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UNIVERSITY OF CALIFORNIA, SAN DIEGO

Investigation of Sulfide-based Solid Electrolytes for Sodium All-Solid-State

Rechargeable Batteries

A Thesis submitted in partial satisfaction of the requirements for the degree

Master of Science

in

NanoEngineering

by

Christopher S. Kompella

Committee in charge:

Professor Ying Shirley Meng, Chair Professor Jian Luo Professor Shyue Ping Ong

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The Thesis of Christopher S. Kompella is approved and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego

2017

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Chapter 1, in part, is a reprint of the material "Room-Temperature All-solid- state Rechargeable Sodium-ion Batteries with a Cl-doped Na₃PS₄ Superionic Conductor" as it appears in Scientific Reports; Chu, I.-H.; Kompella, C. S.; Nguyen, H.; Zhu, Z.; Hy, S.; Deng, Z.; Meng, Y. S.; Ong, S. P. Room-Temperature All-solid-state Rechargeable Sodium-ion Batteries with a Cl-doped Na₃PS₄ Superionic Conductor. Sci. Rep. 6, 33733. The thesis author was the co-primary investigator and co-first author of this paper. All experimental parts were performed by the author.

Chapter 2, in full, is currently being prepared for submission for publication of the material "Elucidating the Effect of Cl-doping on the Decomposition Mechanisms of the Na/Na₃PS₄ Solid-Solid Interphase for All-Solid-State Batteries;" Kompella, C. S.; Lee, J. Z.; Lee, S. C.; Wu, E.; Nguyen, H.; Wang, X.; Meng, Y. S. The thesis author was the primary investigator and first author of this paper. The author designed and performed the experimental work and analyzed all results, except XPS.

Abstract of the Thesis

Investigation of Sulfide-based Solid Electrolytes for Sodium All-Solid-State

Rechargeable Batteries

by

Christopher S. Kompella Master of Science in NanoEngineering University of California, San Diego, 2017 Professor Ying Shirley Meng, Chair

All-solid-state sodium-ion batteries are promising candidates for large-scale energy storage applications. The key enabler for an all-solid-state architecture is a sodium solid electrolyte that exhibits high Na⁺ conductivity at ambient temperatures, as well as excellent phase and electrochemical stability. In this work, we present the synthesis of a novel Cl-doped tetragonal Na₃PS₄ (t-Na_{3-x}PS_{4-x}Cl_x) solid electrolyte with a room-temperature Na⁺ conductivity exceeding 1 mS cm⁻¹. We demonstrate that an all-solid-state TiS₂/ t-Na_{3-x}PS_{4-x}Cl_x/Na cell utilizing this solid electrolyte can be cycled at room-temperature at a rate of

C/10 with a capacity of over 100 mAh g⁻¹ over 10 cycles. Finally, we provide experimental evidence that this excellent electrochemical performance is not only due to the high Na^+ conductivity of the solid electrolyte, but also due to the effect that "salting" Na_3PS_4 has on the formation of an electronically insulating, ionically conducting solid electrolyte interphase.

Introduction

Over the last decade, advances in photovoltaics and other energy-harvesting technologies have led to a dramatic increase in renewable energy generation. In 2015, renewable energy generation, like wind and solar, accounted for more than 13% of total energy production [1], and by 2050, renewables generation is projected to surpass coal as the nation's second largest source of power [2, 3]. However, these sources are often unpredictable and intermittent, and these concerns with reliability make their power difficult to use efficiently on the grid. In order for these technologies to be seamlessly integrated into a smarter, more robust grid, progress in energy storage is critically needed [4].

Batteries, which convert chemical energy into electricity, are a promising candidate to provide safe, low-cost, grid-scale energy storage [4, 5]. A battery comprises a positive electrode (cathode), a negative electrode (anode), and the electrolyte. In a Li-ion battery during discharge, Li^+ ions travel through the electrolyte from anode to cathode, while electrons traverse an external circuit to provide useful power [4]. For rechargeable batteries, this process is reversible to charge the battery. The electrolyte, which conducts ions while preventing electronic conduction is paramount to the performance of the device.

Traditionally, carbonate-based organic liquid electrolytes are selected due to their high ionic conductivity at room temperature (>10 mS/cm) and their ability to conform intimately to electrode surfaces. These chemistries are highly volatile, and have played a role in numerous battery fires and explosions. Moreover, liquid electrolytes are susceptible to dendrite formation, which can short-circuit cells and cause large amounts of energy to

be rapidly released in an uncontrolled, unsafe discharge [5]. If batteries are to remain relevant, their energy and power densities must increase, and the need for safer electrolytes increases with it.

Solid-state electrolytes lend one potential solution. Compared to liquids, they typically have better mechanical, thermal, and chemical stability but finding solids which possess all these properties and have useful ionic conductivities at practical temperatures has been challenging [6, 7]. Furthermore, interfacial impedance between electrolyte grains and between electrolyte and electrodes have become limiting factors in the commercialization of solid-state electrolytes [8]. Densification of the electrolyte layer is important to maximize the contact area between grains because although transport within grains can be fast, ionic transport through the layer is usually limited by grain boundary diffusion. The same is true for interphases between electrolyte and electrode, but densification of electrodes from the electrolyte surface as well as decomposition of the interphase into ionically blocking components almost certainly lead to cell failure.

Sulfide-based glasses and glass-ceramics, such as those in the $yLi_2S + (1-y)P_2S_5$ system, have the advantage of being easily densified [9], as compared to oxide-based ceramics that require energy-intensive, high-temperature sintering steps to minimize grain boundary impedance [8]. Sulfides also have reasonable wettability with Li, which is a known problem with oxide-based ceramics [10]. Most importantly, sulfide-based glasses and ceramics, such as $Li_{10}GeP_2S_{12}$ and $Li_7P_3S_{11}$, have been discovered with room temperature ionic conductivities rivalling those of conventional liquid electrolytes and have since been demonstrated in Li all-solid-state batteries (ASSBs) [11-13].

Due to depleting Li resources, the cost of batteries has skyrocketed. Sodium, on the other hand, is the sixth most abundant element on Earth and more than 10 times cheaper to produce [14]. Grid-scale energy storage applications place large emphasis on the cost-effectiveness, safety, and longevity of the batteries making sodium all-solid-state batteries a promising alternative [15-18]. Nevertheless, the ionic radius on Na⁺ is more than three times that of Li⁺, making the task of finding a material with superionic conductivity all the more trying.

Ionic conduction in solids is the movement of ions by hopping to adjacent stable sites [19]. Ionic conductivity is governed by the following equation:

$$\sigma = ne\mu$$

where *n* is the charge carrier concentration and μ is the ion mobility. In the design of electrolytes, the charge carrier concentration can be increased through the formation of defects, such as vacancies or interstitials [20]. The ion mobility is related to the ease with which it travels the conduction pathway [21]. Because Na⁺ is a larger ion, the channel size needs to be large enough to allow it to pass. Introducing larger elements can help open up the structure and increase ion mobility. Ion conduction is also a thermally activated process, and its temperature dependence follows the Arrhenius equation:

$$\sigma = \sigma_0 e^{-E_a/_{kT}}$$

where σ_0 is the intrinsic ionic conductivity, E_a is the ion migration activation energy, k is the Boltzmann constant, and T is the temperature. Therefore as temperature increases, the ionic conductivity increases. Typically, solid electrolytes have conductivities rivaling that of liquid electrolytes only at high temperatures that are energy-intensive and costly to operate and may even be above the melting point of elemental metal anodes. The ideal solid electrolyte should have an ionic conductivity of at least 1 mS cm⁻¹ at room temperature to used practically in an energy storage device [22].

Sodium sulfide glasses in the $yNa_2S + (1-y)P_2S_5$ system typically reach room temperature conductivities on the order of $10^{-6}-10^{-8}$ S cm⁻¹ [23, 24], however when these glasses are heated, polycrystalline ceramic materials are readily obtained [25-27]. For the y = 0.75 composition, the Na₃PS₄ glass-ceramic is produced, which has cubic and tetragonal polymorphs with room temperature ionic conductivities of about 10^{-4} and 10^{-6} S cm⁻¹, respectively [25, 26]. Various attempts have reached 10^{-3} S cm⁻¹ at room temperature for a sodium superionic conductor have been experimentally or computationally reported, including other chalcogenide (Se and Sb) containing materials [28-31] and materials doped with Group IV metals (Si and Sn), however many have yet to demonstrate the material's performance in a full cell [21, 32, 33].

Herein, we investigate the effects of anion doping with halides in order to design robust, high-performance electrolytes for next-generation rechargeable batteries. Chapter 1 outlines the synthesis and bulk characterization of the novel Cl-doped Na₃PS₄ electrolyte. Chapter 2 investigates the performance of the Cl-doped Na₃PS₄ electrolyte in a device focusing on the metal anode-electrolyte interface.

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Chapter 1

1.1 Introduction

Rechargeable all-solid-state sodium-ion batteries (ss-SIBs), which utilize ubiquitous sodium sources, are a promising low-cost, high-safety alternative to today's lithium-ion batteries, especially for large-scale energy storage applications [1-5]. However, a critical challenge in the development of ss-SIBs is the lack of a sodium solid electrolyte with high ionic conductivity at ambient temperatures and a wide electrochemical window. Although oxide solid electrolytes such as β -alumina and NAtrium Superionic CONductors (NASICON) are well known, they exhibit reasonable ionic conductivities only at higher temperatures [1, 6-10]. Moreover, their synthesis requires high-temperature processing to reduce the grain-boundary resistance, which is incompatible with traditional cathode materials and thus requires special fabrication procedures [1].

Chalcogenide-based (S, Se) chemistries offer the potential for higher ionic conductivities than oxides [11-19]. Though it is likely that sulfide and selenide-based solid electrolytes may exhibit lower *intrinsic* electrochemical stability, the formation of passivating phases at the electrode-solid electrolyte interface can potentially mitigate further reactions [20-22]. Sulfide electrolytes, particularly sodium sulfides, also tend to be softer than oxides [23], which allows intimate contact between electrode and solid electrolyte to be achieved via cold pressing instead of high-temperature sintering.

In recent years, several sodium superionic conductors with ionic conductivities approaching that of traditional organic electrolytes have been identified. For example, the cubic phase of Na₃PS₄ (c-Na₃PS₄) was first reported by Hayashi and co-workers in 2012 with a measured Na⁺ conductivity of 0.2 mS cm⁻¹ [24]. The crystal structure of c-Na₃PS₄ has the $I\bar{4}3m$ space group and is the high-temperature [25], disordered polymorph of tetragonal Na₃PS₄ (t-Na₃PS₄) with space group $P\bar{4}2_1c$ [26]. Since its discovery, there have been a number of successful efforts at further enhancing its room temperature conductivity [25, 27, 28], with the highest value thus far of 0.74 mS cm⁻¹ achieved within the (1*x*)Na₃PS₄-*x*Na₄SiS₄ pseudo-binary system at *x* around 0.06 [28]. A recent first principles investigation by some of the authors of this work 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 [30].

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 [30]. However, previous experimental efforts with (1-*x*)Na₃PS₄-*x*NaI glass-ceramics achieved a Na⁺ conductivity of ~0.1 mS cm⁻¹ [31], 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, suggesting an intrinsic incompatibility of I⁻ ions with the S²⁻ host.

In this work, we demonstrate the stable cycling of a $TiS_2/t-Na_{3-x}PS_{4-x}Cl_x/Na$ 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 the Na_{2.9375}PS_{3.9375}Cl_{0.0625}, and its demonstration in a ss-SIB architecture. We will also present evidence from DFT computations that suggest the superior performance achieved in this cell is not only the result of the high Na⁺ conductivity of the solid electrolyte, but also the formation of electronically-insulating, ionically-conducting passivation layers at the electrode-solid electrolyte interface due to the presence of the Cl⁻ anion.

1.2 Experimental Methods

1.2.1 Synthesis

Pure t-Na₃PS₄ was synthesized from reagent-grade Na₂S (Alfa Aesar, 99%) and P₂S₅ (Sigma Aldrich, 99%). The precursors were ground in agate mortar and pestle in a molar ratio of 75:25, respectively. To introduce the chloride dopant, NaCl (Alfa Aesar, 99.99%) was mixed into the previous precursors following the chemical reaction $(1.5 - x)Na_2S + 0.5P_2S_5 + xNaCl \rightarrow Na_{3-x}PS_{4-x}Cl_x$. The resulting mixtures were then sealed under vacuum in a quartz tube, heated to 1073 K (800 °C) for 4 hours, and then quenched in ice water. Subsequently, the sample was ground in a mortar and pestle and sealed in an ampoule to be heat treated at 693 K (420 °C) for 2 hours to stabilize the tetragonal phase.

The samples were ground back into a powder with mortar and pestle, and re-pelletized. These pellets were then processed via spark plasma sintering (SPS). To prepare the sample, a 10 mm tungsten-carbide circular die was lined with graphite foil and the powder was placed in between two tungsten-carbide plungers, also coated with graphite. The entire setup was placed in the SPS chamber, and the sample was pressed to 100 MPa (100 MPa min⁻¹), heated to 573 K (100 K min⁻¹), and then allowed to dwell under these processing conditions for 5 minutes to reach a densified state. All synthesis steps were performed in a dry, inert (Ar) environment, unless otherwise stated.

1.2.2 Characterization of the solid electrolytes

The structural characterization was performed via X-ray diffraction (XRD). The data was collected by a Rigaku diffractometer over a 2 Θ range of 30–60°, with a step size of 0.02° and a dwell time of 2 seconds. The beam was generated by a Cu-K α source (40 kV, 100 mA). The sample was sealed under Kapton tape to prevent degradation or side-reactions during measurements.

Cross-sectional images of the SPS pellets were obtained using a Phillips XL30 scanning electron microscope (SEM). Pristine and doped pellets were suspended in an acrylic matrix that was polished for imaging. Iridium was sputtered onto the surface of the sample using an Emitech sputter chamber operating at 85 mA for 7 seconds. The sample was imaged using a 10 kV beam. Additionally, an elemental mapping analysis was conducted using an energy dispersive X-ray spectroscopy (EDX) aperture in the SEM. SEM and EDX were conducted under high vacuum.

1.2.3 Electrochemical characterization

The electrochemical performance was evaluated via electrochemical impedance spectroscopy (EIS). The data was collected using a Solartron 1260 impedance analyzer operating from 1 MHz to 1 Hz with a DC bias of 0 V and an applied AC voltage of 25 mV. Carbon was used as blocking electrodes. The pellet was held between two titanium plungers serving as current collectors. The temperature dependence of conductivity was obtained by placing the cell in an electric furnace. The cell was ramped to 453 K (180 °C) from room temperature in 25 K increments. Prior to each measurement, the cell was held at the temperature for one hour to allow the system to reach thermal equilibrium. The sodium ion-migration activation energy was calculated from the slope of the Arrhenius plot. All measurements were taken in a dry, inert (Ar) atmosphere.

A full cell was assembled using a TiS₂ composite cathode against a Na metal anode. TiS₂ was mixed with t-Na_{3-x}PS_{4-x}Cl_x, x = 6.25% in a 1:2 weight ratio. The doped (x = 6.25%) solid electrolyte (200 mg) was cold pressed at 360 MPa in a 13 mm polyetheretherketone (PEEK) die. The cathode blende (10 mg) was cold pressed at 360 MPa on top of the electrolyte layer. Pure Na metal was attached to a titanium current collector and cold pressed into the die at approximately 30 MPa. The cell was cycled using Arbin battery cycler at room temperature. Cycling was performed at a C/10 rate for 10 cycles over a voltage window from 1.2 V to 2.4 V. The cell was cycled inside an Ar glovebox.

1.3 Results

1.3.1 Synthesis and characterization of t-Na_{3-x}PS_{4-x}Cl_x

Pure t-Na3PS4 was synthesized from Na₂S and P₂S₅ precursors. **Figure 1.1** shows the crystal structure of the pristine tetragonal Na₃PS₄. The Cl⁻ dopant was introduced by adding NaCl following the chemical reaction $(1.5-x)Na_2S + 0.5P_2S_5 + xNaCl \rightarrow Na_{3-x}PS_4$. $_xCl_x$. The resulting pellets were then densified via spark plasma sintering (SPS) to minimize porosity of the solid electrolyte. The synthesis details are given in the Experimental Method.

Figure 1.2a 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 [26]. 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 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 1.2**b. The refined lattice constants for the pristine structure are a = b = 6.956 Å and c = 7.088 Å, which are also in excellent agreement with the previously reported values [26]. The isotropic displacement factors were as expected, with P⁵⁺ having the lowest due to its

high coordination. These parameters were then used as an initial model to study the aliovalent substitution of S^{2-} by Cl⁻. Figure 1.2c shows the refined pattern of doped t-Na_{2.9375}PS_{3.9375}Cl_{0.0625}. No unknown phase was detected in the crystal, and no side reactions were observed during the synthesis. Although a trace amount of NaCl was detected in the spectrum, our refinement results show that it comprises less than 1 at%.

Table 1.1 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, we observe an increase in the lattice constants to a = b = 6.970 Å and c = 7.092 Å, associated with the substitution of S²⁻ by Cl⁻. This volumetric expansion is very small and also agrees well with the DFT calculations. We detect Cl⁻ is incorporated into the lattice in the S²⁻ site, and the corresponding decrease in the occupancy of S²⁻ indicates the doping was indeed successful. Finally, we confirm the presence of Na vacancies as shown by the reduction in the Na1 and Na2 occupancies. An observed increase in the isotropic displacement factors is attributable to the distortion of the lattice by the doping of Cl⁻.

Cross-sectional SEM images of the pristine $t-Na_3PS_4$ and doped $t-Na_{2.9375}PS_{3.9375}Cl_{0.0625}$ samples under identical processing conditions are shown in **Figure 1.3a** and **Figure 1.3b**, 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, and the density of the materials was measured.

Though cold pressed sulfides, as compared to oxides, have been shown to be reasonably densified, there is still room for improvement. The increase in conductivity is, in part, owing to the densification of pellets via spark plasma sintering (SPS) which results in a reduction of grain boundary resistance. Grain boundary resistance can be separated into components characteristic of diffusion through the grain and those stemming from a reduced contact area due to porosity. While SPS does not address the intrinsic nature of the grain boundary, it does significantly reduce the porosity of the material, permitting greater contact area between grains. This explains why the ionic conductivity of the pristine t-Na₃PS₄ is an order of magnitude higher than previous reports [26].

Density measurements were conducted to determine the real density of the assynthesized powders and relative densities of the sintered pellets, and the results are shown in **Table1.2**. The densities of the two materials are quite similar and we do not observe a significant difference between them. The real densities of powders were measured using a pycnometer purging helium. The real density measurement was carried out in an inert environment. The pristine and doped materials were 2.268 g mL⁻¹ and 2.262 g mL⁻¹, respectively. These values are within 2% of the theoretical density and well within experimental error. The relative densities of the pristine and doped pellets were 1.99 g mL⁻¹ and 2.08 g mL⁻¹, respectively, which is at least 90% of the theoretical density, 2.22 g mL⁻¹. For this reason, SPS typifies a novel glass-ceramic processing technique which can be effective in both minimizing a material's grain boundary resistance and manufacturing viable all-solid-state batteries by attending to the issue of interfacial contact between the electrode and electrolyte.

EDX elemental mappings of S and Cl were collected from the doped sample and are shown in **Figure 1.3**c and **Figure 1.3**d, respectively. 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.

1.3.2 Ionic conductivity of t-Na_{3-x}PS_{4-x}Cl_x

The ionic conductivity of the material was determined via electrochemical impedance spectroscopy (EIS). The total ionic conductivity has contributions from both the bulk and grain boundary, and was measured based on the intersection of the high-frequency capacitive semicircle and the low-frequency tail. The temperature-dependence of the ionic conductivity follows the equation $\sigma = \sigma_0 e^{(-Ea/kT)}$, so the slope of the Arrhenius plot can be used to calculate the Na⁺ ion migration activation energy. The pristine (x=0%) pellet has the characteristic semicircle and spike typical of ionic conductors. On the other hand, the doped (x=6.25%) pellet does not have a resolvable semicircle though it was measured in the same frequency range as the pristine pellet. This phenomenon has been observed in several other materials, seemingly as the conductivity surpasses 1 mS cm⁻¹. The total room temperature impedances for the pristine and Cl-doped (x = 6.25%) pellets were roughly 12 k\Omega and 400 Ω , respectively.

By normalizing with the factor (l/A), we account for the thickness (l) and crosssectional area (A) of the pellet, and the impedance values were then converted to ionic conductivity. The resulting ionic conductivities for the pristine and Cl-doped (x = 6.25%) cases are 0.05 mS cm⁻¹ and 1.14 mS cm⁻¹, respectively. In these EIS measurements, the pristine and Cl-doped (x = 6.25%) pellets were 2.49 mm thick with a diameter of 9.52 mm and 2.40 mm thick with a 9.67 mm diameter, respectively. It is worth pointing out that these dimensions are quite different from the solid-electrolyte layer in the full-cell assembly, which was 1 mm thick with a 12.95 mm diameter. Note also that the measured impedance of the Cl-doped pellet is of the same order of magnitude for the Si-doped Na₃PS₄ pellet in the previous work by Tanibata et al., in which the resistance of their doped pellet is roughly 350 Ω [25].

The experimental measurement of pristine t-Na₃PS₄ shows a low ionic conductivity of 0.05 mS cm⁻¹ at 303 K, with an activation energy value of 317 meV (see **Figure 1.4**b and **Table 1.3**). The t-Na_{2.9375}PS_{3.9375}Cl_{0.0625} solid electrolyte, on the other hand, shows an extremely high conductivity of 1.14 mS cm⁻¹ at 303 K and a low activation barrier of 249 meV. The measured conductivity and activation barrier are in excellent agreement with the calculated values (see **Table 1.3**). The room temperature Nyquist plots for the pristine t-Na₃PS₄ and doped t-Na_{2.9375}PS_{3.9375}Cl_{0.0625} are given in **Figure 1.4**a, where the total impedance in each structure was used to calculate the room temperature conductivities of each material. A significantly larger semi-circle is observed for the pristine t-Na₃PS₄ compared to doped t-Na_{2.9375}PS_{3.9375}Cl_{0.0625}, indicating a much larger total resistance in the pristine t-Na₃PS₄.

1.3.3 Electrochemical stability of t-Na_{2.9375}PS_{3.9375}Cl_{0.0625}

The electrochemical stability of the Cl-doped t-Na₃PS₄ against Na metal was evaluated. Using a Solartron 1260/1287 analyzer, cyclic voltammetry was performed on a full-cell assembled as described in the Methods section, but using a titanium plunger as a blocking electrode instead of the TiS₂ cathode blende. The voltage was swept from -0.5 V to 5.0 V at 5 mV s⁻¹. The voltammogram shows cathodic and anodic peaks corresponding

to the deposition and dissolution of sodium at 0 V vs. Na/Na⁺ (see **Figure 1.5**a). No other currents are observed up to 5 V vs. Na/Na⁺, suggesting a stable passivation layer at the anode-electrolyte interface.

Impedance measurements of the full-cell were also obtained during the first cycle discharge (see **Figure 1.5**b) using a Solartron 1260/1287. A cell assembled as described in the Methods section was discharged at a C/10 rate, but held at 2.5 V, 2.0 V, 1.75 V, 1.5 V, and 1.2 V while EIS measurements were performed. A 100 mV AC potential was applied and the frequency was swept from 1 MHz to 10 mHz. The cell was fit using an equivalent circuit proposed by Oh and co-workers [34], including contributions from the bulk and interfacial phenomena.

Our results suggest the formation of solid-electrolyte interphase layers as the internal resistance of the cell increases dramatically over the course of the first discharge. We observe that the contributions from the bulk and grain boundary show hardly any deviation from their initial values, while a sharp increase is observed for the interfacial impedance. The capacitances from the interfacial contributions are 2×10^{-7} F, which is within the characteristic range of 10^{-7} - 10^{-5} F [35]. Our results indicate that the increase in interfacial resistance is indeed attributable to a change in the nature of the interface.

1.3.4 Electrochemical performance of t-Na_{2.9375}PS_{3.9375}Cl_{0.0625}

A full-cell was constructed using a TiS_2 charged cathode and a Na metallic anode. The choice of the TiS_2 cathode is motivated by its suitable operating voltage (~1.7 V versus Na/Na⁺), which is well within the limits of the DFT predicted stability window of the t-Na_{2.9375}PS_{3.9375}Cl_{0.0625} solid electrolyte, as well as its fast kinetics for Na⁺ intercalation [46]. 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 charge-discharge profile of the full-cell is shown in **Figure 1.6**a. The theoretical capacity of the TiS₂ active material is 240 mAh g⁻¹. The discharge and charge capacity of the first cycle were ~ 240 mAh g⁻¹ and 80 mAh g⁻¹, respectively. The source of the large irreversible capacity of the first cycle is currently under investigation, and will be the subject of a subsequent study. The subsequent charge and discharge capacities of the cell over 10 cycles were ~80 mAh g⁻¹, with a coulombic efficiency above 98%. Cycling and coulombic efficiency are included in **Figure 1.6**b. Strong polarization, common in Na-ion cells, was also observed at the point of switching from charging to discharging, and vice versa.

1.4 Discussion

The design of an all-solid-state rechargeable battery is a multi-component, multiproperty 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-Na_{2.9375}PS_{3.9375}Cl_{0.0625} solid electrolyte that has been demonstrated in a full ss-SIB cell with good cyclability and capacity.

In this work, the ideal synthesis of the solid electrolyte was paramount. As such, t-Na_{3-x}PS_{4-x}Cl_x, for x = 0% and 6.25%, was synthesized in accordance with the tetragonal $P\overline{4}2_1c$ space group. For the pristine structure, the lattice constants were in excellent agreement with literature [26]. With the introduction of chloride, the lattice constants increased, and presumably this lattice expansion also aids in the superionic conductivity of the bulk material. A corresponding decrease in the occupancies of the S, Na1, and Na2 sites is also observed, confirming the substitution of S^{2-} by Cl⁻ as well as the presence of the desired Na⁺ vacancies. Lastly, an increase in the isotropic displacement factors indicates the distortion of the lattice, which is characteristic of aliovalent doping.

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 **Table 1.3**). This overall conductivity is higher than that of Si-doped c-Na₃PS₄ (0.74 mS cm⁻¹) [28] and is the highest value for sodium thiophosphates achieved thus far. The recently reported Na₃PS₄ has a similar conductivity, but utilizes the more expensive and less stable Se²⁻ anion [19, 33].

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 [24], that performance was achieved with a much lower current density (0.013 mA cm⁻²) against a Na-Sn alloy as the anode. Though the Si-doped c-Na₃PS₄ and Na₃PSe₄ solid electrolytes have higher measured conductivities than c-Na₃PS₄, their room-temperature performance in a full ss-SIB cell has not yet been demonstrated [19, 28]. 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.

1.5 Conclusions

In conclusion, we have demonstrated the prediction and synthesis of a novel Cldoped tetragonal Na₃PS₄ solid electrolyte, or t-Na_{2.9375}PS_{3.9375}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 t-Na_{2.9375}PS_{3.9375}Cl_{0.0625} solid electrolyte exceed 1 mS cm⁻¹, which is one of the highest conductivity reported for any sodium superionic conductor thus far. More importantly, the "salting" of Na₃PS₄ is predicted to improve the characteristics of the interfacial phase equilibria at the anode/solid electrolyte interface, forming an electronically insulating and ionically conducting solidelectrolyte interphase. We also demonstrate the potential of spark-plasma sintering as a technique for achieving a dense sulfide electrolyte with reduced grain boundary resistance.

1.6 References

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1.7 Acknowledgements

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Figure 1.1 Crystal structure of the pristine t-Na₃PS₄. The tetragonal polymorph of the Na₃PS₄ crystal. There are symmetrically distinct Na sites in t-Na₃PS₄, Na1 (4d) and Na2 (2a), and the PS₄⁻ tetrahedra are centered at the 2b positions.



Figure 1.2 X-ray diffraction pattern of pristine and doped t-Na_{3-x}PS_{4-x}Cl_x (a) XRD patterns for t-Na_{3-x}PS_{4-x}Cl_x with x = 0% and 6.25%, and previous study in Ref. 26. (b) Refinement plot of the pristine t-Na₃PS₄. (c) Refinement plot of Cl-doped t-Na₃PS₄. Solid red and black lines denote the observed and calculated XRD patterns, while the green ticks mark the position of the reflections allowed by the space groups of t-Na₃PS₄. (**P42**₁**c**) and NaCl (**Fm3m**). The difference between the observed and calculated patterns is signified by the blue line.





Figure 1.3 Morphology and elemental composition of t-Na_{3-x}**PS**_{4-x}**Cl**_x (a) SEM image of pristine t-Na₃*PS*₄ SPS sample, and (b) SEM image of SPS sample of doped t-Na_{3-x}*PS*_{4-x}*Cl*_x (x = 6.25%). Scale bar is 10 µm. EDX elemental maps of (c) sulfur, and (d) chlorine, corresponding to the doped t-Na_{2.9375}*PS*_{3.9375}*Cl*_{0.0625}. Scale bar is 10 µm.



Figure 1.4 Ionic conductivity of t-Na_{3-x}**PS**_{4-x}**Cl**_x. (a) Electrochemical impedance spectroscopy at room temperature of the doped, on the left, and pristine, on the right, of the t-Na_{3-x} $PS_{4-x}Cl_x$. (b) 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 300 K from AIMD simulations.



Figure 1.5 Electrochemical stability of t-Na_{2,9375}**PS**_{3,9375}**Cl**_{0.0625}. (a) Cyclic voltammogram of the t-Na_{3-x} $PS_{4-x}Cl_x / Na$ (x=0.0625) interface, swept from -0.5 V to 5 V. Here, a titanium plunger was used as the blocking electrode. The stripping and plating of Na metal is observed at 0 V vs. Na/Na⁺, and no other anodic currents are noted up to 5 V. (b) Impedance plots of a discharging TiS₂ / t-Na_{3-x} $PS_{4-x}Cl_x / Na$ full-cell. Measurements were collected at 2.5 V, 2.0 V, 1.75 V, 1.5 V, and 1.2 V. (c) The impedance contributions of bulk and interface are deconvoluted using the results from the provided equivalent circuit.



(b)

Figure 1.6 Electrochemical performance of t-Na_{3-x}PS_{4-x}Cl_x in an all-solid-state full-cell. Chargedischarge profile of TiS₂/t-Na_{2.9375}PS_{3.9375}Cl_{0.0625}/Na full-cell at room-temperature. Cell was cycled under constant current conditions with a current density of 0.149 mA cm⁻² (C/10 rate) from 1.2 V to 2.4 V. The cell was able to routinely deliver 80 mAh g⁻¹ over 10 cycles. Red and black lines in the charge-discharge profile denote charging and discharging, respectively. Similarly, red and black markers signify charge and discharge capacities, while the green circles mark the coulombic efficiency by cycle.

Table 1.1 Rietveld refinement of pristine and doped t-Na_{3-x}**PS**_{4-x}**Cl**_x. Rietveld refinement results of t-Na_{3-x}**PS**_{4-x}**Cl**_x systems, where a, b and c are lattice constants, and V, Occ., and B_{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-Na₃PS₄, the DFT calculated cell parameters are a = b = 6.99 Å, c = 7.12 Å, $V = 348 \text{ Å}^3$, in excellent agreement with the refinement results as well as those by Jansen et al. (Ref. 26): a = b = 6.952 Å, c = 7.076 Å, $V = 341.97 \text{ Å}^3$.

	Pristine ($x = 0\%$), Space Group $P\overline{4}2_1c$				
	a = b = 6.956(5) Å, $c = 7.088(6)$ Å, $V = 342.9(5)$ Å ³				
		$R_b = 3.86\%$,	$R_{wp} = 4.97\%$		
	x	у	z	Occ.	B_{iso} (Å ²)
Na1 (4 <i>d</i>)	0	0.5	0.426(4)	2.00	2.54(9)
Na2 (2 <i>a</i>)	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 $P\overline{4}2_1c$				
	a = b = 6.970(4) Å, $c = 7.092(5)$ Å, $V = 344.5(4)$ Å ³				
		$R_b = 4.29\%$,	$R_{wp} = 5.31\%$		
	xyzOcc. $B_{iso}(Å^2)$				
Na1 (4 <i>d</i>)	0	0.5	0.428(6)	1.99(4)	3.0(2)
Na2 (2 <i>a</i>)	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)

*Table1.2 Density measurements of t-Na*_{3-x} $PS_{4-x}Cl_x$. The real density of the as-synthesized powders and the relative density of the spark plasma sintered pellets.

x	Real Density (g mL ⁻¹)	Relative Density (g mL ⁻¹)
0	2.268	2.085
0.0625	2.262	1.992

Table 1.3 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		Experi	ment
	$\sigma_{300\rm K} ({\rm mS \ cm}^{-1})$	$E_a ({\rm meV})$	$\sigma_{303K} ({\rm mS \ cm}^{-1})$	$E_a ({\rm meV})$
0	N/A	N/A	0.05	317
6.25	1.38 [1.04, 1.82]	232	1.14	249

Chapter 2

2.1 Introduction

Over the past decade, advances in portable electronic devices have led to increased demand for high-capacity, energy-dense sources of power. Moreover, the success of the electric vehicle (EV) market is predicated on achieving an energy density of 500 Wh kg⁻¹, and it is imperative that we innovate in the field of energy storage if this level of performance is to be realized. Two novel chemistries, Li-air and Li-S are predicted to play a pivotal role in the next generation of Li-ion batteries [1-3]. Paramount in these chemistries is the use of elemental metal anodes, such as metallic Li and Na, which have a specific capacity (3876 mAh g⁻¹ and 1170 mAh g⁻¹, respectively) of more than three times conventional carbonaceous anode materials, improving the net gravimetric and volumetric density of the cell [1-5].

The main issue in metal anode batteries is the high activity of Li and Na metal, which make it difficult to find chemistries with which it is intrinsically stable. When placed in contact with most materials, these metals readily react, and this decomposition is further exacerbated by electrochemical activity. As compared to conventional liquid electrolytes, solid electrolytes are better candidates for such systems because of their more favorable stability [6]. Moreover, easily deformable sulfide-based solid electrolytes have been cycled with elemental anodes, and issues with poor wettability and grain boundary impedance that are common in oxide-based electrolytes are mitigated with this chemistry [7-10]. Nevertheless, the poor cyclability and rate capability of all-solid-state batteries are, in part,

ascribed to the incompatibility of the electrolyte in contact with the electrodes and the inability to slow the degradation.

One way to minimize the instability is to form a passivating layer of reactants that prevent further decomposition of the electrolyte. This requires that the decomposed products have favorable ionic conductivities and negligible electronic conductivities. That is, the decomposed products at the electrolyte/anode interface should themselves operate as suitable electrolytes. Formation of a solid-electrolyte interphase (SEI) has been extensively studied in the case of conventional liquid electrolytes and is vital to the stabilization of Li-ion cells [11-13]. In this case, the SEI typically comprises Li₂CO₃ and a Li-containing salt (i.e. LiF), which provides reasonable ionic conductivity through the interface so as not to disrupt the charge-transfer kinetics [14]. In solid electrolytes, studying the solid-solid interphase (SSI) has proven to be a challenging task due to its buried nature which renders it inaccessible for many characterization techniques [15].

In recent work, it has been shown that there is a steady deterioration of lithium sulfide solid electrolytes, such as $Li_7P_3S_{11}$ and $Li_{10}GeP_2S_{12}$ [16-21]. The decomposition products, Li_2S , Li_3P , and $Li_{15}Ge_4$, have low ionic conductivities which can inhibit charge transfer across the device. Li_3P and $Li_{15}Ge_4$ also provide electronic conductivity resulting in steady interface growth until the electrolyte is fully depleted. Computational efforts have further validated these claims, and have found there to be an intrinsic instability between most solid electrolytes and Li metal [22, 23].

Wenzel et al. studied the nature of the pristine Na_3PS_4 (NPS) against Na metal, and determined that it suffers the same issues as in the Li analogs [24]. In this work, we develop a workflow to accurately characterize solid-solid interphase decomposition of the Cl-doped Na₃PS₄ (NPSC), a sodium superionic conductor, to determine the effect of the Cl-doping [25]. We employ a full suite of structural and electrochemical characterization techniques to gain a comprehensive understanding of the decomposition mechanisms of the SSI and the role that NaCl plays in the stability of the cell. Using this information, we can better engineer interfaces and design electrolytes with not only superionic conductivity, but also effective passivation against elemental anodes to enable high performance batteries.

2.2 Experimental Methods

2.2.1 Synthesis and characterization

Pure t-Na₃PS₄ was synthesized from reagent-grade Na₂S (Sigma Aldrich, 99%) and P₂S₅ (Sigma Aldrich, 99%). The precursors were ground in agate mortar and pestle in a molar ratio of 75:25, respectively. To introduce the chloride dopant, NaCl (Alfa Aesar, 99.99%) was mixed into the previous precursors following the chemical reaction $(1.5 - x)Na_2S + 0.5P_2S_5 + xNaCl \rightarrow Na_{3-x}PS_{4-x}Cl_x$. The resulting mixtures were then sealed under vacuum in a quartz tube, heated to 1123 K (850 °C) for 6 hours, and then quenched in ice water. Subsequently, the sample was ground in a mortar and pestle and sealed in an ampoule to be heat treated at 693 K (420 °C) for 3 hours to stabilize the tetragonal phase.

Raman spectroscopy was performed using an inVia Raman microscope (Renishaw) with a 0.5 cm⁻¹ resolution. Samples were sealed on a glass slide using Kapton tape. Powder samples were used for the uncycled solid electrolyte and fragment samples of the SSI on the solid electrolyte were obtained after assembling and cycling a cell as described in the section below. Samples were imaged using a 514 nm laser at 10% laser strength to minimize beam damage. The Raman shift range was from 100 cm⁻¹ to 1000 cm⁻¹.

2.2.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) samples were prepared by removing the current collector on the anode side, exposing the SSI on the solid electrolyte. XPS measurements were carried out in an AXIS Supra (Kratos Analytical) at a chamber pressure of approximately 10^{-7} Pa. A monochromatized Al K α X-ray source was used. Samples were transferred into the UHV chamber through a loadlock from an attached glovebox. Spectral data was evaluated using the CasaXPS software suite. Charge correction was performed relative to the C 1s signal of adventitious carbon (284.8 eV). XPS peak fitting was conducted using Na 1s, O 1s, S 2p, P 2p, and Cl 2p region scans.

2.2.3 Electrochemical characterization

The electrochemical stability of the anode interface was investigated using symmetric cells. The electrolyte powders (150 mg) were uniaxially compressed in a 13 mm polyetheretherketone (PEEK) die to a pressure of about 360 MPa. Na metal foils or Na3Sn powders (50 mg) were attached to either side of the electrolyte pellet. A 50 uA galvanic square-wave was applied for 10 mins and then a reverse current was applied for 10 mins to strip and plate Na metal. The voltage of the symmetric cell was measured and the area-specific resistance (ASR) was calculated following Ohm's law.

A full cell was assembled using a TiS_2 composite cathode against a Na metal anode. TiS₂ was mixed with t-Na_{3-x}PS_{4-x}Cl_x, in a 1:2 weight ratio. The solid electrolyte powders (150 mg) was cold pressed at 360 MPa in a 13 mm polyetheretherketone (PEEK) die. The cathode blende (10 mg) was cold pressed at 360 MPa on top of the electrolyte layer. Pure Na metal was attached to a titanium current collector and cold pressed into the die at approximately 30 MPa. The cell was cycled using Arbin battery cycler at room temperature. Cycling was performed at a C/10 rate for 10 cycles over a voltage window from 1.2 V to 2.4 V. The cell was cycled inside an Ar filled glovebox.

2.3 Results and Discussion

2.3.1 Structural characterization of Na-solid electrolyte SSI

Scanning electron microscopy (SEM) images of the solid-solid interphase (SSI) on Na metal are shown in **Figure 2.1**. The interphase was formed as the cell completed 10 cycles. In the insets, images of the regions corresponding to the SSI and Na metal are shown, and there is a visible difference in the morphology of the two regions. The SSI is more than 100 μ m thick, and there appears to be poorer interfacial contact and density at the interphase.

Raman spectroscopy was used to determine the chemical species present in the SSI. **Figure 2.2** shows the acquired spectra of the pristine NPS and NPSC after cycling. There was no difference between the acquired spectra for the undoped and doped material because the primary byproduct of the doping on the interphase, NaCl, is not Raman active. The acquired Raman spectra for the pristine electrolyte shows sharp peaks at about 415 cm⁻¹, 550 cm⁻¹, and 575 cm⁻¹, and shows broader weaker peaks around 190 cm⁻¹, 210 cm⁻¹, and 280 cm⁻¹. The peak at 415 cm⁻¹ is attributable to the symmetric stretching of [PS₄]³⁻ tetrahedra, which is the major P-S ligand present in the solid electrolyte [26-29]. The other two sharp peaks at 550 cm⁻¹ and 575 cm⁻¹ are due to asymmetric stretching of the

tetrahedral units [26]. The peaks at 190 cm⁻¹ and 210 cm⁻¹ are attributable to Na₂S and P_4S_{10} , respectively, which are precursors in synthesis [26].

The Raman spectra of the cycled SSI shows all the same peaks of the pristine electrolyte, though broadened and less intense. We observe another peak at 380 cm⁻¹ corresponding to symmetric stretching of $[P_2S_6]^{4-}$, which is likely Na₄P₂S₆, the most stable of the compositions in the phase diagram at room temperature [26-28, 30]. Additionally, broad peaks appear at 450 cm⁻¹ and 460 cm⁻¹ which could be due to polysulfides, such as Na₂S₂ and S₈, respectively [26]. The presence of polysulfides as well as the number of P-S bonding structures give rise to the amorphous nature of the interphase, and suggest that the interphase may react slowly through these intermediate polysulfides or may not completely react at all. It also suggests that although there are identifiable short-range orderings (SRO), a sample such as this may not possess the long-range ordering (LRO) to make other techniques, such as diffraction, useful for phase identification.

2.3.2 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed to determine the species present at the interphase. XPS spectra were obtained for pristine and cycled NPS and NPSC and are shown in **Figure 2.3**a. The full spectra were acquired and peaks attributable to Na, P, S, Cl, O, and C were observed with none unaccounted for. The chemical bonding environments of the desired elements were determined using the S 2p, P 2p, and Cl 2p regions and are shown in **Figure 2.3**b, and the binding energies were calibrated to adventitious carbon (248.8 eV). For the pristine undoped sample, we observe two spin-orbit doublets in the S 2p envelope that are characteristic of the P-S-Na and P=S bonding

states. These peaks are found at 161 eV and 162 eV, respectively. In the P 2p region, we detect one doublet associated with the tetrahedrally-coordinated P in $[PS_4]^{3-}$ at 131 eV. Upon cycling, we detect one new spin-orbital doublet in the S 2p region and two more in the P 2p region. Sulfur shifts to a lower binding energy around 159 eV, attributed to the decomposition product Na₂S. Phosphorus also shifts to lower binding energy with Na₃P found at 125 eV and a reduced phosphorus phase at 126 eV. These findings are consistent with those reported in literature [24].

For the doped samples, the pristine spectra is similar to the undoped sample. We observe an additional doublet in the P 2p region, ascribed to S-P-Cl bonding, which suggests the Cl⁻ was successfully incorporated in the $[PS_4]^{3-}$ tetrahedra. After cycling, we detect a shift towards lower binding energy in the Cl 2p region, which we attribute to NaCl at 198 eV. The decomposition products of the interphase are ascribed to Na₂S, Na₃P, reduced P, and NaCl. We note that NaCl and Na₃P are both Raman-inactive and thus, did not appear in the Raman spectra. We speculate that the decomposition reaction is as follows for undoped and doped samples:

 $Na_3PS_4 + 8 Na \rightarrow 4 Na_2S + Na_3P$ $Na_{47}P_{16}S_{63}Cl + 128 Na \rightarrow 63 Na_2S + 16 Na_3P + NaCl$

In this case, $Na_{47}P_{16}S_{63}Cl$ is an analogous stoichiometric ratio to 6.25% at. Cl-doped Na_3PS_4 . We speculate that the presence of polysulfides in the Raman spectra indicates that these reactions have metastable intermediates or progress very gradually towards completion.

2.3.3 Electrochemical characterization of SSI

Symmetric cells using Na metal were assembled to investigate the stability of the Na-solid electrolyte SSI. To quantify the effect of the Cl-doping on the interphase stability, a galvanic square-wave was pulsed through symmetric cells with NPS and NPSC and the voltage was measured. The data is shown in **Figure 2.4**. The area-specific resistance (ASR) was then calculated following Ohm's law using the area of the pellet, which was 1.317 cm². In the undoped sample, the calculated ASR grew from 1986 Ω cm² to 3740 Ω cm². In the doped sample, the ASR grew from 992 Ω cm² to 2139 Ω cm².

Taking the product of the ASR and the current density, the expected voltaic loss across the undoped interphase starts at approximately 100 mV and increases to almost 200 mV. In the doped case, the overpotential increases from just under 50 mV to about 100 mV. A third cell was assembled, using a solid electrolyte with a double the concentration of Cl-doping (12.5% at.). This cell showed very good stability, but with a much larger resistance. This may indicate that increasing the Cl⁻ content in the electrolyte can improve the stability of the interphase, and give credence to the idea of "salting" the interphase. Nevertheless, there must be a compromise between the stability and conductivity. The loss in the third cell remains about 300 mV and this net loss will be detrimental to the cyclability of the cell.

2.3.4 Electrochemical performance

To investigate the effects of decomposition on the cell's performance, full-cells were constructed using a TiS_2 charged cathode and a Na metallic anode. The choice of the TiS_2 cathode is motivated by its suitable operating voltage (~1.7 V versus Na/Na⁺) as well

as its fast kinetics for Na⁺ intercalation [31]. The cell was galvanostatically cycled from 1.2 V to 2.4 V. A current density of approximately 50 μ A cm⁻² was applied, corresponding to a C/10 rate. The charge-discharge profile of the undoped and doped full-cells are shown in **Figure 2.5**a and **Figure 2.5**b, respectively. The theoretical capacity of the TiS₂ active material is 240 mAh g⁻¹. For the undoped cell, the discharge and charge capacity of the first cycle were 180 mAh g⁻¹ and 100 mAh g⁻¹, respectively. For the doped cell, the discharge and charge capacities of the first cycle were 190 mAh g⁻¹ and 135 mAh g⁻¹, respectively. The source of the large irreversible capacity of the first cycle and subsequent cycles is presumably due to the interphase decomposition. After 10 cycles, the final specific capacities of the undoped cells were ~70 mAh g⁻¹ and 110 mAh g⁻¹, respectively.

The doped cell exhibits a larger reversible capacity and lower overpotentials. It also shows better redox kinetics in the cathode which is signified by the appearance of voltage plateaus associated with phase transformations of TiS_2 from octahedral to trigonal prismatic and from trigonal prismatic to trigonal antiprismatic at roughly 2.0 V and 1.5 V, respectively [31]. By comparison, the undoped cell resembles the voltage profile of a solid solution, showing sluggish kinetics in the cathode.

2.5 Conclusion

In conclusion, we have investigated the decomposition mechanism of the Cldoped Na₃PS₄ and find that there is an intrinsic instability against Na metal and this decomposition results in the growth of a thick interphase layer. The reaction is spontaneous, but seemingly gradual, due to the presence of intermediate polysulfides and reduced phosphorus in addition to the expected Na₂S and Na₃P constituents. Increasing the Cl-doping concentration slowed the formation of the interphase at the expense of ionic conductivity, which proved impractical for implementation in a full-cell architecture. Nevertheless, the doped cell had better capacity retention and showed better cathode activation and kinetics. We demonstrate the "salting" effect that Cl-doping has on the interphase and show that there is potential to passivate or stabilize using doping methodologies presented in this work.

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2.7 Acknowledgements

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Figure 2.1 Characterization of Na/NPS interphase. SEM image of solid-solid interphase on Na metal (left), interphase (top-right), and Na metal (bottom-right).



Figure 2.2 Structural characterization of Na-NPSC SSI. Raman spectra of pristine (as-synthesized) solid electrolyte powders and decomposed interphase.



Figure 2.3 Chemical composition of SSI. (a) *Full spectra of undoped and doped pristine electrolyte and interface after cycling.* (b) S 2p, P 2p, and Cl 2p peak fitting models of pristine NPSC and interface after cycling.



Figure 2.4 Na-SE Interphase Stability. Galvanic square-wave cycling of (a) Na|NPS|Na symmetric cell, (b) Na|NPSC|Na (x = 6.25%) symmetric cell, and (c) Na|NPSC|Na (x = 12.5%) symmetric cell. A 50µA current was pulsed for 10 mins in either direction and the voltage of the symmetric cell was recorded. The area-specific resistance (ASR) was calculated following Ohm's law.



Figure 2.5 Electrochemical performance of solid electrolytes. Galvanic cycling of Na-TiS₂ cell using (a) NPS and (b) NPSC. Cells were cycled at room temperature from 1.2 V to 2.4 V at a current density of about 50 μ A cm⁻² which corresponds to a C/10 rate.