

Ion Migration Mechanisms in the Sodium Sulfide Solid Electrolyte $Na_{3-x}Sb_{1-x}W_xS_4$

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Cite This: Chem. Mater. 2022, 34, 4166–4171



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ABSTRACT: The desire to increase the energy density and enhance the safety of batteries has motivated interest in solid-state batteries that employ solid electrolytes. Recently, the sodium solid electrolyte, $Na_{3-x}Sb_{1-x}W_xS_4$, was reported to exhibit an ionic conductivity exceeding that of all lithium (and sodium) solid conductors. Notably, this compound's crystal structure contains complex anions—specifically, tetrahedral SbS_4 and WS_4 . Prior studies on related solid electrolytes have argued that reorientations of the complex anions facilitate cation mobility through the so-called paddlewheel effect. Here, *ab initio* molecular dynamics are used to probe potential contributions of coupled cation—anion dynamics on the mobility of Na-ions. Although Na^+ migration is observed to involve the concerted motion of multiple Na-ions, limited evidence is found for contributions to Na migration from reorientations of the SbS₄ and WS₄ tetrahedra. This implies that the high conductivity is well explained



by a classical vacancy model and a strong overlap of cation vibrational modes with anion librations.

INTRODUCTION

Concerns over safety and the energy density of conventional Li-ion batteries have stimulated interest in the development of solid-state ion conductors. These "solid electrolytes" (SEs) are viewed as an alternative to the liquid electrolytes used in today's Li-ion batteries.¹ Moreover, SEs that employ sodium as the working ion may enable lower-cost and more abundant chemistries relative to Li-based systems.

Toward the goal of developing a Na-based solid-state battery, in 1992, Jansen et al. reported a high ionic conductivity of 4.2×10^{-3} mS cm⁻¹ at 50 °C in sodium thiophosphate, Na₃PS₄.² In 2012, Hayashi et al. demonstrated that crystallization from the glassy state enhanced the conductivity of Na₃PS₄ by nearly 2 orders of magnitude to 0.2 mS cm⁻¹ at ambient temperature.³ In 2016, a conductivity of 1 mS cm^{-1 4-6} was reported for sodium antimony sulfide, Na₃SbS₄. More recently, aliovalent substitutions of tungsten for Sb in this compound, $Na_{3-x}Sb_{1-x}W_xS_4$ (NSWS), have increased the conductivity further to 32 mS cm⁻¹ (x = 0.12) and 41 mS cm⁻¹ (x = 0.10).^{7,8} Jalem et al. used density functional theory to investigate the effects of aliovalent doping of W and Mo in Na₃SbS₄. They concluded that the enhanced conductivity can be explained by a decrease in the activation energy, which correlated with the smaller tetrahedra volume of WS4 and MoS_4 compared to that of SbS_4 .

Recent measurements have shown that several solid electrolytes that exhibit high ionic conductivity and contain complex anions (e.g., PS_4) exhibit rotational dynamics among the anions. These dynamics can couple to the translational motion of the cations through the so-called paddlewheel

effect.^{10–15} For example, the current authors reported that lithium migration in glassy Li₃PS₄ at ambient temperature occurs via a mechanism that combines the concerted motion of lithium ions with large, quasi-permanent reorientations of PS₄^{3–} anions.¹² Earlier studies have also reported that paddlewheel dynamics are common in rotor phases, whose complex anions exhibit significant rotational disorder.¹⁶ Given the extremely high conductivity reported for Na_{3-x}Sb_{1-x}W_xS₄, and the fact that it contains tetrahedral SbS₄^{3–} and WS₄^{2–} anions, it is natural to ask whether anion rotational dynamics contribute to its exceptional mobility for sodium ions.

To answer this question, here Na-ion migration in $Na_{3-x}Sb_{1-x}W_xS_4$ (x = 0.125) is examined in detail at the atomic scale. Specifically, *ab initio* molecular dynamics (AIMD) was used to reveal the mechanisms associated with Na-ion migration and to characterize potential correlations with the dynamics of the surrounding anion "cages". It is observed that Na-ion migration at ambient temperature involves the concerted motion of multiple Na-ions. Nevertheless, during these migration events, limited evidence is observed for the presence of correlated reorientations of the anion tetrahedra, implying that paddlewheel dynamics do not

Received:February 17, 2022Revised:April 6, 2022Published:April 22, 2022





contribute to the high Na-ion conductivity of this phase. Instead, the high conductivity is well explained by a classical vacancy model and a strong overlap of cation vibrational modes with anion librations.

COMPUTATIONAL METHODS

First-principles calculations were performed with the Vienna ab initio simulation package (VASP).^{17–19} Core-valence electron interactions were treated with the projector-augmented wave method²⁰ with valence electron configurations of Na [3s¹], Sb [5s²5p³], W [6s²5d⁴], and S [3s²3p⁴]. The generalized gradient approximation in the formulation of Perdew–Burke–Ernzerhof was used for the exchange and correlation.^{21,22} The plane-wave basis included kinetic energies up to 360 eV. Molecular dynamics (MD) simulations were performed using Parrinello–Rahman dynamics in the NPT ensemble in combination with a Langevin thermostat.^{23,24} The friction coefficient for the atomic species and lattice was 10 ps⁻¹ with a lattice mass of 1000 amu. The MD time step was 2 fs. A Γ-only k-point mesh was used to sample reciprocal space. Velocity scaling was used to heat the system from 300 to 1000 K. All systems were equilibrated for 3 ps followed by 80 ps production runs at one of several different temperatures: 300, 400, 500, 600, 700, 800, 900, and 1000 K.

Figure 1 shows the computational cell of $Na_{3-x}Sb_{1-x}W_xS_4$ (x = 0.125). This cell is a 2 × 2 × 2 enlargement of the conventional unit



Figure 1. Computational cell of $Na_{3-x}Sb_{1-x}W_xS_4$ (x = 0.125). Sodium atoms are depicted as gray spheres, sulfur as yellow spheres, SbS_4 as brown tetrahedra, and WS_4 as green tetrahedra.

cell (*I*-43*m* space group) (a = 7.19 Å) reported by Hayashi et al.⁷ The cell contains 126 atoms, with two WS₄ tetrahedra and two Na vacancies. The vacancy concentration used in the present simulations is similar to those that have been reported in experiments to maximize the Na-ion conductivity, x = 0.12 and 0.10.^{7,8} The initial positions of the vacant Na sites were selected based on an energy minimization across the 1128 possible configurations (Figure S1).

RESULTS

Sodium Migration Mechanism. Sodium migration events were identified during AIMD using a previously employed protocol.¹² A migration event occurs if a Na-ion hops by a minimum distance of 1.6 Å within a transition time of 3 ps and maintains a residence time of 3 ps preceding and following the transition. Using this approach, Figure 2a illustrates that six migration events were identified over an 80 ps AIMD trajectory at 300 K. The number of Na-ions that migrated during this simulation ranged from several single Naion events to an event that included three distinct Na-ions moving simultaneously (labeled as "3" in Figure 2a at ~28 ps). An illustration of this concerted, 3-ion event is shown in Figure 2b. Na positions 5 ps prior to and following the time of the migration event are labeled "B" and "E", respectively. At the beginning of the migration event, a Na vacancy is located at position "E" of the cyan-colored spheres. Subsequently, three Na-ions cooperatively migrate left to right along the horizontal direction (corresponding to the positive direction of the *a*-axis) through adjacent Na sites, displacing the vacancy at a distance equal to three Na lattice sites in the opposite direction. At the end of the migration event, the vacancy is located at position "B" of the orange-colored spheres. The orientation of the neighboring SbS_4 (brown and yellow) and WS_4 (green and yellow) anions is displayed at the event time.

Figure 2c illustrates the rotational motion of the nearestneighbor SbS₄/WS₄ anions during the concerted migration event depicted in Figure 2b. (Rotational motion of all anions within the simulation cell over the course of the simulation time is discussed below.) The displacement of the Na-ions is shown using black lines and corresponds to the left axis, while the rotational displacements of the neighboring anions are shown with blue hues on the right axis. Four lines for each shade of blue are shown, corresponding to rotational displacements of the four vectors from the anion center of mass to its tetrahedrally coordinating S atoms. The top row of plots in Figure 2c shows the dynamics of the three nearestneighbor SbS₄ anions, and the bottom row shows the same behavior for the two neighboring WS₄ anions. These data show that the rotational displacements of the anions during the Naion migration event are small-~10° at most. The displacement of Na is more correlated with SbS₄ compared to that with WS₄ due to the smaller nearest-neighbor distance of SbS₄ anions for the trajectory illustrated. To place the magnitude of these reorientations in context, it is helpful to refer to a similar analysis that was previously performed on PS₄ anion rotations in Li₃PS₄ glass at 300 K. In the glass, much larger sustained reorientations as large as 60° were observed to coincide with cation migration.¹² Correlations between the rotational dynamics of tetrahedral anions and the migration of Na cations were also discussed for the Na-ion conductors $Na_{11}Sn_2SbS_{12}$ and $Na_{11}Sn_2PS_{12}$.¹¹ Specifically, the rotational dynamics of SbS₄ anions in Na₁₁Sn₂SbS₁₂ were reported to be less pronounced compared to those of PS₄ in Na₁₁Sn₂PS₁₂¹¹ due to the stronger ionic bonding present in Sb-S bonds. The small size of the anion rotations in Na_{3-x}Sb_{1-x}W_xS₄ suggests that paddlewheel dynamics are not significant in this compound.

Displacement plots for all migration events shown in Figure 2a and from an additional MD trajectory at 300 K are shown in Figures S2–S5. The rotational displacements for all anions over the course of 80 ps AIMD simulations at 300 and 700 K are shown in Figures S6 and S7. The magnitude of rotational displacements at 300 K is similar to those shown in Figure 2c and does not exceed ~20°. At 700 K, these displacements can be as large as 40°. At temperatures of 800 K and above, the reorientations of a few SbS₄ and WS₄ were observed to be even larger—greater than 100°. However, these temperatures are similar to the melting temperature of the related phase Na₃PS₄, 790 K.² It is not guaranteed that these high-*T* dynamics are representative of the dynamics at ambient temperature.

Ion Dynamics. The preceding analysis has focused on the details of individual migration events. To complement those analyses, time correlation functions have been used to gain insight into the average, collective dynamics of the complex anions. The anion reorientation autocorrelation function,²⁵ C(t), is defined as



Figure 2. Characterization of Na-ion migration events, and their correlation with rotational displacements of SbS₄ and WS₄ anions, in Na_{3-x}Sb_{1-x}W_xS₄ (x = 0.125) at 300 K. (a) Identification of migration events. (b) Illustration of the cooperative Na-ion migration event labeled "3" in panel (a), and the structure of its surrounding anion cage structure. Overlapping colored spheres represent the positions of the three distinct Na-ions during a 10 ps trajectory; the beginning and ending positions of each Na-ion are labeled "B" and "E", respectively. Tetrahedra anions are colored yellow for S, brown for Sb, and green for W. Their instantaneous orientations are shown at the time of the migration event. (c) Displacements of Na-ions (black line, left axis) that participate in the migration event labeled "3" in panel (a) and the coinciding angular displacements of the nearest-neighbor SbS₄ (top panel) and WS₄ (bottom panel) anions (blue hues, right axis). The ID for each Na, SbS₄, and WS₄ anion appears in the top left corner of each plot. Four rotational displacements are plotted for each anion using a common color; these displacements correspond to rotations of the four sulfur atoms about the center of mass of the tetrahedra. Displacement plots for all migration events are shown in Figures S2–S5.

$$C(t) = \frac{1}{N\tau} \sum_{i}^{N} \int_{0}^{\tau} u_{i}(t') \cdot u_{i}(t'+t) dt'$$
(1)

where u_i is the orientation of the *i*-th anion, *N* is the number of anions, and τ corresponds to the simulation time. C(t) is approximately equal to 1 if the anions do not alter their orientations; C(t) will decay to zero if the anions undergo significant reorientations over a time *t*. Figure 3a plots C(t) for the SbS₄ (solid lines) and WS₄ (dashed lines) anions at several temperatures. For both anion types and for all temperatures investigated, C(t) is approximately equal to 1, signifying that their orientations remain "fixed" near their initial orientations. The near-constancy of the anion orientations indicated by the autocorrelation function is consistent with the relatively small rotational displacements observed during Na-ion migration

events (Figure 2) and with the displacement data shown in Figures S6 and S7. The present behavior differs significantly from that observed in Li_3PS_4 glass and $M_2B_{12}H_{12}$, where a rapid decay of C(t) to zero indicated that the anions undergo rapid and large reorientations.^{12,26}

The power spectrum, Z(t), for cation vibration and anion libration was calculated from the Fourier transform of the normalized velocity autocorrelation function, $\langle \mathbf{x}(t') \cdot \mathbf{x}(t' + t) \rangle / \langle \mathbf{x}^2 \rangle$. Here, \mathbf{x} is the linear velocity of the cation or angular velocity of the complex anions. The power spectrum of Na, SbS₄, and WS₄ is shown in Figure 3b and compared to that of the glassy and (crystalline) γ phases of Li₃PS₄. (The dynamics of Li₃PS₄ were investigated in detail in a prior report.¹²) Regarding the spectra for the cations (top panel of Figure 3b), it is evident that the vibrational modes for Na in NSWS have a



Figure 3. (a) Reorientation autocorrelation function for SbS₄ (solid lines) and WS₄ (dashed lines) anions as a function of temperature. (b) Power spectrum of the linear velocity autocorrelation (top panel) and angular velocity autocorrelation (bottom panel) at 300 K in Na_{3-x}Sb_{1-x}W_xS₄ (x = 0.125), glassy-Li₃PS₄, and γ -Li₃PS₄.

higher density of states at lower frequencies compared to that of Li in either Li_3PS_4 phase. In NSWS, the peak in the Na spectrum is relatively narrow and occurs close to 4 THz, whereas in Li_3PS_4 , the peaks fall in the range of 6–10 THz, with a much broader distribution of frequencies. Importantly, the density of vibrational modes for the Na cations at low frequencies is greater than in Li_3PS_4 . Muy et al. have argued that the density of low-frequency modes is an important descriptor for predicting ionic mobility.^{27,28} In agreement with this theory, the relative ordering of the ionic conductivities of the three phases examined in Figure 3b follows their respective peaks in the cation vibrational power spectra in reverse order, i.e., NSWS has the highest conductivity but lowest-frequency peak, LPS glass has intermediate conductivity and peak frequency, etc.

Regarding anion rotational dynamics, the spectra for librations of both SbS4 and WS4 in NSWS exhibit peaks near 5-6 THz, with a lower-frequency shoulder at \sim 2.5 THz. These two features are also present to a lesser degree for PS_4 in the Li_3PS_4 phases,¹² with the primary difference being that the peaks in the SbS₄/WS₄ spectra are narrower and exhibit greater intensity. Different from the behavior of Li and PS_4 in the Li₃PS₄ phases,¹² in NSWS, the Na spectrum exhibits a stronger overlap with the librational spectrum of SbS₄ and WS₄. This suggests that the vibrational coupling of Na-ions with anion librations in NSWS is stronger than between Li and PS₄ in the Li₃PS₄ phases. Despite this strong vibrational/librational coupling in NSWS, Figure 2 demonstrates that large, quasipermanent reorientations of the anions do not occur in this phase. (Rather, anion rotational motions in NSWS involve relatively small excursions about an equilibrium orientation; Figures S6 and S7.) Importantly, the magnitude of the anions' rotational displacements at 300 K (Figure S6) is similar to those shown in Figure 2c and does not exceed $\sim 20^{\circ}$. Hence, the anion reorientations that coincide with Na-ion migration are similar in amplitude to those observed in the absence of migration events. Although we are aware of no angular displacement threshold to identify a paddlewheel mechanism, a hallmark of paddlewheel dynamics is rotational displacements that exceed those typical of thermal motion and that coincide with the migration of neighboring Na-ions.¹² These features are not exhibited by the anions in NSWS. Furthermore, the present behavior differs from that of LPS glass, where the vibrational/librational coupling is less strong, yet large anion

reorientations occur simultaneously with Li-ion migration events. Indeed, the large anion reorientations observed in LPS glass are reminiscent of the orientational disorder reported in rotor phases, and this disorder has been associated with paddlewheel dynamics.^{15,16} In total, it is important to emphasize that vibrational/librational coupling observed here within NSWS is a distinct phenomenon from the large, reorientational anion displacements observed in rotor phases. In prior work, we and others have referred to the latter phenomenon as a paddlewheel effect. Both mechanisms can contribute to cation mobility.

Na-Ion Conductivity. The Na-ion self-diffusivity and migration energy barrier were predicted by calculating the mean-squared displacement (MSD)

$$MSD(t) = \frac{1}{N\tau} \sum_{i}^{N} \int_{0}^{\tau} |r_{i}(t'+t) - r_{i}(t')|^{2} dt'$$
(2)

where r_i is the position of the *i*-th Na-ion and N is the number of Na-ions in the cell (Figure S8). The diffusion coefficient is obtained from the MSD using the Einstein relation

$$D = \lim_{t \to \infty} MSD(t)/6t$$
(3)

The calculated Na-MSD is shown in Figure S8. The corresponding diffusion coefficients are plotted in Figure 4 at



Figure 4. Arrhenius plot of sodium self-diffusion coefficients (diamonds) at 500, 600, and 700 K. The activation energy of 0.15 eV is extrapolated from a linear fit (dotted line). The estimated diffusion coefficient at 300 K is 3.10×10^{-7} cm²/s.

T = 500, 600, and 700 K. The ionic conductivity at 300 K is estimated by extrapolating the diffusivity to 300 K ($D = 3.1 \times$ 10^{-7} cm² s⁻¹) and applying the Nernst–Einstein equation, $\sigma =$ $Dnq^2/k_{\rm B}T$. Here, $k_{\rm B}$ is Boltzmann's constant, T is the absolute temperature, n is the number density of mobile species, and q= 1 is the effective charge of Na-ions. The calculated ionic conductivity at 300 K is 28 mS cm⁻¹. The activation energy, E_{ay} for migration was calculated from the slope of the best-fit line in Figure 4, yielding $E_a = 0.15$ eV. Both the calculated conductivity and activation energy are in close agreement with experimental data. Hayashi et al. reported a conductivity of 32 mS cm⁻¹ and $E_a = 0.18$ eV for an NSWS composition with x =0.12.7 Fuchs et al. reported a conductivity of 41 mS cm⁻¹ and $E_a = 0.18$ eV for the composition with $x = 0.10.^8$ AIMD calculations by Jalem et al. reported a conductivity of 81 mS cm^{-1} with $E_a = 0.10 \text{ eV.}^9$

Discussion. The present analysis has uncovered limited evidence for a paddlewheel effect associated with Na-ion migration in NSWS: strong correlations between Na-ion hopping and large, quasi-permanent reorientations of the SbS₄ and WS₄ anionic tetrahedra are not observed. What, then, is responsible for the exceptionally high ionic conductivity of this material? Jalem et al.⁹ argued that the enhanced conductivity was primarily due to the introduction of WS₄, which has a smaller anion volume, 5.56 Å³, than does SbS₄, 6.83 Å³. On the other hand, the substitution of aliovalent W for Sb also introduces vacancies on the Na-ion sublattice. To probe the impact of an increasing vacancy concentration on



Figure 5. Ionic conductivity of NSWS as a function of composition. Blue circles are experimental data from Fuchs et al., and the orange line is a plot of eq 4.

Na-ion mobility, Figure 5 plots the vacancy-dependent ionic conductivity,²⁹ defined as

$$\sigma = \frac{q^2 z^2 a^2 \nu}{6kT} Nc(1-c) \exp\left(-\frac{E_a}{kT}\right)$$
(4)

where qz is the charge, *a* is the distance between neighboring defect sites, *v* is the attempt frequency, *k* is Boltzmann's constant, *T* is the temperature, *N* is the number of available defect sites per volume, *c* is the site fraction of charge carriers, and E_a is the activation energy. Figure 5 demonstrates that the ionic conductivity of NSWS at 25 °C as a function of composition is well described by the classical vacancy model (eq 4; a = 3.6 Å, $v = 6 \times 10^{13}$ s⁻¹, $E_a = 0.17$ eV, T = 25 °C), which closely matches the experimental data from Fuchs et al. at 25 °C.⁸ The conductivity increases 3 orders of magnitude

for relatively small vacancy concentrations (0 < x < 0.025) and then increases by approximately a factor of 3 up to x = 0.1. Hence, it can be concluded that the high conductivity of NSWS partially arises from the incorporation of vacancies upon aliovalent substitution of W for Sb and from relatively strong vibrational coupling of Na-ions with anion librations. Further support for the importance of vacancies can be found in the behavior of Na₃SbS₄, which exhibits a high conductivity of 3 mS cm⁻¹ with 2.5 mol % Na vacancies⁶ and without the need to substitute W for Sb.

CONCLUSIONS

Understanding the atomic-scale mechanisms that underlie superionic behavior in solids is essential for the design of efficient solid electrolytes and, ultimately, solid-state batteries. Toward these goals, here, ab initio molecular dynamics (AIMD) was used to reveal the Na-ion migration mechanisms that are responsible for the exceptionally high ionic conductivity of the solid electrolyte Na_{3-x}Sb_{1-x}W_xS₄. Correlations between the dynamics of Na-ions and that of the surrounding complex-anion "cage" were characterized to identify whether paddlewheel dynamics contribute to the high cation conductivity. Although Na⁺ migration is observed to involve the concerted motion of multiple Na-ions, limited evidence was found for contributions to Na migration from SbS_4 and WS_4 reorientations. This implies that the high conductivity of Na3-rSb1-rWrS4 does not result from a paddlewheel effect. Rather, the high conductivity is well explained by a classical vacancy model and a strong overlap between cation vibrational modes and anion librations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.2c00526.

Energy of vacancy configurations, cation linear displacement and anion rotational displacement during migration events, angular displacement of all anions at 300 and 700 K, and sodium mean square displacement (PDF)

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Author Contributions

J.G.S. conducted the computational components of the project. All authors contributed to the drafting of the paper. D.J.S. conceived of the project idea.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported as part of the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Science. The authors acknowledge helpful conversations with Yet-Ming Chiang.

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