

Rechargeable sodium ion batteries

Thank you for visiting nature . You are using a browser version with limited support for CSS. To obtain the best experience, we recommend you use a more up to date browser (or turn off compatibility mode in Internet Explorer). In the meantime, to ensure continued support, we are displaying the site without styles and JavaScript.

Chalcogenide-based (S, Se) chemistries offer the potential for higher ionic conductivities than oxides^{11,12,13,14,15,16,17,18,19,20}. 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^{21,22,23}. Sulfide electrolytes, particularly sodium sulfides, also tend to be softer than oxides²⁴, which allows intimate contact between electrode and solid electrolyte to be achieved via cold pressing instead of high-temperature sintering.

Using DFT calculations, we first performed a systematic investigation of the dopability of potential halide X- (X = F, Cl, Br and I) into both the tetragonal and cubic phases of Na₃PS₄. As the DFT predictions for both phases are extremely similar, we will henceforth present only the results of the more stable tetragonal phase for brevity, and interested readers are referred to the Supplemental Information for the results on the cubic phase.

Figure 1 shows the crystal structure of t-Na₃PS₄. There are two symmetrically distinct Na sites in t-Na₃PS₄, Na1 (4d) and Na2 (2a), and the PS₄ tetrahedra are centered at the 2b positions²⁷. The symmetrically distinct Na sites in c-Na₃PS₄ are labeled similarly as cubic Na1 (6b) and Na2 (12d). The Na1 (4d) and Na2 (2a) sites in t-Na₃PS₄ essentially occupy the same positions as the Na1 (6b) sites in c-Na₃PS₄³¹.

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.

A single halide dopant was introduced into a 2 x 2 x 2 supercell of t-Na₃PS₄ by replacing one of the S atoms with X, and simultaneously a Na vacancy was introduced to form Na₄7P16S63X, or t-Na_{3-x}PS_{4-xX} with x = 0.0625. All symmetrically distinct configurations (Kriger-Vink notation is adopted) were evaluated, and the lowest energy configuration was used for subsequent analyses.

Despite the fact that F- doping is predicted to be the most favorable, we have selected Cl- doping for further investigation due to several considerations. First, NaCl, aka table salt, is by far a more commonly available precursor than NaF. Second, fluoride chemistry inherently comes the possibility of HF exposure. Finally, the Cl- anion has an ionic radius that is closest to S²⁻, which would minimize the local structural distortion introduced at the substituted site. The doping concentration of Cl is fixed at x = 0.0625, given that previous work in doping I- (which has a similar dopant formation energy at the same concentration) into c-Na₃PS₄ at x

> 0.1 resulted in formation of unknown phases³².

As demonstrated in recent work by some of the co-authors³⁰, pristine c-Na₃PS₄, i.e., without interstitial or vacancy defects, is predicted to be an extremely poor ionic conductor in AIMD simulations. Using AIMD simulations (see Methods section), a similar result is obtained with t-Na₃PS₄ in this work, which is not surprising given that the small differences in lattice parameters and atomic positions between the cubic and tetragonal polymorphs.

Figure 2a shows the Arrhenius plot of the log of the conductivity-temperature product (σT) versus $1/T$ for t-Na_{2.9375}PS_{3.9375}Cl_{0.0625} obtained from AIMD simulations. With the introduction of a defect pair, the Na⁺ conductivity at 300 K is predicted to be 1.38 mS cm⁻¹ with an activation barrier of 232 meV (see Table 2). During the preparation of this article, it has come to our attention that Klerk et al. has also performed AIMD simulations on halide doping in t- and c-Na₃PS₄³¹. Though the qualitative conclusions of vacancy-induced conductivity are similar, we note that Klerk et al. only performed relatively short AIMD simulations at a single temperature of 525 K; room-temperature Na⁺ conductivities and activation energies were therefore not obtained.

(a) Arrhenius plots of the t-Na_{3-x}PS_{4-x}Cl_x with $x = 0$ (blue) and 6.25% (red) obtained from SPS measurements, and $x = 6.25\%$ (green) from AIMD simulations. The filled green triangle indicates the extrapolated ionic conductivity at 300 K from AIMD simulations. (b) Isosurface of the Na⁺ probability density distribution (P , in green) in the t-Na_{3-x}PS_{4-x}Cl_x ($x = 6.25\%$) at 800 K, with $P = 0.0001$ a₀⁻³ (a₀ is the Bohr radius).

From the Na⁺ probability density distribution (Fig. 2b), we may observe that t-Na_{2.9375}PS_{3.9375}Cl_{0.0625} is predicted to be a 3D diffuser comprising of chains of Na₁ sites along the c direction interconnected via the Na₂ sites, which form a body-centered cubic sublattice. Such a 3D diffusion network is expected to be highly robust against the potential introduction of blocking defects³³.

Plots of Na uptake per formula unit (f.u.) of t-Na_{2.9375}PS_{3.9375}Cl_{0.0625} (red solid), c-Na_{3.0625}Sn_{0.0625}P_{0.9375}S₄ (blue dashed) and c-Na_{3.0625}Si_{0.0625}P_{0.9375}S₄ (green dashed) solid electrolytes against voltage vs Na/Na⁺. At low voltage (high Na chemical potential), each solid electrolyte undergoes reduction and uptakes Na, while at high voltage (low Na chemical potential), each solid electrolyte is oxidized and loses Na. Text indicates the predicted phase equilibria at corresponding regions of the profile. Only selected regions are annotated for brevity.

Contact us for free full report

Web: <https://kary.com.pl/contact-us/>

Email: energystorage2000@gmail.com

WhatsApp: 8613816583346

Rechargeable sodium ion batteries

