Exceptionally High Ionic Conductivity in Na$_{3}$P$_{0.62}$As$_{0.38}$S$_{4}$ with Improved Moisture Stability for Solid-State Sodium-Ion Batteries

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Na-ion batteries (NIBs) have the potential to compete with the widely used Li-ion batteries (LIBs) for stationary energy storage applications and could revolutionize the landscape of electrochemical energy storage, thanks to the abundance of sodium precursor and the cost advantage.[1] Severe safety issues exist in NIBs because of extremely high reactivity of sodium metal in volatile and flammable organic liquid electrolyte.[2] Solid-state NIB with solid-state electrolyte (SSE) is attractive because it can potentially address the safety issues and also achieve long cycle life.[3]

The significant challenge exists in the development of Na-ion SSE with high ionic conductivity that is comparable with liquid counterparts (1–6 mS cm$^{-1}$ at room temperature) to promote fabrication of safe solid-state NIBs.[4] Oxide ceramic and sulfide glass-ceramic Na-ion conductors as potential Na-ion SSE have been explored.[5–6] NASICON-type oxides (such as Na$_{1+x}$Zr$_2$Si$_3$O$_{12}$ with 0 $\leq$ x $\leq$ 3)[6] and β'-alumina[7] are well-known Na-ion SSEs exhibiting high room-temperature ionic conductivity over 1 mS cm$^{-1}$. However, their harsh synthesis conditions (e.g., high synthesis temperature $\approx$1200 °C), high annealing temperature (>1000 °C), and poor room-temperature electrolyte–electrode contact make their large-scale applications complicated and expensive.[8] In contrast to those oxide-based conductors, sulfide-based SSEs are more promising because of their high ionic conductivity, good contact with electrode, low-temperature process capability, and low grain boundary resistance, which have been proved in all-solid-state LIBs.[9]

Inspired by the success of the Li-ion SSEs, considerable efforts have recently been made on the development of Na-ion sulfide-based SSEs. Glass-ceramic electrolyte Na$_3$PS$_4$[7a,10] was found to be with a room-temperature conductivity of 0.2 mS cm$^{-1}$, which was increased to 0.74 mS cm$^{-1}$ by silicon doping[11] and 1.14 mS cm$^{-1}$ by halogen doping.[12] Anion substitution of S by Se (Na$_3$PSe$_4$)[13] and cation substitution of P by Sb (Na$_3$SbS$_4$)[14] further increased the ionic conductivity to 1.16 and 1.05 mS cm$^{-1}$, respectively. Recently, Richards et al.[15] reported a new family of Na$_{10}$MP$_2$S$_{12}$ (M = Sn, Ge, and Si) and predicted a super high ionic conductivity of 10.28 mS cm$^{-1}$ for Na$_3$SiP$_2$S$_4$ based on first-principles simulations. Despite considerable efforts, current Na-ion sulfide-based SSEs, including the aforementioned ones, still suffer from either poor ionic conductivity (<1 mS cm$^{-1}$) or unsatisfied moisture stability at room temperature, motivating the development of Na-ion SSEs, which could address these two challenges.

In the present work, we report a new Na-ion SSE of Na$_{3}$P$_{0.62}$As$_{0.38}$S$_{4}$ (0 $\leq$ x $\leq$ 1). A superior high Na-ion conductivity of 1.46 mS cm$^{-1}$ at room temperature is achieved for x = 0.38 (i.e., Na$_{3}$P$_{0.62}$As$_{0.38}$S$_{4}$)—the highest conductivity reported so far in sulfide-based Na-ion conductors. It is further found that Na$_{3}$P$_{0.62}$As$_{0.38}$S$_{4}$ possesses good moisture stability, dramatically improved in comparison with Na$_3$PS$_4$. The Na-ion conductor of Na$_{3}$P$_{0.62}$As$_{0.38}$S$_{4}$ was further examined in a solid-state NIB, demonstrating a stable electrochemical performance. The exceptionally high conductivity in Na$_{3}$P$_{0.62}$As$_{0.38}$S$_{4}$ with respect to the endmember compounds Na$_3$PS$_4$ (0.2 to 0.46 mS cm$^{-1}$)[7a,11a] and Na$_3$As$_4$ (0.027 mS cm$^{-1}$, see details below) is beyond the current understanding of ionic conductivity for solid-state conductors, for instance, the body-centered-cubic-like anion framework[16] and the increased conductivity with increasing volume.[17] Density functional theory (DFT) calculations uncover that the improvement of conductivity stems from a longer Na–S bond length in the unstable saddle point structure of transition state (TS), regulated by the duel effects of alloying element arsenic (As), i.e., lattice expansion for high conductivity and weaker As–S bond (stronger Na–S bond) for low conductivity. The revealed mechanism opens a new avenue to design SSEs with high ionic conductivity and promising moisture stability.

Figure 1a shows a synchrotron X-ray diffraction (SXRD, wavelength $\lambda$ = 0.117 415 Å) pattern of as-prepared Na$_3$PS$_4$ powder together with the corresponding whole pattern fitting refinement with reference to a tetragonal structure of Na$_3$PS$_4$ (PDF 97-007-2860, space group P$\overline{4}$2$_1$c). Calculated R factor and
Considering the larger ionic radius of As\(^{5+}\) \((0.46 \text{ Å})\) versus P\(^{5+}\) \((0.38 \text{ Å})\), this suggests that alloying element As is successfully substituted for P\(^{5+}\). Figure 1c,d shows the SXRD pattern and the corresponding whole pattern fitting refinement of Na\(_3\)P\(_{0.62}\)As\(_{0.38}\)S\(_4\). Structural parameters as well as calculated \(R\) factor, summarized in Table S1 (Supporting Information), show that lattice parameters \(a\) and \(b\) of Na\(_3\)P\(_{0.62}\)As\(_{0.38}\)S\(_4\) are elongated while lattice parameter \(c\) is slightly compressed, in comparison with Na\(_3\)PS\(_4\). These features of Na\(_3\)P\(_{0.62}\)As\(_{0.38}\)S\(_4\) are favorable for Na-ion conductivity in terms of structure (see DFT results and discussion below). The P/As molar ratio was determined by inductively coupled plasma emission spectrometry (ICP-AES) and found to be 0.62/0.38.

Figure 2a shows Na-ion conductivity in Na\(_3\)P\(_{1-x}\)As\(_x\)S\(_4\) at room temperature as a function of \(x\). The as-prepared Na\(_3\)PS\(_4\) \((x = 0)\) possesses a conductivity \(\sigma\) of 0.2 mS cm\(^{-1}\), agreeing well with the reported value.\([7a]\) The ionic conductivity of Na\(_3\)P\(_{1-x}\)As\(_x\)S\(_4\) increases with increasing As concentration, reaching a maximum value of 1.46 mS cm\(^{-1}\) with \(x = 0.38\) in Na\(_3\)P\(_{1-0.38}\)As\(_{0.62}\)S\(_4\), and then decreases to 0.4 mS cm\(^{-1}\) for Na\(_3\)P\(_{0.5}\)As\(_{0.5}\)S\(_4\) and 0.027 mS cm\(^{-1}\) for Na\(_3\)AsS\(_4\). To the best of our knowledge, 1.46 mS cm\(^{-1}\) is the highest ionic conductivity reported so far in sulfide-based Na-ion conductors. It is even comparable to the conductivities in organic liquid Na-ion electrolytes (1–6 mS cm\(^{-1}\) at room temperature).\([8]\) Figure 2b shows Arrhenius plots and the corresponding impedance plots of Na\(_3\)P\(_{0.62}\)As\(_{0.38}\)S\(_4\) within a temperature range between −120 and 100 °C. The impedance plots indicate that Na\(_3\)P\(_{0.62}\)As\(_{0.38}\)S\(_4\) is a pure ionic conductor, since it consists of a semicircle at high-frequency region and a spike at low-frequency region, corresponding to impedance contributions from (1) the bulk/grain and grain boundary, and (2) the electrode, respectively. The ionic conductivity was calculated based on the total resistance (bulk/grain and grain boundary resistance) obtained from an intercept crossed between the semicircle and the spike on the x-axis. The fitted activation energy is 0.256 eV for Na\(_3\)P\(_{0.62}\)As\(_{0.38}\)S\(_4\) as shown in Figure 2b, which is lower than those of Na\(_3\)PS\(_4\) (0.289 eV), Na\(_3\)P\(_{0.5}\)As\(_{0.5}\)S\(_4\) (0.268 eV), and Na\(_3\)AsS\(_4\) (0.341 eV), as shown in Figure S2 (Supporting Information). Cross-section scanning electron microscopy (SEM) images of Na\(_3\)P\(_{0.62}\)As\(_{0.38}\)S\(_4\) and Na\(_3\)PS\(_4\) pellets (Figure S3, Supporting Information) show the intimate contacts between compact particles obtained
Figure 3. Temperature-dependent ionic conductivities of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ in comparison with the reported Na-ion conductors. Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ exhibits the highest conductivity among sulfides and is comparable with β-alumina (a mixture of β and β” phases).

Figure 4. Stretching force constants (SFCs) of the low energy structure of Na$_3$P$_{0.5}$As$_{0.5}$S$_4$ from DFT calculations. a) The 128-atom supercell marked by the black unit cell lines used for phonon calculations. Two types of Na atoms refer to the ones in the original tetragonal cell (Na$_1$ in 2b site and Na$_2$ in 4d site of space group $P4_{2}1c$). b) Key SFCs between different atomic pairs. The lines are linear fittings of the Na—X (X = S, As, P, and Na) SFCs, showing the Na—S bonding strength is ultrasensitive to bond length change with respect to the other Na—X pairs.

in both of the two pellets, leading to a high density around 1.95 g cm$^{-3}$ for Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ pellet and 1.74 g cm$^{-3}$ for Na$_3$PS$_4$. Compact microstructure with high density is necessary for a fast ionic diffusion.

Figure 3 shows the temperature-dependent ionic conductivities in Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ along with those in Na-ion conductors reported in the literature. Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ shows a similar conductivity with respect to β-alumina (a mixture of β and β” phases) in the temperature range from 25 to 100 °C, and has at least one magnitude higher in conductivity than those in 50Na$_2$S-50P$_2$S$_5$, 60Na$_2$S-40GeS$_2$, 50Na$_2$S-50SiS$_2$, cubic Na$_3$PS$_4$ and Na$_2$Zr$_2$Si$_2$PO$_12$ NASICON. Even though the conductivity is slightly lower than the NASICON-type crystal (produced by Ceramtec), low-temperature process and good electrode-electrolyte contact offered by sulfide-based SSEs grant advantages for Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ to fabricate all-solid-state NIBs (vide infra). Even at low temperatures, it possesses a decent ionic conductivity, such as 0.2 mS cm$^{-1}$ at −20 °C, showing another advantage comparing to organic liquid electrolyte.

Besides the increased ionic conductivity in Na$_3$P$_{0.62}$As$_{0.38}$S$_4$, it is exciting to find that alloying element As could also improve the moisture stability. Figure S4 (Supporting Information) shows the XRD patterns of Na$_3$PS$_4$ and Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ powders exposed to air with 15% humidity at room temperature for 100 h. It clearly shows that Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ powders maintain the same XRD patterns after the exposure, while the new peaks (corresponding to the new phases/compositions due to its reaction with moisture) appearing in Na$_3$PS$_4$ powders. The corresponding impedance plots of the Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ pellet barely change upon the air exposure (Figure S4b, Supporting Information).

In contrast, a large increase in total resistance (bulk/grain and grain boundary resistance) is detected in the Na$_3$PS$_4$ pellet after the air exposure, which may be attributed to the composition or phase changes as indicated by the XRD results. In addition, activation energies for Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ before and after the air exposure are 0.256 and 0.269 eV, respectively. Differently, a huge increase in activation energy from 0.289 to 0.325 eV is found in Na$_3$PS$_4$ after the air exposure due to its composition or phase changes after reacting with H$_2$O. H$_2$S is believed to be one of the products after the reaction with H$_2$O in air. We thus monitor the concentration of H$_2$S by exposing Na$_3$PS$_4$ or Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ powders in air with a higher humidity of 45%. As shown in Figure S4c (Supporting Information), from the sample Na$_3$PS$_4$, the concentration of H$_2$S is detected to be 1.4 ppm after 30 s exposure and gradually increases to 1.8 ppm after 6 min. In contrast, no H$_2$S gas is detected from the Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ powder until the time reaching to 4 min. After 6 min, the concentration of H$_2$S reaches 1.3 ppm, but still lower than that of Na$_3$PS$_4$. The excellent moisture stability of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ mainly results from the moisture reactions shifted from the low energy ones (for example, Na$_3$PS$_4$ + H$_2$O → Na$_3$POS$_3$ + H$_2$S) to the high energy ones (for example Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ + H$_2$O → Na$_3$P$_{0.62}$As$_{0.38}$S$_3$ + H$_2$S and Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ + 8 H$_2$O → Na$_3$P$_{0.62}$As$_{0.38}$S$_4$-8H$_2$O) in terms of DFT calculations (not shown here). The enhanced moisture stability further shows promise of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ for processing and fabrication of solid-state NIBs in practical applications.

In an effort to probe the origin of high conductivity in Na$_3$P$_{1-x}$As$_x$S$_4$, Na-ion migration energies—which link directly to activation energy, and in turn, ionic conductivity—are analyzed by DFT calculations for three tetragonal structures of Na$_3$PS$_4$, Na$_3$AsS$_4$, and the simplest structure of Na$_3$P$_{0.5}$As$_{0.5}$S$_4$ (see the Supporting Information and structural details in Table S2 of the Supporting Information). As demonstrated in one example of Figure 4a, two kinds of sodium (Na$_1$ and Na$_2$)
together with two types of the nearest Na–Na neighbors with bond lengths around 3.5 Å is exist in the tetragonal Na3P1−xAsxS4, in which the Na1−Na2 bond is roughly along the a and b-axis direction and the Na2−Na3 bond along the c-axis direction. In addition, the Na1−Na2 bond length is about 0.02−0.03 Å shorter than the Na2−Na3 case, resulting in lattice parameters c > a, for example, a = 6.952 Å and c = 7.076 Å for Na3P0.5S4 at room temperature.[19c] Calculated migration energies as shown in Figure S7 (Supporting Information) reveal that Na-ion jumps along the Na1 bond are more favorable (with 30−40 meV lower energy) than those along the Na2−Na3 sites, indicating the a and b-directions are the dominant diffusion channels of Na-ion in Na3P1−xAsxS4. However, the general principle regarding the increase of ionic conductivity with increasing volume (or bond length)[16a,17] cannot explain Na-ion migration and the corresponding conductivity as a function of As concentration in the present work (Figure 2a), since the volume and various bond lengths (e.g., Na−Na and Na−S bonds) keep increasing with increasing As concentration in Na3P1−xAsxS4 (Figure 5a and Table S4, Supporting Information).

To examine the determining factor of Na-ion conductivity in Na3P1−xAsxS4, bonding strengths between all atomic pairs[20] are illustrated in Figure 4b: the stretching force constant (SFC) with respect to bond length for a low energy structure (SFC) with respect to bond length for a low energy structure (Figure 4a) from phonon calculations. These force constants are transferable in Na3P1−xAsxS4 by all examined SFCs from the present phonon calculations, agreeing with the finding in metal alloys.[21] Figure 4b shows that the strongest bonding is the P−S pair (≈11.8 eV Å−1) followed by As−S (≈10.9 eV Å−1), indicating the formation of PS3− and AsS42− anions. The present bond lengths and SFCs of P−S and As−S pairs agree reasonably well with the empirical estimations[22] bond length of 2.12 Å and force constant ≈15 eV Å−2 for P−S (PS3−); and bond length of 2.22 Å and force constant ≈14 eV Å−2 for As−S (AsS42−). By examining all the Na−X (X = S, As, P, and Na) SFCs, it is shown that the Na−S bonding strength is ultra-sensitive to the variation of bond length, since the slope of the Na−S linear fitting is 13−16 times steeper than the other Na−X linear fittings (Figure 4b). Hence, the Na−S bond length can serve as a criterion to judge Na-ion diffusivity and conductivity, but it fails to explain the variation of Na-ion conductivity (Figure 2a) based on the stable structures of Na3P1−xAsxS4 as shown in Figure 5a and Table S4 (Supporting Information).

Following the Na migration path in Na3P1−xAsxS4, it is found that the nearest Na−S bond length in the TS structure, an unstable saddle point related to the highest energy along Na-ion migration, correlates well with the Na-ion migration energy. Figure 5a shows that the nearest Na−S bond length in the initial state structure (IS, a stable structure with one Na-vacancy) keeps increasing with increasing As concentration. However, Figure 5b shows that the nearest Na−S bond length in the TS structures reaches the maximum at x = 0.5, showing a trend inversely proportional to the minimum Na-ion migration energy in Figure 5c, in line with the measured Na-ion activation energy and conductivity (Figure 2a and Figure S2, Supporting Information). Based on a binomial fitting for the migration energy data in Figure 5c (70.5, 65.9, and 84.0 meV) together with an additional migration energy of 68.5 meV from the low energy structure of Na3P0.5As0.5S4 (results not shown), the lowest migration energy is found to be at x = 0.38, in accordance with the maximum Na-ion conductivity with x = 0.38 (Figure 2a). The variation of the Na−S bond length in the TS structure (here the mentioned Na is the migrating Na atom) can be understood by the dual effects of alloying element As, viz., (i) lattice expansion as well as bond length (especially Na−S) increase by adding As, promoting the increase of ionic conductivity; and (ii) a weaker As−S bonding compared to the P−S bonding (Figure 4b), making the attraction of Na−S stronger and resulting in a shorter Na−S bond length in the predominant TS structure of Na-ion migration (Figure 5b) when further increasing As concentration, and hence a lower ionic conductivity. It is expected that the present finding about the dual effects of alloying element on Na-ion conductivity exists also in other chalcogenide-based conductors, since a longer bond length together with a weaker bonding (force constants) has been confirmed for various anions, for example, PS3−, AsS42−, AsSe42−, SbS42−, SiS4−, GeS4−, GeSe4−, SnS4−, and SnSe4−.[22] DFT calculations also indicate that Na3P1−xAsxS4 is stable at temperature as low as 100 K (−173 °C) (see the Supporting Information), indicating again Na3P1−xAsxS4 can be used even at low temperatures.

Electrochemical stability of Na3P0.62As0.38S4 was evaluated from cyclic voltammetry (CV) of Na/Na3P0.62As0.38S4/Sn cell at 80 °C, with Na as the counter/reference electrode and Sn as the working electrode. As shown in Figure 6a, both cathodic and anodic currents are observed near 0 V versus Na+/Na, which corresponds to sodiation with and desodiation from Sn, respectively. No significant oxidation current has been detected up to 5 V. The areas under the curves associated with Na deposition and dissolution process are 283.01 and 263.74 μA, respectively. The corresponding coulombic

Figure 5. Nearest Na−S bond length and the minimum migration energy of Na-ion in three 127-atom supercells. The nearest Na−S bond lengths in a) the initial states (IS) and b) the transition states (TS) during Na migrations. One Na vacancy is introduced in each structure, and the simplest Na3P0.5As0.5S4 structure based on the high energy structure of Na3P0.5As0.5S4 with space group P4 is used for simplicity. c) The minimum Na migration energies in these three structures.
efficiency is 263.74/283.01 = 93.2%, indicating that the deposition/dissolution of Na is highly reversible. The CV result indicates that Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ has a good compatibility with sodium metal and a wide electrochemical window.$^{[23,24]}$

All-solid-state Na-ion battery Na-Sn/Na$_3$P$_{0.62}$As$_{0.38}$S$_4$/TiS$_2$ was fabricated by pressing the Na-Sn alloy foil as anodes and the TiS$_2$ power as cathodes onto two faces of the Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ pellet. The obtained three-layer pellet was assembled into a 2032-type coin cell with stainless-steel discs as current collector. Figure 6b shows the charge–discharge curves of the Na-Sn/Na$_3$P$_{0.62}$As$_{0.38}$S$_4$/TiS$_2$ cell at 80 °C, under a current density of 4.8 mAg$^{-1}$ (0.02 C) within the voltage range from 1.17 to 2.4 V. The first discharge and charge capacities are 163 and 118 mAh g$^{-1}$, respectively, corresponding to a high initial coulombic efficiency of 72.4%. After nine cycles, the charging capacity still maintains at 103 mAh g$^{-1}$. The average cell voltage from the first to the ninth cycle is 1.77 V, which corresponds to the potential difference between the Na-Sn counter electrode (≈0.3 V vs. Na$^+$/Na) and the TiS$_2$ working electrode (≈2.0 V vs. Na$^+$/Na). We believe that the specific capacity and cycling performance of the cells could be further enhanced by engineering fabrication of the Na-Sn/Na$_3$P$_{0.62}$As$_{0.38}$S$_4$/TiS$_2$ three-layer pellet with improved interfacial contacts.

The poisonous nature of arsenic compound can raise a concern of toxicity regarding the use of Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ solid-state electrolyte. The poor solubility of arsenic sulfides in water and acid, which is quite different from the toxic oxide counterparts, could reduce the toxicity in preparation of Na$_3$P$_{1-x}$As$_x$S$_4$. However, since Na$_3$P$_{1-x}$As$_x$S$_4$ can react with water eventually generating toxic arsenic compound, great attention should be paid when dealing with sulfide electrolytes.

In summary, a new Na-ion SSE, Na$_3$P$_{0.62}$As$_{0.38}$S$_4$, electrolytes were prepared by ball-mill technique followed by heat treatment. The stoichiometric amounts of Na$_2$S (Alfa Aesar, anhydrous, analytical reagent), P$_2$S$_5$ (Sigma-Aldrich, 99%), and As$_2$S$_5$ (Sigma-Aldrich, 99.99%) were hand-ground before transferring to an agate jar. The mixture was ball-milled for 15 h at a speed of 510 rpm using a planetary ball mill (Across International). The obtained powders were cold pressed at 400 MPa into a pellet, which was 10 mm in diameter and 0.6–1.2 mm in thickness. All the processes were protected under Ar atmosphere. The pellet was sealed in an evacuated glass tube and heated up to 270 °C (1 °C min$^{-1}$). It was kept at 270 °C for 2 h before cooling down to room temperature at the same rate.

Characterization of Solid Electrolytes: Powder XRD measurements were performed on a Rigaku Miniflex II spectrometer with Cu K$_\alpha$ radiation, using XRD holder with beryllium window (Rigaku Corp.) for air sensitive samples. SXRD measurements were conducted at the beamline 11-ID-C of Advanced Photon Source (APS), Argonne National Laboratory, using X-rays with wavelength of 0.11725 Å. The specimens were sealed with Kapton tape in a glove box filled with high purity Ar gas, to avoid any side reactions with the air. Whole pattern fitting refinements on the SXRD data were performed using the JADE 2010 software (Materials Data Corp., California), with polynomial backgrounds fitting model at the order of 3. The cross-section morphology of the SSE pellets was investigated using scanning electron microscope (Nano630 FE-SEM). The P/As ratio was determined by ICP-AES (Perkin-Elmer Optima 5300). For moisture stability characterization, the Nalgene Transparent Polycarbonate Classic Design Desiccator (=16 L in volume, ThermoFisher Scientific Inc.) was employed, in which the humidity was well controlled by tuning the amount of molecular sieve inside and monitored by a hygrometer. Na$_2$P$_4$ and Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ pellets were put into the desiccator for air exposure after the humidity inside stabilized at 15%. Powders and pellets were
used for XRD and impedance measurements, respectively. To compare the amount of H$_2$S gas released from the Na$_3$PS$_4$ and Na$_3$P$_{0.62}$As$_{0.38}$S$_4$ powder samples, 200 mg of each powder was put into the desiccator where the humidity was tuned to 45% in order to accelerate the H$_2$S gas release, the concentration of H$_2$S was detected by a calibrated gas detector (Honeywell Analytics SPM Single Point Monitor). For ionic conductivity measurements, carbon-coated aluminum foils were pressed onto both faces of pellets under the pressure 400 MPa, serving as blocking electrodes. The pellet was assembled into a 2016-type coin with two stainless-steel discs as current collector. Electrochemical impedance spectroscopy measurements were carried out on Solartron ModuLab in the frequency range of 1 MHz to 0.1 Hz with an amplitude of 5 mV. Cyclic voltammetry of Na/Na$_3$P$_x$ (0.02 C, based on the theoretical capacity of TiS$_2$), within the voltage range from 1.17 to 2.4 V using a BTS-5V1mA projector augmented wave method. The selected exchange-correlation functional is the improved generalized gradient approximation for densely packed solids and their surfaces, i.e., the PBE0 functional since it describes well structural and phonon properties of sulfides as well as diffusion properties. In addition, a hybrid X-C functional of Heyd–Scuseria–Ernzerhof (HSE06) was also used to get accurate bandgap energy. The migration energies of Na-ion were predicted by the climbing image nudged elastic band method using five images according to the monovacancy (Va) mediated diffusion mechanism, and all the Na-Va migration pathways were calculated when possible. The reported migration energies were based on an average energy from all initial state structures. Phonon calculations were performed by the supercell method as implemented in the YPHON code with VASP as the computational engine. Other DFT details and results are given in the Supporting Information including, for example, the employed supercells, cutoff energies, and k-points meshes, as well as the predicted structural, thermodynamic, and migration properties, in comparison with experimental data available in the literature.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Z.Y. and S.-L.S. contributed equally to this work. The authors acknowledge financial support partially from the U.S. Department of Energy’s (DOE’s) Office of Electricity Delivery & Energy Reliability (OE) (under Contract No. 57558), and partially from the National Science Foundation (NSF) with Grant Nos. DMR-1310289 and DMR-1610430. The authors also appreciate the technical assistance on H$_2$S gas detection by Dr. Joan Redwing and Mr. Xiaotian Zhang at the Pennsylvania State University, partially on the resources of NERSC supported by the Office of Science of the U.S. DOE under Contract No. DE-AC02-05CH11231, and partially on the resources of XSEDE supported by NSF with Grant No. ACI-1053575. Synchrotron X-ray diffraction characterization was supported by the U.S. DOE’s Office of Energy Efficiency and Renewable Energy (under Contract No. DE-AC02-06CH11357 from the Vehicle Technologies Office). Use of the Advanced Photon Source was supported by the U.S. DOE’s Office of Basic Energy Efficiency and Renewable Energy (under Contract No. DE-AC02-06CH11357).

Received: October 15, 2016
Revised: December 21, 2016
Published online: February 20, 2017