

Achieving Better Anti-Perovskite Solid-State Electrolytes Through Compositional Modifications: A Review

Yunxi Wei

*School of the Environment, Nanjing University, Nanjing, China
724739317@qq.com*

Abstract. Anti-perovskite solid-state electrolytes have attracted increasing attention for solid-state lithium and sodium batteries because of their high concentration of mobile alkali-metal ions, flexible crystal framework and tunable chemical composition. However, their practical application is still limited by insufficient room-temperature ionic conductivity, uncertain electrochemical stability, interfacial incompatibility and grain-boundary resistance. This mini review focuses on recent progress in compositional modification of anti-perovskite solid-state electrolytes. After summarizing their structural features, ionic transport mechanisms, electrochemical properties and current challenges, elemental substitution and polyanion substitution are discussed as two representative modification strategies. The reviewed studies show that compositional modification can tune lattice geometry, defect chemistry, migration pathways and dynamic local environments, thereby improving ionic conductivity and related electrolyte properties. Representative systems include mixed-halide anti-perovskites, fluorine-doped hydroxide anti-perovskites, and BH_4^- , NO_2^- and SO_4^{2-} containing compounds. This review highlights the importance of linking composition, structure and practical battery performance, and provides guidance for the rational design of high-performance anti-perovskite electrolytes for next-generation all-solid-state batteries.

Keywords: anti-perovskite, solid-state electrolyte, compositional modification, polyanion substitution

1. Introduction

Solid-state batteries (SSBs) are promising next-generation energy-storage systems with superior safety and energy density compared to conventional liquid-electrolyte batteries [1, 2], but their practical deployment is limited by solid electrolyte performance, which demands high room-temperature ionic conductivity, a wide electrochemical stability window and stable electrode-electrolyte interfaces [3-5].

Anti-perovskites have emerged as an attractive electrolyte candidate due to their inverse perovskite structure and high mobile alkali-metal ion concentration. The discovery of Li-rich mixed-halide anti-perovskites (e.g., $\text{Li}_3\text{OCl}_{0.5}\text{Br}_{0.5}$) with room-temperature superionic conductivity has further demonstrated their application potential [6].

Compositional engineering is widely used to tailor electrolyte properties via elemental substitution and polyatomic unit incorporation, which modulates local structure, defect chemistry and ion migration pathways to optimize overall performance [7, 8].

While existing research mostly cover the overall development of anti-perovskite electrolytes, a systematic summary focusing specifically on compositional modification strategies is still lacking. This review focuses on anti-perovskite solid-state electrolytes and their compositional modification strategies. The basic structural features, ion-transport mechanisms and electrochemical properties are first introduced, followed by a discussion of elemental substitution and polyanion substitution. Finally, key challenges for battery applications are summarized to highlight the remaining issues in the rational design of improved anti-perovskite electrolytes.

2. Fundamentals of anti-perovskite solid-state electrolyte

2.1. Structural features

Anti-perovskites typically adopt a cubic crystal structure with the space group $Pm\bar{3}m$, in which the cation and anion positions are arranged in an inverted manner compared with conventional perovskites. In the commonly used X_3BA notation, the X site is occupied by cations, while the A and B sites are occupied by anionic species. For Li- and Na-based anti-perovskite electrolytes, the X site is usually occupied by mobile alkali-metal ions such as Li^+ or Na^+ . The basic site arrangement and cubic framework are illustrated in Figure 1a.

Although the ideal anti-perovskite structure is cubic, its actual symmetry depends strongly on the size matching among ions at different lattice sites, which can be evaluated by the Goldschmidt tolerance factor. In general, anti-perovskites with a tolerance factor between 0.85 and 1.0 tend to adopt a cubic structure, whereas values below 0.85 may result in tetragonal, orthorhombic or other lower-symmetry phases. Such lattice distortion is important for solid-state electrolyte applications because it can alter ion migration bottlenecks and transport pathways, thereby affecting phase stability and ionic conductivity.

Meanwhile, the properties of anti-perovskites are also closely related to their characteristic site arrangement. In Li- and Na-rich anti-perovskite electrolytes, the high concentration and arrangement of mobile X-site cations provide a structural basis for fast ion transport. For solid-state electrolyte applications, vacancies and lattice strain are particularly important because they can modify the available migration space, defect formation behaviour and the onset of superionic conduction [6, 9-11]. These structure–property relationships provide a useful basis for rational compositional design.

Benefiting from their structural flexibility and chemical diversity, anti-perovskites can be prepared via various routes. Solid-state reaction is the most common method for bulk powders, and Li-rich synthesis conditions can introduce Li interstitials to enhance ionic conduction [12, 13]. Thin-film deposition and nitridation routes have also been developed for specific anti-perovskite phases in other fields [14, 15].

2.2. Ionic transport mechanism

The ion-transport mechanism of anti-perovskite electrolytes has been mainly investigated via computational simulations, with vacancy migration and interstitial migration being the two most widely discussed pathways.

In 2013, Zhang et al. reported the first computational study on the ion-transport mechanism of Li-rich anti-perovskites, bringing attention to whether ionic conduction is mainly governed by vacancy

or interstitial migration [16]. Their results suggested that Li vacancies and structural disorder are important for Li-ion transport, and later defect studies further supported vacancy migration as a major pathway in stoichiometric systems.

However, interstitial-based mechanisms have also been proposed, since Li interstitial dumbbells can migrate through very low-barrier pathways (Figure 1b). Although Li interstitials generally have higher formation energies, they may become more favourable under specific Li-rich and halide-deficient conditions. Therefore, the dominant ion-transport mechanism in Li-rich anti-perovskites remains strongly dependent on defect chemistry and local composition [17-19].

Overall, the ion-transport mechanism in anti-perovskite electrolytes is still not fully understood and may vary with composition, defect chemistry and local structure. Other processes, including Frenkel defect formation and orientational disorder of anions, may assist ion migration in hydroxide-based systems, while cluster-anion rotation and paddlewheel-type effects can further facilitate ion transport in polyanion-containing compounds. Meanwhile, structural factors such as lattice distortion, anion packing, migration-channel size and local disorder can also regulate migration barriers and defect mobility [20-22]. These factors together provide the mechanistic basis for later doping and polyanion-substitution strategies.

2.3. Electrochemical properties

For solid-state electrolytes (SSEs), a core requirement is high ionic conductivity coupled with negligible electronic conductivity. Anti-perovskite electrolytes generally possess a wide band gap, which effectively suppresses electronic conduction and enables them to act as ion-conducting, electronically blocking separators [23].

Electrochemical stability is another critical property for battery applications. Beyond electronic insulation, redox stability and chemical compatibility with alkali-metal electrodes are key evaluation metrics. Interfacial compatibility further affects the practical electrochemical behaviour of anti-perovskite electrolytes. Poor compatibility with alkali-metal electrodes may lead to side reactions, resistive interphase formation or contact loss at the electrode/electrolyte interface. These factors can increase interfacial resistance and reduce cycling stability, indicating that electrolyte performance is controlled not only by intrinsic conductivity but also by electrode–electrolyte compatibility [24, 25].

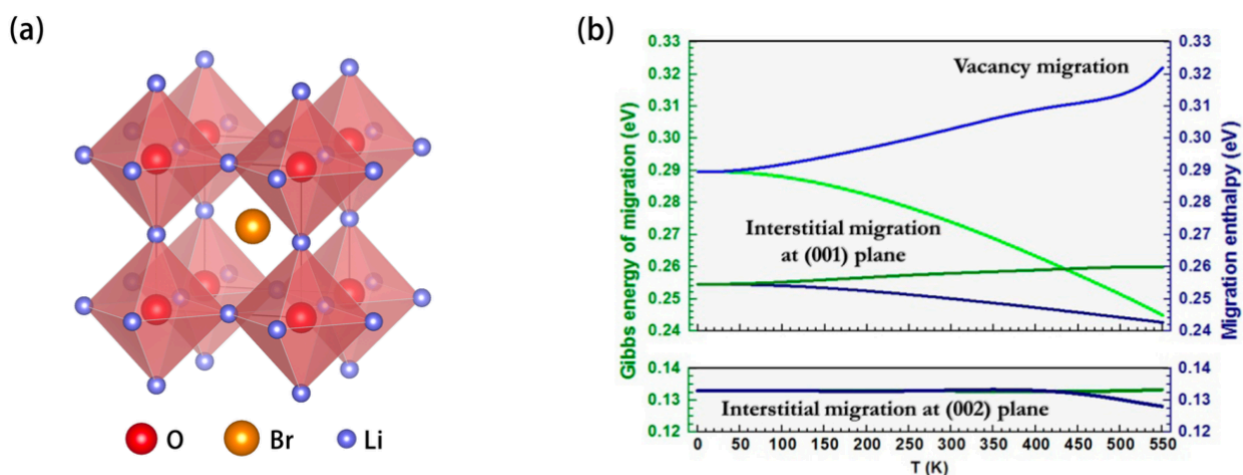


Figure 1. (a) Cubic anti-perovskite structure with the general formula X_3BA . (b) Temperature-dependent migration energetics of vacancy and interstitial pathways [18]

3. Compositional modifications of anti-perovskite materials

3.1. Overview of modification strategies

Compositional modification is an important strategy for tuning the properties of anti-perovskite solid electrolytes. Owing to the structural flexibility and chemical diversity of the anti-perovskite framework, both simple ions and more complex polyatomic units can be introduced into different lattice sites. In this review, recent modification strategies are discussed from two main aspects: elemental substitution and polyanion substitution. Representative examples of these two routes are summarized in Table 1.

3.2. Elemental substitutions

Elemental substitution is the most straightforward modification strategy, enabled by the rich elemental diversity of anti-perovskite structures across different crystallographic sites (Figure 2a) [26]. By adjusting ionic size, bonding strength and local disorder, it can effectively tune lattice geometry, defect chemistry and ion migration pathways [6, 27-30]. Mixed-halide substitution is a representative example of composition-dependent transport regulation. In $\text{Li}_3\text{OCl}_{1-x}\text{Br}_x$, Deng et al. investigated how the Cl/Br ratio affects Li^+ migration at the halide site [31]. Bond-percolation and computational results showed that the probability of low-barrier open bonds depends strongly on Br content, and compositions within $0.235 \leq x \leq 0.395$ were predicted to show improved Li^+ conductivity. In particular, $\text{Li}_3\text{OCl}_{0.75}\text{Br}_{0.25}$ was suggested to have higher Li^+ conductivity than the widely studied $\text{i}_3\text{OCl}_{0.5}\text{Br}_{0.5}$.

Aliovalent or heteroanion doping provides another route to modify defect chemistry and electrochemical behaviour. For example, Li et al. reported the fluorine-doped anti-perovskite $\text{Li}_2(\text{OH})_{0.9}\text{F}_{0.1}\text{Cl}$, where partial F- substitution at the hydroxide-related anion site increased Li^+ conductivity by two orders of magnitude compared with orthorhombic Li_2OHCl and improved its electrochemical tolerance [32]. Mg^{2+} substitution at the mobile Li site in Li_3OCl also illustrates how aliovalent doping can introduce charge-compensating Li vacancies with limited structural distortion [33].

More extensive elemental replacement has also been explored in anti-perovskite-related frameworks. In layered structures constructed from anti-perovskite units, $\text{Na}_3\text{LiS}_{0.5}\text{O}_{0.5}\text{I}_2$ was identified as an optimized composition with a low Na^+ activation energy of 0.12 eV and a room-temperature conductivity of 6.3 mS cm^{-1} (Figure 2b) [34]. In chalcohalide anti-perovskites, Yin et al. investigated the replacement of B-site O^{2-} by chalcogenide anions such as S^{2-} [35]. Such replacement was proposed to weaken the interaction with mobile cations and lower migration barriers, although further progress in phase stabilisation and synthesis control is still required.

3.3. Polyanion substitutions

Compared with elemental substitution, polyanion substitution offers an additional dimension for performance tuning: the rotational and orientational dynamics of polyatomic units can modulate the local environment around mobile ions, affecting both ionic transport and electronic structure [36, 37].

One representative route is to use superhalogen units as halide substitutes in Li-rich anti-perovskites. Superhalogens have higher electron affinities than halogen atoms and can mimic halide-like chemistry, thereby expanding the range of possible A-site substituents. Based on this concept,

BH₄⁻ was introduced into the Li₃OA anti-perovskite framework as a superhalogen substituent. Li₃OBH₄ is particularly notable for its wide band gap (~7 eV), suggesting strong electronic insulation and potential electrochemical stability (Figure 2c) [21].

Later, Sun et al. extended the same BH₄⁻ polyanion strategy to Na-rich anti-perovskites and obtained cubic Na₃OBH₄ [38]. AC impedance measurements showed that hot-pressed pellets achieved a room-temperature ionic conductivity of $4.4 \times 10^{-3} \text{ S cm}^{-1}$, while cold-pressed powders exhibited much higher resistance. This improvement arises from enhanced densification, improved particle contact and reduced grain-boundary resistance.

Other polyanion substitutions have also been explored. In Na₃ONO₂, NO₂⁻ units were reported to assist Na⁺ migration through Na-O interactions, leading to a sharp increase in ionic conductivity at high temperature and a reduced activation energy from 0.81 to 0.385 eV [39]. In another theoretical study, Li₃BrSO₄ was predicted to be a promising anti-perovskite electrolyte containing SO₄²⁻ anion clusters, with high Li⁺ conductivity, a low migration barrier and a wide band gap of 7.69 eV (Figure 2d) [40].

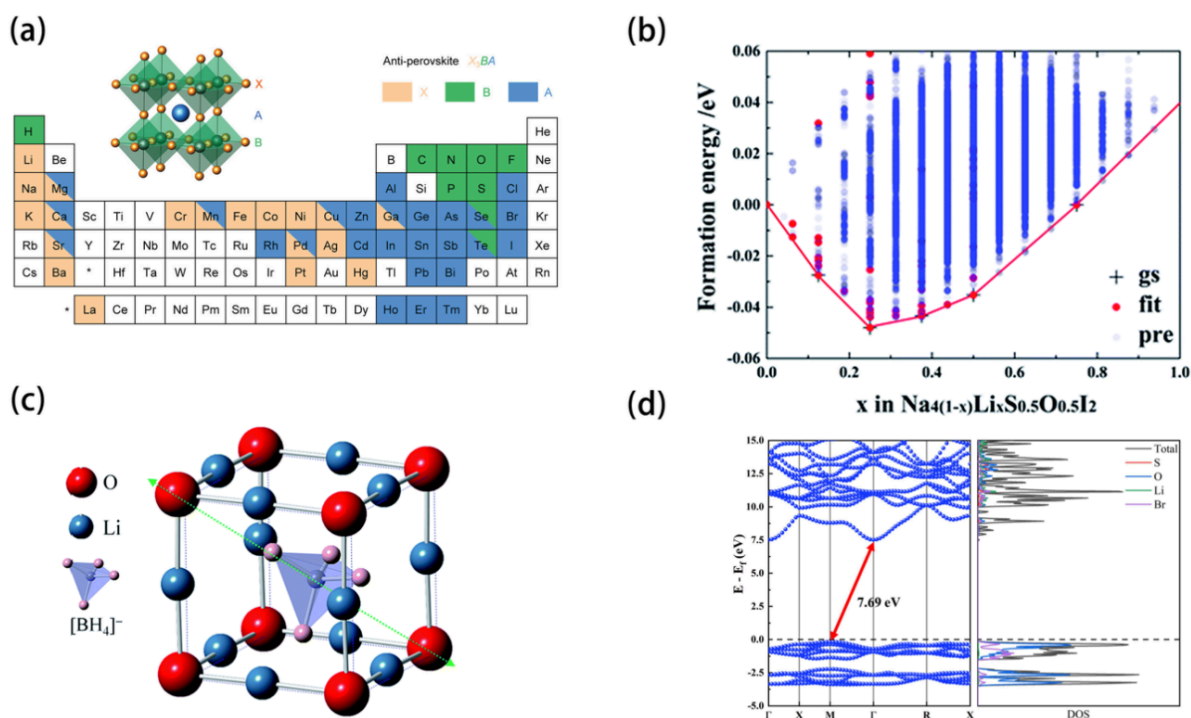


Figure 2. (a) Elemental constituents of known X₃BA anti-perovskites at different crystallographic sites [26]. (b) Convex-hull analysis of Na₄(1-x)Li₃S_{0.5}O_{0.5}I₂, showing the stable composition obtained by partial Li substitution at Na sites [34]. (c) Optimized structure of Li₃O(BH₄) [21]. (d) Calculated electronic band structure and density of states of Li₃BrSO₄ [40]

Table 1. Representative elemental and polyanion substitution strategies in anti-perovskite solid-state electrolytes

Substitution type	Substitution route	Representative composition	Status	Ionic conductivity (S cm ⁻¹)	Ea (eV)	Preparation
Elemental substitution	Br / Li ₃ OCl	i ₃ OCl _{0.5} Br _{0.5} [6].	Experimental	1.94 × 10 ⁻³ (RT)	0.18	Molten synthesis
	F / Li ₂ OHCl	Li ₂ (OH) _{0.9} F _{0.1} Cl [32]	Experimental	3.5 × 10 ⁻⁵ (RT)	0.52	Low-temperature solid-state reaction
	Li / Na ₄ S _{0.5} O _{0.5} I ₂	Na ₃ LiS _{0.5} O _{0.5} I ₂ (predicted) [34]	Predicted	6.3 × 10 ⁻³ (RT)	0.12	— (computational study)
Polyanion substitution	BH ₄ / Li-rich anti-perovskite	Li ₃ OBH ₄ (predicted) [21]	Predicted	0.10 × 10 ⁻³ (RT)	0.301	— (computational study)
	BH ₄ / Na-rich anti-perovskite	Na ₃ OBH ₄ [38]	Experimental	4.4 × 10 ⁻³ (RT)	0.25	Solid-state reaction + hot pressing
	SO ₄ / Li-rich anti-perovskite	Li ₃ BrSO ₄ (predicted) [40]	Predicted	1.206 × 10 ⁻¹ (RT)	0.156	— (computational study)

4. Discussion

The practical battery application is still limited by chemical/electrochemical stability, electrode/electrolyte interfacial compatibility and grain-boundary resistance.

4.1. Chemical and electrochemical stability

Chemical and electrochemical stability is essential for anti-perovskite solid electrolytes under battery-operating conditions. A wide band gap may indicate good electronic insulation, but it does not directly guarantee practical electrochemical stability. For example, Li₃OCl has been predicted to become unstable toward oxidation at relatively low potentials, suggesting that stability should be evaluated under realistic electrochemical conditions rather than inferred only from intrinsic electronic properties [12].

4.2. Electrode/electrolyte interfacial compatibility

Electrode/electrolyte interfacial compatibility also strongly affects practical battery performance. Chemical side reactions, resistive interphase formation and poor physical contact at the metal/electrolyte interface can increase interfacial resistance and reduce cycling stability [24, 25].

4.3. Grain-boundary resistance

Grain-boundary resistance is another major obstacle for polycrystalline anti-perovskite electrolytes. In Li_3OCl , grain-boundary Li^+ conductivity was reported to be nearly one order of magnitude lower than bulk conductivity, with higher activation energies for ion migration [41]. This suggests that densification, hot pressing and microstructure control are important for reducing total resistance and improving practical ionic transport.

5. Conclusion

Anti-perovskite solid-state electrolytes are promising candidates for solid-state batteries because of their flexible crystal framework, high concentration of mobile alkali-metal ions and tunable chemical composition. This review has discussed their structural features, ion-transport mechanisms, electrochemical properties and practical challenges, with particular attention to chemical/electrochemical stability, electrode/electrolyte interfacial compatibility and grain-boundary resistance. Although many Li^- and Na -rich anti-perovskites show favourable ionic conductivity and electronic insulation, their practical performance remains strongly influenced by phase stability, electrode compatibility and microstructure.

Compositional modification provides an important route to address these issues. Elemental substitution can effectively tune lattice geometry, defect formation and carrier concentration, while polyanion substitution further expands the design space by introducing molecular geometry, orientational disorder and dynamic local environments that facilitate ion migration. This combined approach highlights the critical importance of linking composition, structure and processing to optimize overall electrolyte performance.

Due to the scope of this review, the discussion is mainly focused on representative compositional modification strategies rather than a comprehensive comparison of all reported anti-perovskite systems. In addition, some important aspects, such as detailed synthesis control, long-term cycling behaviour and full-cell performance, are only briefly discussed. Therefore, a more systematic evaluation of structure, processing and battery-level performance is still needed to fully assess the practical potential of anti-perovskite solid-state electrolytes.

References

- [1] Joshi, A., Mishra, D. K., Singh, R., Zhang, J., & Ding, Y. (2025). A comprehensive review of solid-state batteries. *Applied Energy*, 386, 125546.
- [2] Dutra, A. C. C., & Dawson, J. A. (2023). Computational design of antiperovskite solid electrolytes. *The Journal of Physical Chemistry C*, 127(37), 18256–18270.
- [3] Ito, D., Kuwata, N., Takemoto, S., Kamiguchi, K., Hasegawa, G., & Takada, K. (2025). Lattice-matched antiperovskite-perovskite system toward all-solid-state batteries. *Nature Communications*, 16(1), 7372.
- [4] Dutra, A. C. C., Quirk, J. A., Zhou, Y., & Dawson, J. A. (2024). Influence of surfaces on ion transport and stability in antiperovskite solid electrolytes at the atomic scale. *ACS Materials Letters*, 6(11), 5039–5047.
- [5] Hatzell, K. B., & Nazar, L. F. (2025). Recent advances in solid-state batteries. *Journal of the American Chemical Society*, 147(18), 14881–14883.
- [6] Zhao, Y., & Daemen, L. L. (2012). Superionic conductivity in lithium-rich anti-perovskites. *Journal of the American Chemical Society*, 134(36), 15042–15047.
- [7] Dawson, J. A., Famprikis, T., & Johnston, K. E. (2021). Anti-perovskites for solid-state batteries: Recent developments, current challenges and future prospects. *Journal of Materials Chemistry A*, 9(35), 18746–18772.
- [8] Xia, W., Zhao, Y., Zhao, F., Adair, K., Zhao, R., Li, S., Zou, R., Zhao, Y., & Sun, X. (2022). Antiperovskite electrolytes for solid-state batteries. *Chemical Reviews*, 122(3), 3763–3819.

- [9] Bannikov, V. V. (2022). Structural and elastic properties of Mn₃InN antiperovskite: The anomalous behavior of compressibility with external pressure and its reasons. *Computational Condensed Matter*, 32, e00729.
- [10] Gao, Z.-Y., Wang, W., Li, B.-C., Sun, L., & Wang, F. (2022). Potential antiperovskite semiconductor compounds Mg₃XN (X = P, As, Sb, Bi): The first-principles study. *Journal of Superconductivity and Novel Magnetism*, 35(11), 3277–3290.
- [11] Sagotra, A. K., & Cazorla, C. (2017). Stress-mediated enhancement of ionic conductivity in fast-ion conductors. *ACS Applied Materials & Interfaces*, 9(44), 38773–38783.
- [12] Emly, A., Kioupakis, E., & Van der Ven, A. (2013). Phase stability and transport mechanisms in antiperovskite Li₃OCl and Li₃OBr superionic conductors. *Chemistry of Materials*, 25(23), 4663–4670.
- [13] Zhang, J., Han, J., Zhu, J., Lin, Z., Braga, M. H., Daemen, L. L., Wang, L., & Zhao, Y. (2014). High pressure-high temperature synthesis of lithium-rich Li₃O(Cl, Br) and Li_{3-x}Ca_{x/2}OCl anti-perovskite halides. *Inorganic Chemistry Communications*, 48, 140–143.
- [14] Zhu, L., Yang, B., Wu, Z., Li, C., Li, H., Li, H., Huang, Y., Zhu, X., Zhu, X., & Sun, Y. (2022). Metal/antiperovskite metal nitride composites Ag/AgNNi₃ as novel efficient electrocatalysts for hydrogen evolution reaction in alkaline media. *Journal of Materials Science & Technology*, 112, 222–229.
- [15] Sun, Y., Wang, C., Na, Y., Chu, L., Wen, Y., & Nie, M. (2010). Investigation of antiperovskite Mn₃CuN_x film prepared by DC reactive magnetron sputtering. *Materials Research Bulletin*, 45(9), 1230–1233.
- [16] Zhang, Y., Zhao, Y., & Chen, C. (2013). Ab initio study of the stabilities of and mechanism of superionic transport in lithium-rich antiperovskites. *Physical Review B*, 87(13), 134303.
- [17] Lu, Z., Chen, C., Baiyee, Z. M., Chen, X., Niu, C., & Ciucci, F. (2015). Defect chemistry and lithium transport in Li₃OCl anti-perovskite superionic conductors. *Physical Chemistry Chemical Physics*, 17(48), 32547–32555. <https://doi.org/10.1039/C5CP05722A>
- [18] Mouta, R., Melo, M. Á. B., Diniz, E. M., & Paschoal, C. W. A. (2014). Concentration of charge carriers, migration, and stability in Li₃OCl solid electrolytes. *Chemistry of Materials*, 26(24), 7137–7144.
- [19] Mouta, R., Diniz, E. M., & Paschoal, C. W. A. (2016). Li⁺ interstitials as the charge carriers in superionic lithium-rich anti-perovskites. *Journal of Materials Chemistry A*, 4(5), 1586–1590. <https://doi.org/10.1039/C5TA07450A>
- [20] Song, A.-Y., Xiao, Y., Turcheniuk, K., Upadhyaya, P., Ramanujapuram, A., Benson, J., Magasinski, A., Olguin, M., Meda, L., Borodin, O., et al. (2018). Protons enhance conductivities in lithium halide hydroxide/lithium oxyhalide solid electrolytes by forming rotating hydroxy groups. *Advanced Energy Materials*, 8(3), 1700971.
- [21] Fang, H., Wang, S., Liu, J., Sun, Q., & Jena, P. (2017). Superhalogen-based lithium superionic conductors. *Journal of Materials Chemistry A*, 5(26), 13373–13381. <https://doi.org/10.1039/C7TA01648D>
- [22] Wang, Y., Richards, W. D., Ong, S. P., Miara, L. J., Kim, J. C., Mo, Y., & Ceder, G. (2015). Design principles for solid-state lithium superionic conductors. *Nature Materials*, 14(10), 1026–1031.
- [23] Wu, M., Xu, B., Lei, X., Huang, K., & Ouyang, C. (2018). Bulk properties and transport mechanisms of a solid state antiperovskite Li-ion conductor Li₃OCl: Insights from first principles calculations. *Journal of Materials Chemistry A*, 6(3), 1150–1160. <https://doi.org/10.1039/C7TA08780B>
- [24] Krauskopf, T., Hartmann, H., Zeier, W. G., & Janek, J. (2019). Toward a fundamental understanding of the lithium metal anode in solid-state batteries—An electrochemo-mechanical study on the garnet-type solid electrolyte Li_{6.25}Al_{0.25}La₃Zr₂O₁₂. *ACS Applied Materials & Interfaces*, 11(15), 14463–14477.
- [25] Wenzel, S., Leichtweiss, T., Weber, D. A., Sann, J., Zeier, W. G., & Janek, J. (2016). Interfacial reactivity benchmarking of the sodium ion conductors Na₃PS₄ and sodium β-alumina for protected sodium metal anodes and sodium all-solid-state batteries. *ACS Applied Materials & Interfaces*, 8(41), 28216–28224.
- [26] Wang, Y., Zhang, H., Zhu, J., Lü, X., Li, S., Zou, R., & Zhao, Y. (2020). Antiperovskites with exceptional functionalities. *Advanced Materials*, 32(7), 1905007.
- [27] Clarke, M. J., Dawson, J. A., Mays, T. J., & Islam, M. S. (2021). Atomistic insights into the effects of doping and vacancy clustering on Li-ion conduction in the Li₃OCl antiperovskite solid electrolyte. *ACS Applied Energy Materials*, 4(5), 5094–5100.
- [28] Dawson, J. A., Chen, H., & Islam, M. S. (2018). Composition screening of lithium- and sodium-rich anti-perovskites for fast-conducting solid electrolytes. *The Journal of Physical Chemistry C*, 122(42), 23978–23984.
- [29] Fan, S., Lei, M., Wu, H., Hu, J., Yin, C., Liang, T., & Li, C. (2020). A Na-rich fluorinated sulfate anti-perovskite with dual doping as solid electrolyte for Na metal solid state batteries. *Energy Storage Materials*, 31, 87–94.
- [30] Braga, M. H., Stockhausen, V., Oliveira, J. C. E., & Ferreira, J. A. (2013). The role of defects in Li₃ClO solid electrolyte: Calculations and experiments. *MRS Online Proceedings Library*, 1526(1), 905.
- [31] Deng, Z., Radhakrishnan, B., & Ong, S. P. (2015). Rational composition optimization of the lithium-rich Li₃OCl_{1-x}Br_x anti-perovskite superionic conductors. *Chemistry of Materials*, 27(10), 3749–3755.

- [32] Li, Y., Zhou, W., Xin, S., Li, S., Zhu, J., Lü, X., Cui, Z., Jia, Q., Zhou, J., Zhao, Y., et al. (2016). Fluorine-doped antiperovskite electrolyte for all-solid-state lithium-ion batteries. *Angewandte Chemie International Edition*, 55(34), 9965–9968.
- [33] Stegmaier, S., Voss, J., Reuter, K., & Luntz, A. C. (2017). Li⁺ defects in a solid-state Li ion battery: Theoretical insights with a Li₃OCl electrolyte. *Chemistry of Materials*, 29(10), 4330–4340.
- [34] Yu, Y., Wang, Z., & Shao, G. (2019). Theoretical tuning of Ruddlesden–Popper type anti-perovskite phases as superb ion conductors and cathodes for solid sodium ion batteries. *Journal of Materials Chemistry A*, 7(17), 10483–10493. <https://doi.org/10.1039/C9TA02166C>
- [35] Yin, L., Murphy, M., Kim, K., Hu, L., Cabana, J., Siegel, D. J., & Lapidus, S. H. (2020). Synthesis of antiperovskite solid electrolytes: Comparing Li₃SI, Na₃SI, and Ag₃SI. *Inorganic Chemistry*, 59(16), 11244–11247.
- [36] Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*, 32(5), 751–767.
- [37] Weller, M. T., Weber, O. J., Henry, P. F., Di Pumpo, A. M., & Hansen, T. C. (2015). Complete structure and cation orientation in the perovskite photovoltaic methylammonium lead iodide between 100 and 352 K. *Chemical Communications*, 51(20), 4180–4183. <https://doi.org/10.1039/C4CC09944C>
- [38] Sun, Y., Wang, Y., Liang, X., Xia, Y., Peng, L., Jia, H., Li, H., Bai, L., Feng, J., Jiang, H., et al. (2019). Rotational cluster anion enabling superionic conductivity in sodium-rich antiperovskite Na₃OBH₄. *Journal of the American Chemical Society*, 141(14), 5640–5644.
- [39] Gao, L., Zhang, H., Wang, Y., Li, S., Zhao, R., Wang, Y., Gao, S., He, L., Song, H.-F., Zou, R., et al. (2020). Mechanism of enhanced ionic conductivity by rotational nitrite group in antiperovskite Na₃ONO₂. *Journal of Materials Chemistry A*, 8(40), 21265–21272. <https://doi.org/10.1039/D0TA07110B>
- [40] Cui, G., Zhang, L., & Dong, Y. (2025). Predictions of anti-perovskite Li₃BrSO₄ electrolyte: A first principles study of electronic, thermal, and mechanical properties, as well as Li-ion conductivity. *Journal of Energy Storage*, 111, 115393.
- [41] Dawson, J. A., Canepa, P., Famprikis, T., Masquelier, C., & Islam, M. S. (2018). Atomic-scale influence of grain boundaries on Li-ion conduction in solid electrolytes for all-solid-state batteries. *Journal of the American Chemical Society*, 140(1), 362–368.