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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:

Professor Shyue Ping Ong, Chair
Professor Prabhakar R. Bandaru
Professor Jian Luo
Professor Ying Shirley Meng
Professor Oleg Shpyrko

2019

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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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Chapter 3, in full, is a reprint of the material “ $\text{Li}_3\text{Y}(\text{PS}_4)_2$ and $\text{Li}_5\text{PS}_4\text{Cl}_2$: New Lithium Superionic Conductors Predicted from Silver Thiophosphates using Efficiently Tiered *Ab Initio* Molecular Dynamics Simulations” as it appears in Chemistry of Materials, Zhuoying Zhu, Iek-Heng Chu and Shyue Ping Ong, 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.

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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 $\text{Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ 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.

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.

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2. H. Liu*, **Z. Zhu***, J. Huang*, X. He, Y. Chen, R. Zhang, R. Lin, Y. Li, S. Yu, X. Xing, Q. Yan, X. Li, M. J. Frost, K. An, J. Feng, R. Kostecki, H. Xin, S. P. Ong and P. Liu, “Elucidating the Limit of Li Insertion into the Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ”, ACS Materials Lett., 2019, 1, 96-102. (* These authors contributed equally)
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ABSTRACT OF THE DISSERTATION

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

using First-Principles Calculations

by

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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 $\text{Li}_3\text{Y}(\text{PS}_4)_2$ and $\text{Li}_5\text{PS}_4\text{Cl}_2$. 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 Na_3PS_4 and evaluated the phase stability, dopant formation energy as well as Na^+ conductivity. Aliovalent M^{4+} (M = Si, Ge, Sn) for P^{5+} substitution in c- Na_3PS_4 introduces Na^+ excess, which is shown to significantly enhance ionic conductivity. AIMD simulations predict that 6.25% Si-doped c- Na_3PS_4 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 S^{2-} , is an alternative strategy for introducing vacancy defects in t- Na_3PS_4 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 $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ and $\text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4$ (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_3PnS_4 and $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ 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 $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ exhibits negative or very small positive mixing enthalpies, including these cation-mixed compositions are likely to form solid solutions. The newly experimental $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ prototype with $I4_1/acd$ 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^{4+} and Pn^{5+} elements. We proposed a new compound of $\text{Na}_{11}\text{Sn}_2\text{AsS}_{12}$ 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 1990s¹ to address potential short circuits caused by dendrite formation during the deposition of Li metal², 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_3N , lithium phosphorus oxynitride (LIPON)⁴ and LISICON $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ ⁵ either suffer severe chemical instability (Li_3N)⁶ or show the room-temperature conductivities several orders of magnitude lower than those of organic electrolytes (LIPON, LISICON). NASICON-type $\text{AM}_2(\text{PO}_4)_3$ ($\text{A} = \text{Li, Na, K}$; $\text{M} = \text{Ge, Zr, Ti}$) was also widely investigated since 1976⁷ with a series of trials to improve the conduction properties. Substitutions in all possible sites prove Al could benefit mostly in the composition of $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($\text{M} = \text{Al, Cr, Ga, Fe, Sc, In, Lu, Y or La}$)^{8,9} for conductivity enhancements whereas another composition of $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ attracts the attention with a relatively wide electrochemical window.¹⁰

The $\text{Li}_{3-x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO)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 $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO),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.¹³

The exciting discovery of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS)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 $\text{Li}_7\text{P}_3\text{S}_{11}$ glass-ceramic conductor, has also been pushed to 17 mS/cm with a low activation energy of 176 meV.^{15,16} More recently, Kato reported two new members in LGPS family with the highest conductivity so far (25 mS/cm for $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$)¹⁷ and high stability with Li metal ($\text{Li}_{9.6}\text{P}_3\text{S}_{12}$).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,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.¹⁹ Another freshly baked work by Kato and Hautier reported that $\text{LiTi}_2(\text{PS}_4)_3$ (LTPS)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 $0.7\text{Li}(\text{CB}_9\text{H}_{10})\cdot 0.3(\text{CB}_{11}\text{H}_{12})$ ²¹ and Li_3YCl_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 SEs²⁴, 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.^{30,31} In 2012, the cubic Na_3PS_4 superionic conductor was firstly reported by Hayashi et al.,³² achieving a relatively high conductivity of 0.74 mS/cm via doping strategies.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_3PS_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 $\text{Na}_{10}\text{MP}_2\text{S}_{12}$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$)³⁴ materials predicted by first-principles calculations were only verified experimentally in $\text{Na}_{10}\text{SnP}_2\text{S}_{12}$. $\text{Na}_7\text{P}_3\text{S}_{11}$,³⁵ derived from $\text{Li}_7\text{P}_3\text{S}_{11}$ 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 $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$.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, $\text{Li}_3\text{Y}(\text{PS}_4)_2$ and $\text{Li}_5\text{PS}_4\text{Cl}_2$, 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_3PS_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_3PS_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_3PS_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 $\text{Na}/\text{Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}/\text{Na}_3\text{V}_2(\text{PO}_4)_3$ is demonstrated with a reversible room-temperature capacity of 100 mAh/g.

In the third project, we give a complete comparison of $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ and $\text{Na}_4\text{TtS}_4\text{--Na}_3\text{PnS}_4$ (where $\text{Pn} = \text{P, As, Sb}$ and $\text{Tt} = \text{Si, Ge, Sn}$) cation mixing systems from prototypes of Na_3PS_4 , Na_4SnS_4 and newly reported $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ structures, in terms of phase stability, electrochemical stability, moisture tolerance and conductivity. In isovalent $\text{Pn}'\text{--Pn}''$ mixing for $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$, high miscibility is observed in this system, especially for P-As mixtures. Arsenic also results in better moisture stability than pure Na_3PS_4 phase. For aliovalent mixed $\text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4$, we found that the newly reported $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ prototype is the most energetically favorable. Through a comprehensive screening of $\text{Tt}\text{--Pn}$ combinations, we identified $\text{Na}_{11}\text{Sn}_2\text{AsS}_{12}$ 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_3PS_4 and use DFT methods to guide halide dopant selection. With the experimental collaboration with the Meng group, we synthesized Cl-doped t- Na_3PS_4 .

And we further investigate how functional defects (Cl and Na vacancy) can individually promote Na diffusion and what is the transport mechanism in $\text{Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ material.

- Chapter 5 presents a comprehensive investigation of cation mixing for stable and high ionic conductivity sodium solid electrolytes in $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ and $\text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4$ (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.

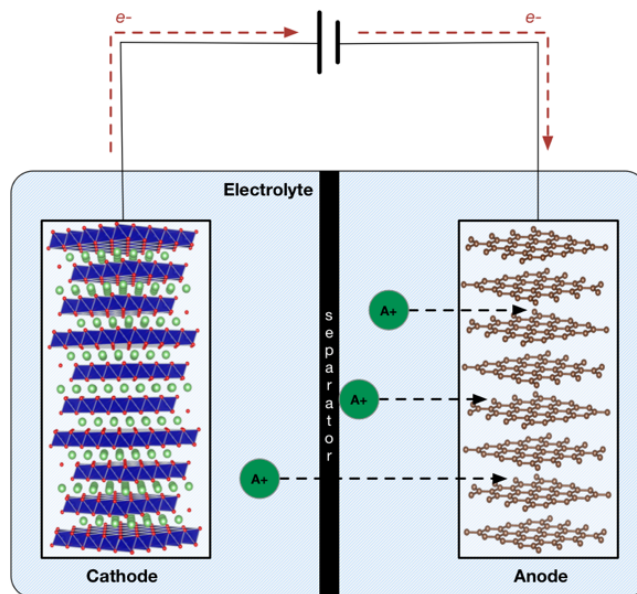


Figure 1.1 Schematic of an alkali-ion battery.³⁸ (Reprinted with permission from Ref 38. Copyright 2016 Nature Research.)

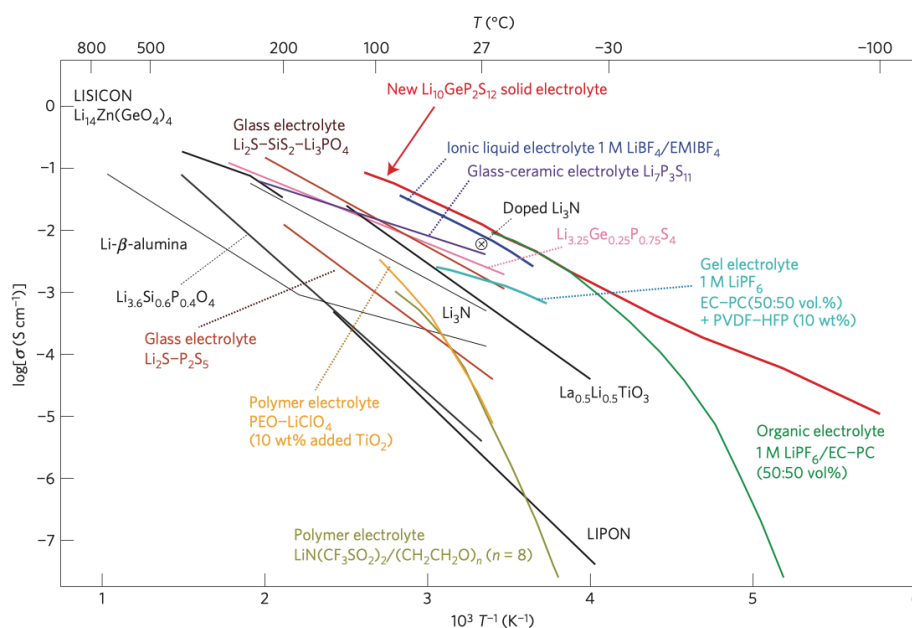


Figure 1.2 Thermal evolution of ionic conductivity of the new $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ phase, together with those of other lithium solid electrolytes, organic liquid electrolytes, polymer electrolytes, ionic liquids and gel electrolytes.¹⁴ (Reprinted with permission from Ref 14. Copyright 2011 Springer Nature.)

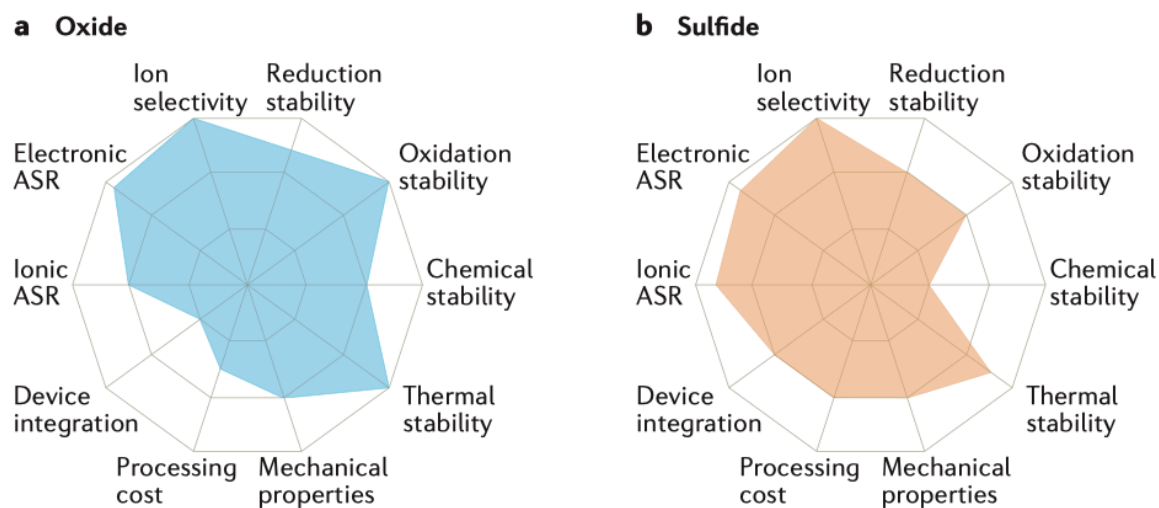


Figure 1.3 Radar plots of the performance properties of (a) oxide solid electrolytes; (b) sulfide solid electrolytes.³⁹ (Reprinted with permission from Ref 39. Copyright 2017 Springer Nature.)

Chapter 2. DFT Methods

First-principles method is a quantum-mechanical based method that does not require any other assumptions such as the empirical model or fitting parameters.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.^{41–43} As predicted by Dirac in 1929, *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.⁴⁴ Today, standard DFT calculations are performed by solving Kohn-Sham equation,⁴⁵ which provides a tractable solution to the Schrödinger equation⁴⁶ for practical materials. First proposed by Hohenberg and Kohn in 1964,⁴⁷ this theory stresses that electron density is the unique quantity that entirely determines the ground-state properties of a given system.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:

- The total energy of a system of electrons and nuclei is a unique functional of the electron density
- The variational minimum of the energy is exactly equivalent to the true ground-state energy

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.^{48–50} Later, this framework was applied to ASICs to understand their multi-properties such as phase and electrochemical stability, and diffusion mechanism,^{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.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.^{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 methods⁵⁷ (e.g., nudged elastic band⁵⁸ and kinetic Monte Carlo⁵⁹) and molecular dynamics simulations^{41,60,61}. In the following subsections, we will focus on the latter, i.e., ab initio molecular dynamics (AIMD) simulation.

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^{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)^{41,65} 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^{66–68}.

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^{65,69}. 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:

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

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:

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

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

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:

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

where ρ 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_σ)⁷⁰:

$$H_R \equiv \frac{D^*}{D_\sigma} \quad (2.5)$$

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

$H_R = 1$ 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^{71–73}. Given that the convergence of D_σ using Eq. (2.6) is often slow, only a few studies have attempted to estimate H_R within the time scales accessible via AIMD simulations³⁴.

Under the assumption of no phase transitions and an abundance of defect carriers, the diffusivity D generally follows an Arrhenius relationship:

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

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 $T \rightarrow \infty$. 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 $P(\mathbf{r})$ 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 structure⁷⁴. P is normalized such that with $\int_0^\Omega P d\mathbf{r} = 1$ with Ω 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:

$$G_s = \frac{1}{4\pi r^2 N_d} < \sum_{i=1}^{N_d} \delta(r - |\mathbf{r}_i(t_0) - \mathbf{r}_i(t + t_0)|) >_{t_0} \quad (2.8)$$

$$G_d = \frac{1}{4\pi r^2 \rho N_d} < \sum_{i \neq j}^{N_d} \delta(r - |\mathbf{r}_i(t_0) - \mathbf{r}_j(t + t_0)|) >_{t_0} \quad (2.9)$$

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. ρ is the average number density which serves as the “normalization factor” in G_d to ensure $G_d \rightarrow 1$ 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 follows⁸⁵:

$$E_f[\text{doped}] = E[\text{doped}] - E[\text{pristine}] - \sum_{i=1}^N n_i \mu_i \quad (2.10)$$

Here, $E[\text{doped}]$ and $E[\text{pristine}]$ are the total energies of the structure with and without the neutral dopant, respectively; μ_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. μ_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

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

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

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.^{86,87} 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.^{14,38,74,88–90}

Thiophosphate lithium superionic conductors have emerged as one of the leading contenders for ss-LIB solid electrolyte applications. For instance, the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) family of materials^{71,83,91,92} and the $\text{Li}_7\text{P}_3\text{S}_{11}$ ^{15,16} glass-ceramic have ionic conductivities exceeding 10

mS/cm, on par or even exceeding that of organic solvent electrolytes.⁹³ More recently, $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$, which also has the LGPS structure, was reported to have an ionic conductivity as high as 25 mS/cm at room temperature.¹⁷ 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, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ is expensive due to the use of Ge, whereas the Sn^{71} and $\text{Si}^{83,92}$ substituted analogues tend to form conducting, nonpassivating phases upon contact with the Li anode.^{94,95} Other candidates, such as $\text{Li}_7\text{P}_3\text{S}_{11}$, are metastable and tend to form nonpassivating layers with the typical LiCoO_2 cathode used in today's LIBs.^{15,96,97} 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, $\text{Li}_7\text{P}_3\text{S}_{11}$ and Li_3PS_4 bear remarkable structural similarity to $\text{Ag}_7\text{P}_3\text{S}_{11}$ and Ag_3PS_4 , respectively.⁹⁸ The highly interesting Li argyrodite superionic conductors with formula $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)⁹⁹ derive their name from the mineral argyrodite (Ag_8GeS_6), and show promising Li^+ conductivities of > 1 mS/cm for $\text{X} = \text{Cl}$ and Br .¹⁰⁰ Many Ag compounds are also known to exhibit extraordinarily high ionic conductivities; for example, $\alpha\text{-AgI}$ is perhaps the best known, and one of the first superionic conductors ever discovered.^{101–103}

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, $\text{Li}_3\text{Y}(\text{PS}_4)_2$ and $\text{Li}_5\text{PS}_4\text{Cl}_2$, 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 $\text{Li}_3\text{Y}(\text{PS}_4)_2$ 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).¹⁰⁴ 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.¹⁰⁵

3.2.2 DFT Calculations

All DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP)¹⁰⁶ within the projector augmented-wave approach.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)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.¹⁰⁹
- **Phase Stability.** The phase stability of a compound was estimated by determining its energy above the convex hull E_{hull} in the relevant Li–P–S and Li–M–P–S phase diagrams.⁵¹ Stable compounds have an E_{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 database¹⁰⁹ using the Materials Application Programming Interface (API).¹¹⁰ To account for overbinding of sulfur in DFT calculations, an energy correction of -0.66 eV per S atom for sulfides was applied.⁷³

- Electrochemical Stability.** The electrochemical stability was assessed using the lithium grand potential phase diagram approach.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 μ_{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 (μ_{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 LiCoO₂ 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.^{75,76} 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 at least 9 Å along each lattice direction. In line with previous studies,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 $D_{300\text{ K}}$ and conductivity $\sigma_{300\text{ K}}$.
- 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,^{112,113} due to the well-known underestimation of band gaps by semilocal functionals.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^{-6} cm²/s. Li⁺ self-diffusivity can be obtained via the following expression:

$$D = \frac{MSD}{2dt} \quad (3.1)$$

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 $MSD_{800K} > 5 \text{ Å}^2$ as the baseline diffusivity criterion. Assuming that the diffusivity follows an Arrhenius relationship as Eq. (2.7), combining combining Eq. (3.1) and Eq. (2.7), we can write:

$$MSD = 2D_0 d t e^{\frac{-E_a}{kT}} \quad (3.2)$$

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

$$\frac{MSD_{1200\text{ K}}}{MSD_{800\text{ K}}} = e^{\frac{-E_a}{1200k} + \frac{E_a}{800k}} \quad (3.3)$$

$$E_a = 2400k \ln \left(\frac{MSD_{1200\text{ K}}}{MSD_{800\text{ K}}} \right) \quad (3.4)$$

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

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 $E_{\text{hull}} < 30 \text{ meV/atom}$, 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_{hull} of 21–25 meV/atom. Second, a lithium superionic conductor must have a high 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 ($\sim 50\,000\text{--}100\,000$ 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.^{117,118} Only materials exhibiting $>1\text{D}$ diffusion networks with a minimum bottleneck size r_c of $1.75\text{ \AA}$, are considered as suitable candidates for lithium superionic conductors. This cutoff is slightly smaller than the channel size for the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ superionic conductor ($1.84\text{ \AA}$). 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+.^{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 ($\text{MSD}_{800\text{ K}}$) and 1200 K ($\text{MSD}_{1200\text{ K}}$). Figure 3.2 shows a log–log plot of the $\text{MSD}_{1200\text{ K}}$ versus $\text{MSD}_{800\text{ K}}$ 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 ($\text{Li}_{10}\text{Si}_{1.5}\text{P}_{1.5}\text{S}_{11.5}\text{Cl}_{0.5}$) for the recently reported $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ superionic conductor, which has the LGPS structure and an extraordinarily high conductivity of 25 mS/cm .¹⁷

We may observe that all known superionic conductors fall within the white region bounded by $\text{MSD}_{800\text{ K}} > 5\text{ \AA}^2$ and $\text{MSD}_{1200\text{ K}}/\text{MSD}_{800\text{ K}} < 7$, 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 ~ 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 Na_3PS_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- Na_3PS_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 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 $\text{Li}_7\text{P}_3\text{S}_{11}$ and Li_3PS_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 $\text{Li}_3\text{Y}(\text{PS}_4)_2$ (LYPS) and $\text{Li}_5\text{PS}_4\text{Cl}_2$ (LPSCl) satisfy all the initial screening criteria: low E_{hull} , $r_c > 1.75 \text{ \AA}$, $\text{MSD}_{800 \text{ K}} > 5 \text{ \AA}^2$ and $\text{MSD}_{1200 \text{ K}}/\text{MSD}_{800 \text{ K}} < 7$. Their $\text{MSD}_{800 \text{ K}}$ are on par with that of the leading LGPS-based candidate, $\text{Li}_{10}\text{Si}_{1.5}\text{P}_{1.5}\text{S}_{11.5}\text{Cl}_{0.5}$, but their $\text{MSD}_{1200 \text{ K}}/\text{MSD}_{800 \text{ K}}$ ratios are slightly higher. Though $\text{Li}_{15}\text{P}_4\text{S}_{16}\text{Cl}_3$, LiZnPS_4 and $\text{LiAl}(\text{PS}_3)_2$ are also predicted to have fairly low E_{hull} and reasonably high $\text{MSD}_{800 \text{ K}}$, their $\text{MSD}_{1200 \text{ K}}/\text{MSD}_{800 \text{ K}}$ 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.¹²⁴ 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.¹²⁴ 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 LPSCl 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 LPSCl 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 LPSCl are 278 and 304 meV, respectively. The extrapolated room-temperature conductivities are 2.16 mS/cm for LYPS and 1.85 mS/cm for LPSCl, 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 LPSCl, 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 Li₇P₃S₁₁ and Li₁₀GeP₂S₁₂.

For LYPS, there are five symmetrically distinct hops between neighboring Li sites, namely, $A \rightarrow B$, $B \rightarrow F$, $B \rightarrow C$, $C \rightarrow E$ and $C \rightarrow H$ (see Figure 3.6). We may observe that the lowest barrier percolating pathway in LYPS is $A \rightarrow B \rightarrow C \rightarrow D$ (Li1–Li1–Li2–Li1) with a barrier of 210 meV. To enable >1D diffusion, the next lowest barrier pathway is $G \rightarrow C \rightarrow H$ (all Li2) along the c direction with an overall barrier of 268 meV. The $E \rightarrow B \rightarrow F$ (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 $E \rightarrow G \rightarrow C \rightarrow B$ 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 LPSCI, 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 ($A \rightarrow B \rightarrow C \rightarrow D$ with overall barrier of 168 meV, and $B \rightarrow E$ with barrier of 217 meV). For 3D diffusion, the $H \rightarrow G \rightarrow F$ 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 LPSCI. 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 ~ 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_2S 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 ~ 1 eV,¹²⁵ and Li_3P . On the solid electrolyte/charged cathode, P_2S_5 is always predicted to be one of the products. However, the presence of S_2Cl_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 $\text{Li}_{10}\text{Si}_{1.5}\text{P}_{1.5}\text{S}_{11.5}\text{Cl}_{0.5}$ model of the recently reported $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ superionic conductor as well as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and $\text{Li}_7\text{P}_3\text{S}_{11}$. Similar to the candidates identified in this work, Li_2S is predicted to be the dominant product at the anode/electrolyte interface in all instances, with the small band gap Li_3P comprising a relatively small fraction. For $\text{Li}_{10}\text{Si}_{1.5}\text{P}_{1.5}\text{S}_{11.5}\text{Cl}_{0.5}$ and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, there is an additional $\text{Li}_{21}\text{Si}_5$ or $\text{Li}_{15}\text{Ge}_4$ phase, which also have a small band gap,

consistent with previous experimental studies.^{94,95} At the cathode/ $\text{Li}_{10}\text{Si}_{1.5}\text{P}_{1.5}\text{S}_{11.5}\text{Cl}_{0.5}$ interface, S_2Cl_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, $\text{Li}_3\text{Y}(\text{PS}_4)_2$ (LYPS) and $\text{Li}_5\text{PS}_4\text{Cl}_2$ (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_{hull}) and excellent topological characteristics (>1D large conduction channels) and are predicted to be electronic insulators with high Li^+ conductivities (exceeding 1 mS/cm). The Li^+ 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 $\text{Li}_7\text{P}_3\text{S}_{11}$ superionic conductor from $\text{Ag}_7\text{P}_3\text{S}_{11}$.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^+ and Li^+ 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 ($E_{\text{hull}} = 2 \text{ meV/atom}$) 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 isovalent 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_{hull} for $\text{Li}_3\text{La}(\text{PS}_4)_2$ 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 $\sim 5\%$ 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 $1 \times 1 \times 2$ 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 $\text{Li}_7\text{P}_3\text{S}_{11}$,¹⁶ the LGPS family ($\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$),^{14,17} 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 $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ superionic

conductor recently reported by Kato et al.¹⁷ has an extraordinarily high room temperature ionic conductivity of 25 mS/cm, its interfacial stability is much poorer than the $\text{Li}_{9.6}\text{P}_3\text{S}_{12}$ composition in the same structure, which has a lower conductivity of ~ 1 mS/cm.¹⁶ The result is that $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which has a voltage of 1.5 V against Li/Li^+ , had to be used as the anode with $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$, lowering achievable energy densities due to the low overall operating voltage of ~ 2.5 V. In contrast, full cell performance at a relatively high operating voltage of up to 4.2 V was demonstrated for $\text{Li}_{9.6}\text{P}_3\text{S}_{12}$ with standard graphitic anodes.

LYPS compares favorably to these known superionic conductors in terms of both phase and electrochemical stability. The calculated E_{hull} of LYPS is only 2 meV/atom, substantially lower than that of $\text{Li}_7\text{P}_3\text{S}_{11}$ (21 meV/atom),¹⁵ $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (25 meV/atom)¹¹¹ and $\text{Li}_{10}\text{Si}_{1.5}\text{P}_{1.5}\text{S}_{11.5}\text{Cl}_{0.5}$ (30 meV/atom). Recently, Richards et al. also reported computational evidence of extraordinarily high Li^+ conductivities exceeding 50 mS/cm in the $\text{Li}_{1+2x}\text{Zn}_{1-x}\text{PS}_4$ solid solution,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_{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 $\text{Li}_{10}\text{Si}_{1.5}\text{P}_{1.5}\text{S}_{11.5}\text{Cl}_{0.5}$ where the presence of Cl is predicted to result in the formation of S_2Cl_2 . On the anode/LYPS interface, the presence of the semiconducting YP phase may be of potential concern, though its band gap (~ 1 eV)¹²⁵ is still higher than the Li–Si alloys (e.g., band gaps of 0.6 eV for $\text{Li}_{12}\text{Si}_7$ and 0.08 eV for Li_7Si_3) predicted to form at the anode/ $\text{Li}_{10}\text{Si}_{1.5}\text{P}_{1.5}\text{S}_{11.5}\text{Cl}_{0.5}$ 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.³⁸

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. $\text{Li}_3\text{Y}(\text{PS}_4)_2$ (LYPS) and $\text{Li}_5\text{PS}_4\text{Cl}_2$ (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 “ $\text{Li}_3\text{Y}(\text{PS}_4)_2$ and $\text{Li}_5\text{PS}_4\text{Cl}_2$: New Lithium Superionic Conductors Predicted from Silver Thiophosphates using Efficiently Tiered *Ab Initio* Molecular Dynamics Simulations” as it appears in Chemistry of Materials, Zhuoying Zhu, Iek-Heng Chu and Shyue 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.

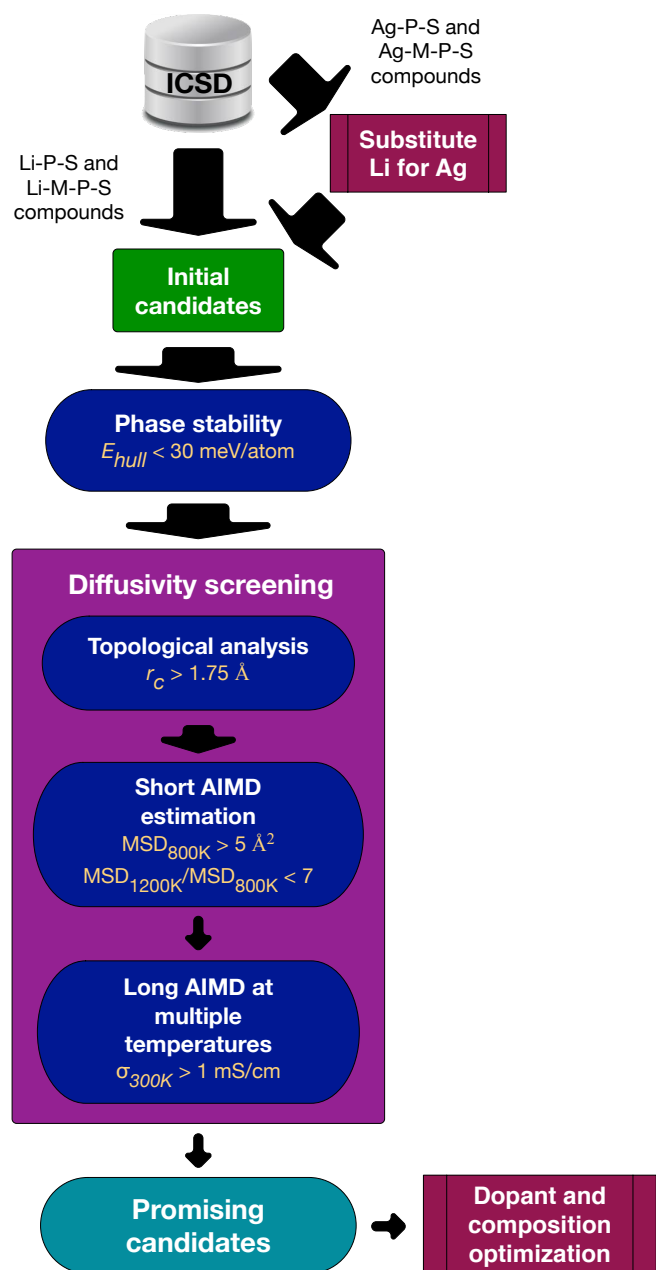


Figure 3.1 Flowchart of the screening procedure for new lithium superionic conductors. M refers to non-redox-active elements. The relative sizes of the arrows indicate the number of candidates remaining after the current screening step.

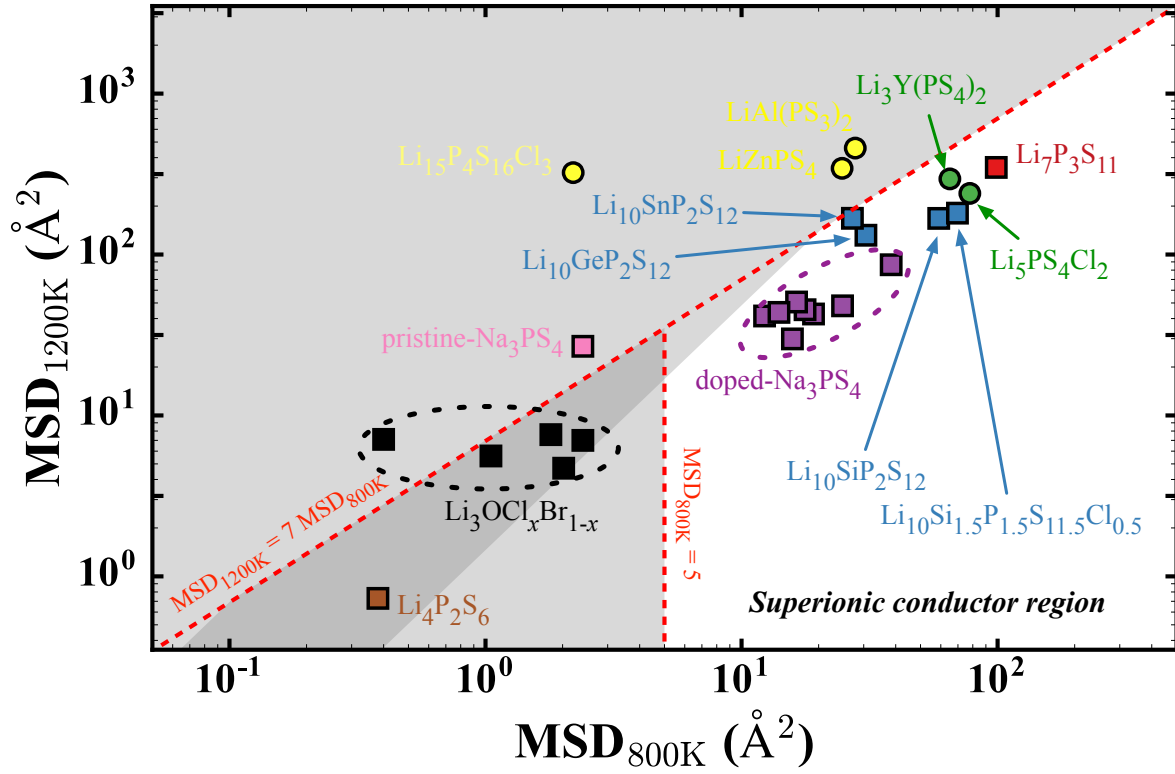


Figure 3.2 Plot of $\text{MSD}_{1200\text{ K}}$ versus $\text{MSD}_{800\text{ K}}$ for a wide range of known alkali conductors and the new candidates in this work. A log-log scale is used for better resolution across orders of magnitude differences in diffusivity/conductivity. Square markers indicate known materials, which include well-established superionic conductors such as $\text{Li}_7\text{P}_3\text{S}_{11}$,¹⁶ the LGPS family^{14,17} ($\text{Li}_{10}\text{SiP}_2\text{S}_{12}$, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$, $\text{Li}_{10}\text{Si}_{1.5}\text{P}_{1.5}\text{S}_{11.5}\text{Cl}_{0.5}$), and doped Na_3PS_4 ^{73,123} as well as relatively poorer conductors such as pristine Na_3PS_4 ^{32,73} and $\text{Li}_3\text{OCl}_x\text{Br}_{1-x}$.^{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 $\text{MSD}_{800\text{ K}} = 5\text{ \AA}^2$ and $\text{MSD}_{1200\text{ K}}/\text{MSD}_{800\text{ K}} = 7$.

Table 3.1 Energy above Hull (E_{hull}), >1D channel size (r_c), and short AIMD (50 ps) results MSD_{800K}, MSD_{1200K}/MSD_{800K} of Li thiophosphates studied in the initial screening. ^a

Compound	Source	E_{hull}	$r_c(\text{\AA})$	MSD _{800K}	MSD _{1200K} /
(space group)	(ICSD number)	(meV/atom)		($\text{\AA}^2$)	MSD _{800K}
Promising candidates					
Li ₃ Y(PS ₄) ₂	Ag ₃ Y(PS ₄) ₂	2	1.88	65.1	4.5
(C2/c)	(417658)				
Li ₅ PS ₄ Cl ₂	Ag ₅ PS ₄ Cl ₂	17	1.76	77.9	3.1
(C2mm)	(416587)				
Candidates failing at least one screening criteria					
Li ₁₅ P ₄ S ₁₆ Cl ₃	Ag ₁₅ P ₄ S ₁₆ Cl ₃	8	1.76	2.2	145.1
(I $\bar{4}$ 3d)	(416586)				
LiZnPS ₄	ICSD	0	1.83	24.7	13.9
(I $\bar{4}$)	(95785)				
LiAl(PS ₃) ₂	ICSD	0	1.82	27.8	16.5
(C2/c)	(425979)				
Li ₂ Zn(PS ₃) ₂	Ag ₂ Zn(PS ₃) ₂	33	1.84		
(C2/c)	(72719)				
LiIn(PS ₃) ₂	AgIn(PS ₃) ₂	0	0		
(P $\bar{3}$ 1c)	(202185)				
LiZnPS ₄	AgZnPS ₄	16	0		
(Pna2 ₁)	(48197)				

^a Measures in which various candidates fail one of the screening criteria are bolded.

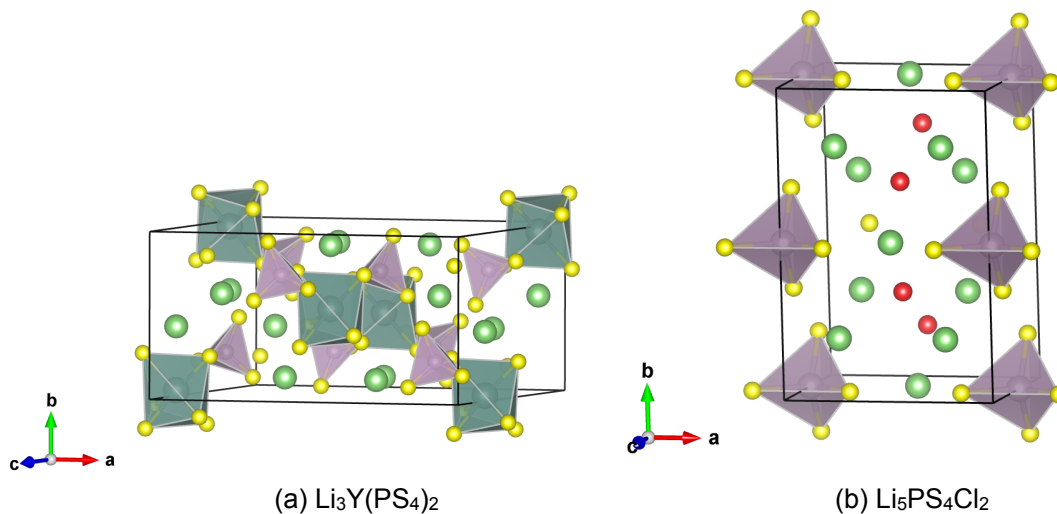


Figure 3.3 Crystal structures (conventional cell) of the identified Li superionic conductor candidates, (a) $\text{Li}_3\text{Y}(\text{PS}_4)_2$ and (b) $\text{Li}_5\text{PS}_4\text{Cl}_2$. Purple tetrahedra, PS_4 ; dark green octahedra, YS_6 ; green spheres, Li; yellow spheres, S; red spheres, Cl.

Table 3.2 Relaxed conventional unit cell lattice parameters for $\text{Li}_3\text{Y}(\text{PS}_4)_2$ and $\text{Li}_5\text{PS}_4\text{Cl}_2$.

Compound	Atoms/cell	a	b	c	α	β	γ
		(Å)	(Å)	(Å)	(deg)	(deg)	(deg)
$\text{Li}_3\text{Y}(\text{PS}_4)_2$	56	17.122	9.290	9.137	90.0	122.3	90.0
$\text{Li}_5\text{PS}_4\text{Cl}_2$	24	7.212	10.494	6.024	90.0	90.0	90.0

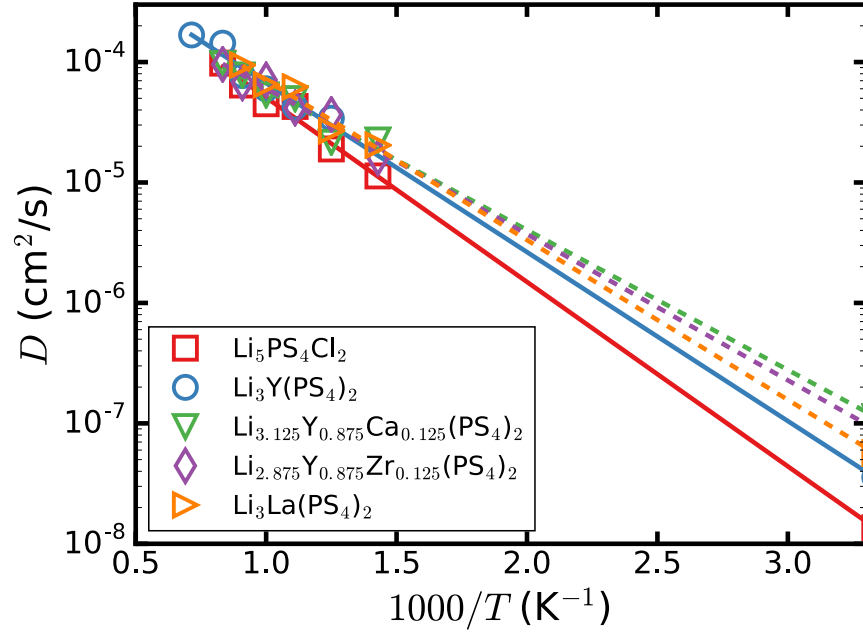


Figure 3.4 Arrhenius plots of promising lithium superionic conductor candidates from AIMD simulations.

Solid lines indicate the initial $\text{Li}_3\text{Y}(\text{PS}_4)_2$ and $\text{Li}_5\text{PS}_4\text{Cl}_2$ candidates. Dashed lines indicate the further optimized candidates obtained via aliovalent doping or substitution of $\text{Li}_3\text{Y}(\text{PS}_4)_2$ ($\text{Li}_3\text{La}(\text{PS}_4)_2$, $\text{Li}_{3.125}\text{Y}_{0.875}\text{Ca}_{0.125}(\text{PS}_4)_2$ and $\text{Li}_{2.875}\text{Y}_{0.875}\text{Zr}_{0.125}(\text{PS}_4)_2$).

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

Formula	$\sigma_{300\text{K}}(\text{mS/cm})$	Error range of	E_a (meV)	$D_{300\text{K}} (\text{cm}^2/\text{s})$
	$\sigma_{300\text{K}}(\text{mS/cm})$			
$\text{Li}_3\text{Y}(\text{PS}_4)_2$	2.16	[1.46, 3.19]	278	3.56×10^{-8}
$\text{Li}_5\text{PS}_4\text{Cl}_2$	1.85	[1.38, 2.47]	304	1.36×10^{-8}

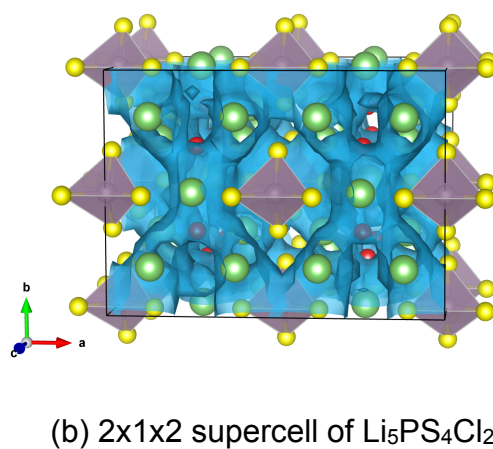
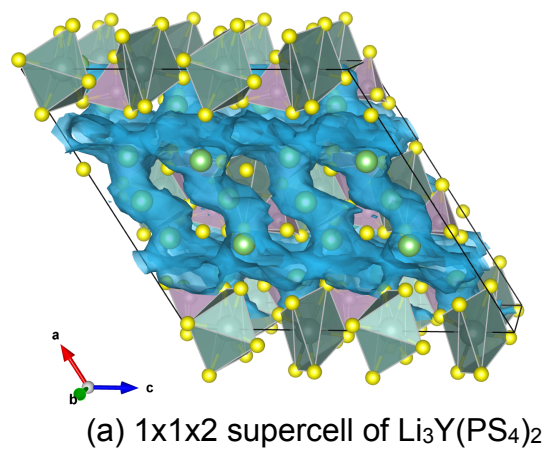


Figure 3.5 Isosurfaces of Li^+ probability density distribution P (light blue) for $\text{Li}_3\text{Y}(\text{PS}_4)_2$ and $\text{Li}_5\text{PS}_4\text{Cl}_2$ from AIMD simulations at 800K with $P = 0.0001 \text{ a}_0^{-3}$ (a_0 is the Bohr radius).

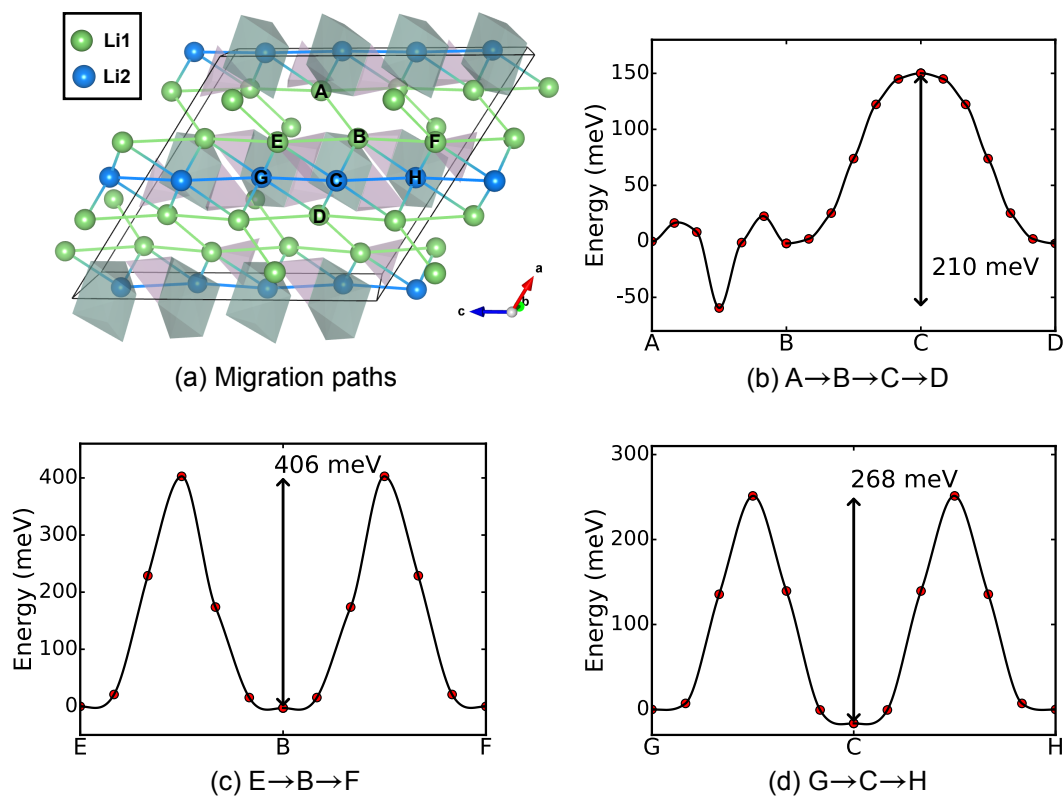


Figure 3.6 Investigated Li vacancy diffusion paths in $\text{Li}_3\text{Y}(\text{PS}_4)_2$ viewed along b direction. Symmetrically distinct Li1 and Li2 are represented by green and blue spheres, respectively. Celadon polyhedra and gray tetrahedra indicate YS_6 and PS_4 . (b–d) Calculated CI-NEB migration barriers for selected percolating paths.

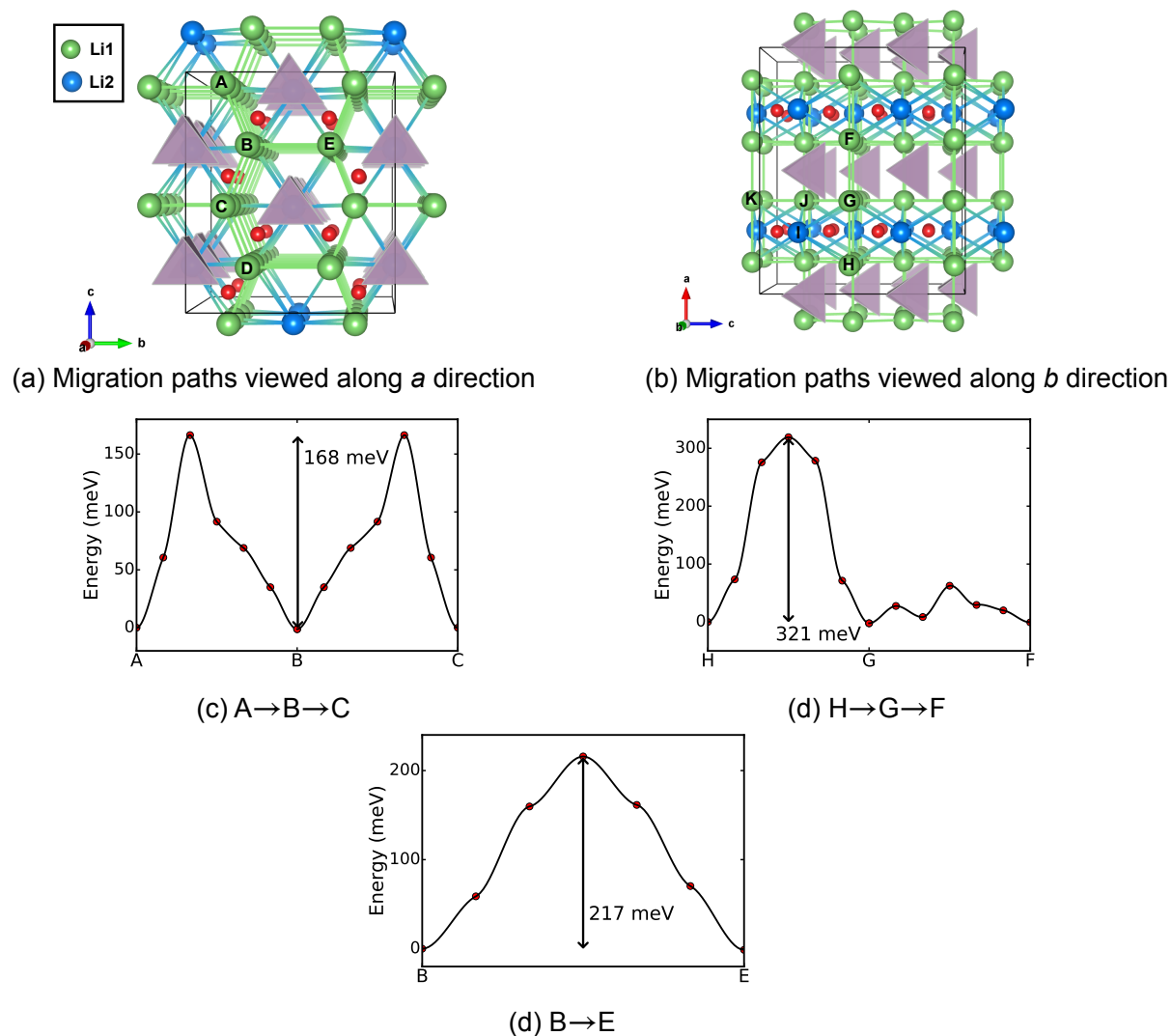
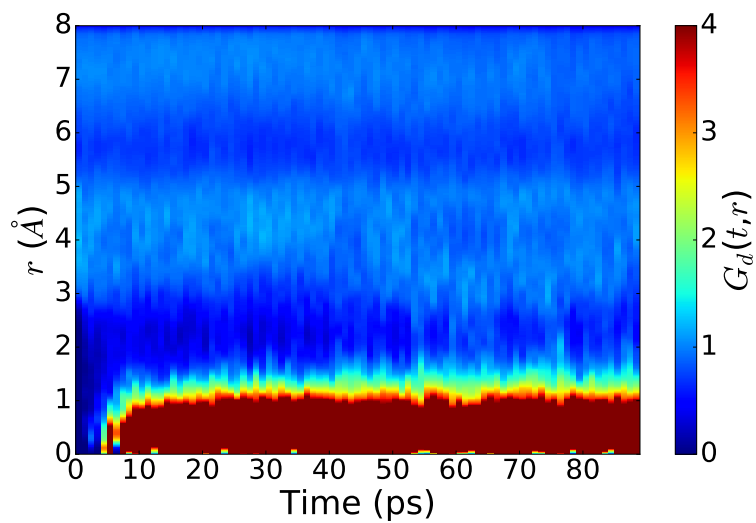
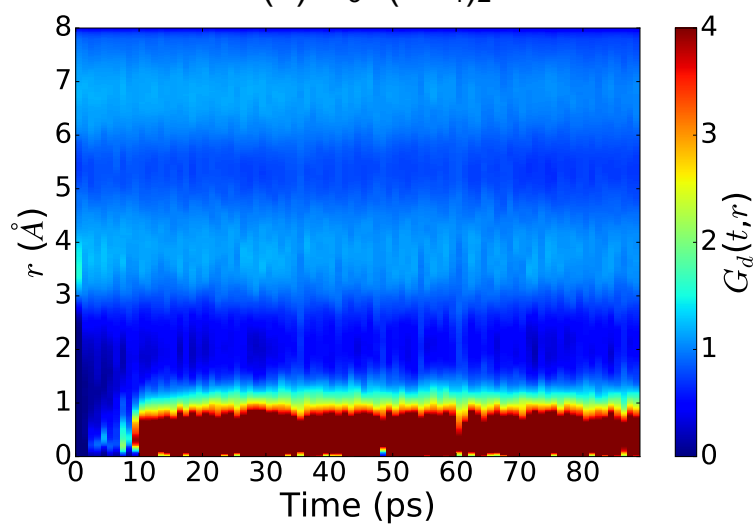


Figure 3.7 Investigated Li vacancy diffusion paths in $\text{Li}_5\text{PS}_4\text{Cl}_2$ viewed along (a) a direction; (b) b direction. Green, blue, red spheres represent Li1, Li2 and Cl atoms, respectively. Gray tetrahedra are PS_4 tetrahedra. (c–e) Calculated CI-NEB migration barriers for selected paths.

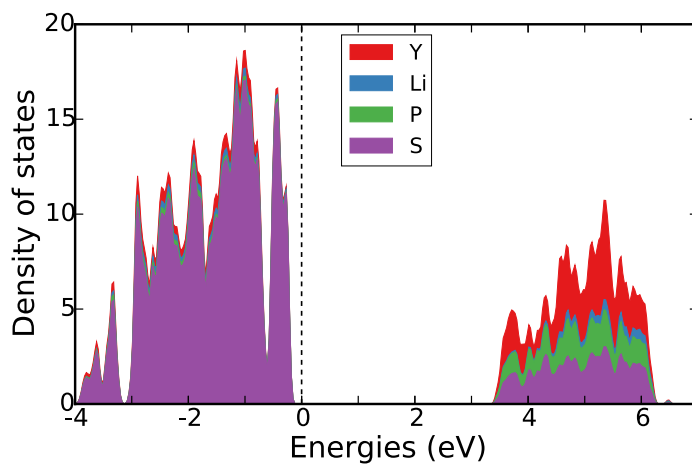


(a) $\text{Li}_3\text{Y}(\text{PS}_4)_2$

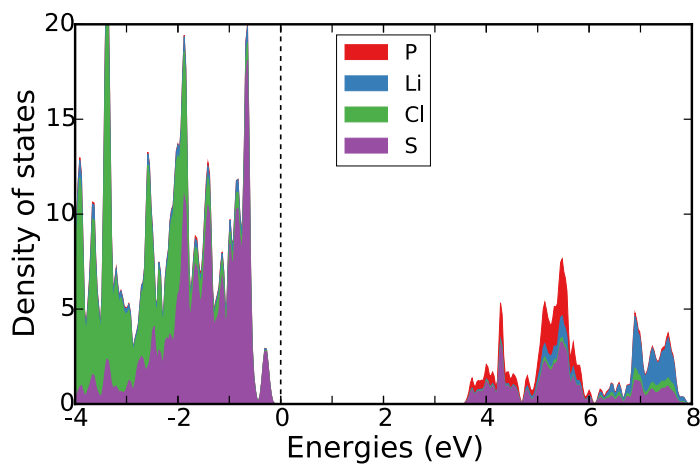


(b) $\text{Li}_5\text{PS}_4\text{Cl}_2$

Figure 3.8 Plots of distinct-part of the van Hove correlation function (G_d) for (a) $\text{Li}_3\text{Y}(\text{PS}_4)_2$ and (b) $\text{Li}_5\text{PS}_4\text{Cl}_2$ 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.



(a) $\text{Li}_3\text{Y}(\text{PS}_4)_2$



(b) $\text{Li}_5\text{PS}_4\text{Cl}_2$

Figure 3.9 Calculated element-projected density of states for (a) $\text{Li}_3\text{Y}(\text{PS}_4)_2$ (band gap $E_g = 3.41$ eV) and (b) $\text{Li}_5\text{PS}_4\text{Cl}_2$ ($E_g = 3.57$ eV) using the HSE screened hybrid functional.

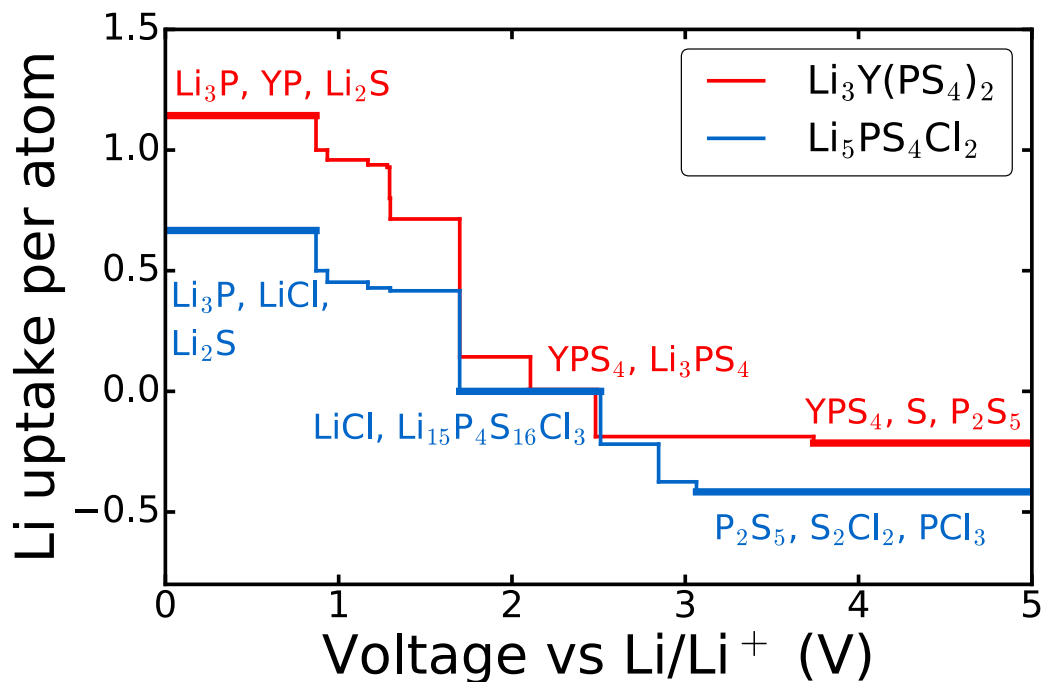


Figure 3.10 Li grand potential phase stability plots for $\text{Li}_3\text{Y}(\text{PS}_4)_2$ and $\text{Li}_5\text{PS}_4\text{Cl}_2$ solid electrolytes. At low voltage, $\text{Li}_3\text{Y}(\text{PS}_4)_2$ and $\text{Li}_5\text{PS}_4\text{Cl}_2$ undergo reduction process and uptake Li whereas at high 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 $\text{Li}_3\text{Y}(\text{PS}_4)_2$ and $\text{Li}_5\text{PS}_4\text{Cl}_2$ candidates as well as other known superionic conductors at 5 V cathode and metallic Li anode.^a

Electrolyte	Phase equilibria at 5 V cathode $\mu_{\text{Li}} = (\mu_{\text{Li}}^0 - 5) \text{ eV}$	Phase equilibria at anode $\mu_{\text{Li}} = \mu_{\text{Li}}^0 \text{ eV}$
Promising candidates		
$\text{Li}_3\text{Y}(\text{PS}_4)_2$	$\text{YPS}_4 + 0.5 \text{ P}_2\text{S}_5 + 1.5 \text{ S}$	$\text{YP} + \text{Li}_3\text{P} + 8 \text{ Li}_2\text{S}$
$\text{Li}_5\text{PS}_4\text{Cl}_2$	$0.067 \text{ PCl}_5 + 0.833 \text{ S}_2\text{Cl}_2 + 0.467 \text{ P}_2\text{S}_5$	$\text{Li}_3\text{P} + 4 \text{ Li}_2\text{S} + 2 \text{ LiCl}$
Known superionic conductors		
$\text{Li}_{10}\text{Si}_{1.5}\text{P}_{1.5}\text{S}_{11.5}\text{Cl}_{0.5}$	$0.75 \text{ P}_2\text{S}_7 + 0.25 \text{ S}_2\text{Cl}_2 + 1.5 \text{ SiS}_2 + 2.75 \text{ S}$	$1.5 \text{ Li}_3\text{P} + 0.3 \text{ Li}_{21}\text{Si}_5 + 0.5 \text{ LiCl} + 11.5 \text{ Li}_2\text{S}$
$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$	$\text{P}_2\text{S}_5 + \text{GeS}_2 + 5 \text{ S}$	$2 \text{ Li}_3\text{P} + 0.25 \text{ Li}_{15}\text{Ge}_4 + 12 \text{ Li}_2\text{S}$
$\text{Li}_7\text{P}_3\text{S}_{11}$	$1.5 \text{ P}_2\text{S}_5 + 3.5 \text{ S}$	$3 \text{ Li}_3\text{P} + 11 \text{ Li}_2\text{S}$

^a Coefficients given per formula unit of solid electrolyte.

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

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

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

Formula	Bulk modulus	Shear modulus	Young's	Poisson's
	(GPa)	(GPa)	modulus	ratio
			(GPa)	
$\text{Li}_3\text{Y}(\text{PS}_4)_2$	27.0	9.7	26.0	0.34
$\text{Li}_5\text{PS}_4\text{Cl}_2$	30.1	13.6	35.4	0.30

Chapter 4. Dopants and Functional Defects for Fast Na⁺

Conduction in Na₃PS₄ Superionic Conductor

In this chapter, we present our investigations of dopants and defects on Na₃PS₄ material. We design the optimization strategy from two sides: M⁴⁺ cation doping (introducing Na⁺ interstitials) and Cl⁻ doping (introducing Na vacancy). We firstly discuss how Na⁺ excess enhances the Na⁺ conductivity in c-Na₃PS₄ by several orders of magnitude higher than tetragonal phase and provide an evaluation of M⁴⁺ dopant effect. Then we present our work on DFT-guided halide doping in t-Na₃PS₄ to improve both conductivity and electrochemical stability. Our prediction is successfully verified by experimental results and Cl-doped t-Na₃PS₄ 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-Na₃PS₄ 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 M⁴⁺ Cation Dopants in Cubic Na₃PS₄

4.1.1 Introduction

Rechargeable Na-ion batteries have enjoyed a resurgence of interest in recent years,^{28,126–128} 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,^{30,129,130} 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.¹³¹ Such organic solvent-based liquid electrolytes are flammable and have limited electrochemical windows.^{3,86,93,132}

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 Na⁺trium Superionic CONductors (NASICON) are wellstudied, but they typically exhibit reasonable ionic conductivities only at higher temperatures.^{30–32,133,134}

An exciting recent development is the discovery of the cubic phase of Na₃PS₄ (c-Na₃PS₄, space group: $I\bar{4}3m$) in 2012.³² 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- Na₃PS₄ to 0.46 mS/cm using crystalline Na₂S with high purity of over 99% followed by heat treatment.¹³⁵ Further efforts at optimizing the conductivity within the (1-x)Na₃PS₄·xNa₄SiS₄ pseudobinary system yield a maximum ionic conductivity as high as 0.74 mS/cm at x around 0.06.^{33,136} Recent first-principles work also shows that Na₃PS₄ is likely to have favorable elastic properties that allow good electrode contact to be achieved with cold-press sintering.²⁴

c-Na₃PS₄ 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-Na₃PS₄ and the effect of doping on its overall conductivity.^{89,91} 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⁺ ionic transport in undoped and M⁴⁺-doped (M = Si, Ge, and Sn) c-Na₃PS₄. We demonstrate that pristine c-Na₃PS₄ is in fact an extremely poor ionic conductor, but with the introduction of Na⁺ interstitials, a reasonably high conductivity can be achieved. We further demonstrate that 6.25% doping of Si⁴⁺ for P⁵⁺ with the concomitant introduction of compensating Na⁺ interstitials result in Na_{3+x}Si_xP_{1-x}S₄ with predicted Na⁺ conductivities that are in excellent agreement with previous experimental results. Furthermore, we show that increased Si⁴⁺ doping (from x = 0.0625 to 0.125) and Sn⁴⁺ doping can potentially achieve even higher conductivities.

4.1.2 Methods

All calculations were performed with the Vienna Ab initio Simulation Package (VASP),¹⁰⁶ within the projector augmented wave (PAW) approach.¹⁰⁷ The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA)¹⁰⁸ was adopted for the exchange correlation functional. Other parameters such as kinetic energy cutoff, *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 library¹⁰⁵ was used for all analyses.

Phase Stability. Cubic Na₃PS₄ (*I* $\bar{4}$ 3*m*) has two symmetrically distinct Na sites: the 6*b* site (Na1) with a partial occupancy of 0.8, and the 12*d* site (Na2) with a partial occupancy of 0.1 (Figure 4.1a).¹³⁶ Structural optimizations were carried out on all symmetrically distinct orderings

of the primitive cell enumerated using the algorithm of Hart et al.¹³⁷ We then selected the lowest energy configuration in subsequent calculations.

We also studied $\text{Na}_{3+x}\text{M}_x\text{P}_{1-x}\text{S}_4$ with $\text{M} = \text{Si}, \text{Ge}, \text{and Sn}$. Since the maximum ionic conductivity reported by Hayashi et al.^{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 $2 \times 2 \times 2$ supercell of the conventional unit cell of $\text{c-Na}_3\text{PS}_4$, in which one P^{5+} is replaced by M^{4+} (Si, Ge, or Sn) and a Na^+ added to maintain overall charge neutrality. For $\text{M} = \text{Si}$, we also studied the effect of dopant concentration by doubling x to 0.125 with corresponding increase in Na^+ 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).¹⁰⁹ The phase stabilities of $\text{c-Na}_3\text{PS}_4$ and $\text{Na}_{3+x}\text{M}_x\text{P}_{1-x}\text{S}_4$ were investigated by constructing the Na–M–P–S phase diagrams⁵¹ using precomputed energies of existing $\text{Na}_x\text{P}_y\text{S}_z$ and $\text{Na}_w\text{M}_x\text{P}_y\text{S}_z$ compounds in the MP database extracted via the Materials Application Programming Interface.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 $\text{Na}_4\text{P}_2\text{S}_6$ and $\text{Na}_2\text{P}_2\text{S}_6$ structures that were reported recently.^{104,138}

For all materials of interest, we computed the decomposition energy (also known as the energy above hull), E_{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_{decomp} of 0, while the higher the E_{decomp} , the more unstable a phase is.

Correction for Sulfur. In our investigations, we found that the binding energy of ground state sulfur (monoclinic S₈) is significantly overestimated by the PBE functional, similar to the well-known overbinding observed for the O₂ 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 S₈ to S²⁻, 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

$$E_f[M] = E_{tot}[M] - E_{tot}[\text{bulk}] - \sum_{i=1}^N n_i \mu_i \quad (4.1)$$

where $E_{tot}[M]$ and $E_{tot}[\text{bulk}]$ are the total energies of the structure with and without the neutral dopant M, respectively; μ_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. μ_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_xP_{1-x}S₄ with M = Si, Ge, and Sn, and $x = 0.0625$, the formation of the defect structure involves an addition of the dopant M⁴⁺ and a Na⁺ interstitial, together with the removal of a host P⁵⁺ ion. The corresponding formation energy E_f can be expressed as follows:

$$E_f[M] = E_f^0[M] - \Delta\mu_M - \Delta\mu_{Na} + \Delta\mu_P \quad (4.2)$$

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

Additional constraints can be applied to the atomic chemical potentials μ_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-Na₃PS₄ framework structure during synthesis

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

where $E_f[Na_3PS_4]$ is the formation energy of the pristine c-Na₃PS₄ 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_xP_{1-x}S₄ with $x = 0.0625$, for example, the formation of the possible secondary phase Na₄SiS₄, as indicated in Table 4.1, should be avoided. This leads to the following inequality:

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

where $E_f[Na_4SiS_4]$ is the formation energy of Na₄SiS₄.

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-Na₃PS₄.¹⁴⁰ 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-Na₃PS₄ 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 × 2 × 2 c-Na₃PS₄ were selected.

Similar AIMD simulation parameters were used as per previous work by the authors.¹¹¹ Non-spin-polarized AIMD simulations were conducted in the *NVT* ensemble at 800–1400 K with a Nose–Hoover thermostat.^{75,76} A smaller plane-wave energy cutoff of 280 eV and a minimal Γ -centered 1×1×1 *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.^{80,141} The central quantity obtained from each AIMD simulation is the Na ion diffusivity that can be expressed as

$$D = \frac{1}{2dt} \langle [\Delta \mathbf{r}(t)]^2 \rangle \quad (4.6)$$

where *d* is the dimensionality factor and equals 3 for 3-D crystal structures, and $\langle [\Delta \mathbf{r}(t)]^2 \rangle$ 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 $D_{300\text{ K}}$. The room-temperature Na ion conductivity $\sigma_{300\text{ K}}$ can then be derived from the Nernst–Einstein equation as follows:

$$\sigma_{300\text{ K}} = \frac{\rho z^2 F^2}{RT} D_{300\text{ K}} \quad (4.7)$$

where ρ 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. $T = 300\text{ K}$ 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-Na₃PS₄ belongs to the $I\bar{4}3m$ space group with a lattice parameter of 6.9965(9) Å.¹³⁶ It is the high-temperature phase of the tetragonal Na₃PS₄ (t- Na₃PS₄). The lattice parameters for t- and c-Na₃PS₄ differ only by around 0.1Å, and the experimental transition temperature from t- Na₃PS₄ to c-Na₃PS₄ is around 540 K.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_{decomp} and the corresponding equilibrium phases for the undoped and doped c- Na_3PS_4 phases are listed in Table 4.1. For the undoped c- Na_3PS_4 , our calculation predicts its E_{decomp} to be only 5 meV/atom, with t- Na_3PS_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.³² 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 $\text{M} = \text{Si}$ 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 synthesizability of Si-doped Na_3PS_4 with similar dopant concentration in experiments.³³ 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_3PS_4 and Na_4MS_4 ($\text{M} = \text{Si}, \text{Sn}$), while the Ge-doped structure has the equilibrium phases of $\text{Na}_6\text{Ge}_2\text{S}_7$, Na_2S , and t- Na_3PS_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_3PS_4 and Na_4SiS_4 remain stable before and after the sulfide correction.

Dopant Formation Energies. The dopant formation energy is an important quantity that measures the synthesizability 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-Na₃PS₄ 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-Na₃PS₄ to be achievable experimentally.

Probability Density and Site Occupancy. The probability density distribution defined on a uniform 3D grid, namely, $P(\mathbf{r})$, 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.⁷⁴ 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 $\int_0^\Omega P d\mathbf{r} = 1$ with Ω being the volume of the unit cell. We define the maximum of $P(\mathbf{r})$ as $P_{\max}$.

Figure 4.3 shows the isosurfaces of probability density distributions for Na ions in Na_{3+x}Si_xP_{1-x}S₄ (x = 0.0625) at 800 K (the lowest temperature at which the AIMD simulations were performed) at various cutoffs. In general, the $P(\mathbf{r})$ 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_xP_{1-x}S₄ (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-Na₃PS₄ (see Table 4.2). For the pristine c-Na₃PS₄, 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-Na₃PS₄ where simulations at only four temperatures were run. Table 4.3 summarizes the extrapolated diffusivities D_{300K} and ionic conductivities σ_{300K} , including the error range for σ_{300K} .

From Figure 4.4a, we may observe that the calculated Na⁺ conductivity is extremely low (1.1×10^{-4} mS/cm) and the activation barrier is extremely high (537 meV) in the pristine c-Na₃PS₄ 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-Na₃PS₄, Na⁺ interstitials can be created by doping the P⁵⁺ sites with M⁴⁺ cations such as Sn⁴⁺, Ge⁴⁺, and Si⁴⁺. The Arrhenius plots for doped Na_{3+x}M_xP_{1-x}S₄ 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}S₄ is 1.66

mS/cm, in excellent agreement with the previously measured experimental value of 0.74 mS/cm for $0.94 \text{ Na}_3\text{PS}_4 \cdot 0.06 \text{ Na}_4\text{SiS}_4$.^{33,136}

Remarkably, the Sn-doped c- Na_3PS_4 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 (P^{5+} , S^{2-} , and M^{4+}), 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 (PS_4 or MS_4), 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_3PS_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_3PS_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_3PS_4 . We find that stoichiometric c- Na_3PS_4 has a very low ionic conductivity, which is similar to reported value of t- Na_3PS_4 .¹⁴² Stoichiometric c- Na_3PS_4 also has relatively low occupancy on the Na2 site (<0.1 at 800 K), similar to t- Na_3PS_4 . Both these observations are not surprising, given the small differences in lattice parameters between t- and c- Na_3PS_4 . It is only

when the Na^+ interstitials are introduced to c- Na_3PS_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_3PS_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_2S 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_2S does not necessarily mean Na^+ interstitials will be formed, a less pure Na_2S 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_3PS_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 $\text{c-Na}_3\text{PS}_4$. 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 $0.94 \text{ Na}_3\text{PS}_4 \cdot 0.06 \text{ Na}_4\text{SiS}_4$ 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. $\text{Na}_{3.0625}\text{Sn}_{0.0625}\text{P}_{0.9375}\text{S}_4$ 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 $\text{c-Na}_3\text{PS}_4$ 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 $\text{Li}_{10}\text{MP}_2\text{S}_{12}$ ($\text{M} = \text{Si, Ge, and Sn}$) superionic conductor⁹¹ leads to the opposite trend in Na^+ conductivity of $\text{Si} > \text{Sn}$. It may be that such different trends are the result of (a) the different dimensionality of diffusion in $\text{Li}_{10}\text{MP}_2\text{S}_{12}$ systems (quasi 1D) and doped Na_3PS_4 systems (3D), and (b) the different diffusing species, i.e., Li^+ in $\text{Li}_{10}\text{MP}_2\text{S}_{12}$ and Na^+ in $\text{c-Na}_3\text{PS}_4$. 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.^{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., $H_R[\text{Li}_{10}\text{SnP}_2\text{S}_{12}] \approx 0.3$).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- Na_3PS_4 and $\text{Na}_{3+x}\text{M}_x\text{P}_{1-x}\text{S}_4$ ($\text{M} = \text{Si}$ with $x = 0.0625$ and 0.125 ; $\text{M} = \text{Ge}, \text{Sn}$ 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- Na_3PS_4 . Si^{4+} , Ge^{4+} , and Sn^{4+} are all viable dopants to introduce Na^+ excess in c- Na_3PS_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- Na_3PS_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- Na_3PS_4 is a potentially promising Na superionic conductor with a significantly higher Na^+ conductivity than 6.25% Si-doped c- Na_3PS_4 .

4.2 Halide Doping Strategy into Tetragonal Na₃PS₄

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-Na₃PS₄, and that Sn⁴⁺ cation doping (for P⁵⁺) may yield greater improvement in conductivity than Si⁴⁺ doping but at the expense of higher dopant formation energy.⁷³ The introduction of defects via aliovalent doping is a common strategy to improve the ionic conductivity of materials.

For Na₃PS₄, previous efforts have mainly focused on the cubic phase and the introduction of Na excess interstitials via substitution of P⁵⁺. An alternative strategy of aliovalent doping is to introduce Na⁺ vacancies in Na₃PS₄. Halide (X⁻) anion doping (for S²⁻) is a potential strategy for Na⁺ vacancy creation.¹⁴⁴ However, previous experimental efforts with (1-*x*)c-Na₃PS₄-*x*NaI glass-ceramics achieved a Na⁺ conductivity of ~0.1 mS cm⁻¹,¹⁴⁵ which is lower than that of the undoped and Si-doped c-Na₃PS₄. Furthermore, an unknown phase was found as the major precipitant when NaI was introduced at *x* ≥ 0.1, suggesting an intrinsic incompatibility of I⁻ ions with the S²⁻ host at such high doping levels.

Besides, we demonstrate the stable cycling of a TiS₂/t-Na_{3-*x*}PS_{4-*x*}Cl_{*x*}/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-Na₃PS₄ 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 S²⁻ 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 $\text{Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$, 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^- ($\text{X}=\text{F}, \text{Cl}, \text{Br}$ and I) into both the tetragonal and cubic phases of Na_3PS_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_3PS_4 . Figure 4.6a shows the crystal structure of t- Na_3PS_4 . There are two symmetrically distinct Na sites in t- Na_3PS_4 , Na1 (4*d*) and Na2 (2*a*), and the PS_4 tetrahedra are centered at the 2*b* positions.¹⁴² It is worth pointing out that the symmetrically distinct Na sites in c- Na_3PS_4 are labeled similarly as cubic Na1 (6*b*) and Na2 (12*d*). The Na1 (4*d*) and Na2 (2*a*) sites in t- Na_3PS_4 essentially occupy the same positions as the Na1 (6*b*) sites in c- Na_3PS_4 .¹⁴⁴

A single halide dopant is introduced into a $2 \times 2 \times 2$ supercell of t- Na_3PS_4 by replacing one of the S atoms with X, and simultaneously a Na vacancy is introduced to form $\text{Na}_{47}\text{P}_{16}\text{S}_{63}\text{X}$, or t- $\text{Na}_{3-x}\text{PS}_{4-x}\text{X}_x$ with $x = 0.0625$. All symmetrically distinct $V'_{\text{Na}} - X_S$ 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 ($E_f = 0.76 \text{ eV/F}^-$), followed by chloride ($E_f = 0.96 \text{ eV / Cl}^-$) and iodide ($E_f = 0.99 \text{ eV / I}^-$). Bromide doping is by far the least favorable with $E_f = 1.11 \text{ eV / Br}^-$. Higher doping levels result in a significantly higher dopant formation energy, e.g., $E_f = 1.77 \text{ eV}$ 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 Na2 site. Nevertheless, the energy differences between different $V'_{\text{Na}} - X_S$ orderings are generally small ($< 10 \text{ meV / atom}$), 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-Na₃PS₄ at $x > 0.1$ result in formation of unknown phases.¹⁴⁵

Ionic conductivity of Cl-doped t-Na₃PS₄. As demonstrated in recent work by some of the co-authors,⁷³ pristine c-Na₃PS₄, 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-Na₃PS₄ 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 $V'_{Na} - Cl'_S$ 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-Na₃PS₄.¹⁴⁴ 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.^{91,153} 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 Na₂S, NaCl and Na₃P in the ratio of 63:1:16. The dominant phase Na₂S is a good electronic insulator with PBE band gap of 2.4 eV, and NaCl has a PBE band gap of 5.0 eV.¹⁰⁹ Na₃P has a small PBE band gap of 0.4 eV (the screened hybrid HSE functional^{149,150} 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-Na₃PS₄ that consists of Na₂S and Na₃P 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 NaPS₃ + 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-Na₃PS₄ + NaCl as the primary component.

Synthesis and characterization of t-Na_{3-x}PS_{4-x}Cl_x. Pure t-Na₃PS₄ was synthesized from Na₂S and P₂S₅ precursors. The Cl⁻ dopant was introduced by adding NaCl following the chemical reaction $(1.5-x) \text{Na}_2\text{S} + 0.5\text{P}_2\text{S}_5 + x \text{NaCl} \rightarrow \text{Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$. 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-Na₃PS₄, 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 S²⁻ 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 $t\text{-Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$. 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 $t\text{-Na}_3\text{PS}_4$ and doped $t\text{-Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$ 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 $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$. The experimental measurement of pristine $t\text{-Na}_3\text{PS}_4$ 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 $t\text{-Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$ 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 $t\text{-Na}_3\text{PS}_4$ compared to doped $t\text{-Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$, indicating a much larger total resistance in the pristine $t\text{-Na}_3\text{PS}_4$.

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 ($\sim 1.7 \text{ V}$ versus Na/Na^+), which is well within the limits of the DFT predicted stability window of the $t\text{-Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$ 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 $\sim 240 \text{ mAh g}^{-1}$ 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 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 $\sim 80 \text{ mAh g}^{-1}$, 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- Na_3PS_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 Na_3PS_4 to be somewhat more favorable than cation (Si^{4+} , Ge^{4+} and Sn^{4+}) doping, with slightly lower dopant formation energies of 0.76 – 1.11 eV vs 1.04 – 1.32 eV for cation.⁷³ 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, Na_2S loss is likely to lower the chemical potentials of Na and S, significantly promoting $V'_{\text{Na}} - X'_\text{S}$ formation.

Both the cation + interstitials and anion + vacancies doping strategies are predicted to be effective in enhancing the ionic conductivity of Na_3PS_4 . In fact, we find no evidence of any significant difference in the predicted bulk Na^+ conductivities between the cubic and tetragonal Na_3PS_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 Na2 (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_3PS_4 phase has been unsuccessful, while the Cl-doped t- Na_3PS_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_3PS_4 , small-gap compounds such as Na_4Si_4 (space group of $C2/c$; PBE band gap of ~ 1.2 eV) and $\text{Na}_{15}\text{Sn}_4$ (space group of $I\bar{4}3d$; PBE band gap of ~ 0 eV) as well as Na_2S and Na_3P are predicted to form at the anode/solid electrolyte interface. For Cl-doped Na_3PS_4 , on the other hand, the anode/solid electrolyte interface comprises predominantly Na_2S with smaller amounts of NaCl and Na_3P . 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 $\text{Na}_3\text{P} + \text{Na}_2\text{S}$ SEI. It should be noted that in all cases (undoped, cation-doped, and halide-doped), the small-gap compound Na_3P (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-Na₃PS₄,³² 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)¹⁵³ 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 Na₃PSe₄,¹⁵⁴ while Na₃SbS₄ requires a more complicated electrolyte bilayer approach using c-Na₃PS₄ to stabilize the interface at the Na anode.¹⁵⁵

We have demonstrated the potential of the t-Na_{2.9375}PS_{3.9375}Cl_{0.0625} 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-Na_{2.9375}PS_{3.9375}Cl_{0.0625} 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-Na_{2.9375}PS_{3.9375}Cl_{0.0625}/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,³² 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- Na_3PS_4 and Na_3PSe_4 solid electrolytes have higher measured conductivities than c- Na_3PS_4 , 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 Na_3PS_4 solid electrolyte, or $\text{t-Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$, 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 $\text{t-Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$ 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 Na_3PS_4 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 $\text{Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$

4.3.1 Introduction

The cubic phase of Na_3PS_4 (c- Na_3PS_4 , an analogue of Li_3PS_4) from the $\text{Na}_2\text{S-P}_2\text{S}_5$ 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).^{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.^{152,165, 167} The tetragonal- Na_3PS_4 (t- Na_3PS_4) phase has a low ionic conductivity of 0.05 mS/cm,¹⁴² which can be significantly improved to reach ~ 1.1 mS/cm by creating structural defects with Cl doping.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.¹²³

In the typical halogen-doped Na_3PS_4 compounds, halide doping for S^{2-} is charge compensated by Na vacancies, i.e., $\text{Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$, 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_3PS_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 ($\text{Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$). 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 P⁵⁺ to P⁴⁺ is also observed from both solid-state ³¹P 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 Na₃PS₄ have been reported, tetragonal- and cubic-phase.^{32,123,142} c-Na₃PS₄ adopts the space group of $I\bar{4}3m$ with the lattice parameter $a = 6.9965$ Å. while t-Na₃PS₄ crystallizes in $P-42_1c$ with lattice parameters of $a = 6.9520$ Å and $c = 7.0757$ Å. These two forms are significantly different in Na positions: in c-Na₃PS₄, Na is reported to occupy the $12d$ site while in t-Na₃PS₄, Na sits at both $2a$ and $4d$ sites. Na-ion conductivity is reported to be on the order of 10^{-4} S/cm for glass-ceramic c-Na₃PS₄,³² but this value is much smaller for glass-ceramic t-Na₃PS₄, 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-Na₃PS₄ (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-Na₃PS₄ is shown in Figure 4.6a, in which P is tetrahedrally coordinated with four S. Na₁ and Na₂ occupy $4d$ and $2a$ sites, respectively. Defects in glass-ceramic t-Na₃PS₄ 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-Na₃PS₄. Most of the diffraction peaks in the XRD patterns collected on t-Na_{3-x}PS_{4-x}Cl_x ($x = 0, 0.0625, 0.1, \text{ and } 0.2$) come from t-Na₃PS₄, except small and broad peaks at around 21° and 44° from the Kapton film

and the stainless-steel holder. The XRD patterns of $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ ($x = 0, 0.0625, 0.1, \text{ and } 0.2$) 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° . This may suggest the exchange of the two Na sites in $t\text{-Na}_3\text{PS}_4$, which makes the structure gradually converge to $c\text{-Na}_3\text{PS}_4$ with increasing x . In addition, some minor peaks from impurities appear in the sample of $\text{Na}_{2.8}\text{PS}_{3.8}\text{Cl}_{0.2}$, which is consistent with calculation results.¹²³ The thermal stability is greatly compromised with increased x value in $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$.

Na⁺ Conduction in $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$. The ionic conductivity of $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ ($x = 0, 0.0625, 0.1, \text{ and } 0.2$) samples is determined with electrochemical impedance spectroscopy (EIS) and the results are shown in Figure 4.12a. The ionic conductivity of $t\text{-Na}_3\text{PS}_4$ is $\sim 10^{-5}$ S/cm at room temperature (Figure 4.12), compared with $\sim 10^{-4}$ S/cm for $c\text{-Na}_3\text{PS}_4$.³² Cl replacement of S in $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ 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., $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}$. Larger or smaller x values yield larger impedance and thus slower ion conduction (Figure 4.12).

The ionic conductivities of $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ 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:

$$\sigma = A \times \exp\left(\frac{-E_a}{RT}\right) \quad (4.8)$$

where A is a constant, R is the universal gas constant with the value of $8.314 \times 10^{-3} \text{ kJmol}^{-1}\text{K}^{-1}$, and T is temperature in Kelvin. The activation energy of $t\text{-Na}_3\text{PS}_4$ is determined to be 0.34 eV, and

it decreases with more Cl $\rightarrow$ S replacement (0.24 eV for $\text{Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$, 0.23 eV for $\text{Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}$, and 0.19 eV for $\text{Na}_{2.8}\text{PS}_{3.8}\text{Cl}_{0.2}$). As a reference, the activation energy for most solid electrolytes is > 0.24 eV.^{123,160,161} The achieved small activation energy in $\text{t-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ 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.

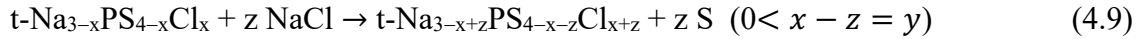
Solid-State ^{23}Na NMR Characterizations of Structural Defects. To identify structural features that contribute to Na-ion conduction in $\text{t-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ ($x = 0, 0.0625, 0.1$, and 0.2), high-resolution solid-state magic-angle-spinning (MAS) ^{23}Na NMR in a high magnetic 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 $\text{t-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$. The ^{23}Na spectrum of $\text{t-Na}_3\text{PS}_4$ 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 $\text{t-Na}_3\text{PS}_4$ 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 $\text{t-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$, 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 $\rightarrow$ S replacement, and the amount of these defects increases with the x values in $\text{t-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ (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 Na₃ sites (~ 10 s) compared with those for Na₁ and Na₂ sites ($< \sim 0.2$ s) in t-Na₃PS₄. For Na₁ and Na₂, the ²³Na NMR T_1 relaxation is driven by quadrupolar interactions and the relaxation time is typically on the order of milliseconds, while for Na₃ and Na₄, 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. Na₃ is assigned to Na sites close to Cl and Na₄ to Na sites in the vicinity of Na vacancies, based on the fact that Na₄ 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 NMR¹⁶² 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., ²³Na, 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 ⁷Li 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 Na₃ and Na₄ resonances after tracer-exchange and increase in Na₁ and Na₂ resonances are observed. The decrease in Na₄ resonance intensity and increase in Na₁ and Na₂ 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.,

Na₄, 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-Na_{2.8}PS_{3.8}Cl_{0.2}. 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-Na_{2.8}PS_{3.8}Cl_{0.2}, 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-Na_{3-y}PS_{4-x}Cl_x. 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-Na_{3-y}PS_{4-x}Cl_x with improved ionic conductivity.



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-Na_{2.9}PS_{3.9}Cl_{0.1} and t-Na_{2.8}PS_{3.8}Cl_{0.2}.

The XRD patterns of the t-Na_{2.9}PS_{3.9}Cl_{0.1}/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-Na_{2.9}PS_{3.9}Cl_{0.1} is successful, manifested as no observed NaCl diffraction peaks. Also, the additional NaCl modifies the t-Na_{2.9}PS_{3.9}Cl_{0.1} 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 $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}$, 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 $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}$ 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 $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}/z\text{NaCl}$ should be less than 0.1 to achieve the goal of partially filling Na vacancies without introducing NaCl impurity. The real formula of $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}/0.1\text{NaCl}$ should be $t\text{-Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$, based on the XRD and NMR results. The optimal z value in $t\text{-Na}_{2.8}\text{PS}_{3.8}\text{Cl}_{0.2}/z\text{NaCl}$ is determined to be 0.2 (Figure 4.20) and the formula for the best sample should be $t\text{-Na}_{3.0}\text{PS}_{3.6}\text{Cl}_{0.4}$.

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

As suggested by tracer-exchange NMR, Na_3 site is responsible for Na conduction. Therefore, Na ionic conductivity can be increased by maximizing $\text{Cl} \rightarrow \text{S}$ replacement and minimizing Na vacancy formation (Na_4). Figure 4.16 presents the results of AC impedance measurements on several $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}/z\text{NaCl}$ ($z = 0.1, 0.3, \text{ and } 0.5$) compounds to validate the proposed strategy. By filling Na vacancies in $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}/z\text{NaCl}$ ($z = 0.1, 0.3, \text{ and } 0.5$), 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 $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}/0.1\text{NaCl}$, nominally $t\text{-Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$. 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 $t\text{-Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$ 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 $t\text{-Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ ($x = 0.0625$ 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 $t\text{-Na}_3\text{PS}_4$ 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 $t\text{-Na}_{2.875}\text{PS}_{3.875}\text{Cl}_{0.125}$ 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 ($\text{Na}_{2.9375}\text{PS}_{3.875}\text{Cl}_{0.125}$), 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 $t\text{-Na}_3\text{PS}_4$ when all Na vacancies are filled ($\text{Na}_3\text{PS}_{4-x}\text{Cl}_x$, $x = 0.0625$ and 0.125). It should be noted that ^{23}Na NMR studies show no sign of Na vacancies for the $\text{Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$ nor $\text{Na}_{3.0}\text{PS}_{3.6}\text{Cl}_{0.4}$ which exhibit highest ionic conductivities of all the $t\text{-Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ 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 $\text{Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$, 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 software¹²⁰ 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. $\text{Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$ vs. $\text{Na}_{2.9375}\text{PS}_{3.875}\text{Cl}_{0.125}$, 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 Å³ to 924 Å³. 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 Na₁ sites along *c* direction and Na₁-Na₂-Na₁ hopping within *ab* plane, which finally form the cubic sub-lattice, similar to that observed in previous studies of Cl-doped Na₃PS₄.¹⁴ 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 → S replacement also leads to changes in the local structural environment of P as seen in ³¹P NMR (Figure 4.21). In addition to ³¹P resonances from t-Na₃PS₄ at ~ 87 ppm, additional ³¹P 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 Li₄P₂S₆ (Li₂PS₃) shows multiple ³¹P NMR peaks > 105 ppm.¹⁶³ Therefore, these additional ³¹P resonances observed for t-Na_{3-y}PS_{4-x}Cl_x compounds suggest the conversion of P⁵⁺ to P⁴⁺ due to Cl → S replacement, and the amount of P⁴⁺ increases with *x* in t-Na_{3-y}PS_{4-x}Cl_x (Figure 4.22). Multiple ³¹P NMR resonances at > 105 ppm suggest an inhomogeneous structural environment due to Cl → S replacement. Both ²³Na and ³¹P NMR indicate that Cl→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 P⁵⁺ to P⁴⁺. Another evidence for the formation of P⁴⁺ is the formation of elemental S. We collected the powder evaporated

during the synthesis of $\text{Na}_{2.8}\text{PS}_{3.8}\text{Cl}_{0.2}$, 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 $\text{Na}_3\text{PS}_{3.9375}\text{Cl}_{0.0625}$ (Figure 4.24). A non-zero integrated spin was observed ($\sim 1/2 \mu_B$ at the radius of 2 Å) for the P in the center of PS_3Cl 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 evidence¹⁶⁴ 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 $\text{t-Na}_3\text{PS}_4$ and $\text{t-Na}_3\text{PS}_{3.8}\text{Cl}_{0.2}$, and the electronic conductivity of $\text{t-Na}_3\text{PS}_{3.8}\text{Cl}_{0.2}$ is $1.2 \times 10^{-8} \text{ S cm}^{-1}$, which is only slightly higher than that for $\text{t-Na}_3\text{PS}_4$, that is, $0.8 \times 10^{-8} \text{ S cm}^{-1}$ (Figure 4.25). Both values are much lower than the measured ionic conductivity $\approx 2 \times 10^{-3} \text{ S cm}^{-1}$ for $\text{t-Na}_3\text{PS}_{3.8}\text{Cl}_{0.2}$.

Full-Cell Performance. The stability of $\text{t-Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ is tested using cyclic voltammetry within a $\text{Na}|\text{Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}|\text{In}$ 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 $\text{Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$ is seen even at a high potential of 10 V , which is attributed to the low electronic conductivity of $\text{Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$, limiting the rate of side reactions. The all-solid-state Na-ion battery using Na as anode, $\text{Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$ as electrolyte, and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ 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}|Na₃V₂(PO₄)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 Ω and it increases to $\approx$ 1300 Ω 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 Na₃V₂(PO₄)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-Na₃PS₄ 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 ²³Na 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-Na₃PS₄, 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 $\text{Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$ is tested in a $\text{Na} \mid \text{Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2} \mid \text{Na}_3\text{V}_2(\text{PO}_4)_3$ cell, which delivers a capacity of 100 mAh/g.

4.3.4 Experimental Section

Synthesis of $\text{t-Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ ($0 \leq y \leq x \leq 0.2$) solid electrolytes: $\text{t-Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ ($0 \leq y \leq x \leq 0.2$) solid electrolytes were prepared via solid-state reactions. All the chemicals (Na_2S , P_2S_5 , and NaCl) were purchased from Sigma-Aldrich and dried under vacuum at 120 °C overnight before use. Na_2S , P_2S_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 $\text{t-Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ ($0 \leq y \leq x \leq 0.2$): 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 $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406$ Å) with a fixed scanning speed of 2°/min from 15° to 60°. The morphologies of $\text{t-Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$

were checked by Scanning Electron Microscopy (SEM) on a NOVA NanoSEM 400 field-emission scanning electron microscope.

Solid-state Nuclear Magnetic Resonance (NMR): ^{23}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}Na is 219.6 MHz. ^{23}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}Na Spin-lattice relaxation time (T_1) measurements were carried out with a saturation recovery pulse sequence. ^{23}Na chemical shift was calibrated to a 0.1 M NaCl solution at 0 ppm. ^{31}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}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}P chemical shift was calibrated to an 85% H_3PO_4 solution at 0 ppm.

Electrochemical tests: Ionic conductivities of $\text{t-Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ pellets at different temperatures were determined using AC impedance measurements. Indium (In) foils with a diameter of 5 mm were attached onto $\text{t-Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ pellets as blocking electrodes and current collectors. The sandwiched cell, $\text{In}|\text{t-Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x|\text{In}$, 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 $^\circ\text{C}$. Cyclic voltammetry measurements were carried out on $\text{Na} | \text{t-Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x | \text{In}$ 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 $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ as cathode, Na metal as anode, and $\text{t-Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$ as solid electrolyte. $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ was prepared via a sol-gel process using citric acid as both chelating agent and carbon source. V_2O_5 , $\text{NH}_4\text{H}_2\text{PO}_4$, CH_3COONa , 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 $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode. The solid electrolyte $\text{t-Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$ (50 mg) was cold-pressed using a 6-mm stainless steel die and then 5 mg composite cathode which contains 60% $\text{t-Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$ and 40% $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ was pressed on top of the $\text{t-Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$ electrolyte layer. Pure Na metal was pressed into a thin film which was attached to the opposite site of the $\text{t-Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}$ 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 $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ 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)¹⁰⁶ within the projector augmented-wave approach.¹⁰⁷ Similar parameters were used as previous works by the authors.^{123,165,166} Briefly, all calculations were performed using the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA) functional.¹⁶⁷ For each composition (Na and Cl concentration), we carried out spin-polarized structure relaxation and total energy calculations of all symmetrically distinct configurations of $\text{v}'_{\text{Na}} - \text{Cl}_5$ in a $2 \times 2 \times 2$ supercell of $\text{t-Na}_3\text{PS}_4$ (16 formula units) using parameters consistent with those in Materials Project (MP),¹⁰⁹ 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 $t\text{-Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ 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.^{75,76} 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 $D_{300\text{K}}$. We derived the room-temperature Na ion conductivity from the Nernst-Einstein equation, $\sigma_{300\text{K}} = \frac{\rho z^2 F^2}{RT} D_{300\text{K}}$ where ρ 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)¹⁰⁵ 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_3PS_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 “Room-Temperature All-Solid-State Rechargeable Sodium-Ion Batteries with a Cl-doped Na_3PS_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 $\text{Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ 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.

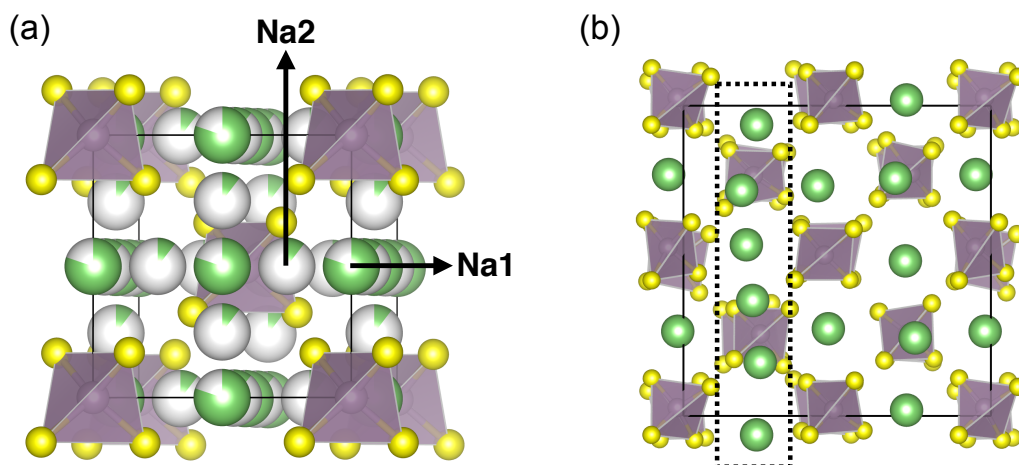


Figure 4.1 (a) Crystal structure of c- Na_3PS_4 primitive cell with green-white spheres, which represent the partially occupied Na sites, whereas dark purple tetrahedrons are PS_4^{3-} . (b) The lowest energy ordering of the $2 \times 2 \times 2$ c- Na_3PS_4 supercell with an Na^+ interstitial (located within the dashed rectangle).

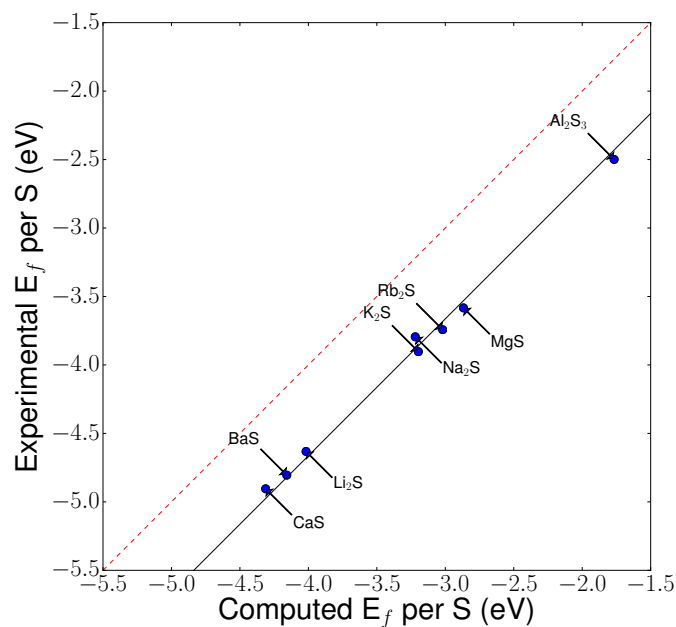


Figure 4.2 Determination of energy difference constant (0.66 eV per S atom) between the DFT and experimental formation energies for sulfides.

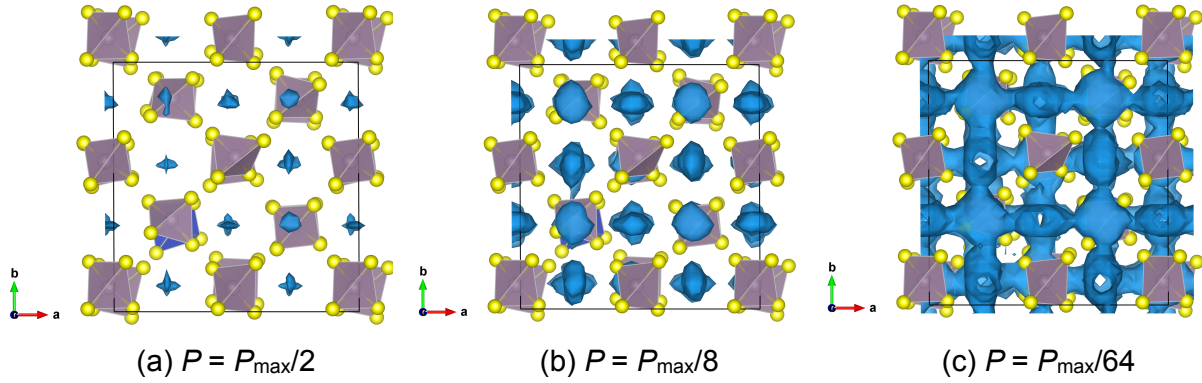


Figure 4.3 Isosurfaces (blue) of Na ion probability density distribution P for $\text{Na}_{3+x}\text{Si}_x\text{P}_{1-x}\text{S}_4$ ($x = 0.0625$) at 800 K.

Table 4.1 Decomposition energies E_{decomp} , the corresponding decomposed products, and neutral dopant formation energies E_{f} of the doped c- Na_3PS_4 compared with undoped case.

Dopant M	x	$E_{\text{f}}(\text{eV/f.u.})$	E_{decomp}	Decomposed
			(meV/atom)	products
undoped	N/A	N/A	5	t- Na_3PS_4
Si	0.125	1.65	30	t- Na_3PS_4 , Na_4SiS_4
Si	0.0625	1.04	13	t- Na_3PS_4 , Na_4SiS_4
Ge	0.0625	1.04	13	t- Na_3PS_4 , Na_4GeS_4
Sn	0.0625	1.32	15	t- Na_3PS_4 , Na_4SnS_4

Table 4.2 Average site occupancies for pristine t-Na₃PS₄, pristine and doped c-Na₃PS₄ compounds with different dopant concentrations x at 800K. To compare with the case of c-Na₃PS₄, we artificially label the Na sites in t-Na₃PS₄ as Na1, whereas the middle points between any two neighboring Na sites are labeled as Na2.

Phase	Structures	x	Na1 site occupancy	Na2 site occupancy
t-Na ₃ PS ₄	pristine	NA	0.88	0.06
c-Na ₃ PS ₄	pristine	NA	0.84	0.08
	Na ⁺ excess	NA	0.68	0.17
	Si-doped	0.0625	0.76	0.13
	Ge-doped	0.0625	0.62	0.20
	Sn-doped	0.0625	0.79	0.12

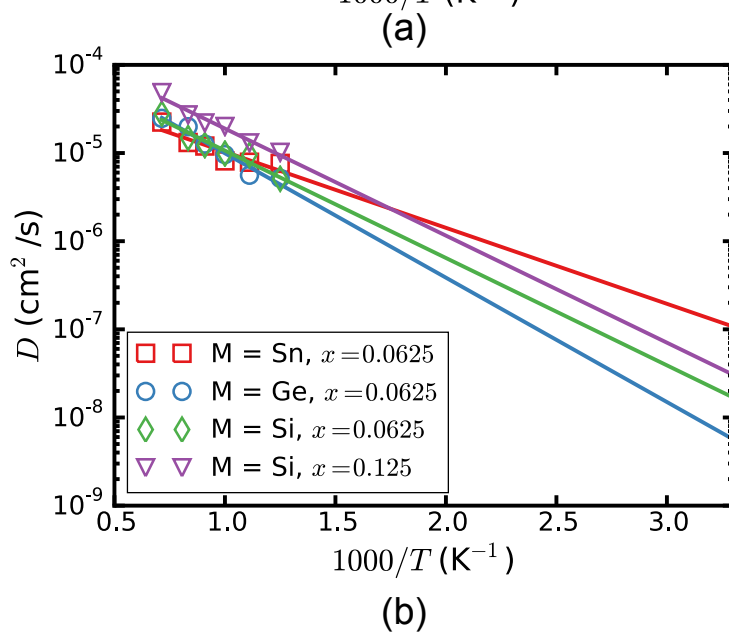
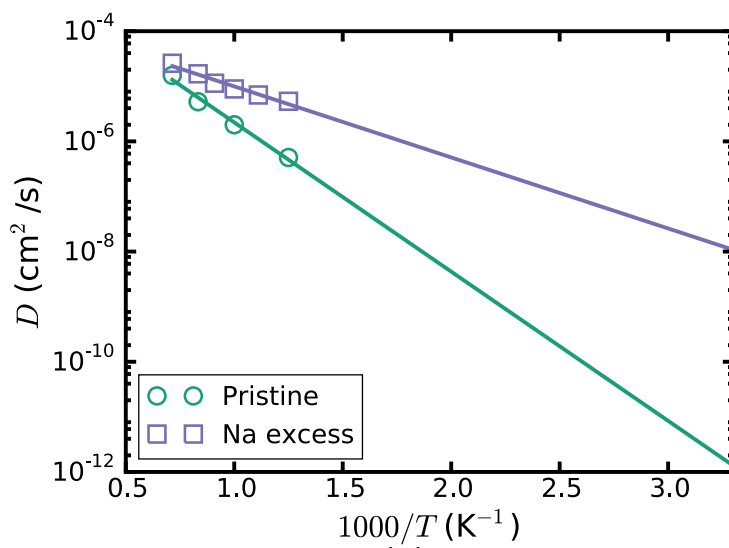


Figure 4.4 Arrhenius plots for (a) c- Na_3PS_4 with Na^+ excess and pristine structures; (b) doped structures $\text{Na}_{3+x}\text{M}_x\text{P}_{1-x}\text{S}_4$ ($\text{M} = \text{Si}, \text{Ge}, \text{or Sn}$).

Table 4.3 Channel size, channel volume, extrapolated Na⁺ conductivity, diffusivity at 300K, and activation energy.

	x	Channel size (Å)	Channel volume (Å ³)	$\sigma_{300\text{ K}}$ (mS/cm)	Error range of $\sigma_{300\text{ K}}$ (mS/cm)	$D_{300\text{ K}}$ (cm ² /s)	E_a (meV)
Pristine	N/A	2.15	863	1.1×10^{-4}	0.68– 1.9×10^{-4}	1.1×10^{-12}	537
Na ⁺ excess	0.0625	2.15	874	1.06	0.79–1.40	9.8×10^{-9}	256
Na _{3+x} Si _x P _{1-x} S ₄	0.125	2.16	879	2.99	2.27–3.94	2.8×10^{-8}	241
Na _{3+x} Si _x P _{1-x} S ₄	0.0625	2.13	869	1.66	1.14–2.41	1.5×10^{-8}	242
Na _{3+x} Ge _x P _{1-x} S ₄	0.0625	2.16	873	0.54	0.38–0.78	5.1×10^{-9}	280
Na _{3+x} Sn _x P _{1-x} S ₄	0.0625	2.16	910	10.7	6.86–16.8	1.0×10^{-7}	171

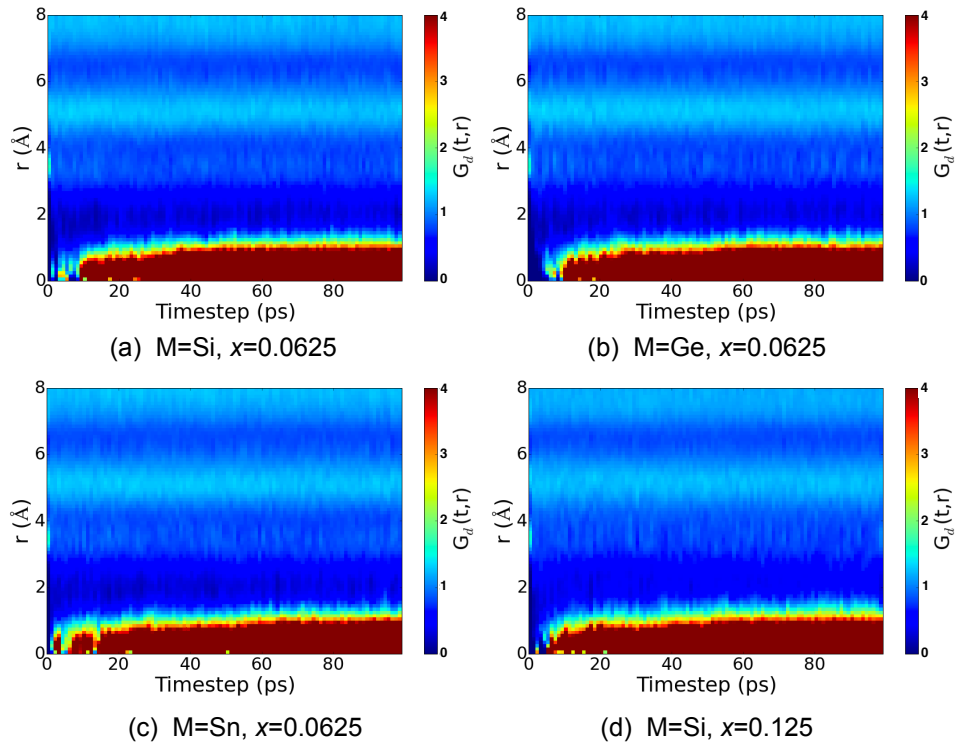


Figure 4.5 Plots of the distinct-part of the van Hove correlation function (G_d) for $\text{Na}_{3+x}\text{M}_x\text{P}_{1-x}\text{S}_4$ at 800K. G_d is a function of the Na–Na pair distance r and time t .

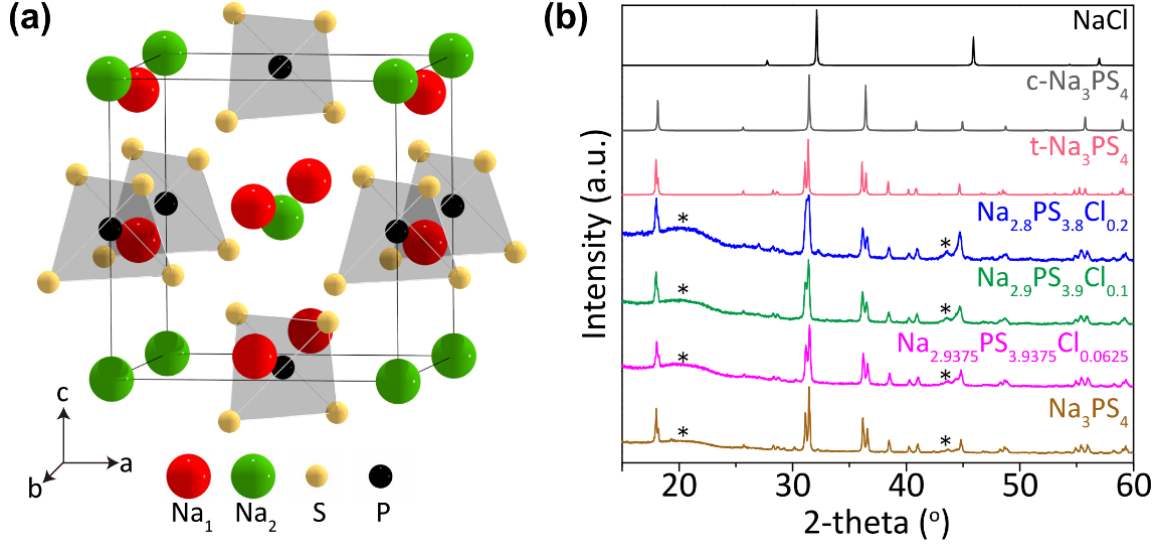


Figure 4.6 Structure and powder X-ray diffraction characterizations of $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$. (a) Crystal structure of pristine tetragonal- Na_3PS_4 (space group = $P\bar{4}2_1c$). Two crystallographically distinct sites Na_1 ($4d$) and Na_2 ($2a$), are shown in green and red, respectively. (b) Powder X-ray diffraction patterns of $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ ($x = 0, 0.0625, 0.1$, and 0.2). Asterisk (*) indicates the background signals from sample holder and Kapton film.

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

Dopant	R_X/R_S	x (%)	E_f (eV/dopant)
F	0.70	6.25	0.76
Cl	0.98	6.25	0.96
Br	1.07	6.25	1.11
I	1.21	6.25	0.99

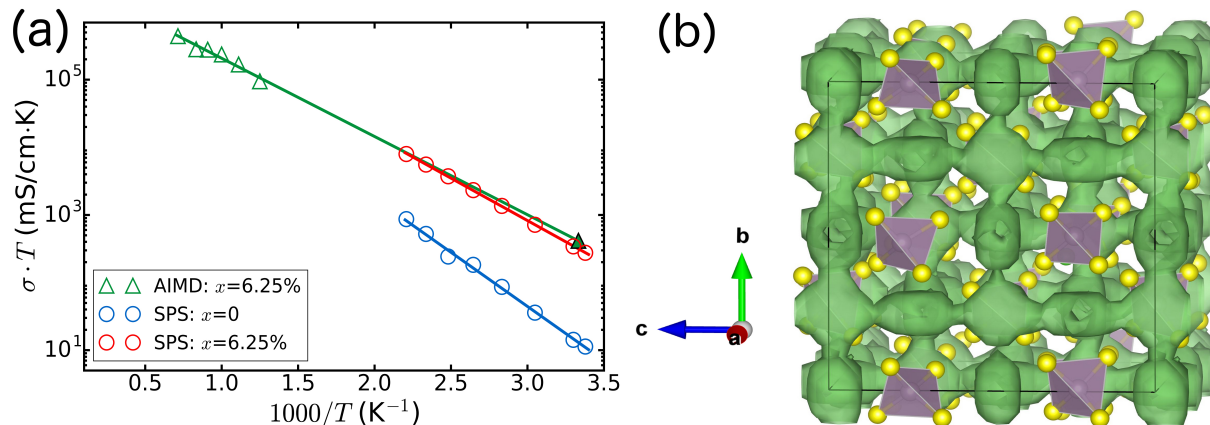


Figure 4.7 Ionic conductivity and Na⁺ probability density distribution of t-Na_{3-x}PS_{4-x}Cl_x. (a) Arrhenius plots of the t-Na_{3-x}PS_{4-x}Cl_x with $x=0$ (blue) and 6.25% (red) obtained from SPS measurements, and $x=6.25\%$ (green) from AIMD simulations. The filled green triangle indicates the extrapolated 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.

x (%)	AIMD simulations		Experiment	
	σ_{300K} (mS cm ⁻¹)	E_a (meV)	σ_{303K} (mS cm ⁻¹)	E_a (meV)
0	N/A	N/A	0.05	317
6.25	1.38 [1.04, 1.82]	232	1.14	249

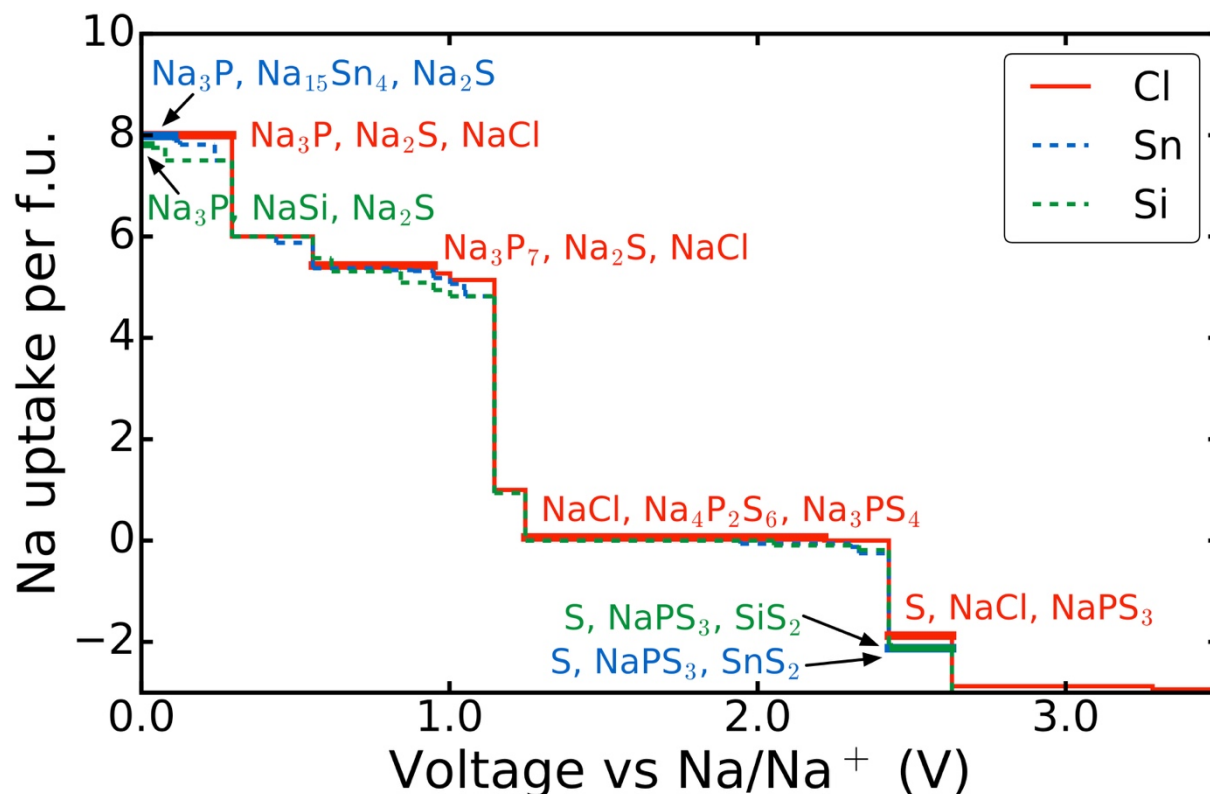


Figure 4.8 Electrochemical decomposition products of doped Na_3PS_4 compounds. Plots of Na uptake per formula unit (f.u.) of t- $\text{Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$ (red solid), c- $\text{Na}_{3.0625}\text{Sn}_{0.0625}\text{P}_{0.9375}\text{S}_4$ (blue dashed) and c- $\text{Na}_{3.0625}\text{Si}_{0.0625}\text{P}_{0.9375}\text{S}_4$ (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 $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$. Rietveld refinement results of $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ systems, where a , b and c are lattice constants, and V , Occ., and B_{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 $t\text{-Na}_3\text{PS}_4$, the DFT calculated cell parameters are $a = b = 6.99 \text{ \AA}$, $c = 7.12 \text{ \AA}$, $V = 348 \text{ \AA}^3$, in excellent agreement with the refinement results as well as those by Jansen et al. (Ref. 27): $a = b = 6.952 \text{ \AA}$, $c = 7.076 \text{ \AA}$, $V = 341.97 \text{ \AA}^3$.

Pristine ($x = 0\%$), Space Group $P\bar{4}2_1c$

$$a = b = 6.956(5) \text{ \AA}, c = 7.088(6) \text{ \AA}, V = 342.9(5) \text{ \AA}^3$$

$$R_b = 3.86\%, R_{wp} = 4.97\%$$

	x	y	z	Occ.	$B_{\text{iso}} (\text{\AA}^2)$
Na1 (4d)	0	0.5	0.426(4)	2.00	2.54(9)
Na2 (2a)	0	0	0	1.00	3.2(1)
P (2b)	0	0	0.5	1.00	0.5(6)
S (8e)	0.315(3)	0.345(2)	0.167(2)	4.00	1.1(6)

Doped ($x = 6.25\%$), Space Group $P\bar{4}2_1c$

$$a = b = 6.970(4) \text{ \AA}, c = 7.092(5) \text{ \AA}, V = 344.5(4) \text{ \AA}^3$$

$$R_b = 4.29\%, R_{wp} = 5.31\%$$

	x	y	z	Occ.	$B_{\text{iso}} (\text{\AA}^2)$
Na1 (4d)	0	0.5	0.428(6)	1.99(4)	3.0(2)
Na2 (2a)	0	0	0	0.99(4)	3.4(3)
P (2b)	0	0	0.5	1.00	0.1(1)
S (8e)	0.316(4)	0.344(3)	0.165(3)	3.94(4)	1.19(9)
Cl (8e)	0.316(4)	0.344(3)	0.165(3)	0.02(4)	1.19(9)

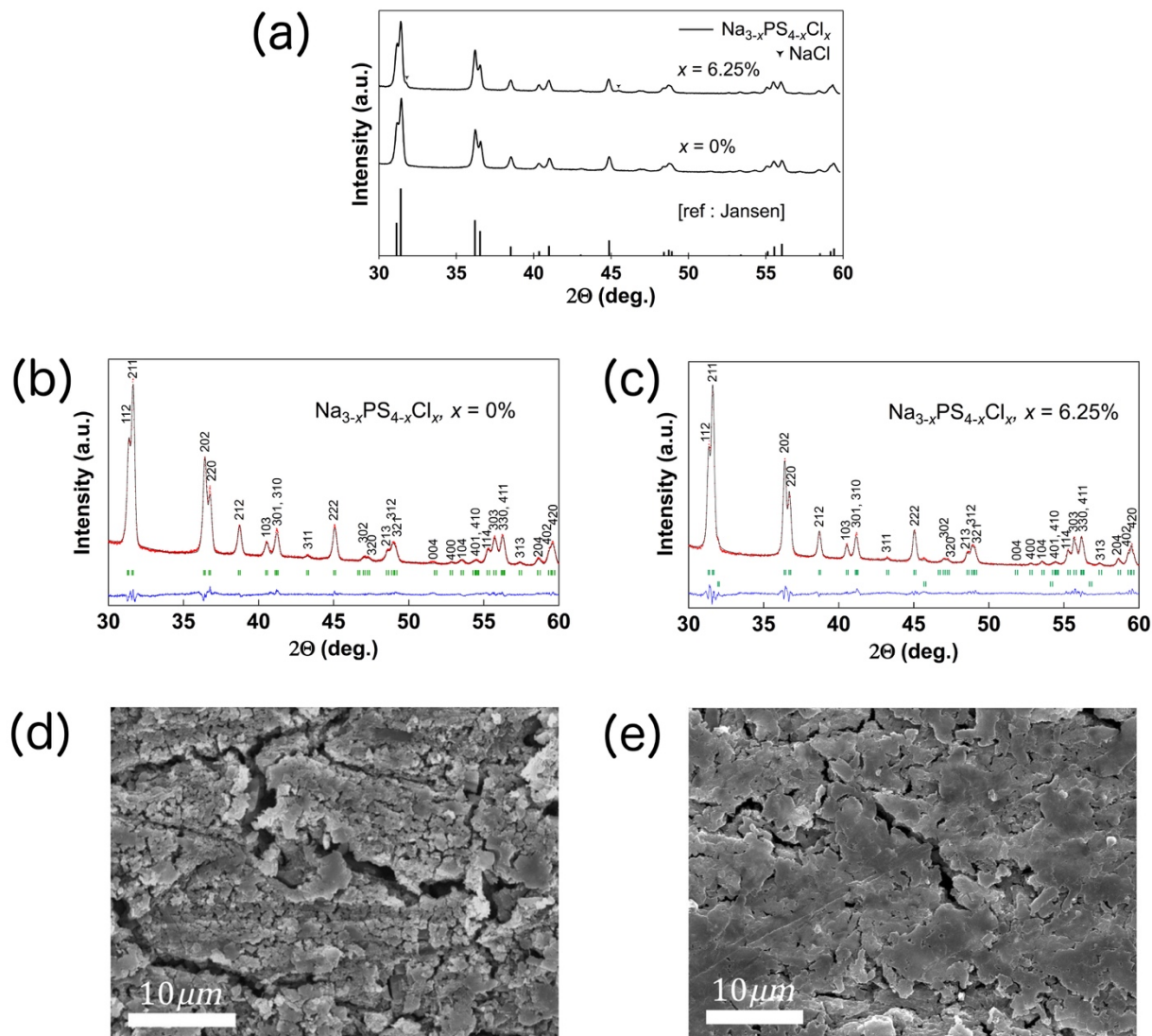


Figure 4.9 Characterization and morphology of $\text{t-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$. (a) XRD patterns for $\text{t-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ with $x = 0\%$ and 6.25% , and previous study in Ref. 27. (b) Refinement plot of the pristine $\text{t-Na}_3\text{PS}_4$. (c) Refinement plot of Cl-doped $\text{t-Na}_3\text{PS}_4$. 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 $\text{t-Na}_3\text{PS}_4$ ($P\bar{4}2_1c$) and NaCl ($Fm\bar{3}m$). The difference between the observed and calculated patterns is signified by the blue line. (d) SEM image of pristine $\text{t-Na}_3\text{PS}_4$ SPS sample, and (e) SEM image of SPS sample of doped $\text{t-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ ($x = 6.25\%$). Scale bar is $10\mu\text{m}$.

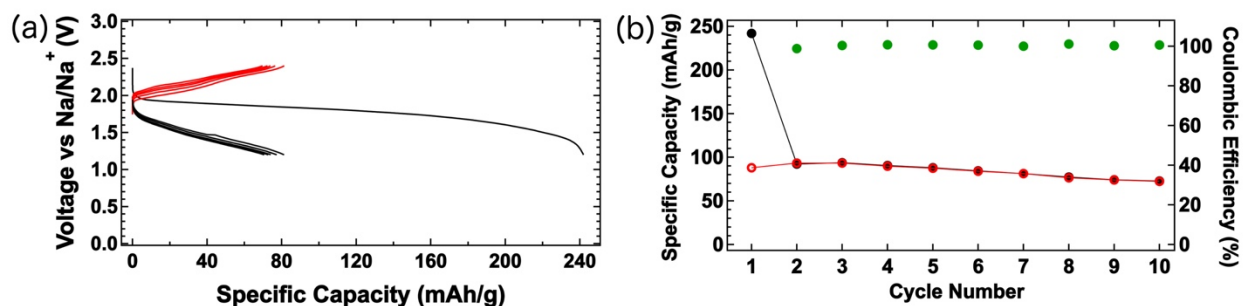


Figure 4.10 Electrochemical performance of $\text{TiS}_2/\text{t-Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}/\text{Na}$ all-solid-state full-cell. Charge-discharge profile of $\text{TiS}_2/\text{t-Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}/\text{Na}$ full-cell at room-temperature. Cell was cycled under constant current conditions with a current density of 0.149 mA cm^{-2} ($\text{C}/10$ 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.

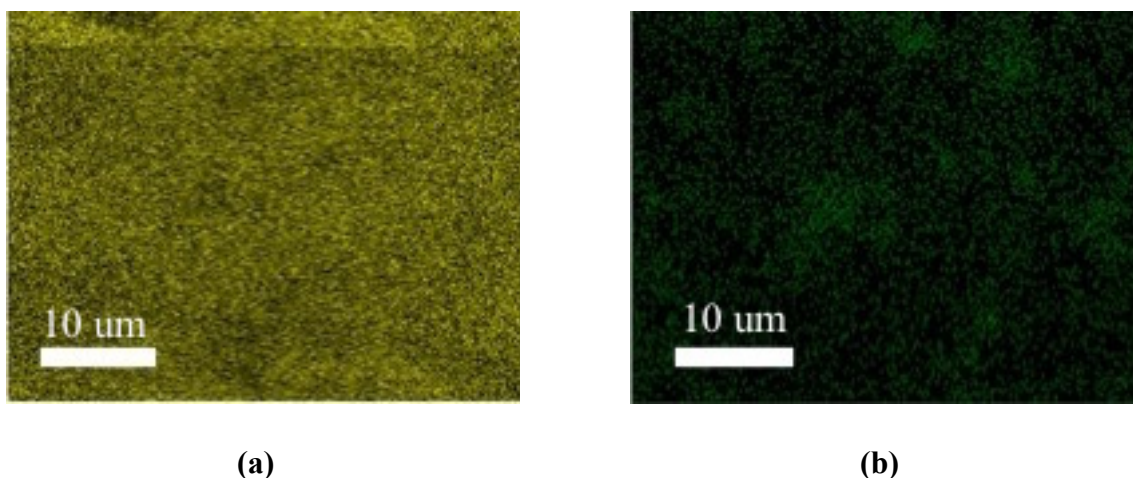


Figure 4.11 EDX element maps of doped sample ($x = 6.25\%$) for (a) S and (b) Cl. Maps correspond to SEM image (Figure 4e). Scale bar is $10 \mu\text{m}$.

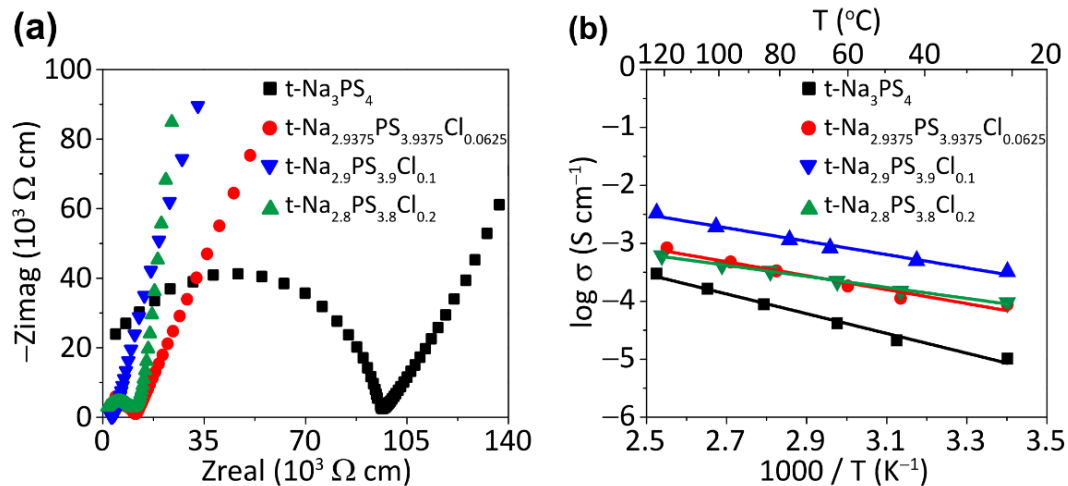


Figure 4.12 Electrochemical Impedance measurements at 21 °C and Nyquist plots of $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$. (a) Nyquist plots of $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ ($x = 0, 0.0625, 0.1$, and 0.2). (b) Arrhenius plot of $t\text{-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ ($x = 0, 0.0625, 0.1$, and 0.2).

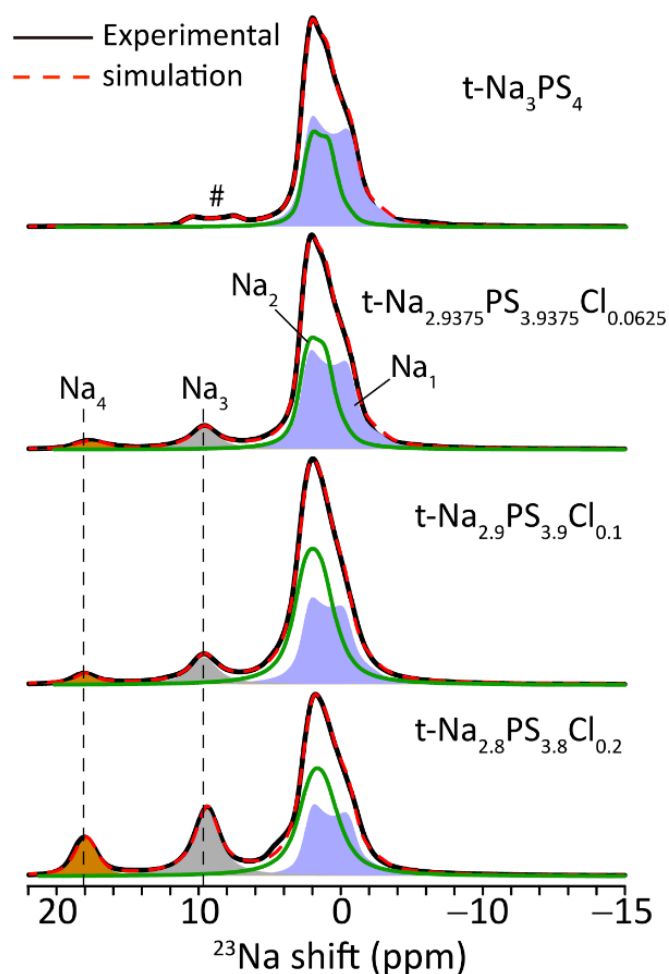


Figure 4.13 Evolution of structural defects in $\text{t-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ ($x = 0, 0.0625, 0.1$, and 0.2) electrolytes probed by ^{23}Na solid-state magic-angle-spinning (MAS) NMR. ^{23}Na MAS NMR spectra together with simulation results of $\text{t-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ ($x = 0, 0.0625, 0.1$, and 0.2).

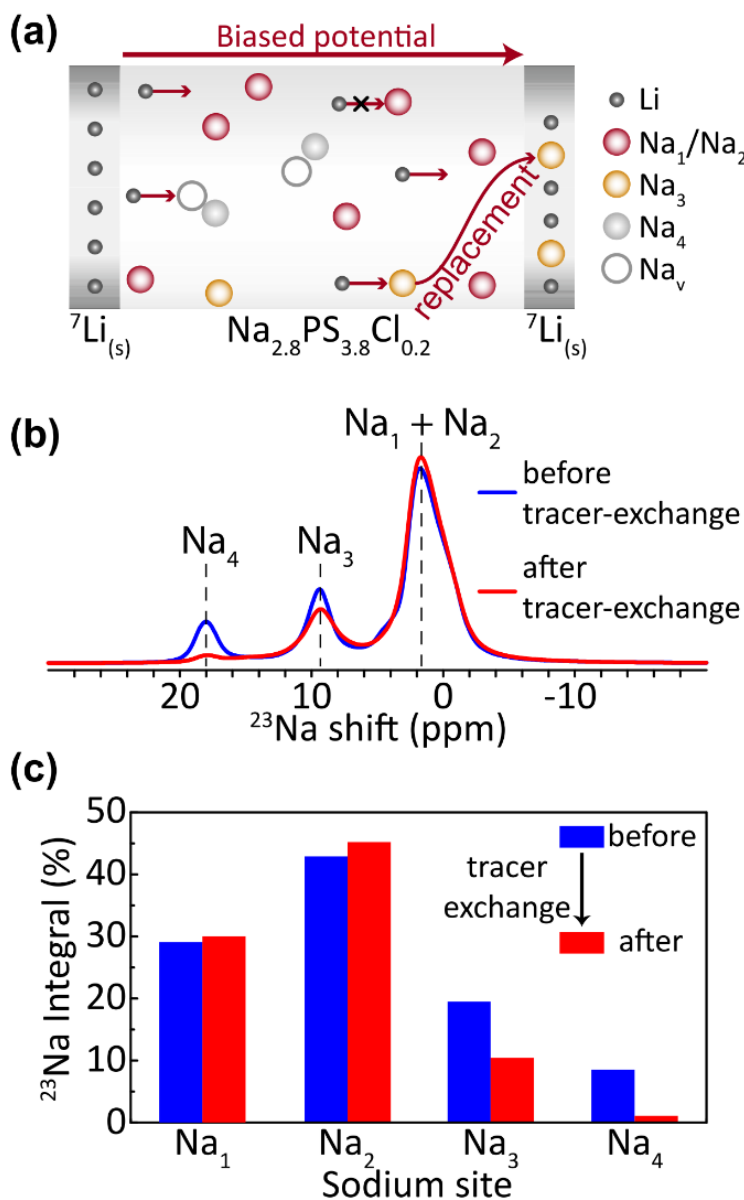


Figure 4.14 Identification of functional defects with tracer-exchange NMR and ${}^{23}\text{Na}$ solid-state magic-angle-spinning (MAS) NMR. (a) Schematic of electrochemically driven ${}^7\text{Li} \rightarrow {}^{23}\text{Na}$ tracer-exchange method. ${}^{23}\text{Na}$ MAS NMR spectra (b) and quantification (c) of $\text{t-Na}_{2.8}\text{PS}_{3.8}\text{Cl}_{0.2}$ before/after ${}^7\text{Li} \rightarrow {}^{23}\text{Na}$ tracer-exchange.

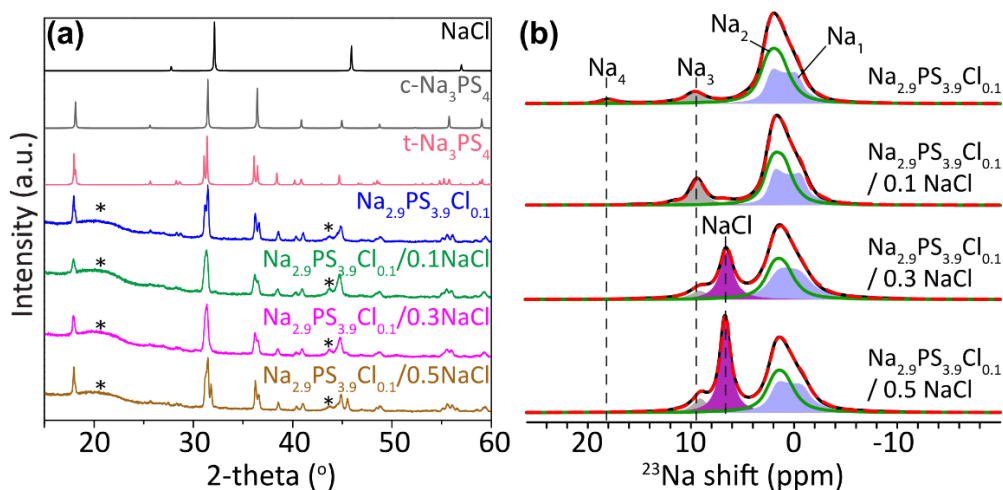


Figure 4.15 Structure characterizations of synthesized $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}/z\text{NaCl}$ ($z = 0, 0.1, 0.3$, and 0.5). (a) Powder X-ray diffraction patterns and (b) ^{23}Na MAS NMR spectra of $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}/z\text{NaCl}$ ($z = 0, 0.1, 0.3$, and 0.5). Asterisk (*) indicates the background signals from sample holder and polyimide film.

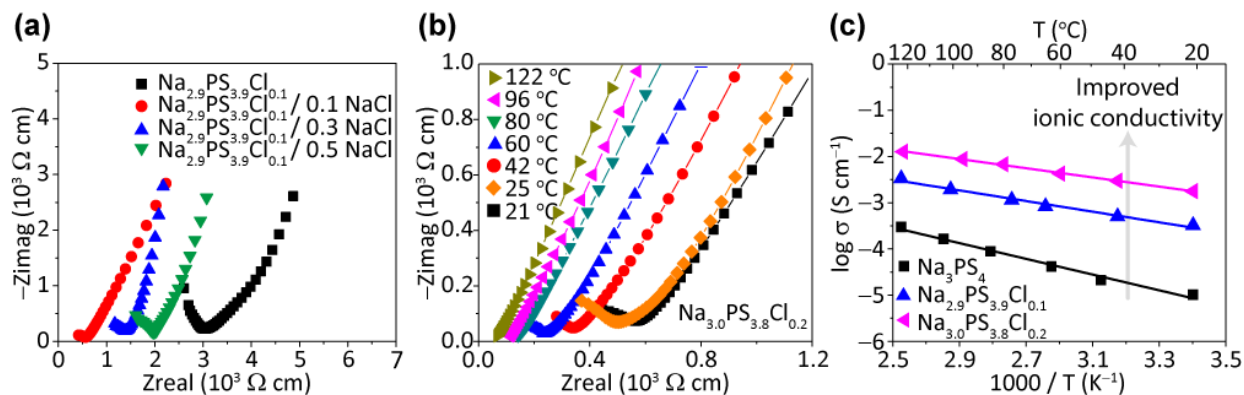


Figure 4.16 Enhanced ionic conductivities of $t\text{-Na}_{3-x}\text{PS}_{4+x}\text{Cl}_x$. (a) Nyquist plots of $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}/z\text{NaCl}$ ($y = 0, 0.1, 0.3$, and 0.5). (b) Variable-temperature impedance spectra of $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}/0.1\text{NaCl}$. (c) Arrhenius plots of $t\text{-Na}_3\text{PS}_4$, $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}$, and $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1}/0.1\text{NaCl}$.

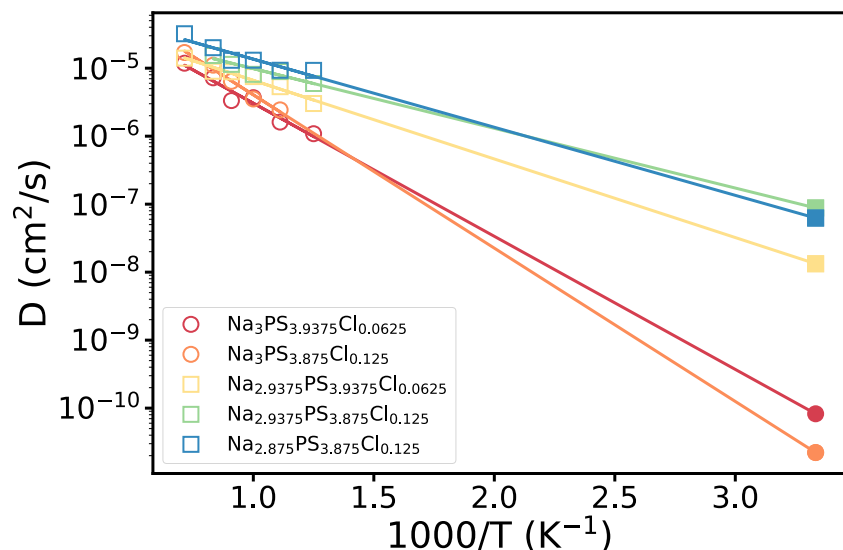


Figure 4.17 Ionic conductivity of t- $\text{Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ from AIMD simulations. Arrhenius plots for $\text{Na}_3\text{PS}_{3.9375}\text{Cl}_{0.0625}$ (red), $\text{Na}_3\text{PS}_{3.875}\text{Cl}_{0.125}$ (orange); $\text{Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$ (yellow); $\text{Na}_{2.9375}\text{PS}_{3.875}\text{Cl}_{0.125}$ (green), and $\text{Na}_{2.875}\text{PS}_{3.875}\text{Cl}_{0.125}$ (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- $\text{Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ ($x = 0.0625$ 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.

Composition	$\sigma_{300\text{K}}$ (mS/cm)	E_a (eV)	Error range of $\sigma_{300\text{K}}$ (mS/cm)	Channel volume ($\text{\AA}^3$)
$\text{Na}_3\text{PS}_{3.9375}\text{Cl}_{0.0625}$	0.009	0.388	[0.005, 0.014]	937
$\text{Na}_3\text{PS}_{3.875}\text{Cl}_{0.125}$	0.002	0.447	[0.002, 0.004]	947
$\text{Na}_{2.9375}\text{PS}_{3.9375}\text{Cl}_{0.0625}$	1.38	0.232	[1.04, 1.82]	924
$\text{Na}_{2.9375}\text{PS}_{3.875}\text{Cl}_{0.125}$	9.03	0.174	[5.74, 14.2]	948
$\text{Na}_{2.875}\text{PS}_{3.875}\text{Cl}_{0.125}$	6.38	0.199	[5.89, 6.91]	932

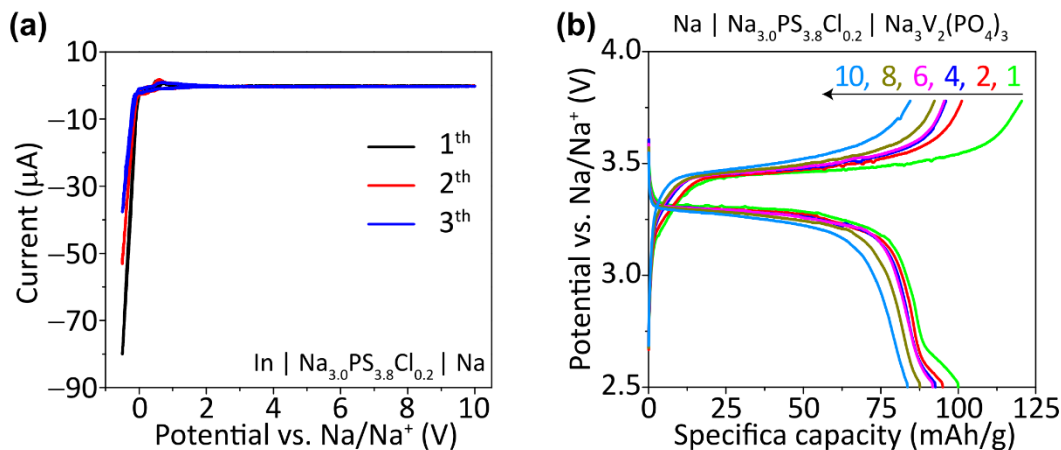


Figure 4.18 Cyclic Voltammetry and electrochemical performance of a full cell solid-state battery made of Na | t-Na_{3.0}PS_{3.8}Cl_{0.2} | Na₃V₂(PO₄)₃. (a) CV of a Na | t-Na_{3.0}PS_{3.8}Cl_{0.2} | In cell, (b) The charge and discharge profiles of Na | t-Na_{3.0}PS_{3.8}Cl_{0.2} | Na₃V₂(PO₄)₃ performed at room temperature with a current density of 10 mA/g calculated based on the mass of Na₃V₂(PO₄)₃.

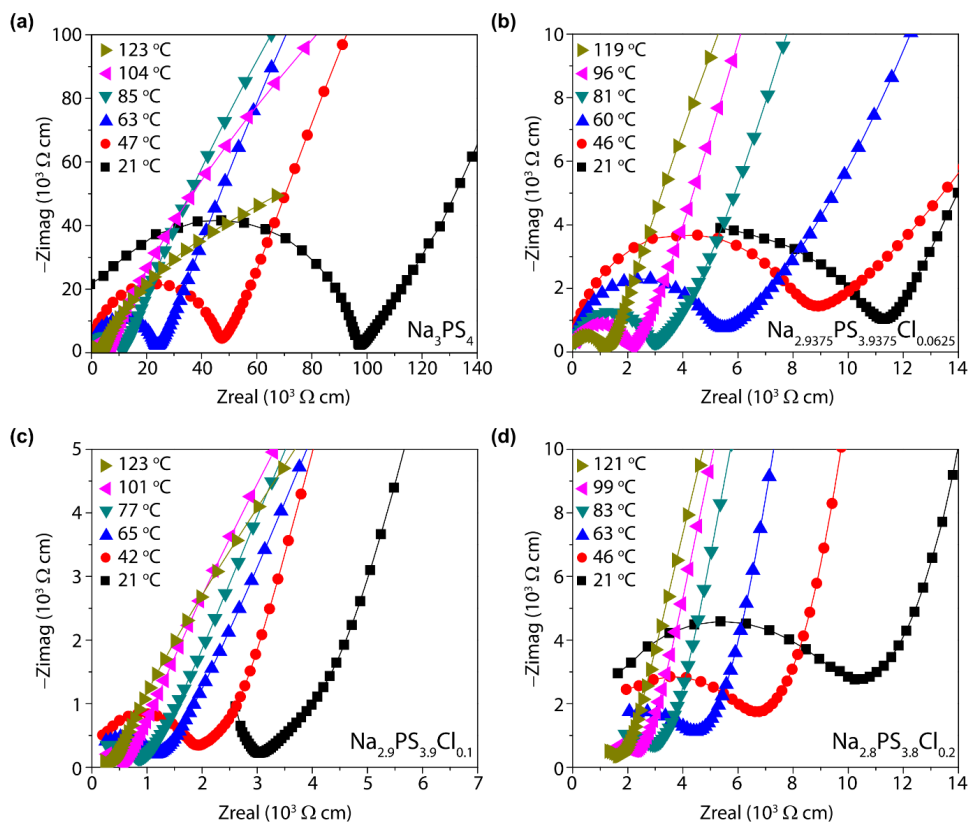


Figure 4.19 Variable-temperature Nyquist plots of (a) t-Na₃PS₄, (b) t-Na_{2.9375}PS_{3.9375}Cl_{0.0625}, (c) t-Na_{2.9}PS_{3.9}Cl_{0.1}, and (d) t-Na_{2.8}PS_{3.8}Cl_{0.2}.

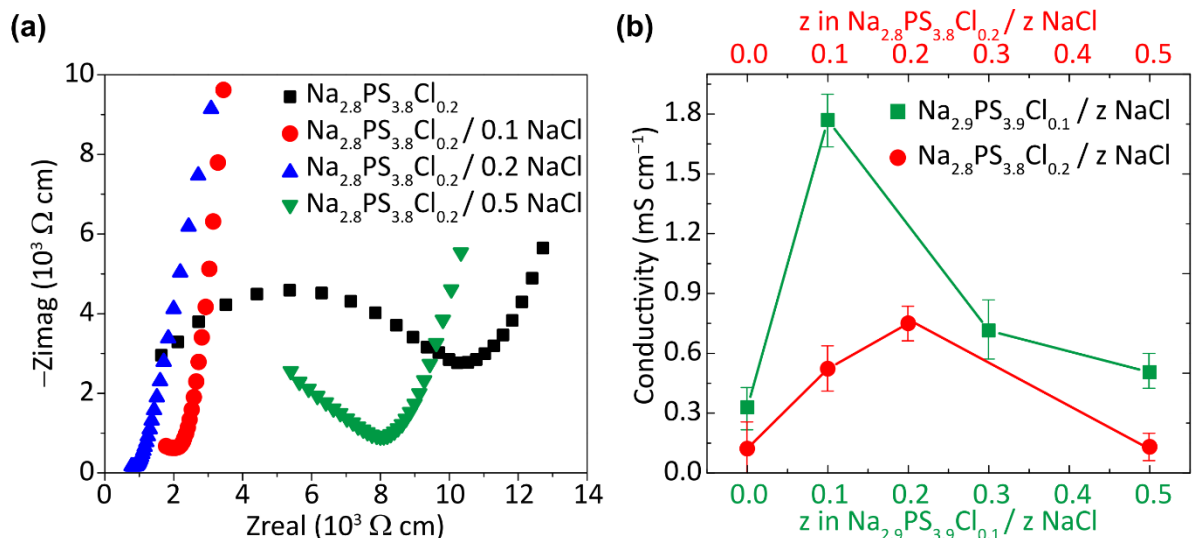


Figure 4.20 (a) Nyquist plots of $t\text{-Na}_{2.8}\text{PS}_{3.8}\text{Cl}_{0.2} / z \text{NaCl}$ ($z = 0, 0.1, 0.2$, and 0.5). (b) Summary of ionic conductivity in $t\text{-Na}_{2.9}\text{PS}_{3.9}\text{Cl}_{0.1} / z \text{NaCl}$ ($z = 0, 0.1, 0.3$, and 0.5) and $t\text{-Na}_{2.8}\text{PS}_{3.8}\text{Cl}_{0.2} / z \text{NaCl}$ ($z = 0, 0.1, 0.2$, and 0.5) at 21°C .

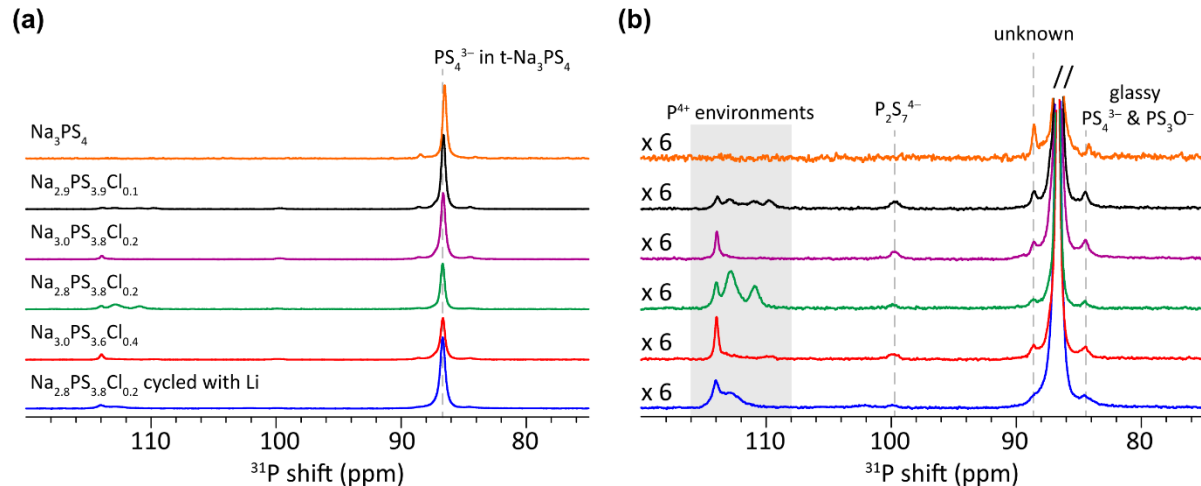


Figure 4.21 Changes in phosphorous local environment of $t\text{-Na}_{3-y}\text{PS}_{4-x}\text{Cl}_x$ detected by ^{31}P MAS NMR. (a) ^{31}P NMR spectra of five selected samples. (b) 6-fold magnification of (a) to show the changes in the spectral range of 90–120 ppm.

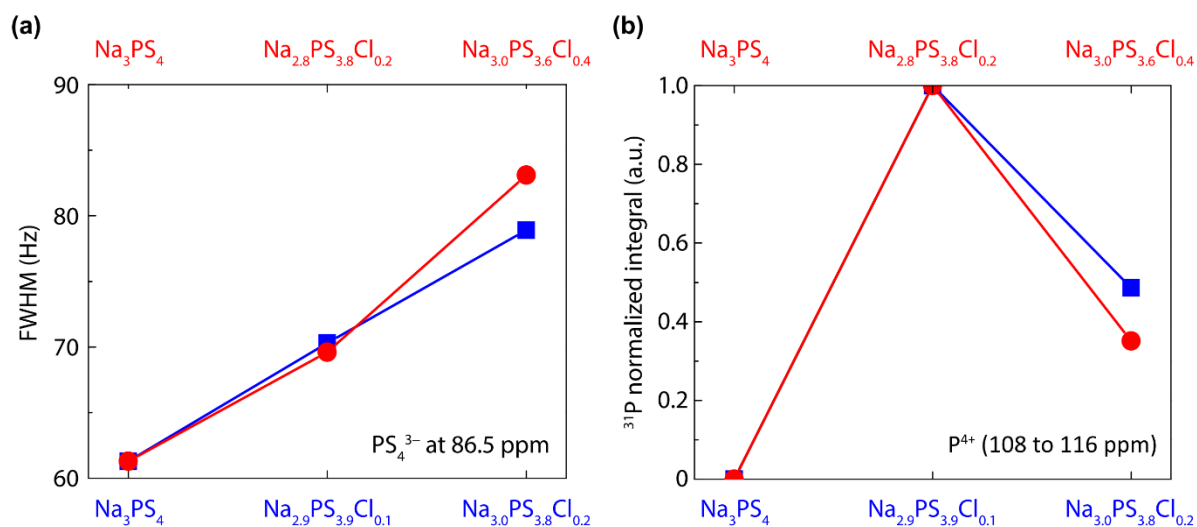


Figure 4.22 Summary of ³¹P MAS NMR spectra. (a) FWHM of PS₄³⁻ unit at 86.5 ppm in t-Na₃PS₄ structural framework. (b) Normalized ³¹P integral of P⁴⁺ signals (108 to 116 ppm) induced by Cl⁻ doping.

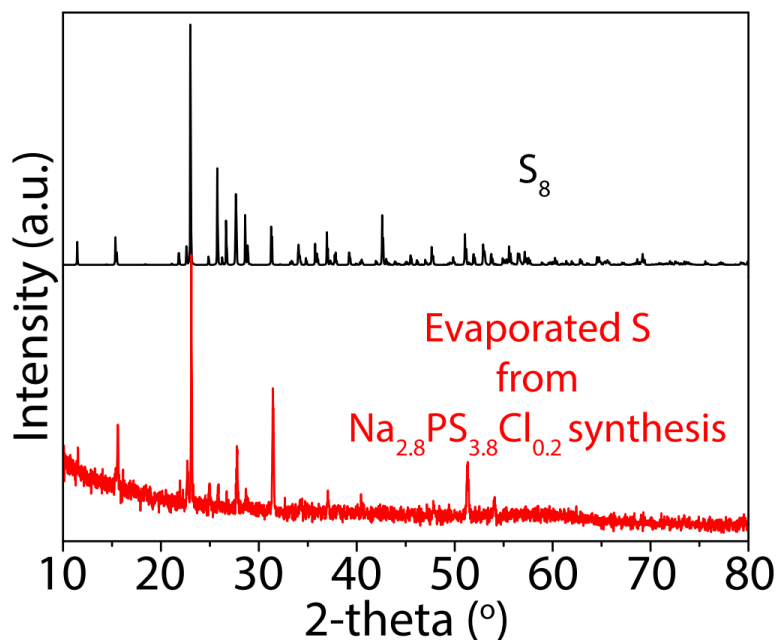


Figure 4.23 XRD patterns of the evaporated S from the synthesis of t-Na_{2.8}PS_{3.8}Cl_{0.2} and standard S₈.

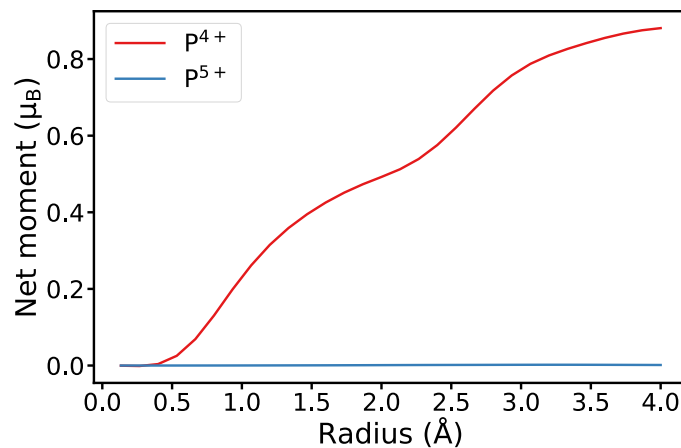


Figure 4.24 Calculated integrated spin charge density as a function of radius cutoff around P in $\text{t-Na}_3\text{PS}_{3.9375}\text{Cl}_{0.0625}$.

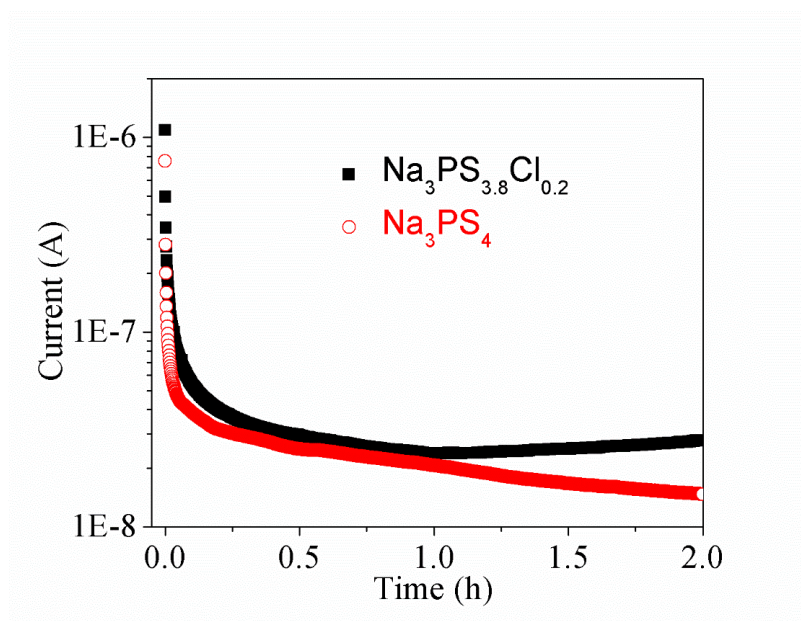


Figure 4.25 DC polarization curve of Na_3PS_4 and $\text{Na}_3\text{PS}_{3.8}\text{Cl}_{0.2}$ under 1 V (diameter of In current collector is 5 mm, thickness is 1mm)

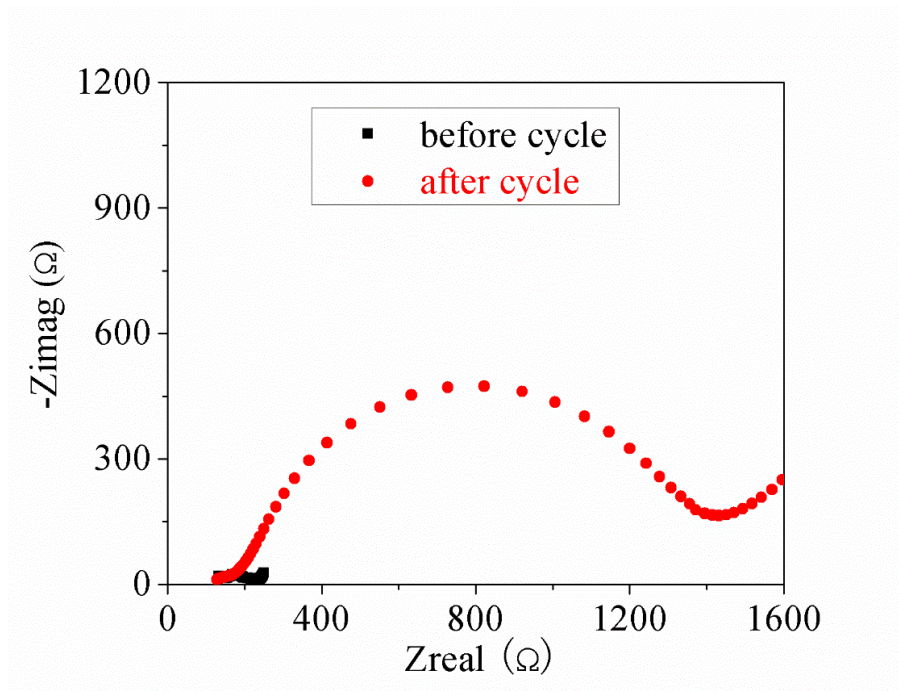


Figure 4.26 AC impedance of $\text{Na}[\text{Na}_{3.0}\text{PS}_{3.8}\text{Cl}_{0.2}]\text{Na}_3\text{V}_2(\text{PO}_4)_3$ full cell before and after cycling.

Chapter 5. Cation Mixing in Stable, High Conductivity

Sodium Solid Electrolytes

In this chapter, we present our work on $\text{Na}_3\text{Pn}'\text{S}_4\text{--Na}_3\text{Pn}''\text{S}_4$ isovalent and $\text{Na}_4\text{TtS}_4\text{--Na}_3\text{PnS}_4$ 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_3PS_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., P⁵⁺ for Sn⁴⁺)^{37,73} and anion (e.g., S²⁻ 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 Na₃PnS₄-Na₄TtS₄ system with composition Na₁₁Tt₂PnS₁₂ (Pn = P/Sb, Tt = Sn) and a tetragonal *I4*₁/*acd* space group.^{36,161} Na₁₁Sn₂PS₁₂ 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 Na₁₁Sn₂SbS₁₂ 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 Na₃PnS₄-Na₄TtS₄ (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 Na₃PnS₄, 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_xS₄ phases, including the recently-reported Na₁₁Tt₂PnS₁₂ 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 Na₁₁Sn₂AsS₁₂ 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 Na_3PnS_4 (t- Na_3PnS_4 and c- Na_3PnS_4 , respectively), Na_4TtS_4 and $\text{Na}_{11}\text{Tt}_2\text{PnS}_{12}$ 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 $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ ($\text{Pn}', \text{Pn}'' = \text{P, As or Sb}$) structures with x in intervals of 1/16 were generated by enumerating all symmetrically distinct configurations¹³⁷ using $2 \times 2 \times 2$ supercell of t- and c- Na_3PS_4 .
2. Aliovalent mixed $\text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4$ structures were with x in intervals of 1/4 generated by enumerating all symmetrically distinct Na vacancy and Tt/Pn orderings in $2 \times 1 \times 1$ supercells of Na_3PS_4 ($P\bar{4}2_1c$), Na_4SnS_4 ($P\bar{4}2_1c$). 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 $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ ($I4_1/acd$).

5.2.2 DFT Calculations

All DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) within the projector augmented-wave approach.¹⁰⁷ The Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA) exchange-correlation functional¹⁰⁸ was used for all calculations.

For structural relaxations and energy calculations of the Na_3PnS_4 - Na_4TtS_4 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)).¹⁰⁹ 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 $1 \times 1 \times 1$ 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_{hull}), an estimate of the phase stability, can be obtained for each phase of interest. In addition, the 0K pseudo-binary $\text{Na}_3\text{Pn}'\text{S}_4$ – $\text{Na}_3\text{Pn}''\text{S}_4$ stability diagram were constructed for each Pn'–Pn'' combination, from which the mixing enthalpies of $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ 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:

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

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 Na₃Pn'_xPn''_{1-x}S₄

Cubic VS Tetragonal. Table 5.1 lists the composition space that we investigated in this work including Na₃Pn'_xPn''_{1-x}S₄ from two sources (t- and c-Na₃PS₄). As reported previously,^{73,178} cubic and tetragonal Na₃PS₄ have great structural similarities and relatively small energy difference

(~ 5 meV/atom). Na_3SbS_4 and Na_3AsS_4 were isostructures substituted from t- and c- Na_3PS_4 . We listed the lattice parameter and energy above hull (E_{hull}) in Table 5.2. The lattice parameters increase along with Pn^{5+} ionic radius following the order of $\text{Na}_3\text{PS}_4 < \text{Na}_3\text{AsS}_4 < \text{Na}_3\text{SbS}_4$. The zero value of E_{hull} for t- Na_3PnS_4 (Pn=P, As, Sb) implies it is the most stable phase compared with c- Na_3PnS_4 .

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 $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$. 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 Na_3PnS_4 is Na_3PS_4 (5.4 meV/atom) $>$ Na_3SbS_4 (4.3 meV/atom) $>$ Na_3AsS_4 (3.5 meV/atom). $\text{Na}_3\text{P}_x\text{Sb}_{1-x}\text{S}_4$ show energy-favorable intermediate phase at $x \sim 0.25$, 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- $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ 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 $\text{Na}_3\text{As}_x\text{P}_{1-x}\text{S}_4$ system, which is in good agreement with previous study (a negligibly positive mixing enthalpy of < 1 meV/atom) by Shang et al.¹⁷⁵ For $\text{Na}_3\text{Sb}_x\text{As}_{1-x}\text{S}_4$ 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 $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ systems show a good solubility through the entire composition space. We checked the arrangements of 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), PS_4 and SbS_4 tetrahedrons alternate in the same column or row within ab plane, forming the roughly centrosymmetric pattern in ab plane. When Pn' and Pn'' have the same ratio, the queue of PnS_4 tetrahedrons along c direction keeps homogeneous and the non-interval chain of Na1 (Wyckoff site: $4d$, following the symbols in pristine $t\text{-Na}_3\text{PS}_4$) sites along c direction are interconnected via Na2 (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 Na–Sn–P–S. In addition to the isovalent $\text{Pn}'\text{--Pn}''$ mixing, we probe another chemical space of Na–Sn–P–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: $I4_1/acd$).³⁶ The two ternary parent structures, $t\text{-Na}_3\text{PS}_4$ and Na_4SnS_4 , display high similarity in polyhedron arrangements and belong to the same space group of $P\bar{4}2_1c$ with the only disparity of Na sites as shown in Figure 5.1. When mixing Sn and P from either side, we introduced proper Na defects for the sake of total charge neutrality. Substitutions of Sn for P in Na_3PS_4 requires the equivalent Na excess. To the contrary, Na vacancies form in Na_4SnS_4 when replacing P for Sn in Na_4SnS_4 .

$\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$, a novel superionic conductor first reported by Nazar's group, has a different single crystal structure (see Figure 5.4a) in contrast to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and Na_3PS_4 . This new prototype with 5 geometrically distinct Na sites (corrected to 6 by the same group in a follow-up paper)¹⁷⁷ 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.³⁶ Shortly after, a higher conductivity (3.7 mS/cm) was reported by Duchardt and coworkers, but with a higher activation energy (0.39 eV).¹⁶⁹ Moreover, quaternary analogs not limited to Na–Sn–P–S space group were found recently: Sb-version $\text{Na}_{11}\text{Sn}_2\text{SbS}_{12}$ ¹⁷⁶ and selenium-based non-stoichiometric $\text{Na}_{11.1}\text{Sn}_{2.1}\text{P}_{0.9}\text{Se}_{12}$.^{179,180} 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 $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ compared with $2\times 2\times 2$ supercell of Na_3PS_4 . We can observe the exceeding disorder in Na sites of $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ 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 $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ and Na_3PS_4 is given in the Discussion section. We show the phase stability (E_{hull}) of $\text{Na}_{4-x}\text{Sn}_{1-x}\text{P}_x\text{S}_4$ from three prototype sources (Na_3PS_4 , Na_4SnS_4 , $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$) in Figure 5.4d covering the maxing ratio of $x = 1/4, 1/2, 3/4$ and additional $x = 1/3$ for $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$. 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 $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ prototype is more thermodynamically stable than the other two at various x values. Moreover, Sn-rich $\text{Na}_{4-x}\text{Sn}_{1-x}\text{P}_x\text{S}_4$ ($x < 0.5$) have lower E_{hull} than P-rich composition ($x > 0.5$) as shown in Table 5.3. The same tendency holds for

$\text{Na}_{11}\text{Sn}_2\text{SbS}_{12}$ as well (see Figure 5.10). In the following, we will only focus on the new $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ prototype.

Optimized Stoichiometry and Elements for $\text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4$. Figure 5.5 shows the complete E_{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_{hull} of < 8 meV/atom. Particularly, we observe that the mixing ratio of $x = 1/3$ (normalized formula: $\text{Na}_{3.67}\text{Tt}_{0.67}\text{Pn}_{0.33}\text{S}_4$) leads to the lowest E_{hull} among all mixing ratios. The overall feasibility of $\text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4$ is high, especially at $x = 0.33$. Under this ratio, P and As-containing compounds have the E_{hull} of 0 meV/atom regardless of Tt species. Sb-containing compounds have slightly higher E_{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_{hull} values have the general trend of increasing with x . When $x = 3/4$, the maximum of E_{hull} is in the range of $5 \sim 8$ 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.¹⁸¹ 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) $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ by isovalent mixing (top panel) and (2) $\text{Na}_{11}\text{Tt}_2\text{PnS}_{12}$ by aliovalent mixing (bottom panel). The reactivity of $\text{Na}_3\text{P}_x\text{Sb}_{1-x}\text{S}_4$ with H_2O is the highest among all $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ systems. The collective reaction products are NaSbS_2 , $\text{Na}_3\text{PS}_3\text{O}$, and NaHS for the entire P-Sb

mixing region. NaS_2 and Na_3SbS_3 are exclusively formed in S-rich region ($x = 0.0625\text{--}0.375$); Na_2S_5 , $\text{t-Na}_3\text{PS}_4$ appear at moderate P-Sb mixing ratio ($x = 0.4375$); Na_2S_5 and H_2S (gaseous phase at room temperature) form in P-rich concentration ($x = 0.5625\text{--}0.9375$). Considering the fact that Na_3PS_4 reacts with H_2O but Na_3SbS_4 does not, we think the high reactivity of P-Sb mixed intermediate compounds, which is even poorer than pure Na_3PS_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 H_2S and water-resist Na_3AsS_4 . Impressively, all $\text{Na}_3\text{Sb}_x\text{As}_{1-x}\text{S}_4$ compounds are stable with H_2O . If we plan to modify the moisture stability based on well-known Na electrolyte Na_3PS_4 , though both Na_3AsS_4 and Na_3SbS_4 do not react with H_2O , introducing As and Sb into Na_3PS_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 $\text{Na}_{11}\text{Si}_2\text{PnS}_{12}$ ($\text{Pn} = \text{P}, \text{As}, \text{Sb}$), which may result from the formation of very stable SiO_2 in reaction with H_2O . $\text{Na}_{11}\text{Ge}_2\text{PnS}_{12}$ 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 Na_3AsS_4 (1.94–2.12V) reported in the previous work⁵⁶ was attributed by the missing entry of Na_3AsS_4 in the database. After properly including all entries, we obtained a much wider EC window of 1.57–2.47 V for Na_3AsS_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 Na_4GeS_4 (1.05–2.06V) and Na_3SbS_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 Bang Gap

Due to the poor moisture stability of Si phase and high expenses of Ge, we selected promising candidates of Sn-containing compounds $\text{Na}_{11}\text{Sn}_2\text{PnS}_{12}$ (Pn=P, As, 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 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 $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ and 0.34 eV for $\text{Na}_{11}\text{Sn}_2\text{SbS}_{12}$).

Figure 5.13 shows calculated densities of states (DOS) for $\text{Na}_{11}\text{Sn}_2\text{PnS}_{12}$ 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 $\text{Na}_{11}\text{Sn}_2\text{PnS}_{12}$ (Pn = P, As, Sb) compositions have very close band gaps. Similar features are found in pure Na_3PnS_4 (Figure 5.14) and Na_4TtS_4 (Figure 5.15), although the E_g varies from 2.18 (Na_3AsS_4) to 2.92 eV (Na_3PS_4) for Na_3PnS_4 and 2.73 eV (Na_4SnS_4) to 3.4 eV (Na_4SiS_4) for Na_4TtS_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 $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$

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 ($E_{\text{cubic}} - E_{\text{tetra}}$) for pure Na_3PnS_4 is accordantly positive, i.e., t- Na_3PnS_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_3PS_4 (0.60 eV/defect) and t- Na_3PS_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_3PS_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_3PnS_4 , in which Na vacancies are more easily formed than t- Na_3PnS_4 . And it is not a distinct phenomenon only appearing in cation mixed $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$, but also applicable in anion mixed $\text{Na}_3\text{PS}_x\text{Se}_{4-x}$.¹⁵² Thus, the formation energy of Na vacancy plays a significant role on diffusivity and conductivity within such vacancy-driven Na_3PnS_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.^{135,178}

The thermodynamic driving force of cation mixing is reflected through mixing enthalpy of $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ (Figure 5.2), from which we can demonstrate great miscibility in this system especially $\text{Na}_3\text{As}_x\text{P}_{1-x}\text{S}_4$ compounds. Borrowing the concept of Hume-Rothery rules¹⁸³ from metallurgy field, $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ 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 scale¹⁸⁴), same crystal structure and valency. The close resemblance between Na_3PS_4 , Na_3AsS_4 and Na_3SbS_4 implies solid solution phases between any two end members may exist, providing an effective method to tailor the chemical/physical properties of $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ 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.¹⁸⁵

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 Na_3MOS_3 to $\text{Na}_3\text{MO}_3\text{S}$ (M is the hard acid element) to replace sulfur (the soft base). Correspondingly, Na_3PS_4 (P is hard acid) in air and moisture is less stable/more active than Na_3AsS_4 and Na_3SbS_4 . By introducing the softer species (As and Sb) and taking advantage of the composition engineering, the mixing systems of $\text{Na}_3\text{As}_x\text{P}_{1-x}\text{S}_4$ and $\text{Na}_3\text{Sb}_x\text{As}_{1-x}\text{S}_4$ show a better moisture stability than pure Na_3PS_4 . The high reaction activity in $\text{Na}_3\text{P}_x\text{Sb}_{1-x}\text{S}_4$ particularly when x is close to 0.5, can be attributed to the positive mixing enthalpy of $\text{Na}_3\text{P}_x\text{Sb}_{1-x}\text{S}_4$. Previous experimental/DFT studies by Yu, Shang and co-workers verified our predicted trend in $\text{Na}_3\text{As}_x\text{P}_{1-x}\text{S}_4$ case and reported the optimized compound of $\text{Na}_3\text{As}_{0.38}\text{P}_{0.62}\text{S}_4$ with high conductivity of 1.46 mS/cm.¹⁶⁵ The trend of EC window width for pure Na_3PnS_4 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, Na_4GeS_4 with possible redox-active Ge from 4+ to 2+ oxidation states exhibit the narrower EC window than Na_4SiS_4 and Na_4SnS_4 . 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 ($\text{Na}_3\text{SbS}_4 \cdot 8\text{H}_2\text{O}$) as a passivating layer.

The studies on Na_3PnS_4 family rose from the high conductivity achieved in c- Na_3PS_4 back in 2012.³² Analogs like Na_3SbS_4 ¹⁸⁷ and Na_3PSe_4 ^{79,188} 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 Pn^{5+} cation mixing effects in $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ in the following aspects: (i) Solid solution phases tend to be formed with complete solubility in the order of $\text{Na}_3\text{As}_x\text{P}_{1-x}\text{S}_4$, $\text{Na}_3\text{Sb}_x\text{As}_{1-x}\text{S}_4$ and $\text{Na}_3\text{P}_x\text{Sb}_{1-x}\text{S}_4$ (from ease to difficulty);

(ii) Arsenic involvements help to improve the moisture stability of Na_3PS_4 whereas Sb-P mixing makes it more negative of reaction energy between H_2O and $\text{Na}_3\text{P}_x\text{Sb}_{1-x}\text{S}_4$ 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 $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ 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 $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ 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 $\text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4$

The discovery of $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ 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 $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ from XRD refinement shows it a distinct geometry from either quasi-1D LGPS conductor or pure Na_3PS_4 . Comparing the unit volume of $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ ($5046.4 \text{ \AA}^3$, quadrupling of LGPS unit cell size)³⁶ and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ ($965.5 \text{ \AA}^3$),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 Na₃PS₄. All of these make it an excellent framework model considered as superior 3D Na⁺ conductor.

On account of the great framework similarity between Na₃PS₄ and Na₄SnS₄ (Figure 5.1), more ratios in Na_{4-x}Tt_{1-x}Pn_xS₄ start the trial substitutions from two parent ternaries and turn out to be less thermodynamic stable than those derived from Na₁₁Sn₂PS₁₂. The phase stability of Na_{4-x}Tt_{1-x}Pn_xS₄ 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 Na₁₁Tt₂PnS₁₂ 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 Na₁₁M₂PS₁₂(M=Ge, Sn)¹⁹⁰ comparison, the authors reported a high E_{hull} of 14.5 meV/atom for Na₁₁Sn₂PS₁₂ by only calculating 20 lowest electrostatic energy configurations among 40,000 enumerated structures. We selected a smaller cell size (formula: Na₄₄Sn₈P₄S₄₈) 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 ($E_{\text{hull}} = 0$ meV/atom). Consequently, a narrower EC window was claimed from the same paper (1.16–1.91 V in the reference¹⁹⁰ 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, NaS₂, Na₂S₅) in phase diagram and grand potential analysis, to avoid the over-correction caused by sulfur correction exclusively for S²⁻.

We claimed the superiority of Na₁₁Tt₂PnS₁₂ 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 $\text{Na}_{11}\text{Tt}_2\text{PnS}_{12}$. The hard acid Si (IV) results in high reactivity of $\text{Na}_{11}\text{Si}_2\text{PnS}_{12}$ 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 $\text{Na}_{11}\text{Sn}_2\text{PnS}_{12}$ 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., $\text{Li}_4\text{Cu}_8\text{Ge}_3\text{S}_{12}$.¹⁹¹ More options like Cu (I), Zn (II), Bi (III) are also worth trying as the substitution for hard acids (Si(IV) and P(V)).¹⁹²

Our predicted conductivities for $\text{Na}_{11}\text{Sn}_2\text{PnS}_{12}$ are in excellent agreement with two synthesized phases ($\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ and $\text{Na}_{11}\text{Sn}_2\text{SbS}_{12}$), 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 $\text{Na}_{11}\text{Sn}_2\text{SbS}_{12}$ revealing a 3-fold lower conductivity compared with $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ (0.56 mS/cm¹⁷⁷ vs 1.4 mS/cm³⁶). The optimal conductivity appears in $\text{Na}_{11}\text{Sn}_2\text{AsS}_{12}$ given its weaker $\text{Na}^+ - \text{S}^{2-}$ 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 $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ and $\text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4$, respectively, which are derived from Na_3PS_4 , Na_4SnS_4 and $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ prototype parent structures. Among $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ systems, $\text{Na}_3\text{As}_x\text{P}_{1-x}\text{S}_4$ compositions have super low or even negative enthalpy of mixing, indicating highly miscibility and complete solubility as solid solution phases. In the aliovalent mixed $\text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4$, Na concentration and Tt/Pn ratios are adjustable simultaneously and compounds substituted from experimentally-reported $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ 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 $\text{Na}_{11}\text{Sn}_2\text{AsS}_{12}$ 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.

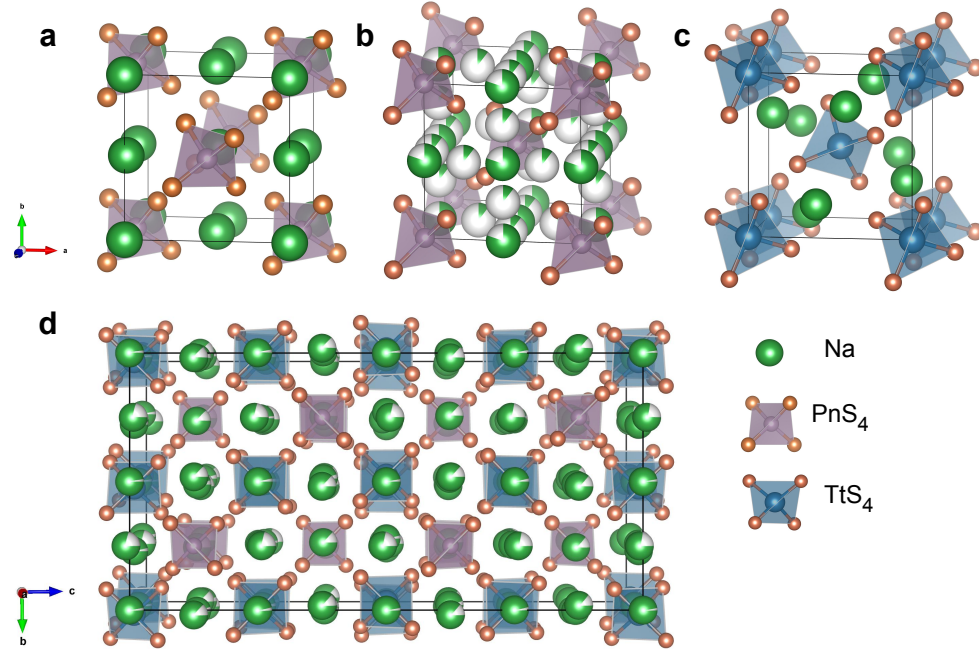


Figure 5.1 Crystal structures of (a) tetragonal Na_3PnS_4 (space group: $P\bar{4}2_1c$), (b) cubic Na_3PnS_4 (space group: $I\bar{4}3m$), (c) Na_4TtS_4 (space group: $P\bar{4}2_1c$) and (d) $\text{Na}_{11}\text{Tt}_2\text{PnS}_{12}$ (space group: $I4_1/acd$). Purple tetrahedrons, PnS_4 ; blue tetrahedrons, TtS_4 ; green spheres, Na.

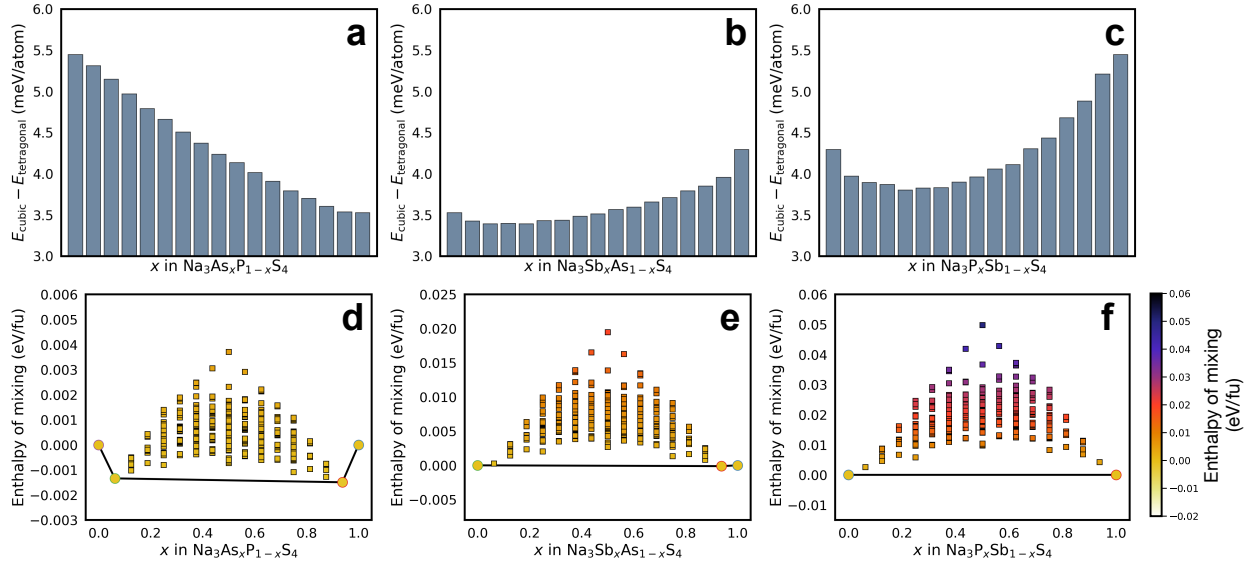


Figure 5.2 Polymorph stability and mixing enthalpy of $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ ($\text{Pn}', \text{Pn}'' = \text{P, As, Sb}$). (a-c) Energy difference between the cubic and tetragonal phase ($E_{\text{cubic}} - E_{\text{tetra}}$) and (d-f) mixing enthalpy of t- $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$. Squares and circles markers are for unstable and stable structures, respectively. The mixed $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ systems are successively (from left to right): $\text{Na}_3\text{As}_x\text{P}_{1-x}\text{S}_4$; $\text{Na}_3\text{Sb}_x\text{As}_{1-x}\text{S}_4$ and $\text{Na}_3\text{Sb}_x\text{P}_{1-x}\text{S}_4$.

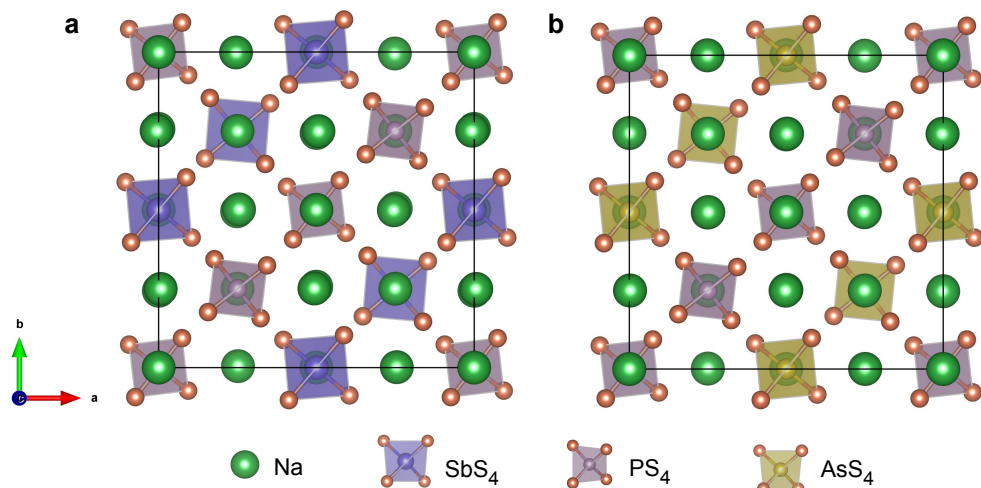


Figure 5.3 Ordering pattern (top view along c direction) of the most stable structure for (a) $\text{Na}_3\text{Sb}_{0.5}\text{P}_{0.5}\text{S}_4$ and (b) $\text{Na}_3\text{As}_{0.5}\text{P}_{0.5}\text{S}_4$.

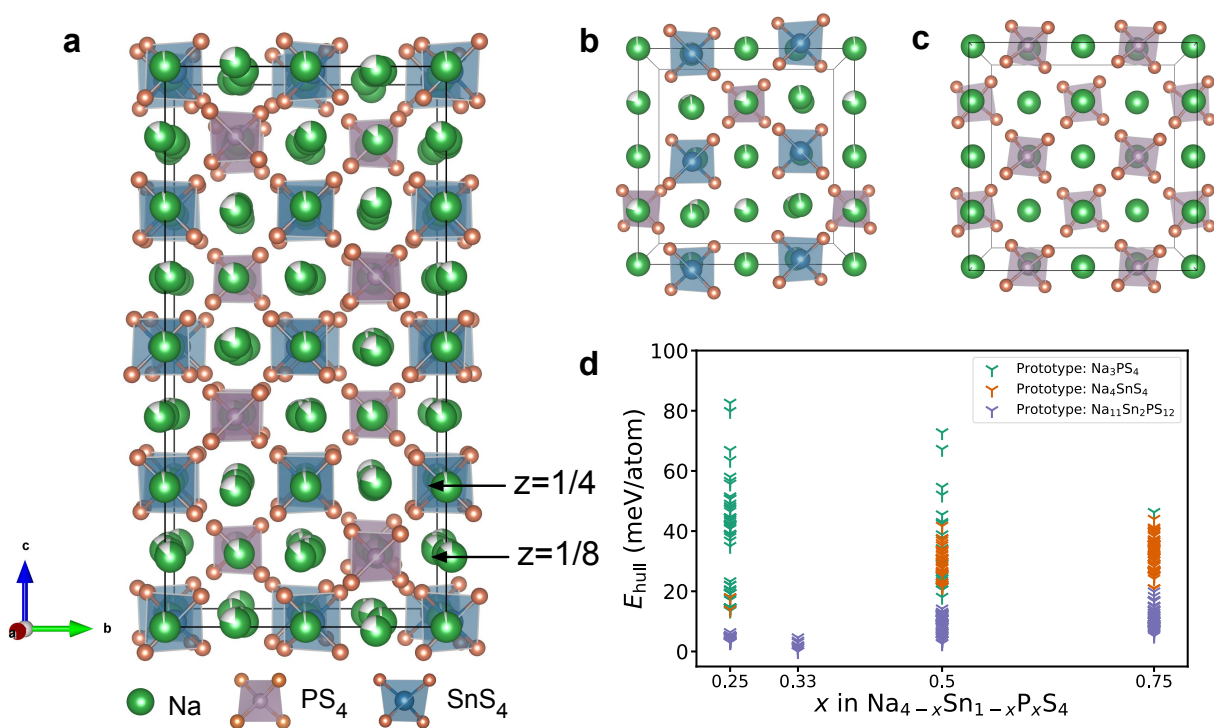


Figure 5.4 $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$, Na_3PS_4 crystal structures and E_{hull} of $\text{Na}_{4-x}\text{Sn}_{1-x}\text{P}_x\text{S}_4$ substituted from different prototypes. (a) $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ viewed from a direction; (b) $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ viewed from c direction showing 3 PS_4 and 6 SnS_4 tetrahedrons in $z=1/8$ and $z=1/4$ layer, respectively. (c) $2 \times 2 \times 2$ supercell of Na_3PS_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: Na_3PS_4 , Na_4SnS_4 and $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$.

Table 5.1 Cation mixed compositions we studied: isovalent Pn'–Pn'' mixing in $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ and aliovalent Tt–Pn mixing in $\text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4$. Cation species are Pn=P, As, Sb; Tt=Si, Ge, Sn.

Compound	Source (Space group)	Mixing type	Mixing ratio (x)
$\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$	t- Na_3PS_4 ($P\bar{4}2_1c$)	Isovalent	$x = i/16$
	c- Na_3PS_4 ($I\bar{4}3m$)		i is an integer
			between 1 and 16
$\text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4$	t- Na_3PS_4 ($P\bar{4}2_1c$)	Aliovalent	$x = 1/4, 1/2, 3/4$
	Na_4SnS_4 ($P\bar{4}2_1c$)		$x = 1/4, 1/3, 1/2, 3/4$
	($I4_1/acd$)		

Table 5.2 Space group, lattice parameter after structural optimization and phase stability (E_{hull}) for t- and c- Na_3PnS_4 (Pn=P, As, Sb).

Pure Na_3PnS_4	Lattice parameter	E_{hull} (meV/atom)
t- Na_3PS_4	$a=7.016\text{\AA}$, $c=7.148\text{\AA}$	0
c- Na_3PS_4	$a=7.048\text{\AA}$	5.4
t- Na_3AsS_4	$a=7.104\text{\AA}$, $c=7.235\text{\AA}$	0
c- Na_3AsS_4	$a=7.129\text{\AA}$	3.5
t- Na_3SbS_4	$a=7.228\text{\AA}$, $c=7.377\text{\AA}$	0
c- Na_3SbS_4	$a=7.253\text{\AA}$	4.3

Table 5.3 E_{hull} values of $\text{Na}_{4-x}\text{Ti}_{1-x}\text{Pn}_x\text{S}_4$ ($x = 1/4, 1/3, 1/2, 3/4$) from the different prototypes (Na_3PS_4 , Na_4SnS_4 and $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ structures).

Prototype	$x = 1/4$	$x = 1/3$	$x = 1/2$	$x = 3/4$
	(meV/atom)	(meV/atom)	(meV/atom)	(meV/atom)
Na_3PS_4	13	N/A	12	29
Na_4SnS_4	14	N/A	22	21
$\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$	3	0	3	5

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

Composition	$\sigma_{300\text{K}}$ (mS/cm)	Error range of	E_a (eV)	E_g (eV)
	$\sigma_{300\text{K}}$ (mS/cm)			
$\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$	2.77	[2.62, 2.93]	0.243	2.53
$\text{Na}_{11}\text{Sn}_2\text{AsS}_{12}$	4.52	[4.23, 4.82]	0.216	2.62
$\text{Na}_{11}\text{Sn}_2\text{SbS}_{12}$	0.45	[0.41, 0.48]	0.289	2.50

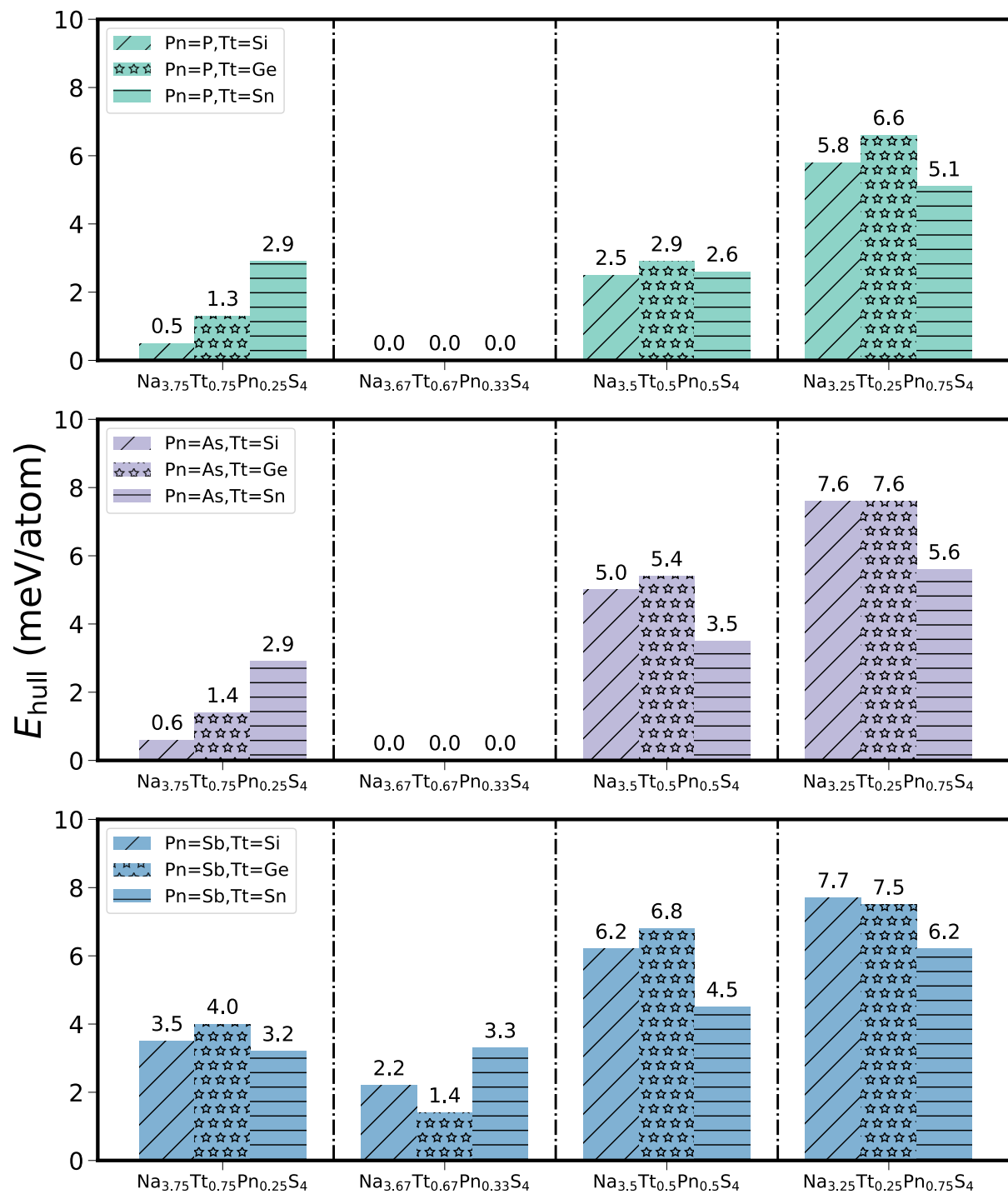


Figure 5.5 Thermodynamic stability of $\text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4$ ($x=1/4, 1/3, 1/2, 3/4$). When $x = 1/3$, $\text{Na}_{3.67}\text{Tt}_{0.67}\text{Pn}_{0.33}\text{S}_4$ is the normalized formula, which is equivalent to $\text{Na}_{11}\text{Tt}_2\text{PnS}_{12}$.

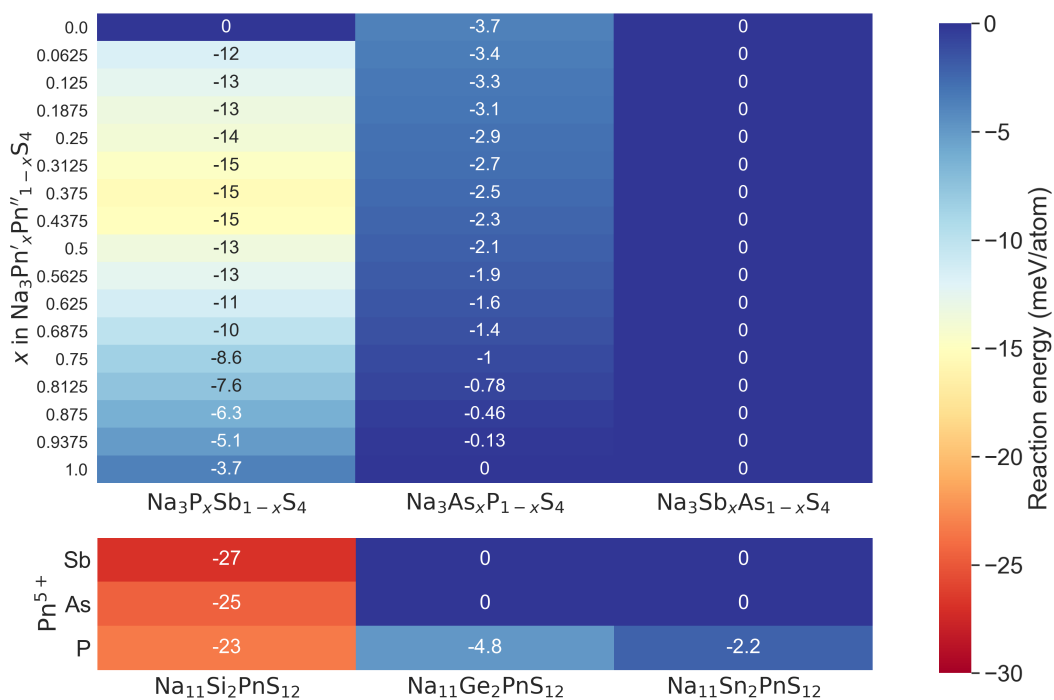


Figure 5.6 Reaction energy with H_2O for $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ (top) and $\text{Na}_{11}\text{Tt}_2\text{PnS}_{12}$ (bottom).

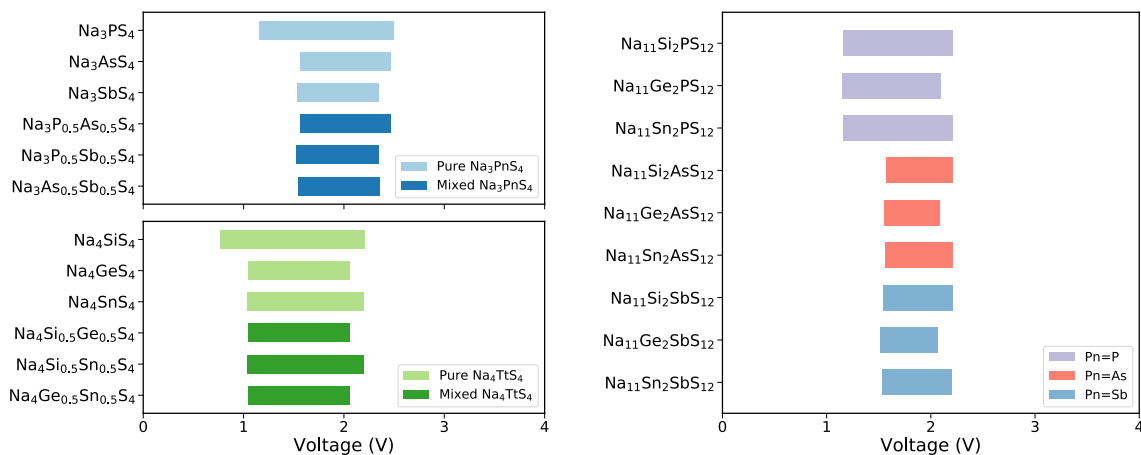


Figure 5.7 Electrochemical stability of pure and mixed Na_3PnS_4 (top left), Na_4TtS_4 (bottom left) and $\text{Na}_{11}\text{Tt}_2\text{PnS}_{12}$ (right) where $\text{Pn} = \text{P, As, Sb}$ and $\text{Tt} = \text{Si, Ge, Sn}$.

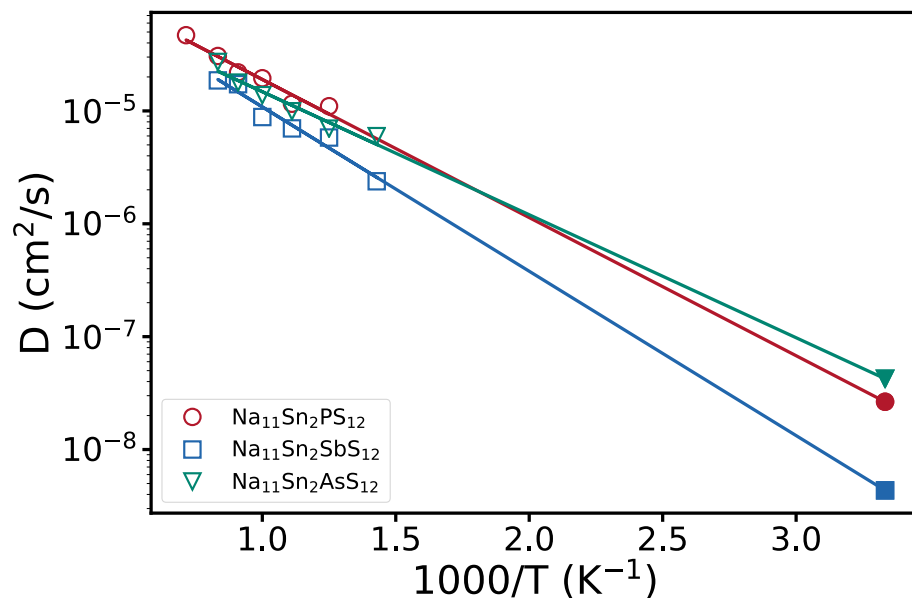


Figure 5.8 Arrhenius plots for $\text{Na}_{11}\text{Sn}_2\text{PnS}_{12}$ ($\text{Pn} = \text{P}, \text{As}, \text{Sb}$) obtained from AIMD simulations. Unfilled markers indicate the operation temperatures at which we run AIMD calculations, while filled markers are the extrapolated room temperature of 300 K.

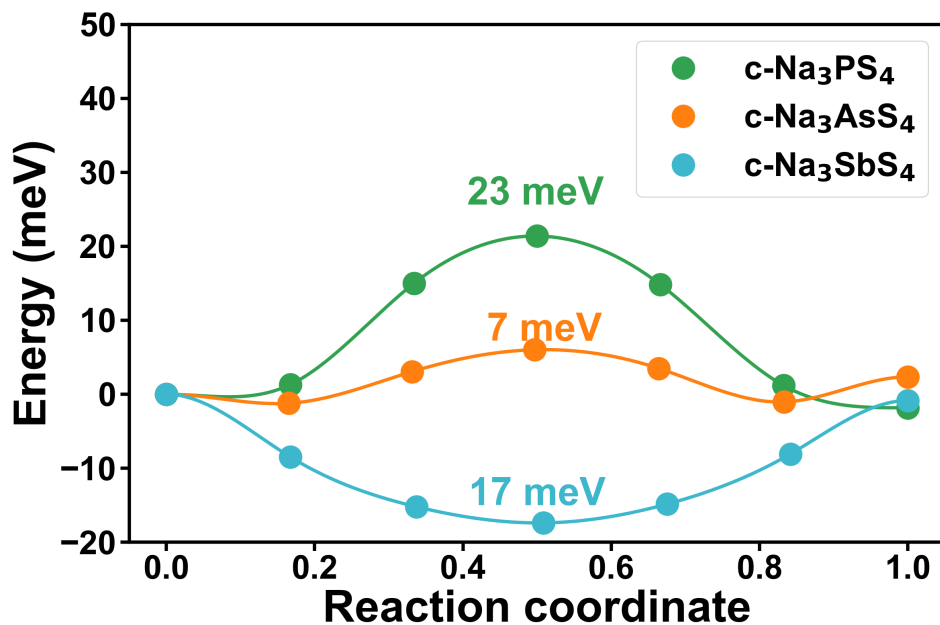


Figure 5.9 NEB migration barriers for the solely distinct path in $\text{c-Na}_3\text{PnS}_4$ ($\text{Pn} = \text{P}, \text{As}, \text{Sb}$).

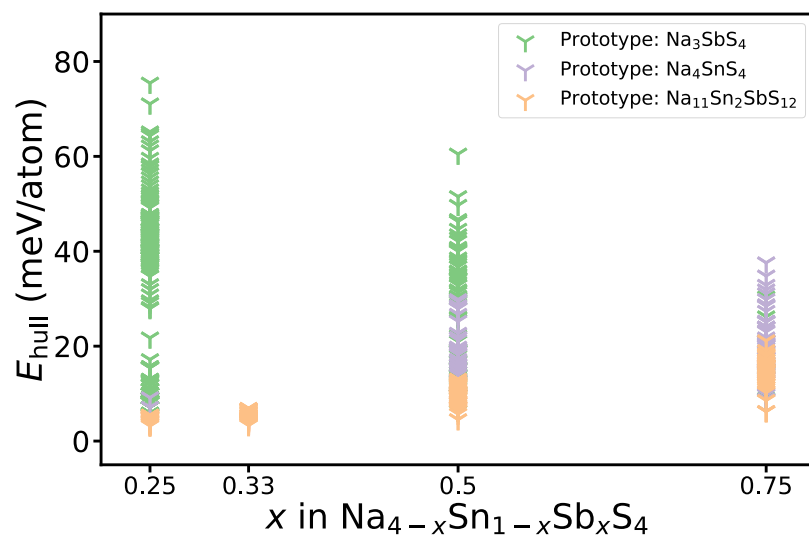


Figure 5.10 Thermodynamic stability (E_{hull}) of $\text{Na}_{4-x}\text{Sn}_{1-x}\text{Sb}_x\text{S}_4$ substituted from different prototypes.

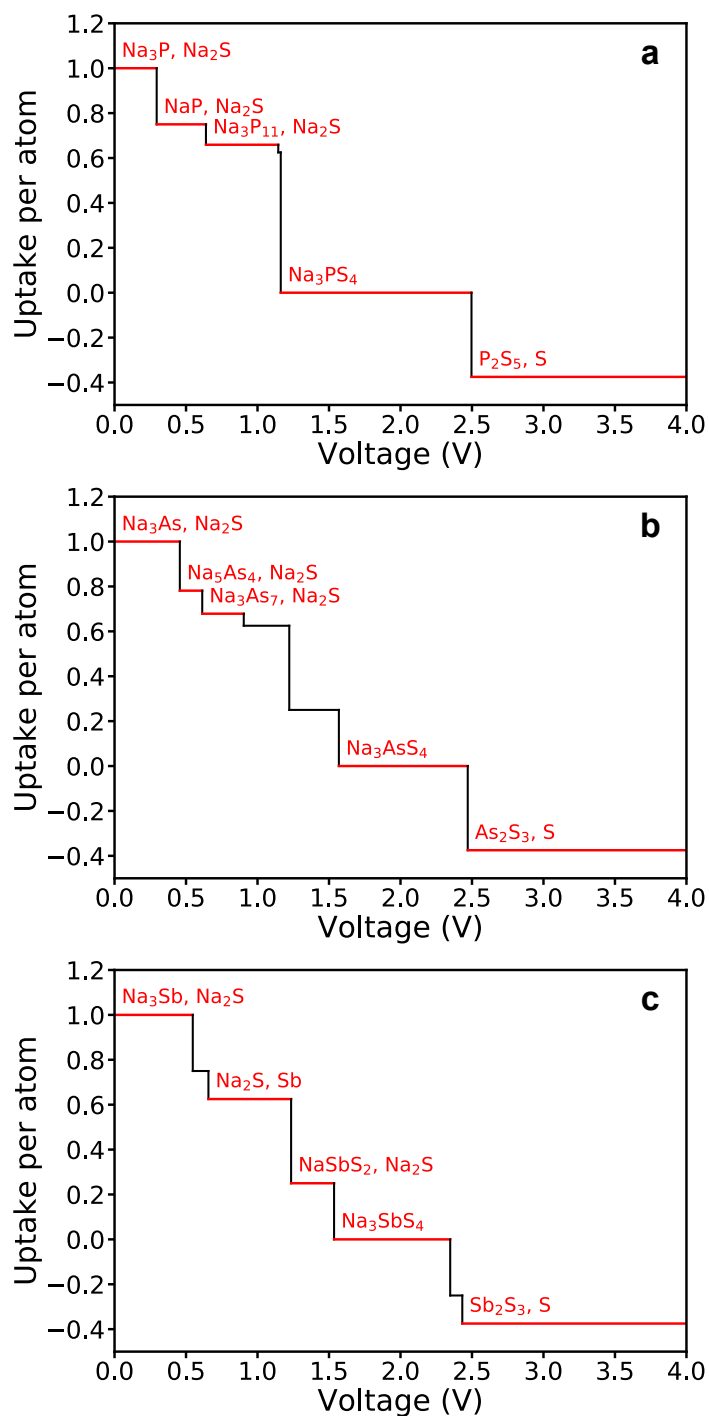


Figure 5.11 Plots of Na uptake per atom against voltage vs Na/Na^+ (V) of various solid electrolytes: (a) Na_3PS_4 ; (b) Na_3AsS_4 ; (c) Na_3SbS_4 . In anode region, the decomposed products are Na_2S and Na_3Pn while at high voltage up to 4 V, P_2S_5 , As_2S_3 and Sb_2S_3 are predicted to form.

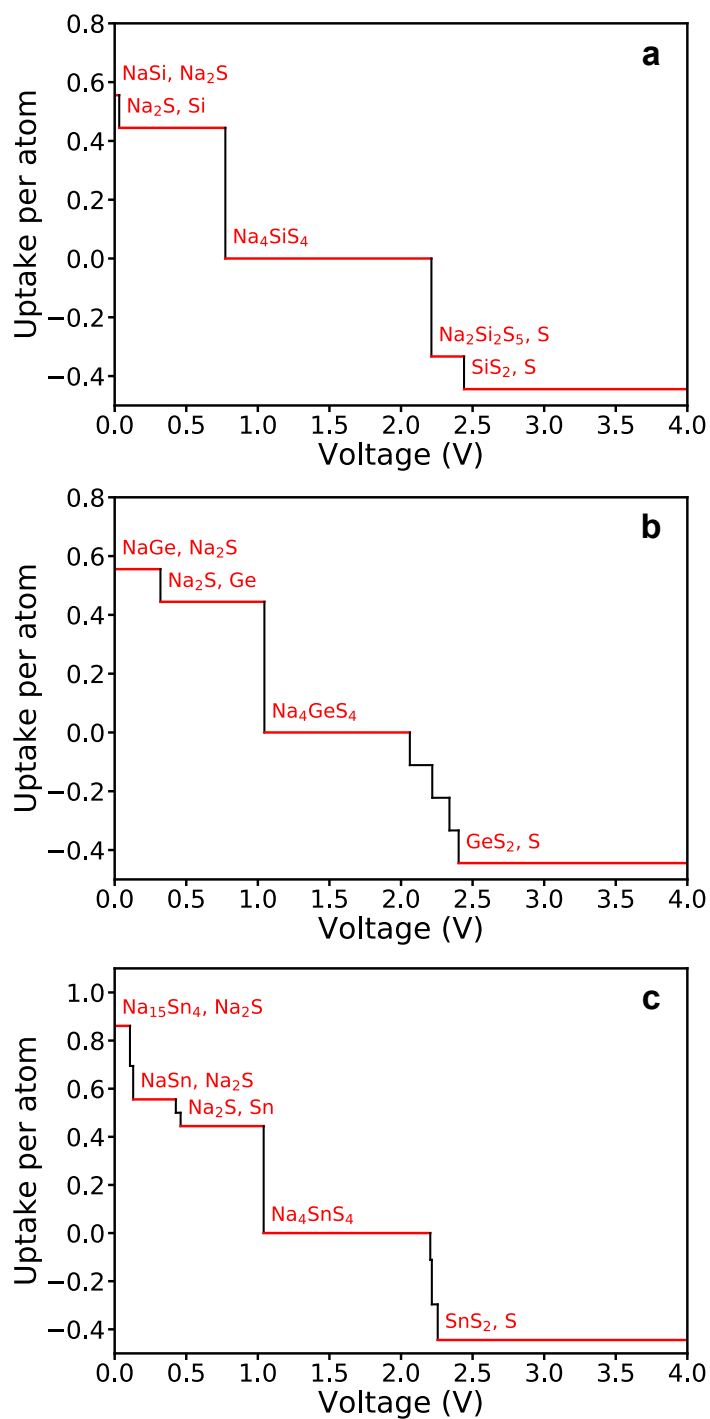


Figure 5.12 Plots of Na uptake per atom against voltage vs Na/Na⁺ (V) of various solid electrolytes: (a) Na₄SiS₄; (b) Na₄GeS₄; (c) Na₄SnS₄. In anode region, Na_xTt_y compounds and Na₂S are the main products whereas universal formula of TtS₂ and S form at high voltage cathode region.

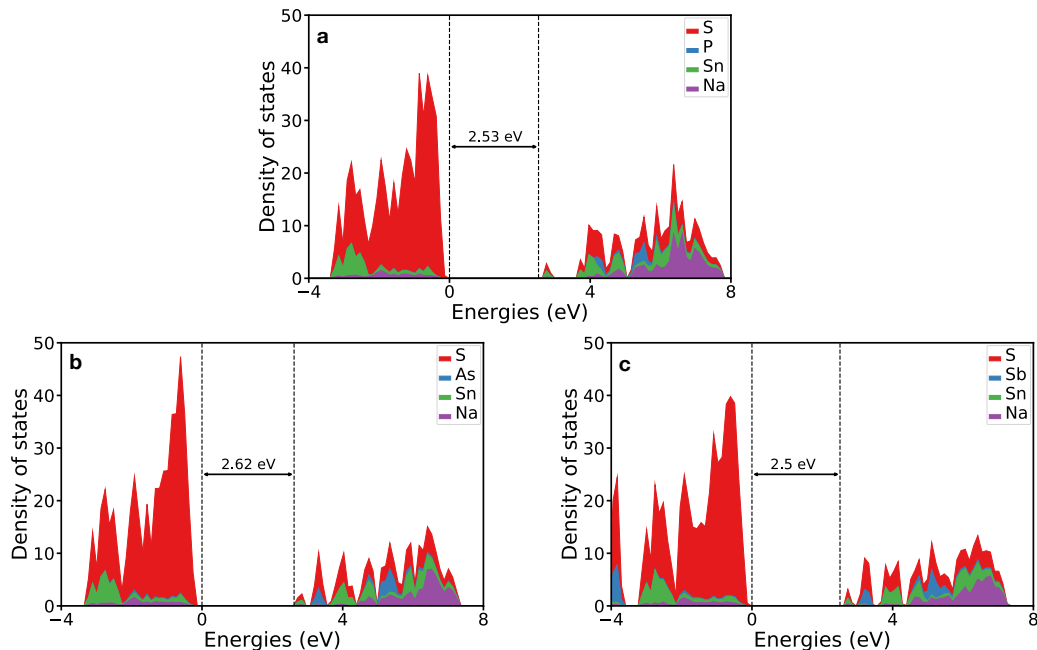


Figure 5.13 Calculated element-projected density of states (DOS) for (a) $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ (band gap $E_g = 2.53$ eV) (b) $\text{Na}_{11}\text{Sn}_2\text{AsS}_{12}$ ($E_g = 2.62$ eV) and (c) $\text{Na}_{11}\text{Sn}_2\text{SbS}_{12}$ ($E_g = 2.5$ eV) using the HSE06 screened hybrid functional.

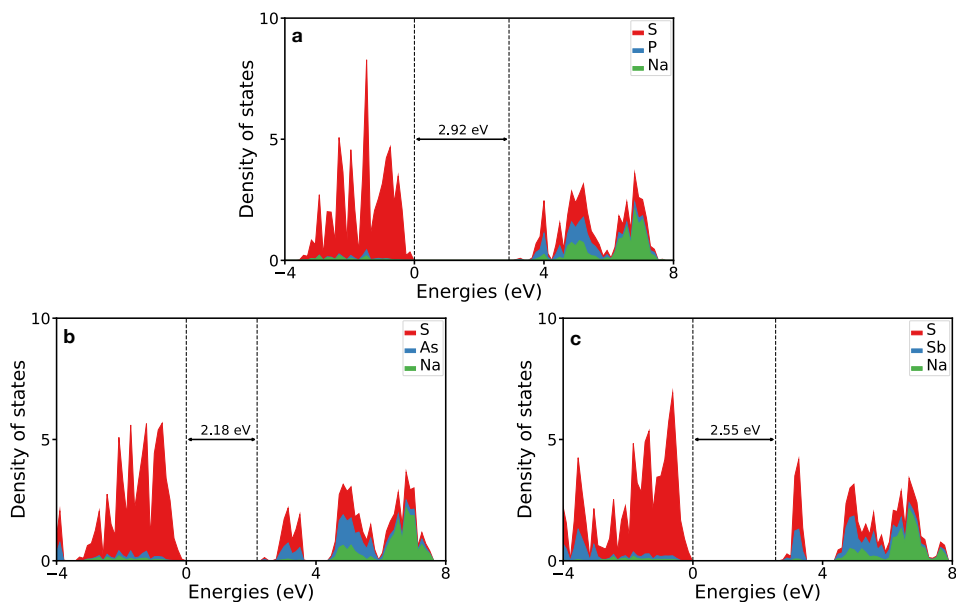


Figure 5.14 Calculated element-projected density of states (DOS) for (a) Na_3PS_4 (band gap $E_g = 2.92$ eV) (b) Na_3AsS_4 ($E_g = 2.18$ eV) and (c) Na_3SbS_4 ($E_g = 2.55$ eV) using the HSE06 screened hybrid functional.

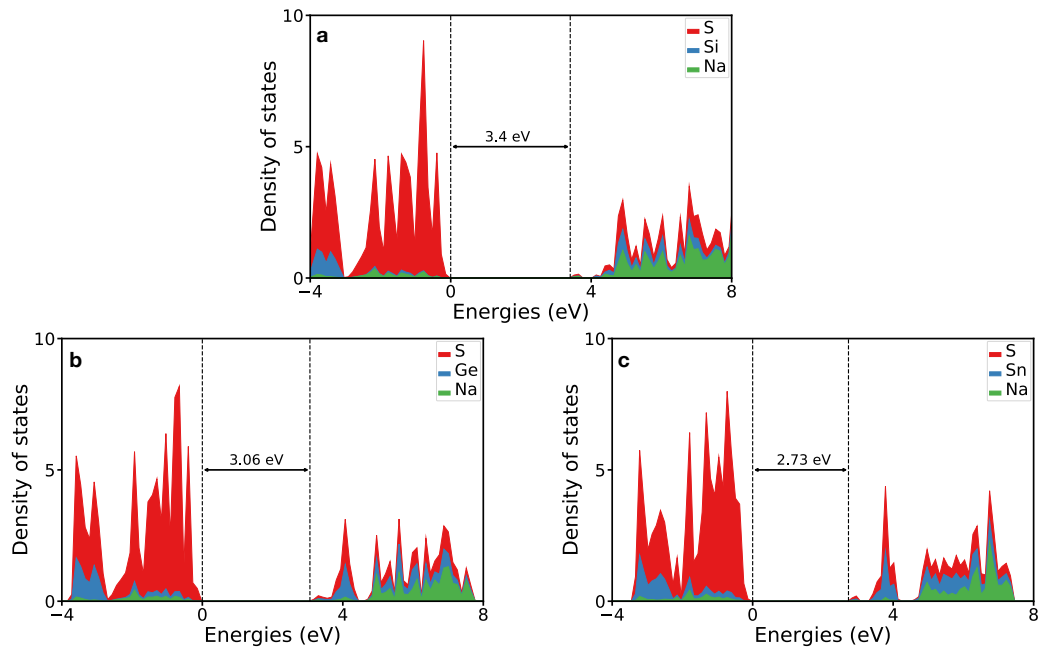


Figure 5.15 Calculated element-projected density of states (DOS) for (a)Na₄SiS₄ (band gap $E_g = 3.4$ eV) (b)Na₄GeS₄ ($E_g = 3.06$ eV) and (c) Na₄SnS₄ ($E_g = 2.73$ eV) using the HSE06 screened hybrid functional.

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 Na_3PS_4 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- Na_3PS_4 is in excellent agreement with the experimental results. Besides, M^{4+} dopants (Si, Ge, Sn) are taken into consideration for P^{5+} 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,³⁷ 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.¹²³ Then we deepen our understanding of the transport mechanism in Cl-doped t- Na_3PS_4 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 Na_3 (Na close to Cl) and eliminating Na_4 (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 P^{5+} to P^{4+} guarantees Na and Cl concentrations can be tuned independently.

Finally, we present a comprehensive investigation on $\text{Na}_4\text{TtS}_4\text{--Na}_3\text{PnS}_4$ (where $\text{Pn} = \text{P}, \text{As}, \text{Sb}$ and $\text{Tt} = \text{Si}, \text{Ge}, \text{Sn}$) cation mixing using first principles calculations. The composition systems include prototypes of Na_3PS_4 , Na_4SnS_4 and newly reported $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$. Isovalent mixed $\text{Na}_3\text{Pn}'_x\text{Pn}''_{1-x}\text{S}_4$ is highly miscible solid solution with complete solubility, particularly for P-As mixing. $\text{Na}_3\text{P}_x\text{As}_{1-x}\text{S}_4$ compositions also exhibit better moisture stability compared with Na_3PS_4 . For aliovalent mixed $\text{Na}_{4-x}\text{Tt}_{1-x}\text{Pn}_x\text{S}_4$, structures substituted from $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ show better phase stability than those from Na_3PS_4 and Na_4SnS_4 . A new mixed composition $\text{Na}_{11}\text{Sn}_2\text{AsS}_{12}$ 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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