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Materials Design of Sodium Chloride Solid Electrolytes Na₃MCl₆ for All-Solid-State Sodium-Ion Batteries

Dongsu Park,a,b Kwangnam Kim,c Gin Hyung Chun,a,b Brandon C. Wood,c Joon Hyung Shim,b,* and Seungho Yua,b,*

All-solid-state sodium-ion batteries have attracted increasing attention owing to the low cost of sodium and the enhanced safety compared to conventional Li-ion batteries. Recently, halides have been considered as promising solid electrolytes (SEs) due to their favorable combination of high ionic conductivity and chemical stability against high-voltage cathode materials. Although a wide variety of lithium chloride SEs, LiₓMClₓ, have been developed for high-voltage all-solid-state batteries, only a limited number of sodium chloride SEs have been reported. This study aims to offer a material design insight for the development of sodium chloride SEs through systematic assessment of the phase stability, electrochemical stability, and transport properties of novel NaₓMClₓ SEs. Structural calculations indicate that NaₓMClₓ exhibits trigonal P3̅1c, monoclinic P2₁/n, and trigonal R̅3 phases, and the stable phase of NaₓMClₓ is dependent on the type and ionic radius of M. NaₓMClₓ typically exhibits a high oxidation potential, demonstrating good electrochemical stability against cathodes. The bond-valence site energy and ab initio molecular dynamics calculations revealed that NaₓMClₓ with P2₁/n and R̅3 phases showed low ionic conductivity, whereas the P3̅1c phase slightly improved the ionic conductivity of NaₓMClₓ. The formation of Na vacancies by aliovalent substitution considerably increased the ionic conductivity up to four orders of magnitude for pristine NaₓMClₓ, exhibiting ~10⁻⁶ S/cm for trigonal P3̅1c and R̅3 phases, which is comparable to the highest ionic conductivity among the reported Na chloride SEs. The formation of defects could further enhance the ionic conductivity of NaₓMClₓ, and the optimization of defect type and ratio can be helpful in developing superionic Na chloride SEs. The material design of NaₓMClₓ in this study will be fundamental guidelines for the development of novel sodium halide SEs for all-solid-state sodium-ion batteries.

Introduction

The development of next-generation batteries has been widely conducted for emerging applications such as energy storage systems (ESSs) and electric vehicles.1 All-solid-state batteries (ASSBs) are promising candidates for next-generation batteries owing to their high energy density and enhanced safety.2 Solid electrolytes (SEs) in ASSBs enable the use of metallic anodes exhibiting higher energy density than graphite anodes. SEs also significantly enhance safety by replacing flammable organic liquid electrolytes in conventional Li-ion batteries.3 Recently, ASSBs employing Na-ion SEs have been considered due to the low cost of sodium and enhanced safety compared to conventional Li-ion batteries.4, 5 The abundance of sodium particularly facilitated the development of low-cost batteries for large-scale applications such as ESSs.6

Among the various types of Na-ion SEs, sulfide SEs have been widely investigated owing to their high ionic conductivities.7–11 For example, Na₃PS₄, Na₃SbS₄, and Na₁₁Sn₂P₄S₁₂ exhibited conductivities of 0.1–10 mS/cm,7, 10 and W-substituted Na₃SbS₄ showed a high conductivity of 41 mS/cm.9, 12 However, sulfide SEs exhibit a narrow electrochemical stability window, resulting in poor compatibility with metal anodes and typical cathode materials.13, 14 In addition, phosphorus-based sulfide SEs are unstable against humid air and are prone to generate toxic H₂S gas.15, 16 Oxide SEs such as NASICONs and β-alumina exhibit good chemical stability, but they require sintering process to address interfacial resistances.17, 18

Recently, halide SEs have been considered as promising alternative SEs due to their favorable combination of high ionic conductivity, wide electrochemical stability window, and chemical stability against high-voltage cathodes.19–28 Lithium ternary chlorides, LiₓMClₓ, exhibit high ionic conductivity (0.5–3 mS/cm for LiₓMClₓ with M = Y, Er, In, Sc, and Yb) and chemical stability against 4 V-class oxide cathode materials.22–28 The ionic conductivity of LiₓMClₓ (M = Y, Er, Fe, In, and Yb) was further improved by the aliovalent substitution of M³⁺ to Zr⁴⁺.28–32
Theoretical studies also revealed the high ionic conductivity of Li$_3$MCli and Li$_3$M$_{1-x}$ZrCl$_6$, above 10 ms/cm and high oxidation potential of approximately 4.3 V.\textsuperscript{33-36} Although lithium chloride SEs, Li$_3$MCli are considered promising candidates for high-voltage ASSBs, very few investigations of sodium chloride SEs, such as Na$_3$MCli (M = Y and Er), Na$_3$ZrCl$_6$ and Zr-substituted Na$_3$M$_{1-x}$ZrCl$_6$ (M = Y and Er),\textsuperscript{37,42} have been reported in the literature. Therefore, a systematic screening of Na$_3$MCli with a broad variety of elements, M$^{3+}$, would be a fundamental guideline for developing novel sodium chloride SEs. In this study, we provided a material design strategy for sodium chloride SEs by assessing the phase stability, electrochemical stability, and transport properties of Na$_3$MCli SEs with 26 M$^{3+}$ elements.

Structural calculations indicated that Na$_3$MCli exhibited the crystal structures of the $P\overline{3}1c$, $P2_1/n$, and $R\overline{3}$ phases, and the stable phase of Na$_3$MCli was dependent on the type and ionic radius of M. Na$_3$MCli typically exhibited a high oxidation potential, demonstrating good electrochemical stability at high voltages. The Na-ion migration pathways and migration energy barriers in Na$_3$MCli from the bond-valence site energy (BVSE) method indicated that Na-ion migration in monoclinic $P2_1/n$ and trigonal $R\overline{3}$ phases was slower than that in the trigonal $P\overline{3}1c$ phase. \textit{Ab initio} molecular dynamics (AIMD) simulations further revealed that Na$_3$CrCl$_6$ ($P\overline{3}1c$-phase) had higher ionic conductivity than Na$_3$ErCl$_6$ ($P2_1/n$ phase) and Na$_3$GdCl$_6$ ($R\overline{3}$ phase). Although the $P2_1/n$ and $R\overline{3}$ phases exhibited low ionic conductivity, the aliovalent substitution of M$^{3+}$ with Zr$^{4+}$ significantly increased the ionic conductivity up to four orders of magnitude. Ionic substitutions in Na$_3$MCli would be a promising approach for the enhancement of ionic transport, and the optimization of the element type and ratio of substitution can further increase the ionic conductivity of Na$_3$MCli.

**Methods**

First principles calculations were conducted using density functional theory (DFT) with a plane-wave basis set and the projector-augmented wave method,\textsuperscript{41} as implemented in the Vienna \textit{Ab initio} Simulation Package.\textsuperscript{42} The generalized gradient approximation of Perdew, Burke, and Ernzerhof was employed for the exchange–correlation energy.\textsuperscript{44} A van der Waals density functional (vdW-DF, optB86b-vdW)\textsuperscript{45} was used to address the interaction in layered chloride structures based on previous works.\textsuperscript{34} An energy cutoff of 520 eV was used for the plane-wave basis, and the k-point grids were generated using the Python Materials Genomics (Pymatgen) code,\textsuperscript{46} where the k-point densities were at least 1000/atom. The ionic positions were relaxed until the forces were less than 0.01 eV Å$^{-1}$, and the convergence criterion for the electronic self-consistency loop was set to 10$^{-5}$ eV. Spin-polarized calculations were performed for the transition metals and lanthanides.

The simulation cells of Na$_3$MCli were generated using the experimental structures of Na$_3$MCli, exhibiting trigonal $P\overline{3}1c$ (space group number, S.G., #163),\textsuperscript{37,48} monoclinic $P2_1/n$ (S.G. #14),\textsuperscript{37,49} and trigonal $R\overline{3}$ (S.G. #148)\textsuperscript{50} crystal structures. In addition, the experimental structures of lithium ternary chlorides Li$_3$MCli, including monoclinic C2/m (S.G. #12)\textsuperscript{24,26} and trigonal $P\overline{3}1m$ (S.G. #164)\textsuperscript{72,35} structures were also used to generate the simulation cells of Na$_3$MCli. A total of 26 M$^{3+}$ cations were selected for Na$_3$MCli, including 3d transition metals (Cr, V, Fe, and Ti), group 3 elements (Sc, Lu, and Y), group 13 and 15 elements (Al, Ga, In, Ti, and Bi), and lanthanides (Yb, Tb, Er, Ho, Dy, Tb, Gd, Eu, Sm, Pm, Nd, Pr, Ce, and La). For the partially occupied Na sites in the Na$_3$MCli structures, the ionic configuration with the lowest total energy was selected for subsequent calculations.

The phase stability of Na$_3$MCli was examined using Na-M-Cl phase diagrams in the Materials Project (MP) database.\textsuperscript{51} Competing stable decomposition phases for Na$_3$MCli (e.g., MCli, Na$_3$MCl$_4$, and NaCl) were collected to evaluate the energy above the convex hull ($E_{\text{null}}$) of Na$_3$MCli. The Na$_3$MCli phase with an $E_{\text{null}}$ value below 25 meV/atom was considered as the stable phase, which can be stabilized by entropic effects. The electrochemical stability window of Na$_3$MCli was calculated using the grand potential phase diagram as a function of the chemical potential of Na:

$$\mu_{Na^{0}}(\varphi) = \mu_{Na^{0}} - e\varphi, \quad (1)$$

where $\mu_{Na^{0}}$ is the chemical potential of Na metal, $e$ is the elementary charge, and $\varphi$ is the applied potential referenced to the Na metal anode. The Pymatgen code was used to generate the grand phase diagram and determine the electrochemical stability window. The total energies of Na$_3$MCli were recalculated using consistent settings in the MP for the electrochemical stability calculations.

Na-ion migration pathway and its energy barrier were predicted using the BVSE method as implemented in the SoftBV software.\textsuperscript{52} Na site energies were calculated for a dense grid with a resolution of 0.1 Å using the Morse type interaction potential. The Na-ion migration path was identified based on the isosurface of the Na site energy, whereas the minimum energy required to connect a migration path was calculated for the migration energy barrier.

Na-ion diffusivity in Na$_3$MCli was obtained using AIMD simulations. Because AIMD simulations require significant computational effort, a lower energy cut-off of 350 eV, gamma point-only k-point grid, and the NVT ensemble with a Nosé-Hoover thermostat were employed. The mean squared displacement (MSD) was evaluated at 700, 750, 800, 900, and 1000 K for the 40–75 ps window, and the time step for all AIMD calculations was 2 fs. The diffusion coefficient, $D$, was calculated using the MSD of the Na ions:

$$D = \frac{1}{2d^2} \langle [r(t + \tau) - r(t)]^2 \rangle \quad (2)$$

where $d$ is the dimensionality of the system, $\tau$ is the initial time, $t$ is the time for MSD, and the angled brackets indicate the average overall Na ions. For the statistical reliability of the AIMD simulations, the average diffusion coefficient and its standard deviation were evaluated using three independent AIMD simulations at each temperature. The ionic conductivity of Na, $\sigma$, was calculated using the Nernst–Einstein equation:
Fig. 1 (a) Crystal structures of sodium chlorides Na₃MCl₆ (M=Cr, Er, and Gd) with NaCl octahedra (yellow) and MCl₆ octahedra. (b-d) Structural preference of Na₃MCl₆ among the trigonal P₃̅1c, monoclinic P₂₁/n, and trigonal R̅3̅ systems. (b) Energy differences among the crystal structures of P₃̅1c, P₂₁/n, and R̅3̅, as a function of the effective ionic radii of M. (c-d) Energy difference between (c) trigonal P₃̅1c and monoclinic P₂₁/n, and (d) monoclinic P₂₁/n and trigonal R̅3̅ structures of Na₃MCl₆, as a function of the volume of structures. The values in (b-d) were divided into four groups based on M: 3d transition metals, group 3 elements, group 13 and 15 elements, and lanthanides.

\[ \sigma = \frac{(z\varepsilon)^2D}{kT} \]  

where \( z \) is the valence of the Na ion, \( \varepsilon \) is the elementary charge, \( c \) is the concentration of the Na ion, and \( D \) is the diffusion coefficient of Na ions. The ionic trajectories of Na during the AIMD simulations were recorded using a grid with dimensions of 25 × 25 × 25 to visualize Na-ion migration. Iso-surfaces of the ionic probability densities were obtained with respect to the mean ionic probability density \( P_0 \).

Results

The structure of sodium chloride Na₃MCl₆ was determined by comparing the total energy among the trigonal P₃̅1c, monoclinic P₂₁/n, and trigonal R̅3̅ phases based on the experimental structures of Na₃MCl₆. The crystal structures of the P₃̅1c, P₂₁/n, and R̅3̅ phases (from Na₃CrCl₆, Na₃ErCl₆, and Na₃GdCl₆, respectively), are presented in Figure 1(a) with NaCl₆ polyhedra (yellow) and MCl₆ octahedra. The structural preference of Na₃MCl₆ was evaluated by calculating the total energy differences \( \Delta E \) between the phases (\( \Delta E \) between trigonal R̅3̅ and monoclinic P₂₁/n \( (E_{R̅3̅} - E_{P₂₁/n}) \) phases, and between trigonal R̅3̅ and trigonal P₃̅1c \( (E_{R̅3̅} - E_{P₃̅1c}) \) phases), as shown in Figure 1(b). The negative values of \( \Delta E \) in Figure 1(b) indicate the preference of the trigonal R̅3̅ phase, whereas the positive values of \( \Delta E \) demonstrate the preference of the P₃̅1c and P₂₁/n phases compared to the R̅3̅ phase. The values of \( \Delta E \) decreased as the size of M increased, indicating that Na₃MCl₆ with relatively large M cations preferred the trigonal R̅3̅ phase. The energy differences among the phases in Figure 1(b) are also presented as a function of the volume of the structures in Figure S1. The values of \( \Delta E \) decreased as the volume of Na₃MCl₆ increased, suggesting a preference for the trigonal R̅3̅ phase for Na₃MCl₆ with relatively large M cations. The values of \( \Delta E \) and volume of Na₃MCl₆ for the P₃̅1c, P₂₁/n, and R̅3̅ phases are listed in Tables S1 and S2, respectively.

The structural preference of the monoclinic P₂₁/n phase compared to the trigonal P₃̅1c and R̅3̅ phases was examined using the values of \( \Delta E \), as shown in Figures 1(c) and (d), respectively. As shown in Figure 1(c), Na₃MCl₆ generally preferred the monoclinic P₂₁/n phase as the volume of Na₃MCl₆ increased. Na₃MCl₆ with relatively large M cations, such as group
Table 1. Stable phase, $E_{\text{hull}}$, and decomposition phases of Na$_x$MCl$_6$.

<table>
<thead>
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<th>M</th>
<th>M</th>
<th>$M_{\text{bulk}}$ (pm)</th>
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<th>Stable phase</th>
<th>$E_{\text{hull}}$ (meV/atom)</th>
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3 elements and lanthanides, exhibited a monoclinic $P2_1/n$ phase. Na$_3$MCl$_6$ with 3d transition metals slightly preferred the monoclinic $P2_1/n$ phase, whereas Na$_3$MCl$_6$ with a relatively small Cr preferred the trigonal $P\bar{3}1c$ phase, which was consistent with the experimental results. The preference tendency of the monoclinic phase was slightly different for Na$_3$MCl$_6$ with group 13 elements (Al, Ga, In, and Tl), exhibiting trigonal $P\bar{3}1c$. The preference tendency of the trigonal $R3$ phase compared to the monoclinic $P2_1/n$ phase for Na$_3$MCl$_6$ is illustrated in Figure 1(d). Na$_3$MCl$_6$ with relatively large M cations exhibited a trigonal $R3$ phase, and the transition from the monoclinic to trigonal phase occurred with an ionic radius of 90 pm. The phase transition to the trigonal $R3$ phase was consistent among the groups of 3, 13, and 15, and lanthanides.

The most stable phase of Na$_3$MCl$_6$ among the trigonal $P\bar{3}1c$, monoclinic $P2_1/n$, and trigonal $R3$ phases is shown in Table 1. Na$_3$MCl$_6$ with relatively small M cations (Cr) and group 13 elements (Al, Ga, In, and Tl) preferred the trigonal $P\bar{3}1c$ phase, whereas Na$_3$MCl$_6$ with relatively large M cations (>90 pm, Y, Bi, Er, Ho, Dy, Tb, Gd, Eu, Sm, Pm, Nd, Pr, Ce, and La) preferred the trigonal $R3$ phase. Monoclinic $P2_1/n$ was the preferred phase of Na$_3$MCl$_6$ with M cations exhibiting moderate ionic radii, such as V, Fe, Ti, Sc, Lu, Yb, and Tm. Additionally, the stability of Na$_3$MCl$_6$ structures with monoclinic $C2/m$ or trigonal $P\bar{3}m1$ phases from the Li$_3$MCl$_6$ structures was also investigated by comparing the total energy differences among the phases. Table S3 shows the most stable phase of Na$_3$MCl$_6$ among the $P\bar{3}1c$, $P2_1/n$, and $R3$ phases, and the energy differences of the Na$_3$MCl$_6$ phase against the $C2/m$ and $P\bar{3}m1$ phases. The positive values of $\Delta E$ indicate that the Na$_3$MCl$_6$ structures with the $C2/m$ and $P\bar{3}m1$ phases were unstable phases, compared to the Na$_3$MCl$_6$ structures based on the $P\bar{3}1c$, $P2_1/n$, and $R3$ phases. The values of $\Delta E$ were $\sim$45 meV/atom, suggesting that $C2/m$ and $P\bar{3}m1$ from Li$_3$MCl$_6$ structures are unfavorable phases for Na$_3$MCl$_6$.

The phase stability of Na$_3$MCl$_6$ was determined using the $E_{\text{hull}}$ of Na$_3$MCl$_6$ against competing decomposition phases, as shown in Table S4. The decomposition phases generally consisted of NaCl and MCl$_3$ (Tables S5 and S6), and NaMCl$_6$ ($M = Fe$, Sc, Lu, Al, Ga, Tm, and Tb) phases were also considered as stable decomposition phases. In Table 1, Na$_3$MCl$_6$ phases with $E_{\text{hull}}$ values higher than 25 meV/atom, such as Na$_3$MCl$_6$ ($M = Fe$, Ti, Ga, Sm, Pm, Nd, Pr, Ce, and La) were considered as unstable phases, whereas Na$_3$MCl$_6$ phases with a positive value of $E_{\text{hull}}$ below 25 meV/atom such as Na$_3$MCl$_6$ ($M = Cr$, V, Al, Ho, Dy, Tb, Gd, and Eu) were considered as metastable phases, which can be stabilized by entropic effects. Na$_3$MCl$_6$ with Sc, Lu, Y, In, Ti, Bi, Yb, Tm, and Er exhibited negative values of $E_{\text{hull}}$ indicating that these phases were stable against the decomposition phases. The heat map in Figure 2 presents the $E_{\text{hull}}$ of Na$_3$MCl$_6$ among the crystal structures of $P\bar{3}1c$, $P2_1/n$, $R3$, $C2/m$, and $P\bar{3}$.
m1, where the most stable phase is indicated by a black box. Stable Na3MCl6 phases were colored with light blue, and changed to light green, yellow, orange, and red, as $E_{\text{null}}$ increased.

The electrochemical stability window of Na3MCl6 was examined using the grand potential diagram as a function of the Na chemical potential, as shown in Figure 3. The most stable phase of Na3MCl6 (Table 1) was used to calculate the electrochemical stability of Na3MCl6 against reduction and oxidation. The oxidation potential of most Na3MCl6 was approximately 3.8 V, suggesting good stability against oxidation. Phase decomposition by oxidation reactions occurs at a higher voltage than that from these theoretical thermodynamic calculations, owing to the kinetic barrier of the reaction and protective decomposition layers. The high oxidation potential of Na3MCl6 enables its use in cathodes, demonstrating a considerable advantage compared to sulfide SEs, which exhibit low oxidation potentials (e.g., 2.49 V for Na3PS4 and 2.35 V for Na3SbS4)\textsuperscript{53}. The oxidation potential of Na3VCl6 was lower (2.8 V) than that of Na3MCl6 because of the decomposition phase of VCl6.

The reduction potential of Na3MCl6 with group 3 elements and lanthanides was approximately 0.5 V, exhibiting a wide electrochemical stability window (0.5–3.8 V). The reduction potential of Na3MCl6 with p-block elements (M = Al, In, Ti, and Bi) and 3d transition metals (Cr and V) was higher than 1.5 V, indicating that these elements were unstable against reduction reaction in contact with anodes. These results are in agreement with those of previous studies for lithium chlorides, Li3MCl6, which revealed the wide electrochemical window (0.7–4.3 V) of Li3MCl6 with group 3 elements and lanthanides, whereas Li3MX6 with p-block elements (M = In, Bi, and Ti) was unstable against reduction reaction in contact with anodes.\textsuperscript{34} Although Na3MCl6 with group 3 elements and lanthanides showed wide electrochemical window with low reduction potential of approximately 0.5 V, the reduction products of Na3MCl6 included metal M, which enable to conduct electrons, resulting in continuous reduction reactions.\textsuperscript{34} Na3MCl6 also exhibited the instability against the Na metal, and reduction products included metal M, as shown in Table S7. Therefore, adequate coatings should be considered to stabilize the interface between Na3MCl6 and anodes.\textsuperscript{55} The reduction and oxidation potentials of Na3MCl6 and their corresponding phase equilibria are listed in Table S8.

The chemical stability of Na3MCl6 against cathode materials was evaluated by calculating the reaction energy between Na3MCl6 and four cathode materials (NaCrO2, NaNiO2, NaCoO2, and NaNiO2) as shown in Figure S2. Na3MCl6 exhibited the reaction energy approximately 0.1 eV/atom, which was significantly lower than that of sulfide SE, Na3PS4. Although the negative value of reaction energy suggested the thermodynamically favorable reaction between Na3MCl6 and cathode materials, kinetic barrier could prevent the decomposition due to the low reaction energy, while decomposition phases at the interface could also prevent further decomposition of the bulk phase.

The Na-ion migration pathway in Na3MCl6 was predicted using the BVSE method, as shown in Figure 4. The Na-ion migration paths within Na3CrCl6 (trigonal $P\overline{3}1c$), Na3ErCl6 (monoclinic $P2_1/n$), and Na3GdCl6 (trigonal $R\overline{3}$) are illustrated in Figures 4(a), (b), and (c), respectively, using the isosurface (light blue) of the Na site energy. The trigonal $P\overline{3}1c$ and $R\overline{3}$ phases exhibited a one-dimensional migration path along the z-axis between octahedral sites (Oct.–Oct.), and three-dimensional migration paths between octahedral sites via tetrahedral interstitial sites (Oct.–Tet.–Oct.). The monoclinic $P2_1/n$ phase included the Na-ion migration path between octahedral and...
prism sites (Oct.–Prism), and between octahedral and prism sites via tetrahedral interstitial sites (Oct.–Tet.–Prism), which was in good agreement with a previous study. Details of Na-ion migration paths for trigonal $P\bar{3}1c$, monoclinic $P2_1/n$, and trigonal $R\bar{3}$ phases are presented in Figures S3, S4, and S5, respectively.

The energy barriers of Na-ion migration through face sharing octahedral sites (Oct.–Oct.), and three-dimensional path between octahedral sites via tetrahedral interstitial sites (Oct.–Tet.–Prism), and migration paths between octahedral and prism sites via tetrahedral interstitial sites (Oct.–Tet.–Prism). Details of migration pathways are shown in Figures S3–5. (d–f) Na-ion migration energy barriers along the migration paths in (d) Na$_2$CrCl$_6$, (e) Na$_2$ErCl$_6$, and (f) Na$_2$GdCl$_6$.

The Na-ion diffusivity in Na$_x$MCl$_6$ (M = Cr, Er, and Gd) was calculated using the MSD derived from the AIMD simulations. Na$_2$ErCl$_6$ and Na$_2$GdCl$_6$ exhibited negligible values of Na-ion MSD (~1 Å) during 100 ps at 1000 K (Figure S6), indicating the poor ionic conductivity of Na$_2$ErCl$_6$ and Na$_2$GdCl$_6$. Earlier theoretical studies for non-conductive materials suggested that the ionic conductivity was assumed as approximately $10^{-7}$ S/cm at room temperature, when inter-site hopping was not found in the MSD plot at 900 K. Based on the low values of Na-ion MSD for Na$_2$ErCl$_6$ and Na$_2$GdCl$_6$, the diffusion barriers for these materials would exhibit 0.5 eV or higher values. Using these upper bound values, the ionic conductivities at room temperature were estimated by the extrapolation of Arrhenius relation, resulting in $2\times10^{-8}$ S/cm for Na$_2$GdCl$_6$ and Na$_2$ErCl$_6$. When the experimental activation energy of Na$_2$ErCl$_6$ (0.65 eV) was used for the calculation, the ionic conductivity was estimated to be $3\times10^{-10}$ S/cm, which is in good agreement with the experimental ionic conductivity of $10^{-8}$ S/cm. In contrast, the Na-ion MSD was improved in Na$_2$CrCl$_6$, as shown in Figure S7, indicating a higher Na-ion diffusivity of the trigonal $P\bar{3}1c$ phase compared to the monoclinic $P2_1/n$ and trigonal $R\bar{3}$ phases. These results are in good agreement with the energy barrier calculations obtained using the BVSE method, as shown in Figure 4. The Arrhenius plot of Na-ion diffusivity in Figure 5 indicates an activation energy of 0.57 eV for Na$_2$CrCl$_6$, resulting in an ionic conductivity of $2\times10^{-7}$ S/cm at room temperature.

Based on the relatively low ionic conductivities of Na$_x$MCl$_6$, an additional material design strategy should be applied to improve the ionic conductivity of Na$_x$MCl$_6$. One meaningful approach to increase the ionic conductivity is the formation of Na vacancies in Na$_x$MCl$_6$ by the aliovalent substitution of M$^{3+}$.
Fig. 5 Arrhenius plots of Na-ion (a) diffusivity and (b) conductivity for Na2CrCl6, Na2.5Er2Zr0.5Cl6 (NCZC), Na2.5Er2Zr0.5Cl6 (NEZC), Na2.5Gd2Zr0.5Cl6 (NGZC). The open symbols in (b) denote the ionic conductivities obtained using the extrapolation of the Arrhenius plots for high temperature data.

with Zr4+, which resulted in an increase of the ionic conductivity of Na2.3ErCl6 (10^{-6} S/cm) by approximately four orders of magnitude compared to that of Na2.3Er2Zr0.5Cl6 (4\times10^{-5} S/cm). The phase stability of Zr-substituted Na2MCl6 (Na2.5M1.5ZrCl6) was determined as a function of the substitution levels (x=0, 0.25, 0.5, 0.75, and 1), as listed in Table S9. All the Zr-substituted phases, Na2.5M1.5ZrCl6 (M=Cr, Er, and Gd), were considered as stable compounds (E_{\text{hull}} < 25 meV) against competing decomposition phases NaCl, MCl6, and ZrCl6. Zr-substitution in Na2MCl6 (M=Er and Gd) increased the reduction potential to 1.7 V (Table S10), while the effect of Zr substitution on the oxidation potential of Na2MCl6 was negligible.

The Arrhenius plots of the Na-ion diffusivities of Na2.3M0.5Zr0.5Cl6 were obtained using AIMD calculations, as shown in Figure 5 for Na2.3Cr0.5Zr0.5Cl6 (NCZC), Na2.5Er0.5Zr0.5Cl6 (NEZC), and Na2.5Gd0.5Zr0.5Cl6 (NGZC). The activation energy of Na2.3M0.5Zr0.5Cl6 was 0.44, 0.46, and 0.43 eV for NCZC, NEZC, and NGZC, respectively, suggesting that aliovalent substitution is a promising method to enhance the ionic diffusion in Na2MCl6. The predicted Na-ion conductivities at room temperature were 1.3\times10^{-5}, 2.2\times10^{-6}, and 1.3\times10^{-5} S/cm for NCZC, NEZC, and NGZC, respectively, exhibiting ionic conductivities up to four orders of magnitude higher than that in the pristine Na2MCl6. The predicted ionic conductivities of Zr-substituted Na2MCl6 phases (approximately 10^{-5} S/cm) are comparable to the highest ionic conductivity among the reported Na chloride SEs.37-39

Na-ion trajectories were obtained to visualize Na-ion diffusion in Na2MCl6 and Na2.5M0.5Zr0.5Cl6 as shown in Figure 6. The isosurfaces of the Na-ion probability densities during 40 ps AIMD calculations at 1000 K were plotted using an isosurface value of 4P_0 for Na2CrCl6 and Na2GdCl6, which exhibited localized displacements, confirming the lower Na-ion mobility in Na2ErCl6 and Na2GdCl6. Na-ion isosurfaces were more connected through the migration path in Na2CrCl6 compared to that in Na2ErCl6 and Na2GdCl6, which was consistent with the higher diffusivity of Na2CrCl6. Na-ion paths were improved in Na2.5M1.5ZrCl6, indicating that Na vacancies by the aliovalent substitution facilitated Na-ion diffusion. The difference in size between the M and Zr octahedra also led to the disorder of the diffusion path, increasing the Na-ion mobility. Based on the improvement of ionic mobility by ionic substitutions, the optimization of defects in Na2MCl6 is a promising strategy for developing superionic Na chloride SEs. Na2MCl6 with the aliovalent substitution of Ti4+ and Hf4+ also exhibited good phase stability (E_{\text{hull}} < 30 meV) as listed in Table S11, indicating that Ti and Hf can be potential candidates for the substitution in Na2MCl6.

Conclusions

Halide SEs have been reported as promising alternative SEs to other types of SEs owing to their high ionic conductivity and wide electrochemical stability window. In this study, systematic assessments of the phase stability, electrochemical stability, and transport properties of Na2MCl6 were performed to provide design insights for sodium chloride SEs. Structural calculations revealed that sodium chloride Na2MCl6 exhibited the crystal structures of the P2_1c, P2_1/n, and R3 phases, and that the phase preference was dependent on the types and ionic radii of M. Na2MCl6 with relatively small M cations and group 13 elements preferred the trigonal P2_1c phase, whereas Na2MCl6 with
moderate ionic radii preferred the monoclinic $P2_1/n$ phase. $Na_3MCl_6$ generally showed a preference for the trigonal $R3$ phase with relatively large $M$ cations above 90 pm. Phase stability calculations indicated that $Na_3MCl_6$ ($\text{M} = \text{Cr}, \text{V}, \text{Sc}, \text{Lu}, \text{Y}, \text{Al}, \text{In}, \text{Ti}, \text{Bi}, \text{Yb}, \text{Sm}, \text{Er}, \text{Ho}, \text{Dy}, \text{Tb}, \text{Gd}$, and $\text{Eu}$) can be considered as stable structures. $Na_3MCl_6$ typically exhibits a high oxidation potential, demonstrating considerable advantages compared to sulfide SEs. The electrochemical stability window was wide (0.5–3.8 V) for $Na_3MCl_6$ with $p$-block elements and $3d$ transition metals was higher than 1.5 V. The Na-ion migration pathway and energy barriers in $Na_3MCl_6$ were predicted using the BVSE method. The energy barriers in the monoclinic $P2_1/n$ and trigonal $R3$ phases were higher than those in the trigonal $P31c$ phase. AIMD simulations were performed to examine Na-ion diffusion in $Na_3MCl_6$. $Na_3CrCl_6$ had a higher ionic conductivity than $Na_3ErCl_6$ and $Na_3GdCl_6$, but all $Na_3MCl_6$ phases displayed low ionic conductivity. The aliovalent substitution of $M^{3+}$ with $Zr^{4+}$ increased the ionic conductivity up to four orders of magnitude compared to that of the pristine phase, suggesting that Na vacancy formation in $Na_3MCl_6$ is a crucial approach to improve the ionic conductivity.

Conflicts of interest

There are no conflicts to declare.

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