



A first principle study of the phase stability, ion transport and substitution strategy for highly ionic conductive sodium antiperovskite as solid electrolyte for sodium ion batteries

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HIGHLIGHTS

- Ab initio study on the promising solid electrolyte material Na₃OCl.
- Substituting alkali earth metal elements leads to increased Na migration barrier.
- Ca being identified as a potential candidate for substitution.

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ABSTRACT

Materials in the Na-rich antiperovskite family are promising candidates as solid electrolytes (SEs) for all-solid-state Na-ion batteries (NIBs). In this work, we carry out *ab-initio* calculations to study various properties of Na₃OCl, namely the formation energies of various neutral defect pairs, the defect hopping barriers, the solution energies of high valence alkali earth metal substitutes to the Na atoms, and the effect of such substitution to the Na migration. While the introduction of alkali earth metal ions increases the Na vacancy concentration, the activation energy of Na transport also increases. Furthermore, we identify Ca as the most promising alkali earth metal to be doped into Na₃OCl due to its low binding energy and relatively small impact on the migration barrier. Our work provides a theoretical framework for further improving the Na conductivity of materials in the antiperovskite family for all-solid-state NIBs.

1. Introduction

The growing interest in renewable power sources has been accompanied by an increase in the demand for reliable energy storage systems. Although Li-ion batteries (LIBs) have been widely applied to electronic devices due to their high capacities and technological maturity, their prospects in large-scale grid-level storage of renewables are restricted by the limited availability of Li [1,2]. Because of the higher abundance of Na compared to Li [3], Na ion batteries (NIBs) have recently gained increasing attention [4–7]. It should be noted that safety is also an important issue for conventional LIBs and NIBs. To minimize the hazards, which include leakage of corrosive, toxic, and flammable organic liquid electrolytes, solid electrolytes (SEs) have been suggested as alternatives to traditionally used organic liquids [8–10].

In order to achieve reasonable performance, the SEs of the solid-state NIBs must possess an ionic conductivity of greater than

1 mS cm⁻¹, a negligible electronic conductivity, and a high chemical stability with respect to the applied voltage [11,12]. In light of this, β -alumina [8,13,14], which has an ionic conductivity of 2 mS cm⁻¹ at room temperature [4], and Na_{1+x}Zr₂Si_xP_{3-x}O₁₂ (NASICON) based material [9,15,16], with ambient ionic conductivity as high as 3.5 mS cm⁻¹ (for Na_{3.1}Zr_{1.95}Mg_{0.05}Si₂PO₁₂ [17]), have been widely investigated. Other popular materials within the research community include sulfide based Na conducting materials [18], such as the Na₃PS₄ glass [19,20]. Such materials are under intensive investigation due to their wide electrochemical window and electrode-electrolyte interface stability.

Nevertheless, the researches of novel Na-ion SEs are often inspired by materials that have been developed as Li SEs. This is not surprising as both Li and Na are in the alkali metal group. The alkali-metal-rich antiperovskite with chemical formula M₃OA (M= Li/Na, A= halogen) are among one of the most promising Li and Na SE materials [21]. The

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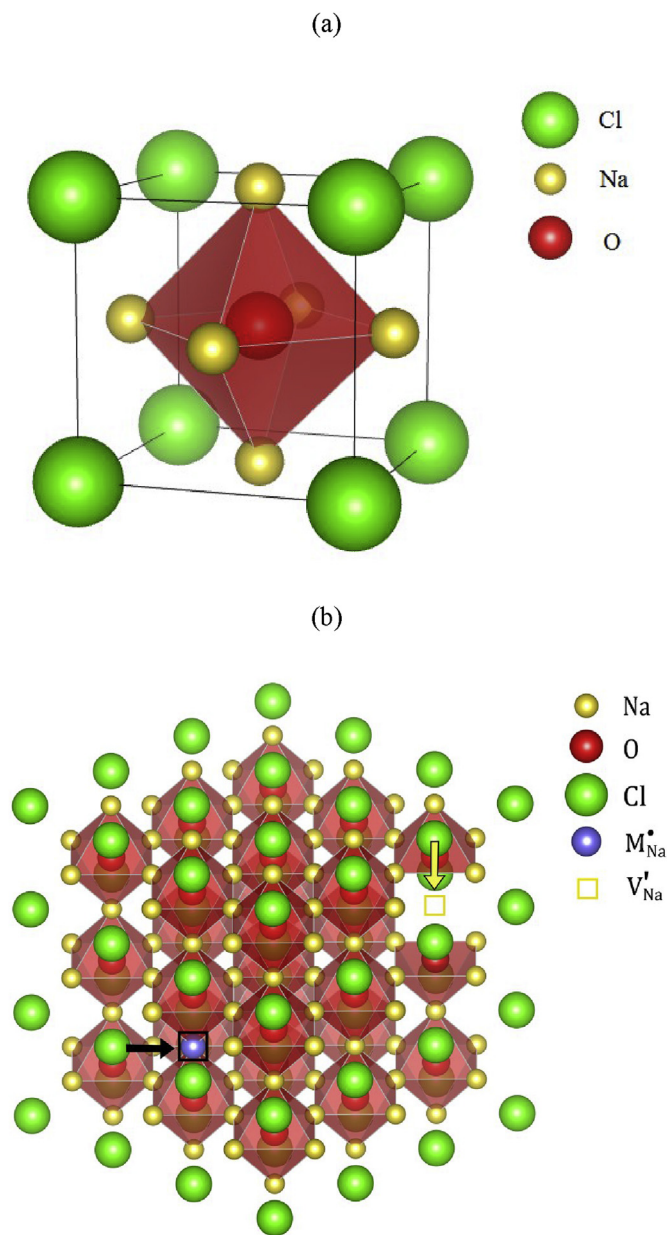


Fig. 1. (a) Atomic structure of Na₃OCl and (b) illustration of substituting alkaline earth metal into Na₃OCl. The purple sphere denotes the substitutional defect and yellow squared frame being V'_{Na} associated. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

prefix “anti” refers to the fact that the alkali metal cations occupy the O sites of typical perovskite oxides (*i.e.* ABO₃), while the halide and oxygen anion occupy the A site and B site, respectively. The structure of an anti-perovskite is shown in Fig. 1a.

Li-rich antiperovskite has shown excellent ionic conductivities as high as 1 mS cm⁻¹ at room temperature and 10 mS cm⁻¹ at 250 °C [21]. Although, the Na-rich antiperovskite has a lower ionic conductivity of 0.22 mS cm⁻¹ at 240 °C [22], researchers have improved the Na conductivity using elemental substitution. For example, Wang et al. [22] have shown that Na_{2.9}Sr_{0.05}OBr_{0.6}I_{0.4} has an order of magnitude greater ionic conductivity compared to its un-modified counterpart, Na₃OBr, at 200 °C. Moreover, the Goodenough group has recently reported that amorphous Na antiperovskites are superionic conductors with conductivity as high as 100 mS cm⁻¹ at around 150 °C, far above the values obtained with other state-of-the-art SEs [23–25].

Due to the tremendous potential of Na-rich antiperovskites, compositional modification strategies for enhancing the ionic conductivity, *e.g.* the partial substitution of the Na site, are worth additional investigation. In this regard, we carried out an *ab-initio* study on the defect energy, substitutional energy, and Na transportation in Na₃OCl. We considered Na₃OCl because it is a prototypical antiperovskite, structurally analogous to the highly conductive Li₃OCl, and is less studied than Na₃OBr [26] and Na₄O₂ [27]. In this work, we first investigated the defect formation energies of various plausible defects in Na₃OCl [28]. We considered three different types of neutral charged defect pairs: i) the Na Frenkel defect; ii) the NaCl Schottky defect pair; and iii) the Na₂O Schottky pair. For Na Frenkel defect pair, a lattice Na_{Na}^x ion is shifted to an interstitial site (Na_i^x) leading to the formation of a Na vacancy V'_{Na} as follows:



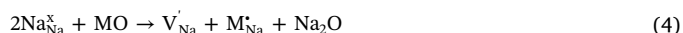
The NaCl Schottky defect pair refers to the coexistence of a V'_{Na}, and a Cl vacancy, V'_{Cl}, formed by the following reaction:



The Na₂O Schottky pair corresponds to the formation of two V'_{Na}, and one O vacancy, V''_O, by the following reaction:



Our defect calculations suggest that NaCl Schottky defect pair is the energetically most stable among the three studied. This conclusion is similar to the one we have previously drawn for Li₃OCl [28]. The presence of V'_{Na} due to the NaCl Schottky defect pair suggests that the vacancy migration is the dominant diffusion mechanism. Since the diffusion of Na in the antiperovskite is likely mediated by V'_{Na}, an increase in the concentration of that defect may enhance the ionic conductivity. Hence, one strategy to improve the ionic conductivity of V'_{Na} is by partially substituting group II metal elements (*e.g.* Mg, Ca, Sr and Ba) into the Na site resulting in the creation of a M'_{Na} defect. In turn, this leads to the formation of V'_{Na} by charge compensation. Consequently, we studied the impact of such substitution on the conductivity and we calculated the substitutional energies, *i.e.*, the energy necessary to form M'_{Na} – V'_{Na} defect pairs via the following reaction:



We also calculated the M'_{Na} – V'_{Na} binding energy corresponding to the energy required for a V'_{Na} to detach from the attraction of a neighboring M'_{Na}. We then studied the impact of the substitution on the Na migration by both nudged elastic band (NEB) and *ab-initio* molecular dynamics (AIMD) simulations. Our results illustrate that although M'_{Na} substitution effectively increases V'_{Na} concentration in Na₃OCl, the M'_{Na} – V'_{Na} attraction leads to an increased activation energy for the migration of Na. This results in a lower conductivity given an identical V'_{Na} concentration. One can select a M'_{Na} substitutional defect with weaker M'_{Na} – V'_{Na} attraction to minimize the increase in migration barrier. Because of a relatively smaller binding energy and, hence, a weaker Ca'_{Na} – V'_{Na} attraction, we propose that Ca is a potential candidate for substitution of Na₃OCl.

2. Computational methods

In this study, the density functional theory (DFT) simulations were carried out using the VASP code [29]. The projector augmented wave (PAW) method was used with the Perdew–Burke–Ernzerhof generalized gradient approximation [30]. The defect formation and substitutional energies were calculated by the structural relaxation of the initial lattice. These relaxations were carried out on 3 × 3 × 3 supercell with 135 atoms. A 3 × 3 × 3 Monkhorst-Pack grid was used to sample the Brillouin zone [31]. For the three elements of the original material, *i.e.*, Na, O and Cl, we used pseudopotentials with 2p⁶3s¹, 2s²2p⁴, and 2s²2p⁵

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