stability at both high and low voltages is limited by the least stable cation (whether Pn or Tt). Finally, a new composition Na\(_{11}\)Sn\(_2\)AsS\(_{12}\) is proposed with potentially improved ionic conductivity as well as moisture stability over all previously reported compositions in this space.

5.2 Methods

5.2.1 Structure Preparation
The prototypical crystal structures of the tetragonal and cubic forms of Na₃PnS₄ (t-Na₃PnS₄ and c-Na₃PnS₄, respectively), Na₄TtS₄ and Na₁₁Tt₂PnS₁₂ are shown in Figure 5.1. The mixed compounds investigated in this work are listed in Table were generated in the following manner:

1. Isovalent mixed Na₃Pₙ₋ₓPₙ₋₁ₓS₄ (Pₙ’,Pₙ”=P, As or Sb) structures with x in intervals of 1/16 were generated by enumerating all symmetrically distinct configurations using 2×2×2 supercell of t- and c-Na₃PS₄.

2. Aliovalent mixed Na₄₋ₓTtₓ₋₁ₓPₙS₄ structures were with x in intervals of 1/4 generated by enumerating all symmetrically distinct Na vacancy and Tt/Pn orderings in 2×1×1 supercells of Na₃PS₄ (P₄̅2₁c), Na₄SnS₄ (P₄̅2₁c). In addition, substitutions of different Tt and Pn in different ratios, charge balanced by modifications in Na concentration, were carried out on the primitive cell of Na₁₁Sn₂PS₁₂ (I4₁/acd).

5.2.2 DFT Calculations

All DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) within the projector augmented-wave approach. The Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA) exchange-correlation functional was used for all calculations.

For structural relaxations and energy calculations of the Na₃PnS₄-Na₄TtS₄ phases of primary interest, spin-polarized calculations were performing with an energy cutoff of 520 eV and a k-point density of at least 1000/(number of atoms were applied, similar to those used in the Materials Project (MP). These energies were then combined with pre-computed energies for other phases in the MP for phase stability, moisture stability and electrochemical stability analysis.
For the *ab initio* molecular dynamics (AIMD) simulations, non-spin-polarized calculations were carried out with a smaller plane-wave energy cutoff of 280 eV, a minimal Γ-centered 1×1×1 k-point mesh. The timestep was 2 fs. The AIMD simulations were done in the *NVT* ensemble at six temperatures (800 -1400 K or 700-1200 K depending on melting temperature of the structure) with a Nose-Hoover thermostat,75,76 with the volume (*V*) fixed as GGA-relaxed volume at 0K, in line with typical approximations used in prior works.91

All DFT and AIMD simulations were carried out using fully-automated workflows173 built on the Python Materials Genomics (pymatgen)105 library and automated scientific workflow package.141

### 5.2.3 Property Analysis

The 0K Na–Pn′–Pn”–S and Na–Tt–Pn–S phase diagrams were constructed by taking the convex hull of the energies of all phases in the respective compositional spaces.51 From the 0K phase diagram, the energy above the convex hull (*E*<sub>hull</sub>), an estimate of the phase stability, can be obtained for each phase of interest. In addition, the 0K pseudo-binary Na₃Pn’S₄–Na₃Pn”S₄ stability diagram were constructed for each Pn′–Pn” combination, from which the mixing enthalpies of Na₃Pn’ₓPn”₁₋ₓS₄ can be obtained.

To estimate the electrochemical stability, the Na grand canonical phase diagrams51 were constructed to determine the range of Na chemical potentials for which each solid electrolyte composition is against Na extraction or uptake, in line with the approach developed by Ong et al.91, Mo et al.111 for analysis of lithium superionic conductors. In this approach, the SE/cathode and
SE/anode interfaces are modelled as an open system where the SE is in contact with a Na sink at low Na chemical potential and Na source at high Na chemical potential, respectively.

The moisture sensitive of each SE is estimated by the reaction energy of the SE with H₂O at 0K. This is done by constructing the Na–Pn’–Pn”–S–H–O or Na–Tt–Pn–S–H–O phase diagram and identifying the most exothermic reaction along the tie-line between the SE composition and H₂O.¹⁵,⁵⁵,⁹¹ The more negative the reaction energy, the more sensitive the SE is to moisture.

Finally, the diffusivity $D$ of each SE at each AIMD simulation temperature was obtained by performing a linear fit of the mean square displacements (MSD) of Na in the AIMD trajectories with time, according to the following equation:

$$D = \frac{MSD}{2dt}, \text{ where } MSD = \langle |\Delta r(t)|^2 \rangle$$  \hspace{1cm} (5.1)

An Arrhenius plot was then constructed by plotting log($D$) versus $1/T$, where $T$ is the temperature, from which the activation barrier for conductivity and the extrapolated room temperature conductivities and diffusivities can be obtained.

### 5.3 Results

#### 5.3.1 Isovalent Cation Mixing in $\text{Na}_3\text{Pn'}_x\text{Pn''}_{1-x}\text{S}_4$

**Cubic VS Tetragonal.** Table 5.1 lists the composition space that we investigated in this work including $\text{Na}_3\text{Pn'}_x\text{Pn''}_{1-x}\text{S}_4$ from two sources (t- and c-$\text{Na}_3\text{PS}_4$). As reported previously,¹³,¹⁷⁸ cubic and tetragonal $\text{Na}_3\text{PS}_4$ have great structural similarities and relatively small energy difference.
(~ 5 meV/atom). Na₃SbS₄ and Na₃AsS₄ were isostructures substituted from t- and c-Na₃PS₄. We listed the lattice parameter and energy above hull ($E_{\text{hull}}$) in Table 5.2. The lattice parameters increase along with Pn⁵⁺ ionic radius following the order of Na₃PS₄ < Na₃AsS₄ < Na₃SbS₄. The zero value of $E_{\text{hull}}$ for t-Na₃PnS₄ (Pn=P, As, Sb) implies it is the most stable phase compared with c-Na₃PnS₄.

We calculated energy difference between the cubic and tetragonal phase ($E_{\text{cubic}} - E_{\text{tetra}}$) to show the trend of phase preference at various mixing ratio (0 < $x$ < 1) in Na₃PnₓPn''₁⁻ₓS₄. From Figure 5.2(a-c), we can see that the value is subtly positive in the range of 3~6 meV/atom, which indicates cubic phase is slightly unstable compared to tetragonal phase. The ranking of polymorph energy difference for pure Na₃PnS₄ is Na₃PS₄ (5.4 meV/atom) > Na₃SbS₄ (4.3 meV/atom) > Na₃AsS₄ (3.5 meV/atom). Na₃PₓSb₁⁻ₓS₄ show energy-favorable intermediate phase at $x$ ~ 0.25, while was not observed in arsenic-containing compounds.

**Miscibility and Ordering Pattern.** Figure 5.2 shows the predicted 0 K enthalpy of mixing for t-Na₃PnₓPn''₁⁻ₓS₄ supercell involving 128 atoms. We observe that P-As mixing leads to a slightly negative value of enthalpy of mixing (~ -1 meV/formula unit) attesting an excellent miscibility in Na₃AsₓP₁⁻ₓS₄ system, which is in good agreement with previous study (a negligibly positive mixing enthalpy of < 1 meV/atom) by Shang et al.¹⁷⁵ For Na₃SbₓAs₁⁻ₓS₄ mixing, we find the mixing enthalpy turns to be positive but no larger than 5 meV/f.u. (< 3 meV/f.u. even when $x$ = 0.5) as shown in the center of Figure 5.2. The mixing enthalpy for P-Sb mixing is the largest: the enthalpy of mixing is always positive at any ratio of $x$ and we can see an increased miscibility gap of 10 meV/f.u. at $x$ = 0.5. These results clearly show that the larger lattice or ionic radius difference of two end members, the higher enthalpy of mixing between them.
The even distribution of mixing enthalpy respect to \( x = 0.5 \) indicates that preferential phase segregation introduced by certain elements is unlikely to happen and \( \text{Na}_3\text{Pn}'\text{Pn}''_1\text{Pn}''_2\text{S}_4 \) systems show a good solubility through the entire composition space. We checked the arrangements of \( \text{PnS}_4 \) tetrahedrons for the most stable configurations to find the inerratic ordering patterns. Taking \( \text{Na}_3\text{Sb}_{0.5}\text{P}_{0.5}\text{S}_4 \) as an example (Figure 5.3a), \( \text{PS}_4 \) and \( \text{SbS}_4 \) tetrahedrons alternate in the same column or row within \( \text{ab} \) plane, forming the roughly centrosymmetric pattern in \( \text{ab} \) plane. When \( \text{Pn}' \) and \( \text{Pn}'' \) have the same ratio, the queue of \( \text{PnS}_4 \) tetrahedrons along \( \text{c} \) direction keeps homogeneous and the non-interval chain of \( \text{Na}1 \) (Wyckoff site: \( 4d \), following the symbols in pristine \( \text{t-Na}_3\text{PS}_4 \) sites along \( \text{c} \) direction are interconnected via \( \text{Na}2 \) (Wyckoff site: \( 2a \) sites. The same ordering pattern shown in \( \text{Na}_3\text{As}_{0.5}\text{P}_{0.5}\text{S}_4 \) (Figure 5.3b) verifies the trend is universal regardless of \( \text{Pn}'--\text{Pn}'' \) combination. In addition, any complementary mixing ratio, e.g., \( \text{Na}_3\text{As}_{0.2}\text{P}_{0.8}\text{S}_4 \) vs \( \text{Na}_3\text{As}_{0.8}\text{P}_{0.2}\text{S}_4 \), gives the similar orderings with the only difference of \( \text{Pn}'--\text{Pn}'' \) position swapping.

### 5.3.2 Aliovalent Cation Mixing in \( \text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4 \)

**Prototype Comparison in \( \text{Na}--\text{Sn}--\text{P}--\text{S} \).** In addition to the isovalent \( \text{Pn}'--\text{Pn}'' \) mixing, we probe another chemical space of \( \text{Na}--\text{Sn}--\text{P}--\text{S} \) by either aliovalent mixing of \( \text{Na}_3\text{PS}_4--\text{Na}_4\text{SnS}_4 \) or tailoring from the newly-reported \( \text{Na}_{11}\text{Sn}_2\text{PS}_{12} \) prototype (space group: \( \text{I4}_1/acd \)).\(^{36}\) The two ternary parent structures, \( \text{t-Na}_3\text{PS}_4 \) and \( \text{Na}_4\text{SnS}_4 \), display high similarity in polyhedron arrangements and belong to the same space group of \( \text{P42}_1\text{c} \) with the only disparity of \( \text{Na} \) sites as shown in Figure 5.1. When mixing \( \text{Sn} \) and \( \text{P} \) from either side, we introduced proper \( \text{Na} \) defects for the sake of total charge neutrality. Substitutions of \( \text{Sn} \) for \( \text{P} \) in \( \text{Na}_3\text{PS}_4 \) requires the equivalent \( \text{Na} \) excess. To the contrary, \( \text{Na} \) vacancies form in \( \text{Na}_4\text{SnS}_4 \) when replacing \( \text{P} \) for \( \text{Sn} \) in \( \text{Na}_4\text{SnS}_4 \).
Na$_{11}$Sn$_2$PS$_{12}$, a novel superionic conductor first reported by Nazar’s group, has a different single crystal structure (see Figure 5.4a) in contrast to Li$_{10}$GeP$_2$S$_{12}$ and Na$_3$PS$_4$. This new prototype with 5 geometrically distinct Na sites (corrected to 6 by the same group in a follow-up paper) exhibits the underlying isotropic 3D fast-ion diffusion and shows a high room-temperature conductivity of 1.4 mS/cm as well as the low activation energy of 0.25 eV. Shortly after, a higher conductivity (3.7 mS/cm) was reported by Duchardt and coworkers, but with a higher activation energy (0.39 eV). Moreover, quaternary analogs not limited to Na–Sn–P–S space group were found recently: Sb-version Na$_{11}$Sn$_2$SbS$_{12}$ and selenium-based non-stoichiometric Na$_{11.1}$Sn$_{2.1}$P$_{0.9}$Se$_{12}$. All of these findings reveal that Na–Tt–Pn–S should be a fruitful and promising composition space and this distinct prototype of tetragonal phase ($I4_1/acd$) shows great superiority worth sufficiently exploration.

Figure 5.4 gives the unit cell of Na$_{11}$Sn$_2$PS$_{12}$ compared with 2×2×2 supercell of Na$_3$PS$_4$. We can observe the exceeding disorder in Na sites of Na$_{11}$Sn$_2$PS$_{12}$ and PS$_4$ and SnS$_4$ 2D slabs in the ab plane alternate at $z = 1/8$ and $z = 1/4$, respectively. Sn (Wyckoff site: 16e) and P (Wyckoff site: 8a) occupy two distinct sites leaving more vacant volume that can be used for Na diffusion. A comparison in terms of channel density between Na$_{11}$Sn$_2$PS$_{12}$ and Na$_3$PS$_4$ is given in the Discussion section. We show the phase stability ($E_{\text{hull}}$) of Na$_{4-x}$Sn$_{1-x}$P$_x$S$_4$ from three prototype sources (Na$_3$PS$_4$, Na$_4$SnS$_4$, Na$_{11}$Sn$_2$PS$_{12}$) in Figure 5.4d covering the maxing ratio of $x = 1/4$, 1/2, 3/4 and additional $x = 1/3$ for Na$_{11}$Sn$_2$PS$_{12}$. The structures are generated by substituting Sn for P (or the opposite way) and tuning Na concentration (create Na defect or change Na occupancy) simultaneously. Figure 5.4d clearly shows that Na$_{11}$Sn$_2$PS$_{12}$ prototype is more thermodynamically stable than the other two at various x values. Moreover, Sn-rich Na$_{4-x}$Sn$_{1-x}$P$_x$S$_4$ ($x < 0.5$) have lower $E_{\text{hull}}$ than P-rich composition ($x > 0.5$) as shown in Table 5.3. The same tendency holds for
Na$_{11}$Sn$_2$SbS$_{12}$ as well (see Figure 5.10). In the following, we will only focus on the new Na$_{11}$Sn$_2$PS$_{12}$ prototype.

Optimized Stoichiometry and Elements for Na$_{4-x}$Tt$_{1-x}$Pn$_x$S$_4$. Figure 5.5 shows the complete $E_{\text{hull}}$ data for three Tt (Si, Ge, Sn) and three Pn elements (P, As, Sb) at 4 mixing ratios ($x = 1/4$, 1/3, 1/2, 3/4). In general, all compounds we calculated have a relatively small $E_{\text{hull}}$ of $< 8$ meV/atom. Particularly, we observe that the mixing ratio of $x = 1/3$ (normalized formula: Na$_{3.67}$Tt$_{0.67}$Pn$_{0.33}$S$_4$) leads to the lowest $E_{\text{hull}}$ among all mixing ratios. The overall feasibility of Na$_{4-x}$Tt$_{1-x}$Pn$_x$S$_4$ is high, especially at $x = 0.33$. Under this ratio, P and As-containing compounds have the $E_{\text{hull}}$ of 0 meV/atom regardless of Tt species. Sb-containing compounds have slightly higher $E_{\text{hull}}$ values which is still no larger than 3.5 meV/atom. Excluding this special ratio ($x = 1/3$), in which 16e and 8a sites are fully occupied by Tt and Pn element, respectively, the $E_{\text{hull}}$ values have the general trend of increasing with $x$. When $x = 3/4$, the maximum of $E_{\text{hull}}$ is in the range of 5 ~ 8 meV/atom.

5.3.3 Moisture Stability

The poor chemical stability in the ambient environment is a major drawback of sulfide electrolytes because of the high reactivity between sulfides and oxygen/moisture in the air. It is essential to understand the determinative factors that affect the moisture stability for sulfide electrolytes so that we can avoid the harmful elements during our consideration for promising sulfide candidates. Figure 5.6 shows the moisture stability of the two groups of compounds: (1) Na$_3$Pn$_x$Pn$_{1-x}$S$_4$ by isovalent mixing (top panel) and (2) Na$_{11}$Tt$_2$PnS$_{12}$ by aliovalent mixing (bottom panel). The reactivity of Na$_3$P$_x$Sb$_{1-x}$S$_4$ with H$_2$O is the highest among all Na$_3$Pn$_x$Pn$_{1-x}$S$_4$ systems. The collective reaction products are NaSbS$_2$, Na$_3$PS$_3$O, and NaHS for the entire P-Sb
mixing region. $\text{NaS}_2$ and $\text{Na}_3\text{SbS}_3$ are exclusively formed in Sb-rich region ($x = 0.0625-0.375$); $\text{Na}_2\text{S}_5$, t-$\text{Na}_3\text{PS}_4$ appear at moderate P-Sb mixing ratio ($x = 0.4375$); $\text{Na}_2\text{S}_5$ and $\text{H}_2\text{S}$ (gaseous phase at room temperature) form in P-rich concentration ($x = 0.5625-0.9375$). Considering the fact that $\text{Na}_3\text{PS}_4$ reacts with $\text{H}_2\text{O}$ but $\text{Na}_3\text{SbS}_4$ does not, we think the high reactivity of P-Sb mixed intermediate compounds, which is even poorer than pure $\text{Na}_3\text{PS}_4$, can be attributed to the phase instability of $\text{Na}_3\text{P}_x\text{Sb}_{1-x}\text{S}_4$.

$\text{Na}_3\text{As}_x\text{P}_{1-x}\text{S}_4$ compounds show a better moisture stability with reaction products of $\text{Na}_3\text{PS}_3\text{O}$, gaseous $\text{H}_2\text{S}$ and water-resist $\text{Na}_3\text{AsS}_4$. Impressively, all $\text{Na}_3\text{Sb}_x\text{As}_{1-x}\text{S}_4$ compounds are stable with $\text{H}_2\text{O}$. If we plan to modify the moisture stability based on well-known Na electrolyte $\text{Na}_3\text{PS}_4$, though both $\text{Na}_3\text{AsS}_4$ and $\text{Na}_3\text{SbS}_4$ do not react with $\text{H}_2\text{O}$, introducing As and Sb into $\text{Na}_3\text{PS}_4$ has opposite influence: As-mixing enhance while Sb-mixing do harm the moisture stability.

For quaternary $\text{Na}_{11}\text{Tt}_2\text{PnS}_{12}$ compounds, the most moisture-active ones are Si-containing $\text{Na}_{11}\text{Si}_2\text{PnS}_{12}$ ($\text{Pn} = \text{P, As, Sb}$), which may result from the formation of very stable SiO$_2$ in reaction with $\text{H}_2\text{O}$. $\text{Na}_{11}\text{Ge}_2\text{PnS}_{12}$ and $\text{Na}_{11}\text{Sn}_2\text{PnS}_{12}$ share a similar trend with $\text{Na}_3\text{Pn'}_x\text{Pn''}_{1-x}\text{S}_4$ that P-containing compounds are slightly more reactive with water.

### 5.3.4 Electrochemical Stability

Figure 5.7 shows the predicted electrochemical (EC) window of selected pure and mixed $\text{Na}_3\text{PnS}_4/\text{Na}_4\text{TtS}_4$ as well as $\text{Na}_{11}\text{Tt}_2\text{PnS}_{12}$ calculated using the grand potential phase diagram approach. Note that extremely narrow EC window of $\text{Na}_3\text{AsS}_4(1.94–2.12\text{V})$ reported in the previous work$^{56}$ was attributed by the missing entry of $\text{Na}_3\text{AsS}_4$ in the database. After properly including all entries, we obtained a much wider EC window of 1.57–2.47 V for $\text{Na}_3\text{AsS}_4$. The
electrochemical reactions products at different potentials of pure compositions can be found in Figure 5.11 and Figure 5.12.

From Figure 5.7 we can observe that the EC window of a given mixed composition highly agrees with the overlapping EC windows of its components no matter in isovalent or aliovalent mixing cases. For example, the EC window of \( \text{Na}_{11}\text{Ge}_2\text{SbS}_{12} \) (1.52–2.07V) coincides with the overlapping part of \( \text{Na}_4\text{GeS}_4 \) (1.05–2.06V) and \( \text{Na}_3\text{SbS}_4 \) (1.54–2.35V), which is 1.54–2.06V with a negligible deviation of 0.02 V. The greatest error found after enumerating all the combinations is only 0.04V. This indicates that the EC window of a mixed sulfide is limited by the overlap region of its components.

### 5.3.5 Conductivity and Band Gap

Due to the poor moisture stability of Si phase and high expenses of Ge, we selected promising candidates of Sn-containing compounds \( \text{Na}_{11}\text{Sn}_2\text{PnS}_{12} \) (\( \text{Pn}=\text{P}, \text{As}, \text{Sb} \)) to calculate their ionic conductivities and electronic band gaps, which were calculated using AIMD simulations and HSE hybrid functional, respectively. Figure 5.8 shows the Arrhenius plots for \( \text{Na}_{11}\text{Sn}_2\text{PnS}_{12} \) in an \( NVT \) ensemble at six temperatures varying from 700K to 1400K. At least 200 ps of AIMD simulations were performed to get reliable \( \text{Na}^+ \) ionic conductivity and activation energy. Framework trajectories were inspected at the highest temperatures (1400K for \( \text{Na}_{11}\text{Sn}_2\text{PS}_{12}, \) 1200K for \( \text{Na}_{11}\text{Sn}_2\text{AsS}_{12} \) and \( \text{Na}_{11}\text{Sn}_2\text{SbS}_{12} \)) to avoid framework melting and ensure no phase transition within simulation temperatures. We listed key conduction results in Table 5.4: the extrapolated conductivities are 2.77 mS/cm for \( \text{Na}_{11}\text{Sn}_2\text{PS}_{12} \), 4.52 mS/cm for \( \text{Na}_{11}\text{Sn}_2\text{AsS}_{12} \) and 0.45 mS/cm for \( \text{Na}_{11}\text{Sn}_2\text{SbS}_{12} \), i.e., two of them (\( \text{Na}_{11}\text{Sn}_2\text{PS}_{12} \) and \( \text{Na}_{11}\text{Sn}_2\text{SbS}_{12} \)) are in excellent agreement with experimental results (\( \text{Na}_{11}\text{Sn}_2\text{PS}_{12} \): 1.4–3.7 mS/cm; \( \text{Na}_{11}\text{Sn}_2\text{SbS}_{12} \): 0.2–0.56
mS/cm). The estimated activation energies ($E_a$) for P phase (0.24 eV) and Sb phase (0.29 eV) are in the same trend and close to previously reported experimental data (0.25 eV for Na$_{11}$Sn$_2$PS$_{12}$ and 0.34 eV for Na$_{11}$Sn$_2$SbS$_{12}$).

Figure 5.13 shows calculated densities of states (DOS) for Na$_{11}$Sn$_2$PnS$_{12}$ using HSE hybrid functional. All of the three candidates are relatively large band gap (2.5∼2.62 eV) insulators. S-$p$ electrons contribute to valence band maximum while the conduction band minimum is dominated by framework cations (especially Sn) and S anion. That is why the three Na$_{11}$Sn$_2$PnS$_{12}$(Pn = P, As, Sb) compositions have very close band gaps. Similar features are found in pure Na$_3$PnS$_4$ (Figure 5.14) and Na$_4$TtS$_4$ (Figure 5.15), although the $E_g$ varies from 2.18 (Na$_3$AsS$_4$) to 2.92 eV (Na$_3$PS$_4$) for Na$_3$PnS$_4$ and 2.73 eV (Na$_4$SnS$_4$) to 3.4 eV (Na$_4$SiS$_4$) for Na$_4$TtS$_4$. Note that the band gap is the upper limit for the intrinsic stability of the material against reduction and oxidation. Cathodes such as layered transition-metal oxides with moderate potentials (2.7–3.2 V vs Na$^+$/Na)$^{182}$ and proper anodes need to be assorted to avoid electronic conductivity in these solid electrolytes when operating.

5.4 Discussion

5.4.1 Cation Mixing Effect in Na$_3$Pn$'_x$Pn$''_{1-x}$S$_4$

From the preceding part, we provided a systematic study on isovalent Pn$^{5+}$ mixing and their effects on a spectrum of properties, including phase stability, miscibility, moisture stability, EC window, etc. The overall tendency of cubic/tetragonal energy difference ($E_{cubic}$ – $E_{tetra}$) for pure Na$_3$PnS$_4$ is accordantly positive, i.e., t-Na$_3$PnS$_4$ is always more stable than cubic phase. Arsenic phase with small energy difference between cubic and tetragonal helps to favor cubic phase. Our
neutral Na vacancy formation energies for c-Na$_3$PS$_4$ (0.60 eV/defect) and t-Na$_3$PS$_4$ (0.33 eV/defect) are consistent with previous work by Bo et al. (0.57 eV and 0.34 eV for c- and t-Na$_3$PS$_4$, respectively). The facility of Na diffusion is dominated by the joint effect of Na vacancy formation and migration. Substantially small vacancy migration barriers less than 25 meV (see Figure 5.9) are found in c-Na$_3$PnS$_4$, in which Na vacancies are more easily formed than t-Na$_3$PnS$_4$. And it is not a distinct phenomenon only appearing in cation mixed Na$_3$Pn'$_x$Pn''$_{1-x}$S$_4$, but also applicable in anion mixed Na$_3$PS$_x$Se$_{4-x}$. Thus, the formation energy of Na vacancy plays a significant role on diffusivity and conductivity within such vacancy-driven Na$_3$PnS$_4$-type materials and it is not surprising that high conductivity in this family of electrolytes are achieved by ball milling approach which can promote the concentration of generated Na vacancy.

The thermodynamic driving force of cation mixing is reflected through mixing enthalpy of Na$_3$Pn'$_x$Pn''$_{1-x}$S$_4$ (Figure 5.2), from which we can demonstrate great miscibility in this system especially Na$_3$As$_x$P$_{1-x}$S$_4$ compounds. Borrowing the concept of Hume-Rothery rules from metallurgy field, Na$_3$Pn'$_x$Pn''$_{1-x}$S$_4$ system satisfied the requirements for substitutional solid solution with close atomic radii (195 pm for P; 185 pm for As; 206 pm for Sb) and electronegativity (2.19 for P; 2.18 for As; 2.05 for Sb in the unit of Pauling scale), same crystal structure and valency. The close resemblance between Na$_3$PS$_4$, Na$_3$AsS$_4$ and Na$_3$SbS$_4$ implies solid solution phases between any two end members may exist, providing an effective method to tailor the chemical/physical properties of Na$_3$Pn'$_x$Pn''$_{1-x}$S$_4$ compounds as promising solid electrolytes. On the basis of similar ordering patterns (Figure 5.3) and small mixing enthalpy (Figure 5.2), we assert the homogeneous distribution of any two constituents and complete solubility are similar to binary alloys, e.g., Cu-Ni.
According to hard and soft acid and base (HSAB) theory, the sulfides with hard acid species as framework are prone to react with oxygen (the hard base) and form products varying from Na₃MOS₃ to Na₃MO₃S (M is the hard acid element) to replace sulfur (the soft base). Correspondingly, Na₃PS₄ (P is hard acid) in air and moisture is less stable/more active than Na₃AsS₄ and Na₃SbS₄. By introducing the softer species (As and Sb) and taking advantage of the composition engineering, the mixing systems of Na₃AsₓP₁₋ₓS₄ and Na₃SbₓAs₁₋ₓS₄ show a better moisture stability than pure Na₃PS₄. The high reaction activity in Na₃PₓSb₁₋ₓS₄ particularly when x is close to 0.5, can be attributed to the positive mixing enthalpy of Na₃PₓSb₁₋ₓS₄.

Previous experimental/DFT studies by Yu, Shang and co-workers verified our predicted trend in Na₃AsₓP₁₋ₓS₄ case and reported the optimized compound of Na₃As₀.₃₈P₀.₆₂S₄ with high conductivity of 1.46 mS/cm.¹⁶⁵ The trend of EC window width for pure Na₃PnS₄ as we discussed in our previous paper⁵⁶ is determined by whether Pn element is redox-active or not: As/Sb with oxidation state of 5+ and 3+ show a narrower EC window than P version. Similarly, Na₄GeS₄ with possible redox-active Ge from 4+ to 2+ oxidation states exhibit the narrower EC window than Na₄SiS₄ and Na₄SnS₄. Besides tuning the element, a recent work by Tian et al.¹⁸⁶ provided a novel train of thought to improve interface stability versus Na metal by coating a newly discovered protective hydrated phase (Na₃SbS₄·₈H₂O) as a passivating layer.

The studies on Na₃PnS₄ family rose from the high conductivity achieved in c-Na₃PS₄ back in 2012.³² Analogs like Na₃SbS₄¹⁸⁷ and Na₃PSe₄⁷⁹,¹⁸⁸ as well as picked cation/anion mixing systems were investigated both experimentally and computationally by different groups soon after.¹⁸³,¹⁵² This work provides a comparison and assessment of Pn⁵⁺ cation mixing effects in Na₃PnₓPn''₁₋ₓS₄ in the following aspects: (i) Solid solution phases tend to be formed with complete solubility in the order of Na₃AsₓP₁₋ₓS₄, Na₃SbₓAs₁₋ₓS₄ and Na₃PₓSb₁₋ₓS₄ (from ease to difficulty);
(ii) Arsenic involvements help to improve the moisture stability of Na$_3$PS$_4$ whereas Sb-P mixing makes it more negative of reaction energy between H$_2$O and Na$_3$P$_x$Sb$_{1-x}$S$_4$ implying a detrimental to tolerance to moisture; (iii) The narrowest EC window of any ternary constituent determines the limitation of that for mixed quaternary compounds; (iv) The competing effects of cubic-tetragonal phase transition (t-phase always more thermodynamic favorable) lead to the adjustable conductivities.

We did not provide the AIMD data for Na$_3$Pn$'_x$Pn$''_{1-x}$S$_4$ compositions given to the poor Arrhenius relationship in our trials when x=0.5 and the huge fluctuation of diffusivity close to 1000 K (900K to 1100K) indicating the likelihood of phase transition occurring. Within our capability and reasonable computational expense, we launch the light to composition engineering in Na$_3$Pn$'_x$Pn$''_{1-x}$S$_4$ and give reliable predictions on concerned materials properties such as thermodynamic/moisture/electrochemical stability. Under the guidance of DFT simulations, there is still more space left for experimentalists to explore in conductivity optimization, full cell performance and buffer layers choosing for better cycling.

5.4.2 Novel Promising Prototype Na$_{4-x}$Tt$_{1-x}$Pn$_x$S$_4$

The discovery of Na$_{11}$Sn$_2$PS$_{12}$ initialized the exploration of this new prototype (space group: I4$_1$/acd) in Na–Tt–Pn–S chemical space. Though it looks like the relatives of LGPS family with similar formula, the experimental evidence of Na$_{11}$Sn$_2$PS$_{12}$ from XRD refinement shows it a distinct geometry from either quasi-1D LGPS conductor or pure Na$_3$PS$_4$. Comparing the unit volume of Na$_{11}$Sn$_2$PS$_{12}$ (5046.4 Å$^3$, quadrupling of LGPS unit cell size)$^{36}$ and Li$_{10}$GeP$_2$S$_{12}$ (965.5 Å$^3$),$^{14}$ we found Na$^+$ version can enlarge the cell volume by 30% increase for equivalent cell. The half-amount of PS$_4$ polyhedrons in z = 1/8 layer (Figure 5.4a-c) leads to a 23% decrease of
polyhedral density (polyhedron number/cell volume) and a 12% larger of Na\(^+\) channel volume per unit volume compared with Na\(_3\)PS\(_4\). All of these make it an excellent framework model considered as superior 3D Na\(^+\) conductor.

On account of the great framework similarity between Na\(_3\)PS\(_4\) and Na\(_4\)SnS\(_4\) (Figure 5.1), more ratios in Na\(_{4-x}\)Tt\(_{1-x}\)Pn\(_x\)S\(_4\) start the trial substitutions from two parent ternaries and turn out to be less thermodynamic stable than those derived from Na\(_{11}\)Sn\(_2\)PS\(_{12}\). The phase stability of Na\(_{4-x}\)Tt\(_{1-x}\)Pn\(_x\)S\(_4\) is not primarily depending on Tt/Pn elements, but highly related to the \(x\) value (Figure 5.5). The optimal Tt/Pn ratio is equal to 2, which results in the formula of Na\(_{11}\)Tt\(_2\)PnS\(_{12}\) and thus we use this stoichiometry as a testing case to assess other properties including moisture, electrochemical stability. It is noted that in a recent work for Na\(_{11}\)M\(_2\)PS\(_{12}\)(M=Ge, Sn)\(^{190}\) comparison, the authors reported a high \(E_{\text{hull}}\) of 14.5 meV/atom for Na\(_{11}\)Sn\(_2\)PS\(_{12}\) by only calculating 20 lowest electrostatic energy configurations among 40,000 enumerated structures. We selected a smaller cell size (formula: Na\(_{44}\)Sn\(_8\)P\(_4\)S\(_{48}\)) with the same Na occupancy settings but only an enumeration of ~700 orderings and calculated more than 100 configurations based on ewald energy implemented in pymatgen code. It is merited that we are more likely to capture a more stable ordered structure \((E_{\text{hull}} = 0 \text{ meV/atom})\). Consequently, a narrower EC window was claimed from the same paper (1.16–1.91 V in the reference\(^{190}\) vs 1.16–2.21 V in this work): EC window predicted by grand potential method is related to energy of the compounds. Additionally, we excluded polysulfides (such as NaS, NaS\(_2\), Na\(_2\)S\(_3\)) in phase diagram and grand potential analysis, to avoid the over-correction caused by sulfur correction exclusively for S\(^{2-}\).

We claimed the superiority of Na\(_{11}\)Tt\(_2\)PnS\(_{12}\) in terms of phase stability based on the foregoing Results section and thus employ this particular ratio for the following discussions. As
indicated before, sulfides follow HSAB theory, which is also reflected in the moisture stability of Na$_{11}$Tt$_2$PnS$_{12}$. The hard acid Si (IV) results in high reactivity of Na$_{11}$Si$_2$PnS$_{12}$ and form super stable SiO$_2$ as a decomposed product. Ge (IV) and Sn (IV) which are softer than Si (IV), demonstrate a better moisture stability, especially Na$_{11}$Sn$_2$PnS$_{12}$ with relatively lower expense compared with Ge resources. According to HSAB theory, soft acids mitigating the reactivity with oxygen and moisture in air are utilized to design stable superionic conductors under ambient conditions, i.e., Li$_4$Cu$_8$Ge$_3$S$_{12}$. More options like Cu (I), Zn (II), Bi (III) are also worth trying as the substitution for hard acids (Si(IV) and P(V)).

Our predicted conductivities for Na$_{11}$Sn$_2$PnS$_{12}$ are in excellent agreement with two synthesized phases (Na$_{11}$Sn$_2$PS$_{12}$ and Na$_{11}$Sn$_2$SbS$_{12}$), which gives us the confidence of accurate prediction for arsenic version showing a superior conductivity of 4.52 mS/cm. The Na$^+$ ions diffuse in the isostructural 3D pathways as described before, but contribute to different conductivities, implying Pn elemental properties do have an effect on conduction. A lower electronegativity of Sb$^{5+}$ compared with P$^{5+}$ (2.05 vs 2.19) elucidates a more negative effective charge of SbS$_4$ tetrahedron (higher electron density in $S^{2-}$) which ensures stronger interactions between Na$^+$ and surrounding framework lattice. Moreover, the additional effect from lower site occupancy in interstitial “Na6” makes Na$_{11}$Sn$_2$SbS$_{12}$ revealing a 3-fold lower conductivity compared with Na$_{11}$Sn$_2$PS$_{12}$ (0.56 mS/cm$^{177}$ vs 1.4 mS/cm$^{36}$). The optimal conductivity appears in Na$_{11}$Sn$_2$AsS$_{12}$ given its weaker Na$^+$-$S^{2-}$ interaction versus Sb version based on electronegativity (2.18 for As; 2.05 for Sb) and slightly larger volume compared with P phase.

5.5 Conclusion
To conclude, we performed a comprehensive study of isovalent and aliovalent cation mixing in Na$_3$Pn’$_x$Pn’’$_{1-x}$S$_4$ and Na$_{4-x}$Tt$_{1-x}$Pn$_x$S$_4$, respectively, which are derived from Na$_3$PS$_4$, Na$_4$SnS$_4$ and Na$_{11}$Sn$_2$PS$_{12}$ prototype parent structures. Among Na$_3$Pn’$_x$Pn’’$_{1-x}$S$_4$ systems, Na$_3$As$_x$P$_{1-x}$S$_4$ compositions have super low or even negative enthalpy of mixing, indicating highly miscibility and complete solubility as solid solution phases. In the aliovalent mixed Na$_{4-x}$Tt$_{1-x}$Pn$_x$S$_4$, Na concentration and Tt/Pn ratios are adjustable simultaneously and compounds substituted from experimentally-reported Na$_{11}$Sn$_2$PS$_{12}$ prototype with space group of $I4_1/acd$ show greater phase stability and larger 3D channels. Following HSAB theory, P- and Si-containing chemistries have the drawback of instability in air and moisture, which would be improved by introducing soft acids like Sn and As. Buffer layer needs to be considered since EC windows and HSE band gaps are relatively small compared with oxides and halides. We proposed a novel promising mixed composition Na$_{11}$Sn$_2$AsS$_{12}$ which is very likely to be synthesized and potentially possesses higher conductivity of 4.52 mS/cm and better chemical stability than the P/Sb versions already reported experimentally.

Chapter 5, in full, is currently being prepared for submission for publication of the material “Cation Mixing for Stable, High Ionic Conductivity Sodium Solid Electrolytes” Zhuoying Zhu, Hanmei Tang, Xiang-Guo Li and Shyue Ping Ong. The dissertation author was the primary investigator and author of this paper. Most of the calculations and corresponding data analyses were done by the author. The moisture stability analyses were done by collaborator and coauthor of this paper, Hanmei Tang.
Figure 5.1 Crystal structures of (a) tetragonal Na₃PnS₄ (space group: $P\bar{4}2_1c$), (b) cubic Na₃PnS₄ (space group: $I4_3m$), (c) Na₄TtS₄ (space group: $P\bar{4}2_1c$) and (d) Na₁₁Tt₂PnS₁₂ (space group: $I4_1/acd$). Purple tetrahedrons, PnS₄; blue tetrahedrons, TtS₄; green spheres, Na.

Figure 5.2 Polymorph stability and mixing enthalpy of Na₃PnₓPn"₁₋ₓS₄ (Pn’, Pn”=P, As, Sb). (a-c) Energy difference between the cubic and tetragonal phase ($E_{cubic} - E_{tetra}$) and (d-f) mixing enthalpy of t- Na₃PnₓPn"₁₋ₓS₄. Squares and circles markers are for unstable and stable structures, respectively. The mixed Na₃PnₓPn"₁₋ₓS₄ systems are successively (from left to right): Na₃AsₓP₁₋ₓS₄; Na₃SbₓAs₁₋ₓS₄ and Na₃SbₓP₁₋ₓS₄.
Figure 5.3 Ordering pattern (top view along c direction) of the most stable structure for (a) $\text{Na}_3\text{Sb}_{0.5}\text{P}_{0.5}\text{S}_4$ and (b) $\text{Na}_3\text{As}_{0.5}\text{P}_{0.5}\text{S}_4$.

Figure 5.4 $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$, $\text{Na}_3\text{PS}_4$ crystal structures and $E_{\text{bulk}}$ of $\text{Na}_4-x\text{Sn}_{1-x}\text{P}_x\text{S}_4$ substituted from different prototypes. (a) $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ viewed from a direction; (b) $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ viewed from c direction showing 3 PS$_4$ and 6 SnS$_4$ tetrahedrons in $z=1/8$ and $z=1/4$ layer, respectively. (c) $2\times2\times2$ supercell of $\text{Na}_3\text{PS}_4$ viewed from c direction. Unlike $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$, the numbers of PS$_4$ tetrahedrons are the same in each layer. (d) Thermodynamic stability of $\text{Na}_4-x\text{Sn}_{1-x}\text{P}_x\text{S}_4$ substituted from three different prototypes: $\text{Na}_3\text{PS}_4$, $\text{Na}_4\text{SnS}_4$ and $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$.
Table 5.1 Cation mixed compositions we studied: isovalent Pn’–Pn” mixing in Na₃PnₓPn”₁₋ₓS₄ and aliovalent Tt–Pn mixing in Na₄₋ₓTt₁₋ₓPnₓS₄. Cation species are Pn=P, As, Sb; Tt=Si, Ge, Sn.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Source</th>
<th>Mixing type</th>
<th>Mixing ratio (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₃PnₓPn”₁₋ₓS₄</td>
<td>t-Na₃PS₄ (P42₁c)</td>
<td>Isovalent</td>
<td>$x = i/16$</td>
</tr>
<tr>
<td></td>
<td>c-Na₃PS₄ (I43m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$i$ is an integer</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>between 1 and 16</td>
</tr>
<tr>
<td>Na₄₋ₓTt₁₋ₓPnₓS₄</td>
<td>t-Na₃PS₄ (P42₁c)</td>
<td>Aliovalent</td>
<td>$x = 1/4, 1/2, 3/4$</td>
</tr>
<tr>
<td></td>
<td>Na₄SnS₄ (P42₁c)</td>
<td></td>
<td>$x = 1/4, 1/3, 1/2, 3/4$</td>
</tr>
<tr>
<td></td>
<td>(I4₁/acd)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2 Space group, lattice parameter after structural optimization and phase stability ($E_{\text{hull}}$) for t- and c-Na$_3$PnS$_4$ (Pn=P, As, Sb).

<table>
<thead>
<tr>
<th>Pure Na$_3$PnS$_4$</th>
<th>Lattice parameter</th>
<th>$E_{\text{hull}}$ (meV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Na$_3$PS$_4$</td>
<td>a=7.016Å, c=7.148Å</td>
<td>0</td>
</tr>
<tr>
<td>c-Na$_3$PS$_4$</td>
<td>a=7.048Å</td>
<td>5.4</td>
</tr>
<tr>
<td>t-Na$_3$AsS$_4$</td>
<td>a=7.104Å, c=7.235Å</td>
<td>0</td>
</tr>
<tr>
<td>c-Na$_3$AsS$_4$</td>
<td>a=7.129Å</td>
<td>3.5</td>
</tr>
<tr>
<td>t-Na$_3$SbS$_4$</td>
<td>a=7.228Å, c=7.377Å</td>
<td>0</td>
</tr>
<tr>
<td>c-Na$_3$SbS$_4$</td>
<td>a=7.253Å</td>
<td>4.3</td>
</tr>
</tbody>
</table>
Table 5.3 $E_{\text{hull}}$ values of Na$_{4-x}$Tt$_x$Pn$_4$S$_4$ ($x = 1/4, 1/3, 1/2, 3/4$) from the different prototypes (Na$_3$PS$_4$, Na$_4$SnS$_4$ and Na$_{11}$Sn$_2$PS$_{12}$ structures).

<table>
<thead>
<tr>
<th>Prototype</th>
<th>$x = 1/4$ (meV/atom)</th>
<th>$x = 1/3$ (meV/atom)</th>
<th>$x = 1/2$ (meV/atom)</th>
<th>$x = 3/4$ (meV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_3$PS$_4$</td>
<td>13</td>
<td>N/A</td>
<td>12</td>
<td>29</td>
</tr>
<tr>
<td>Na$_4$SnS$_4$</td>
<td>14</td>
<td>N/A</td>
<td>22</td>
<td>21</td>
</tr>
<tr>
<td>Na$_{11}$Sn$<em>2$PS$</em>{12}$</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 5.4 Na$^+$ conductivity at 300 K ($\sigma_{300K}$), error range of $\sigma_{300K}$, activation energy ($E_a$) obtained from AIMD simulations as well as HSE band gap ($E_g$) of Na$_{11}$Sn$_2$PnPn$_{12}$ (Pn=P, As, Sb).

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\sigma_{300K}$ (mS/cm)</th>
<th>Error range of $\sigma_{300K}$ (mS/cm)</th>
<th>$E_a$ (eV)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_{11}$Sn$<em>2$PS$</em>{12}$</td>
<td>2.77</td>
<td>[2.62, 2.93]</td>
<td>0.243</td>
<td>2.53</td>
</tr>
<tr>
<td>Na$_{11}$Sn$<em>2$AsS$</em>{12}$</td>
<td>4.52</td>
<td>[4.23, 4.82]</td>
<td>0.216</td>
<td>2.62</td>
</tr>
<tr>
<td>Na$_{11}$Sn$<em>2$SbS$</em>{12}$</td>
<td>0.45</td>
<td>[0.41, 0.48]</td>
<td>0.289</td>
<td>2.50</td>
</tr>
</tbody>
</table>
Figure 5.5 Thermodynamic stability of Na$_{4-x}$Tt$_1-x$Pn$_x$S$_4$ ($x=1/4, 1/3, 1/2, 3/4$). When $x=1/3$, Na$_{3.67}$Tt$_{0.67}$Pn$_{0.33}$S$_4$ is the normalized formula, which is equivalent to Na$_{11}$Tt$_2$PnS$_{12}$.
Figure 5.6 Reaction energy with H$_2$O for Na$_3$Pn’$_x$Pn”$_{1-x}$S$_4$ (top) and Na$_{11}$Tt$_2$PnS$_{12}$ (bottom).

Figure 5.7 Electrochemical stability of pure and mixed Na$_3$PnS$_4$ (top left), Na$_4$TtS$_4$ (bottom left) and Na$_{11}$Tt$_2$PnS$_{12}$ (right) where Pn=P, As, Sb and Tt=Si, Ge, Sn.
Figure 5.8 Arrhenius plots for Na$_{11}$Sn$_2$Pn$_{12}$ (Pn = P, As, Sb) obtained from AIMD simulations. Unfilled markers indicate the operation temperatures at which we run AIMD calculations, while filled markers are the extrapolated room temperature of 300 K.

Figure 5.9 NEB migration barriers for the solely distinct path in c-Na$_3$Pn$_4$ (Pn = P, As, Sb).
Figure 5.10 Thermodynamic stability ($E_{\text{hull}}$) of $\text{Na}_4\text{Sn}_1-\text{Sb}_x\text{S}_4$ substituted from different prototypes.
Figure 5.11 Plots of Na uptake per atom against voltage vs Na/Na$^+$ (V) of various solid electrolytes: (a) Na$_3$PS$_4$; (b) Na$_3$AsS$_4$; (c) Na$_3$SbS$_4$. In anode region, the decomposed products are Na$_2$S and Na$_3$Pn while at high voltage up to 4 V, P$_2$S$_5$, As$_2$S$_3$ and Sb$_2$S$_3$ are predicted to form.
Figure 5.12 Plots of Na uptake per atom against voltage vs Na/Na\(^+\) (V) of various solid electrolytes: (a) Na\(_4\)SiS\(_4\); (b) Na\(_4\)GeS\(_4\); (c) Na\(_4\)SnS\(_4\). In anode region, Na\(_x\)Tt\(_y\) compounds and Na\(_2\)S are the main products whereas universal formula of TtS\(_2\) ans S form at high voltage cathode region.
Figure 5.13 Calculated element-projected density of states (DOS) for (a) Na$_{11}$Sn$_2$PS$_{12}$ (band gap $E_g = 2.53$ eV) (b) Na$_{11}$Sn$_2$AsS$_{12}$ ($E_g = 2.62$ eV) and (c) Na$_{11}$Sn$_2$SbS$_{12}$ ($E_g = 2.5$ eV) using the HSE06 screened hybrid functional.

Figure 5.14 Calculated element-projected density of states (DOS) for (a) Na$_3$PS$_4$ (band gap $E_g = 2.92$ eV) (b) Na$_3$AsS$_4$ ($E_g = 2.18$ eV) and (c) Na$_3$SbS$_4$ ($E_g = 2.55$ eV) using the HSE06 screened hybrid functional.
Figure 5.15 Calculated element-projected density of states (DOS) for (a) Na$_4$SiS$_4$ (band gap $E_g = 3.4$ eV) (b) Na$_4$GeS$_4$ ($E_g = 3.06$ eV) and (c) Na$_4$SnS$_4$ ($E_g = 2.73$ eV) using the HSE06 screened hybrid functional.
Chapter 6. Summary and Outlook

The inorganic solid electrolyte is a critical component of all-solid-state batteries and an ultimate solution to the safety concerns caused by traditional organic liquid electrolytes. Ideally, we expect the electrolyte materials not only exhibit high ionic conductivity and negligible electronic conductivity (electronic insulating), but also show the stability under ambient environment (moisture, O₂, CO₂). Interfacial stability between electrolytes and electrodes is essential as well. Once incorporating the electrolytes with good electrochemical stability and low interfacial resistance, the full cell performance is expected to be one step forward. High capacity, excellent cycling performance and high energy density are things to be considered for real applications and it is not trivial to reach for solid electrolytes. In this dissertation, we have applied first principles calculations based on density functional theory (DFT) to evaluate the multiple properties for candidate materials.

The interesting observation that existing lithium thiophosphates have their Ag analogs aroused our interest to explore novel lithium conductor from silver compounds and this strategy has been proven a success with the fruitful harvest of predicted Li₃Y(PS₄)₂ (LYPS) and Li₅PS₄Cl₂ (LPSCl). The two compounds are predicted to satisfy a necessary combination of good phase stability, electrochemical stability, high Li⁺ ionic conductivity and wide band gap. From the first principles calculations, LYPS is predicted to be a particularly promising novel superionic conductor with further improved conductivity via Ca doping. An efficiently tiered workflow is essential to filtering the superionic conductors. We developed the hierarchy of diffusivity screening from primary channel size cutoff to short AIMD estimations. The high-throughput
workflow is universal for any ion conductor screening after adjusting suitable parameters accordingly.

Next, we present the optimizations and better understanding of Na₃PS₄ material combining computational and experimental methods. The early-stage attempts on cation dopants help to understand the crucial factor that significantly enhances the conductivity in the cubic phase is the existence of the defects, more particularly, Na interstitials. The AIMD predicted room-temperature conductivity of 6.25% Si-doped c-Na₃PS₄ is in excellent agreement with the experimental results. Besides, M⁴⁺ dopants (Si, Ge, Sn) are taken into consideration for P⁵⁺ site substitution. Sn dopant is predicted to future improve the conductivity to more than 10 mS/cm. Independent experimental results from Rao et al. proved the potential of Sn dopant with a very low activation energy of 0.18 eV, although the targeting conductivity is not achieved yet. For the trial of halide doping, we first used DFT calculations to guide the species choice and ensure Cl is a potential dopant to try. Then we deepen our understanding of the transport mechanism in Cl-doped t-Na₃PS₄ by the feat of solid-state nuclear magnetic resonance (NMR) method. From the trend of conductivity fluctuation versus peak intensities of Na sites in various environments, we find that aggrandizing Na₃ (Na close to Cl) and eliminating Na₄ (Na in the vicinity of Na vacancies) would be an efficient way to enhance the conductivity. A series of AIMD results find that in the presence of a small amount of Na vacancy, an increase of Cl doping concentration significantly improves the Na⁺ conductivity. Independent tuning of Cl and Na vacancy amount can lead to optimized conduction performance. Change of P oxidation state from P⁵⁺ to P⁴⁺ guarantees Na and Cl concentrations can be tuned independently.
Finally, we present a comprehensive investigation on Na₄TtS₄−Na₃PnS₄ (where Pn = P, As, Sb and Tt = Si, Ge, Sn) cation mixing using first principles calculations. The composition systems include prototypes of Na₃PS₄, Na₄SnS₄ and newly reported Na₁₁Sn₂PS₁₂. Isovalent mixed Na₃Pn’ₓPn”₁₋ₓS₄ is highly miscible solid solution with complete solubility, particularly for P-As mixing. Na₃PₓAs₁₋ₓS₄ compositions also exhibit better moisture stability compared with Na₃PS₄. For aliovalent mixed Na₄₋ₓTt₁₋ₓPnₓS₄, structures substituted from Na₁₁Sn₂PS₁₂ show better phase stability than those from Na₃PS₄ and Na₄SnS₄. A new mixed composition Na₁₁Sn₂AsS₁₂ is proposed with potentially higher conductivity and better chemical stability than those already reported experimentally.

To conclude, we have demonstrated our works on the design and optimization of alkali superionic conductors in this dissertation. We display the high-throughput workflow for solid electrolytes search, which can ideally inspire more works in future materials discovery. We showcase the joint efforts from the combination of computational and experimental sides to deepen the understanding of a particular material and to provide optimization strategy. The useful toolkits like probability density function and van Hove function are contributed to the open-source pymatgen-diffusion package. The study on Na-Tt-Pn-S cation mixing fills the gap of the unclear zone on how cations affect multiple intrinsic properties like stability. We hope that our computational exploration can serve as an inspiration for future researchers to make efforts in this field. We realize there is plenty of space for methodology improvements. Emerging directions appear with the developments of other interdisciplinary subjects. For example, currently, not an individual type of solid electrolyte can satisfy the practical requirements for real applications. Considering hybrid electrolytes combining two or more SEs with complementary advantages may be a potential next move. With the aid of supercomputer rising, high-performance computing
makes it possible for computational high-throughput and this concept is also employed in experimental science. Rapid developments in machine learning and artificial intelligence recently can be a new, robust hammer for materials informatics. The fundamental science of materials discovery is meaningful, but we should always look back to the technologic improvements for practical engineering issues since it is equally, if not more important.
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