

Potential Solid-State Electrolytes with Good Balance between Ionic Conductivity and Electrochemical Stability: $\text{Li}_{5-x}\text{M}_{1-x}\text{M}'_x\text{O}_4$ ($\text{M} = \text{Al}$ and Ga and $\text{M}' = \text{Si}$ and Ge)

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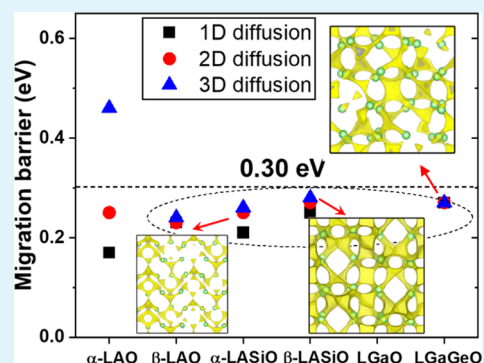
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ABSTRACT: Exploring new solid-state electrolyte (SSE) materials with good electrochemical stability and high Li-ion conductivity for all-solid-state Li-ion batteries is vital for the development of technologies. Herein, we employ two lithium aluminates, α - and β - Li_5AlO_4 (α - and β -LAO), as the model framework, which have an orthorhombic crystal structure and isolated AlO_4 tetrahedron units connected in lithium atoms, exhibiting large band gaps, low migration barriers (0.30–0.40 eV), fast Li-ion conductivity (LIC, in a magnitude of 10^{-4} S/cm), and a good electrochemical stability window (ESW, [0.01–3.20 V] vs Li^+/Li). We tabulate the expected decomposition products at the interface, while considering cathodes in combination with the LAO electrolyte to discuss their compatibility. We also examine the electrochemical stability, $\text{H}_2\text{O}/\text{CO}_2$ stability, and Li-ion mobility of $\text{Li}_{4.6}\text{Al}_{0.6}\text{Si}_{0.4}\text{O}_4$ (LASO), Li_5GaO_4 (LGaO), and $\text{Li}_{4.6}\text{Ga}_{0.6}\text{Ge}_{0.4}\text{O}_4$ (LGaGeO) compounds. In general, there is usually a trade-off between the LIC and the ESW; however, LAO features a good balance between an outstanding LIC and a wide ESW, making the compound a promising candidate for next-generation SSE materials.

KEYWORDS: Li_5AlO_4 , solid-state electrolyte, ionic conductivity, stability, first-principles calculations, all-solid-state lithium-ion battery



1. INTRODUCTION

New solid-state electrolyte (SSE) materials that can fast transport Li-ions from one electrode to the other are required to increase energy density and decrease safety concerns in all-solid-state lithium-ion batteries (ASSLBs).^{1,2} Such SSE materials can thus help to alleviate technological challenges associated with the adoption of electric vehicles and accelerate the transition to a low-carbon economy. The most commonly used SSE materials, such as sulfide-based lithium superionic conductors (LISICON),^{3,4} oxide-based NASICON-like conductors (sodium superionic conductors),⁵ garnet,^{6,7} and perovskites,^{8,9} have Li-ion conductivities approaching those of liquid electrolytes. However, current SSE materials are not stable against lithium-ion battery electrodes, especially for cathode materials.^{10,11} Moreover, we could count on one hand the number of oxide SSE materials. Therefore, there is an urgent need for new SSE materials with high Li-ion conductivity and electrochemical (chemical) stability.¹²

In our present work, we investigate the less-studied lithium aluminate, Li_5AlO_4 (LAO), which is previously used as a coating material on $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ cathodes,^{13,14} a gate dielectric,¹⁵ and a high-temperature CO_2 -capturing material.¹⁶ This crystalline LAO has two polymorphs that are α - and β -crystallized LAO phases, and both phases crystallize in an orthorhombic structure, characterized by the $Pbca$ space group with $a = 9.087$, $b = 8.947$, and $c = 9.120$ Å and the $Pmmn$ space

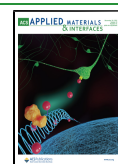
group with $a = 6.420$, $b = 6.302$, and $c = 4.620$ Å, respectively. Both structures are ordered derivatives of the antiperovskite (Li_2O) structure and the cation atoms' (Li and Al) ordered arrangement causes an orthorhombic distortion from cubic symmetry. LAO can potentially permit a high ionic conductivity with a three-dimensional (3D) percolating diffusion network. Therefore, it is anticipated that bulk LAO can have high ion conductivity. Nevertheless, to date, only two early experiments^{17,18} have been reported on the utilization of this material as a SSE except a computation research using a high-throughput method,¹⁹ but the analysis of structure–property relationships in LAO and Si/Ge-substituted compositions for SSE has been unknown.

Herein, we apply first-principles density functional theory (DFT) to understand their stability and ion conductivity.²⁰ We calculate the formation energies of several defects in the range of 0–4.5 V versus Li/Li^+ . We evaluate the electrochemical stability window and $\text{H}_2\text{O}/\text{CO}_2$ stability of LAO, LASO,

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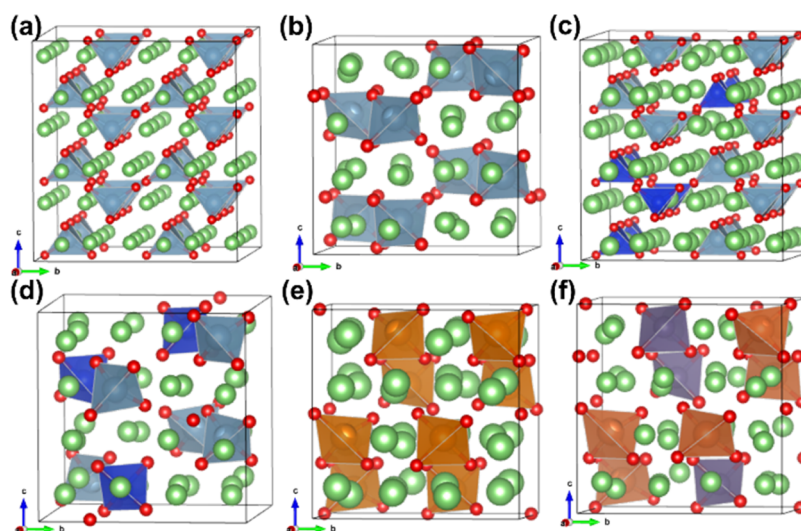


Figure 1. (a–f) Side view of α -LAO with the $Pmmn$ space group, β -LAO with the $Pbca$ space group, α - $\text{Li}_{4.6}\text{Al}_{0.6}\text{Si}_{0.4}\text{O}_4$ (α -LASiO), β - $\text{Li}_{4.6}\text{Al}_{0.6}\text{Si}_{0.4}\text{O}_4$ (β -LASiO), Li_5GaO_4 (LGaO) with the $Pbca$ space group, and the $\text{Li}_{4.6}\text{Ga}_{0.6}\text{Ge}_{0.4}\text{O}_4$ (LGaGeO) crystal structure, respectively. The green and red spheres, dusty blue tetrahedrons, orange and gray red tetrahedrons represent the Li and O atoms, AlO_4 and SiO_4 units, GaO_4 , and GeO_4 units, respectively.

LGaO, and LGaGeO compounds and tabulate the expected decomposition products at the cathode/LAO and cathode/LGaO interfaces. We employed the bond valence site energy (BASE) method and DFT-based climbing image nudged elastic band (CI-NEB) simulations to evaluate the Li-ion mobility and found that the ion conductivity of LAO and LGaO is on a par with known SSE materials, which is critical for the operation of ASSLBs.

2. COMPUTATIONAL DETAILS

All calculations in this work were performed with a general gradient approximation applying the Perdew–Burke–Ernzerhof functional,^{21,22} in the program of the Vienna Ab initio Simulation Package (VASP).²³ Valence electron configurations are expanded with the projector augmented wave basis set.²⁴ Monkhorst–Pack k -point meshes ($2 \times 2 \times 2$) and ($3 \times 3 \times 3$) were used to sample the Brillouin zones for a $p(2 \times 2 \times 2)$ α -LAO supercell and β -LAO unit cell, respectively. The cutoff energy for plane-wave expansion was set to 500 eV. Residual force less than 0.01 eV/Å and total energy less than 10^{-5} eV were utilized for all the calculations.

The substitution of each M^{3+} by M'^{3+} needs to delete a Li atom for charge compensation. According to the calculated configuration energy, Si/Ge-dopants in LAO/LGaO tend to have a dispersed distribution rather than agglomeration, and the Li vacancies are nearby the M'^{3+} cations. To evaluate the interaction between one Li-ion and one XO_4 unit ($\text{X} = \text{Al}, \text{Si}, \text{Ga}, \text{and Ge}$), one Li and one XO_4 are set in a $20 \times 20 \times 20$ Å lattice. To calculate the bond dissociation energy of $\text{X}-\text{O}$, one XO_4 and one XO_3 are set in a $20 \times 20 \times 20$ Å lattice, respectively. During the relaxation, the atomic positions of XO_4 are fixed but Li is allowed to relax. The $\text{X}-\text{O}$ bond lengths were obtained from Li_5AlO_4 (COD-1523841), Li_4SiO_4 (COD-4124128), Li_5GaO_4 (COD-1528895), and Li_4GeO_4 (COD-9008154). COD represents the Crystallography Open Database.

The formation energy E_f of a defect is defined as the following equation

$$E_f = E_{\text{tot}}(\text{defect}, q) - E_{\text{tot}}(\text{bulk}) - n_i \mu_i + q(E_{\text{VBM}} + \mu_e) \quad (1)$$

Herein, $E_{\text{tot}}(\text{defect}, q)$ is the total energy of the defect system with charge q , $E_{\text{tot}}(\text{bulk})$ is the total energy of a bulk supercell of the same size as the defected one, and $n_i \mu_i$ is the reference energy of n_i added atoms of an element at chemical potential μ_i . Applied voltage V can be directly converted to lithium chemical potential μ_{Li} using the equation $\mu_{\text{Li}} = \mu_{\text{Li}}^0 - eV$, where μ_{Li}^0 is the lithium chemical potential in the Li metal and e is the elementary charge. The term in the parenthesis accounts for the chemical potential of the electron involved in charging the defect. E_{VBM} is the valence band maximum for the bulk phase and μ_e is the electron chemical potential and is treated as the Fermi level (E_f). A negative E_f value suggests that the formation of a defect is exothermic and favorable. To search for the possible Li-ion migration pathways and the corresponding migration barriers, the BASE calculations using the softBV software tool^{25,26} and the CI-NEB method^{27,28} were carried out. A γ -only k -point in the $p(2 \times 2 \times 2)$ α -LAO supercell and β -LAO unit cell is considered. In the ab initio molecular dynamics (AIMD) simulations, an NVT ensemble was simulated using a time step of 2 fs with a period of 10 ps and a Nosé–Hoover thermostat. The Li-ion diffusion coefficient is calculated using the following formula.

$$D_{\text{Li}} = \frac{1}{2} \nu (\Delta x)^2 e^{-E_A/k_B T} \quad (2)$$

where Δx is the hop distance, ν is the lattice vibrational frequency with a typical value of 10^{13} Hz, T is the temperature, k_B is the Boltzmann constant, and E_A is the migration barrier. The Li-ion conductivity (σ_{Li}) is estimated from the Nernst–Einstein relation

$$\sigma_{\text{Li}} = n_{\text{Li}} D_{\text{Li}} \left(\frac{q^2}{k_B T} \right) \quad (3)$$

where n_{Li} is the concentration of Li-ions, q is the electrical charge of the diffusion carrier (Li), D_{Li} is calculated from eq 2, and T is the temperature.

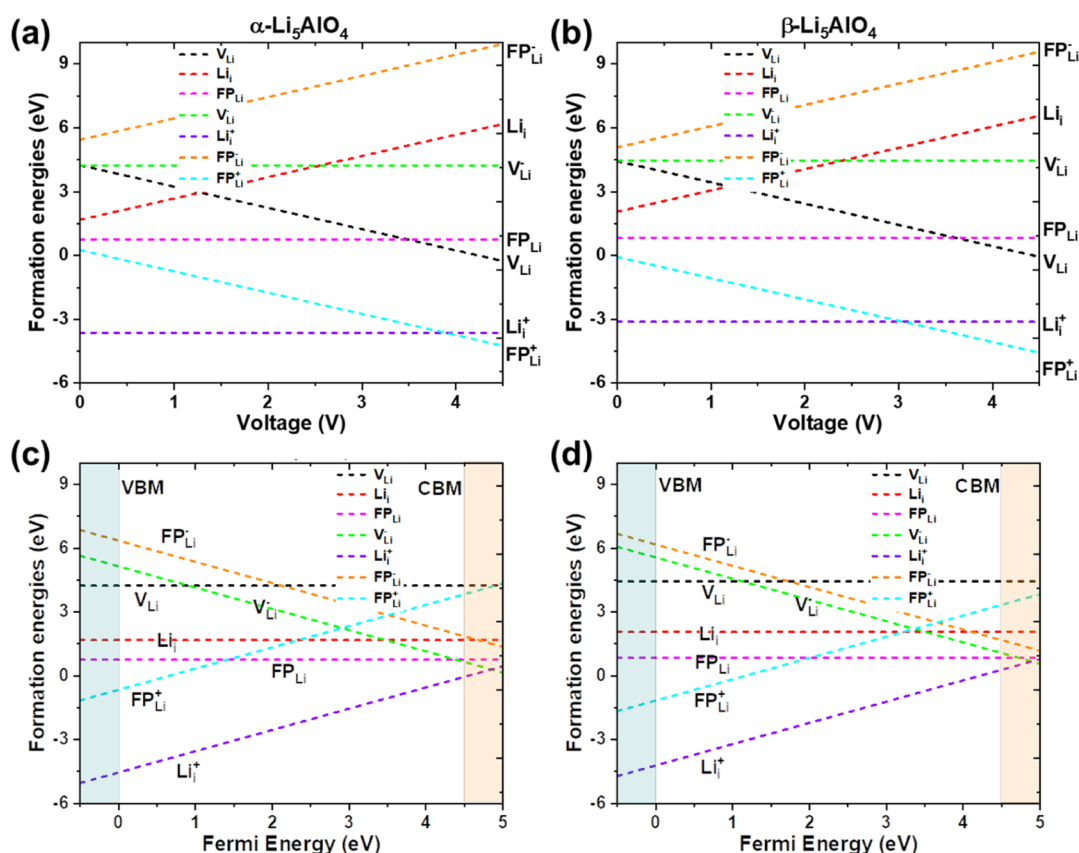


Figure 2. Formation energies, E_f , for point defects as a function of applied voltage when the Fermi level at the valence-band maximum (a,b) and the Fermi level when the electrode potential is 0 V (c,d) in α - and β -LAO, respectively.

The electrochemical stability window of SSE materials means that they are stable at the applied voltage V . The electrochemical stability window (exactly on the grand potential convex hull) is determined by grand canonical linear programming (GCLP).^{29,30} The grand potential convex hull at a given voltage is formed by the grand potentials of a set of phases and their linear combinations that minimize the grand potential at each composition. More information about the calculations of electrochemical stability is detailed in previous studies.^{31–35} To study the H_2O and CO_2 stability of LAO, we calculate $\Delta E_{\text{mixing-energy}}$ of the reactions: $x\text{LAO} + (1-x)\text{H}_2\text{O} \rightarrow C_{\text{equilibrium}}$ and $x\text{LAO} + (1-x)\text{CO}_2 \rightarrow C_{\text{equilibrium}}$, which is defined as

$$\Delta E_{\text{mixing-energy}} = [E(C_{\text{equilibrium}}) - (1-x)E(\text{CO}_2) - xE(\text{LAO})]/n_{\text{atoms}} \quad (4)$$

$$\Delta E_{\text{mixing-energy}} = [E(C_{\text{equilibrium}}) - (1-x)E(\text{H}_2\text{O}) - xE(\text{LAO})]/n_{\text{atoms}} \quad (5)$$

where n_{atoms} represents the total number of atoms involved in the mixing reaction.

3. RESULTS AND DISCUSSION

3.1. Structure Modeling and Defect Chemistry. All crystal structures used in this work including α - and β -LAO, α -LASiO, β -LASiO, LgaO, and LGaGeO are shown in Figure 1a–f, respectively. Both structures of α - and β -LAO (see Figure S1a,b in the Supporting Information) have an

orthorhombic symmetry and are composed of isolated AlO_4 units and corner-sharing or edge-sharing LiO_4 units, which are linked together to form 3D diffusion channels. There are two and eight formula units in α - and β -LAO unit cells, respectively. Table S1 in the Supporting Information lists the calculation results of lattice parameters for both structures. The total density of states (TDOS) (see Figure S1c) shows that the bandgap of α - and β -LAO is 4.87 and 4.98 eV, respectively, indicating that LAO materials are good electron insulators and thus block the electron leakage and protect against electron corrosion. In addition, the $Pbca$ -phase LGaO also exhibits a large bandgap of 3.70 eV (see Figure S1c).

Calculations on intrinsic defects in the LAO system are performed on the optimized structure. Following eq 1, we obtain the formation energies of several defects (V_{Li} : Li vacancy, Li_i : Li interstitial, FP_{Li} : Li Frenkel pair, and the + and – superscripts represent a hole and an electron, respectively). For V_{Li} and Li_i defects, the most stable configurations are considered in the plots of Figure 2, which show the defect formation energies with applied voltage. It is found that the V_{Li} and Li_i are unfavorably thermodynamic at 0 K in the voltage range of 0–4.0 V because of the valence state of Al. The formation energy of V_{Li} (4.24 eV in α -LAO and 4.44 eV in β -LAO) is much higher than that of Li_i (1.68 eV in α -LAO and 2.06 eV in β -LAO) at 0 V (corresponding to the lithium metal anode). This translates into a concentration over 43 and 30 orders of magnitude higher than that of V_{Li} according to $c = N \exp(-E_f/kT)$ in α -LAO and β -LAO, respectively, indicating that Li_i is the dominant conduction carrier under anodic conditions. However, the formation energy of V_{Li} (–0.26 eV in

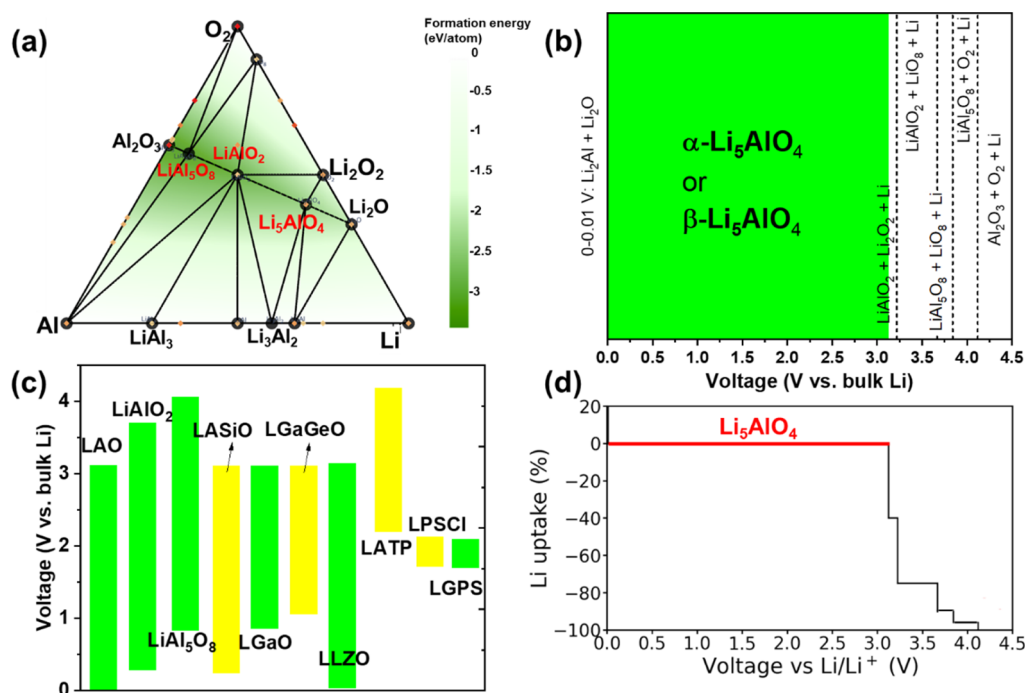


Figure 3. (a) Li–Al–O₂ phase diagram at 0 K computed from the LAO DFT data combined with Materials Project data, respectively. The green regions in the phase diagram become darker as the formation energy values are more negative. (b) Voltage profile and phase equilibria of LAO upon the lithiation and delithiation. The green-shaded region is determined after consideration of the energy of the Li insertion/extraction only without any mixing reaction from electrodes. (c) Electrochemical stability windows (green bar) for Li₅AlO₄, LiAlO₂, LiAl₃O₈, Li₇La₃Zr₂O₁₂ (LLZO), Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP), Li₆PS₅Cl (LPSCI), and Li₁₀GeP₂S₁₂ (LGPS) (for comparison) are shown. The yellow region reflects the possible extension of the voltage window. (d) Li uptake vs voltage for the LAO system.

α -LAO and -0.06 eV in β -LAO) is much lower than that of Li_i (6.18 eV in α -LAO and 6.56 eV in β -LAO) at 4.5 V (corresponding to the high-voltage cathode environment), indicating that under cathodic conditions, the concentration of V_{Li} is larger than that of Li_i. It can be also seen that the formation energies of FP_{Li}⁺ and Li_i⁺ are lower than those of FP_{Li} and Li_i, implying that interstitial Li would spontaneously ionize in LAO. This can be rationalized by the fact that during Li-ion battery operation, FP_{Li} and Li_i will change the charge state of Al and O and thus lead to phase transformations of LAO. For synthetic crystals by experiment, LAO can hardly exhibit off-stoichiometric composition as the valence state of Al ions is hard to change. It is known, however, the concentrations of intrinsic defects can be introduced into the system by cation-doping, such as the partial substitution of M³⁺ by M⁴⁺ or Zn²⁺.

3.2. Electrochemical Stability, Interfacial Stability, and H₂O/CO₂ Stability. Next, we employ the LAO as a model framework to evaluate the phase stability and electrochemical stability at 0 K computed from DFT data combined with python materials genomics code.^{31,32,34,35} The Li–Al–O ternary 0 K phase diagrams of Figure 3a depict the phase equilibria of LAO at different Li or O chemical potentials. The higher Li or O chemical potential, the farther away from the Li metal or the O₂ endpoint in the phase diagram, and vice versa. Within the Li₂O–Al₂O₃ combination, from the Al-rich side to Li-rich side, there are three Li_xAl_yO_z compounds: Li₅AlO₄, LiAlO₂, and LiAl₃O₈. Based on the formation energy (in different shades of color), the more the negative formation energy, the more stable the compound is likely to be. Figure 3b,d shows the electrochemical phase equilibria and Li uptake versus voltage for the LAO system, respectively. LAO exhibits

an anodic (cathodic) limit of 0.01 V (3.20 V) versus Li/Li⁺. It is noticeable that LAO will be unstable at high voltage and the phase decomposition, Li₅AlO₄ → LiAlO₂ + Li₂O₂ + Li, begins to occur at 3.2 V. Figure 3c shows that the intrinsic stability windows of these three Li_xAl_yO_z compounds are relatively wide. The detailed voltage profile and phase equilibria of LASiO, LGaO, and LGaGeO upon lithiation and delithiation are shown in Figures S2–S4 in the Supporting Information, respectively. The comparison of the electrochemical stability window between Li_xAl_yO_z compounds and typical SSE materials suggests that LAO is on a par with LLZO. As compared with LATP, LPSCI, and LGPS materials, the electrochemical stability of LAO is much more superior. The comparison of the electrochemical stability window between the Li_xAl_yO_z compounds and typical SSE materials suggests that LAO is on a par with LLZO. It is worth mentioning that LAO has the lowest reduction voltage among all listed materials, indicating that although LAO has less phase stability compared to other Li_xAl_yO_z compounds, it still holds promise for use in Li–metal anodes. As compared with LATP, LPSCI, and LGPS materials, the electrochemical stability of LAO is much more superior.

To understand the interfacial electrochemical reaction between the LAO and conventional cathodes, we also apply the above method and consider all possible electrochemical reactions: $x\text{Cathode} + (1-x)\text{LAO} + ne^- \rightarrow C_{\text{equilibrium}}$, where $C_{\text{equilibrium}}$ is the low-energy phase equilibrium determined from the phase diagram and x is the mixing parameter varying from 0 and 1. The chemical reaction of LAO with cathode ($x\text{Cathode} + (1-x)\text{LAO} \rightarrow C_{\text{equilibrium}}$) and pure redox decomposition reaction of LAO ($\text{LAO} + ne^- \rightarrow C_{\text{equilibrium}}$) are also shown in the second and third columns in Table 1,

Table 1. Predicted Chemical Reaction between the Cathode and LAO ($x\text{Cathode} + (1-x)\text{LAO} \rightarrow C_{\text{equilibrium}}$), LAO Redox Decomposition at Cathode Potential ($\text{LAO} + ne^- \rightarrow C_{\text{equilibrium}}$), and the Electrochemical Reaction Products for the Cathode/LAO ($x\text{Cathode} + (1-x)\text{LAO} + ne^- \rightarrow C_{\text{equilibrium}}$) Mixing Reaction at Cathode Potential

cathode/LAO	chemical reaction	LAO redox decomposition at cathode potential ^a	electrochemical reaction with mixing at cathode potential ^a
LiCoO ₂ /Li ₅ AlO ₄	none	Li ₂ O, Al ₂ O ₃	none
LiNiO ₂ /Li ₅ AlO ₄	none	Li ₂ O, Al ₂ O ₃	Al ₂ NiO ₄ , Li ₂ O
LiMnO ₂ /Li ₅ AlO ₄	none	LiAl ₅ O ₈ , Li ₂ O	LiAl ₅ O ₈ , Li ₄ Mn ₅ O ₁₂
NCM532 ^b /Li ₅ AlO ₄	none	Li ₂ O, Al ₂ O ₃	Li ₂ O, MnNiO ₃ , CoO ₂ , Al ₂ NiO ₄
NCM811 ^b /Li ₅ AlO ₄	none	Li ₂ O, Al ₂ O ₃	Li ₂ O, MnNiO ₃ , CoO ₂ , Al ₂ NiO ₄
LiMn ₂ O ₄ /Li ₅ AlO ₄	LiMnO ₂ , LiAlO ₂ , Li ₂ MnO ₃	LiAl ₅ O ₈ , Li ₂ O	LiAl ₅ O ₈ , Li ₄ Mn ₅ O ₁₂
LiFePO ₄ /Li ₅ AlO ₄	FeO, LiAlO ₂ , Li ₃ PO ₄	LiAlO ₂ , Li ₂ O	LiAlO ₂ , Li ₃ PO ₄ , Fe ₂ O ₃

^aThe cathode potentials versus bulk Li (in V): LiCoO₂: 4.2; LiNiO₂: 4.5; LiMnO₂: 4.0; NCM532 and NCM811: 4.2; LiMn₂O₄: 4.0; and LiFePO₄: 3.50. ^bNCM532: Li₆Ni₃Co₂Mn₁O₁₂; NCM811: Li₁₂Co₁₀Mn₁Ni₁O₂₄.

respectively. Thermodynamically feasible chemical reactions between the electrolyte and various cathodes, namely, layered LiMO₂ (M = Co, Ni, and Mn), spinel LiMn₂O₄, and LiFePO₄ are detailed in Table 1 and Figures S5–S6 in the Supporting Information. We found that there is no chemical reaction between LAO and layered cathode materials (LXO₂, X = Co, Ni, and Mn; NCM) listed in the second column in Table 1. However, LAO undergoes a chemical reaction (the second column in Table 1) and an electrochemical reaction (the fourth column in Table 1) at the LiMn₂O₄/LAO and LiFePO₄/Li₅AlO₄ interfaces and results in the formation of SEI-like (solid-electrolyte interphase, SEI) products. For LAO + $ne^- \rightarrow C_{\text{equilibrium}}$, LAO will undergo redox decomposition forming SEI-like products with all cathodes at cathodic

potential as listed in the third column in Table 1. The SEI-like composition as the interfacial phase could facilitate the Li passivation in LAO and could be beneficial for cyclability.

To assess the H₂O and CO₂ stability of LAO, we extend the above method and consider the reactions: $x\text{LAO} + (1-x)\text{H}_2\text{O} \rightarrow C_{\text{equilibrium}}$ and $x\text{LAO} + (1-x)\text{CO}_2 \rightarrow C_{\text{equilibrium}}$, where $C_{\text{equilibrium}}$ is the low-energy phase equilibrium determined from the phase diagram and x is the mixing parameter varying from 0 and 1. According to the definition (see eqs 4 and 5 in the method), a negative value signifies the thermodynamic feasibility toward $C_{\text{equilibrium}}$ generation. Table S2 in the Supporting Information shows the chemical reaction equation with maximum reaction energy from the SSE compound and H₂O/CO₂ molecules into possible products. In the range of 0 and 1 of the mixing parameter, the most favorable reaction of LAO with H₂O (CO₂) is $0.4\text{Li}_3\text{GaO}_4 + 0.8\text{H}_2\text{O} \rightarrow 1.6\text{LiHO} + 0.4\text{LiGaO}_2$ ($0.8\text{CO}_2 + 0.4\text{Li}_3\text{AlO}_4 \rightarrow 0.8\text{Li}_2\text{CO}_3 + 0.4\text{LiAlO}_2$), with a reaction energy of -0.05 eV/atom (-0.22 eV/atom). In Figure 4 and Table S2 in the Supporting Information, we can find that most of the SSE materials (all sulfides, Li₃OCl, and LLZO) would react with H₂O and CO₂ with negative mixing reaction energies, except LTP and LPO. We also note that the extent of H₂O and CO₂ instability for Li₃CIO (-0.08 and -0.27 eV/atom) and Li₆PS₅Cl (-0.09 and -0.25 eV/atom) is even larger than that for LAO. Moreover, the extent of LAO instability against H₂O is close to that of LLZO (-0.01 eV/atom). Many experiments have successfully demonstrated the assemblage of Li₃CIO and Li₆PS₅Cl in a battery setup with an argon atmosphere although they are thermodynamically unstable against H₂O and CO₂. Thus, thermodynamic H₂O/CO₂ instability of LAO is less problematic in practice if we can avoid excess exposure to the air.

3.3. Li-Ion Diffusivity in LAO. For Li-ion diffusivity in LAO, we first evaluate Li-ion diffusion channels of LAO by the bond valence (BV) theory, as shown in Figure 5a,b. For α -LAO, after careful examination of the bond valence pathway, it is seen that the Li diffusion pathway is constructed piece by piece, by interconnecting the saddle-shaped region (SSR) to form a whole 3D diffusion channel. Our model predicts that

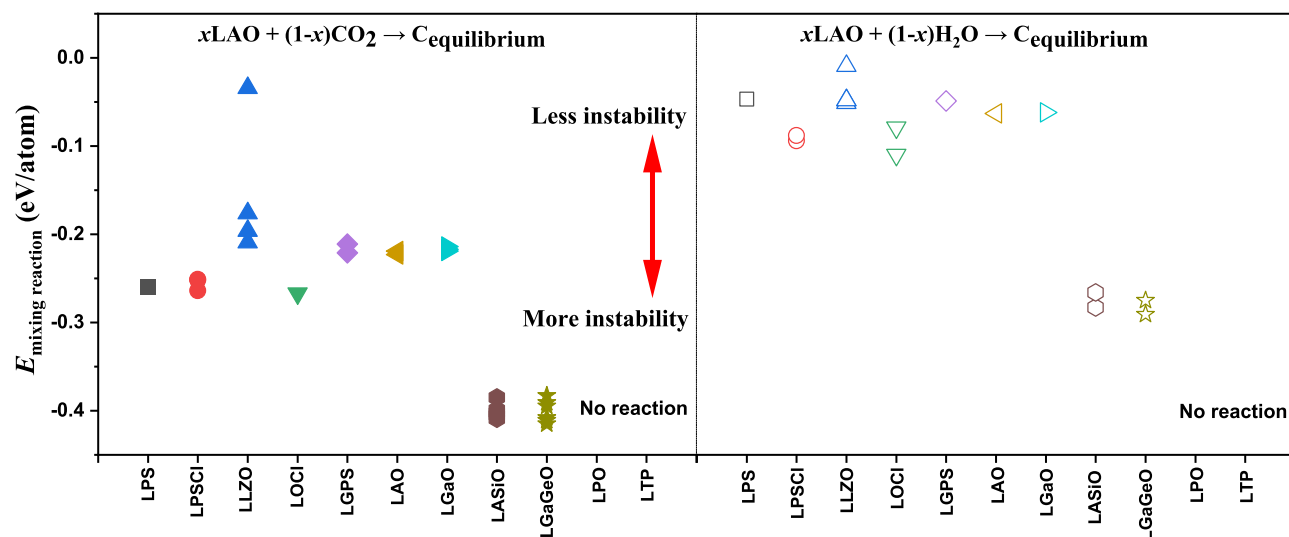


Figure 4. CO₂ stability (left) and moisture stability (right) for LAO, LGO, LAISiO, LGaGeO, and other SSEs (for comparison) are shown. Li₃PS₄ (LPS), Li₃OCl (LOCl), Li₃PO₄ (LPO), and LiTi₂(PO₄)₃ (LTP).

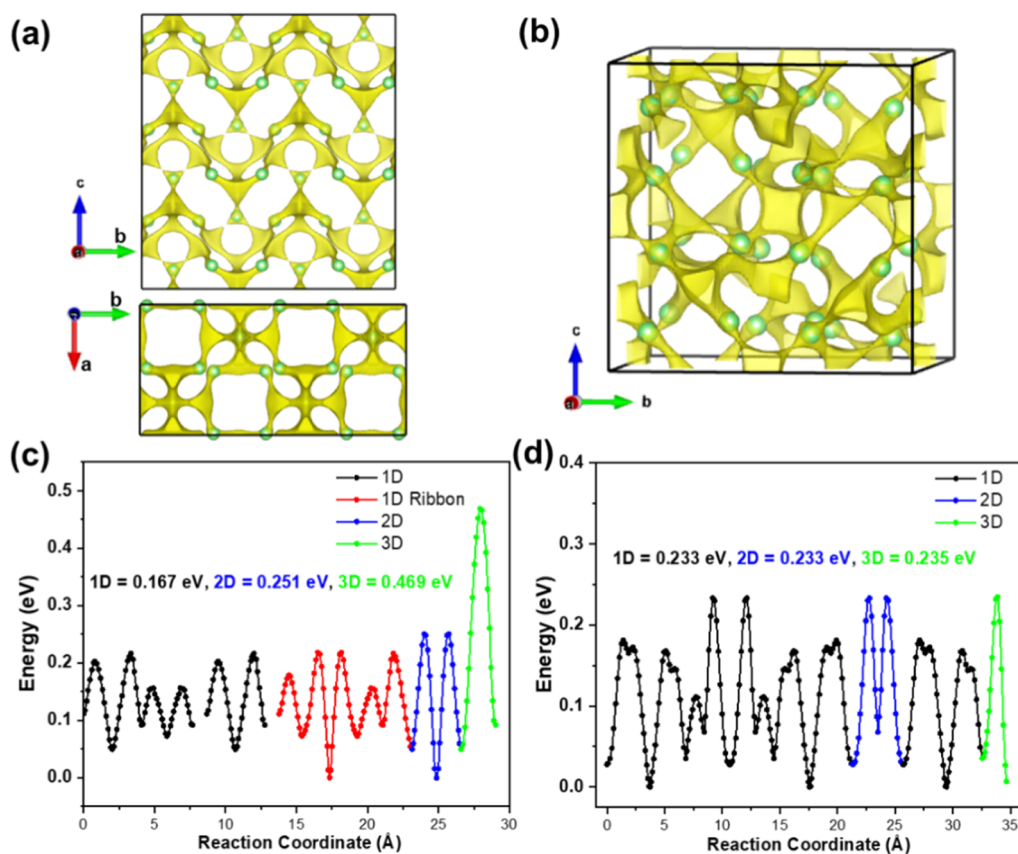


Figure 5. (a,b) Li-ion diffusion channels (obtained from bond valence simulations) in α - and β -LAO are shown in yellow isosurfaces, respectively. (c,d) BVSE-recommended path and the Li migration barrier in α - and β -LAO, respectively.

the most favorable interstitial site is just at the saddle-point concerning the Li BV diffusion channel (i.e., I1 and I3 sites shown in the following Figure 7a). For β -LAO in Figure 5b (BV analysis), there is a 3D diffusion channel. The BVSE results (Figure 5c,d) show the 1D, 2D, and 3D migration barriers in α - and β -LAO. It can be seen that the 1D migration barriers in α -LAO and 3D migration barriers in β -LAO are sufficiently low that the Li-ions can diffuse within them. For example, the 1D migration barrier is 0.17 eV in α -LAO, which is even less than that for LGPS (0.20 ± 0.02 eV). Such a low energy potential surface in LAO also suggests that there may be plenty of Li interstitial sites (or metastable sites) along the Li diffusion path. To prove the diffusion pattern, the AIMD simulations at 850 K are performed within α - and β -LAO (Figure S7 in the Supporting Information). The mean square displacement (MSD) results of Li-ions are consistent with the suggestion of BVSE. There is definitely anisotropic diffusion in α -LAO and a nearly isotropic 3D diffusion in β -LAO. α -LAO exhibits negligible diffusion along the a -axis direction but a significant diffusion along the c -axis direction. Therefore, we suggest that there is an anisotropic and a nearly isotropic diffusion in pure α - and β -LAO, respectively.

The above diffusion calculations suggest that the layout of AlO_4 and LiO_4 units causes the anisotropic ion transport in α -LAO. Previous studies suggested that the formation of solid solutions can significantly improve the ionic conductivity and tune Li diffusion paths, such as in the range of compounds Li_4SiO_4 , $\text{Li}_{4-x}\text{Si}_{1-x}\text{P}_x\text{O}_4$, $\text{Li}_{4+x}\text{Si}_{1-x}\text{Al}_x\text{O}_4$, or $\text{Li}_4\text{Al}_x\text{Si}_{1-2x}\text{P}_x\text{O}_4$.^{36,37} Therefore, the motif-based design of a polyanion mixing class of $(\text{Si}/\text{Al})\text{O}_4$ and $(\text{Ga}/\text{Ge})\text{O}_4$ units

may modify the potential energy surface and lower the migration barriers. It is well known that a 3D diffusion pattern is more robust than a 1D diffusion one. To further lower the migration barrier of Li, we calculate the migration barrier along with three directions in α -LASiO, β -LASiO, LGaO, and LGaGeO, as shown in Figure 6 (the original copy of Figure 5 is

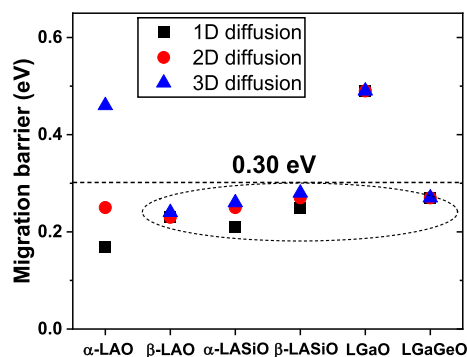


Figure 6. Li migration barrier obtained from BVSE in α - and β -LAO, α -LASiO, β -LASiO, LGaO, and LGaGeO. The short-dashed circle suggests the compounds with low migration barriers.

listed in Figures S8–S13 in the Supporting Information). We note that Si-substitution of Al in α -LASiO and Ge-substitution of Ga in LGaGeO can significantly decrease the Li migration barrier of their parent structures, which is consistent with an effect called the “mixed polyanion” effect. The mixed polyanion effect also causes the substituted composition of

α -LASiO to show a 2D–3D transition in the Li diffusion pattern.

To evaluate the correlation between the chemical composition and the structure evolution, several intrinsic structural and energy characteristics of XO_4 tetrahedra ($\text{X} = \text{Al}^{3+}$, Ga^{3+} , Si^{4+} , and Ge^{4+}) are listed in Table 2. Based on the

Table 2. Tetrahedral Anion Charge ($(\text{XO}_4)^{n-}$), the X–O Distance in the XO_4 unit of Li_xXO_4 ($d_{(\text{X}-\text{O})}$), X–O Dissociation Energy in the XO_4 unit ($\text{Ed}_{(\text{X}-\text{O})}$), the Li–X Distance in the Li– XO_4 configuration ($d_{(\text{Li}-\text{X})}$), and the Binding Energy between Li and the (XO_4) Unit ($\text{Eb}_{(\text{Li}-\text{XO}_4)}$)

$(\text{XO}_4)^{n-}$	$d_{(\text{X}-\text{O})}(\text{\AA})$	$\text{Ed}_{(\text{X}-\text{O})}(\text{eV})$	$d_{(\text{Li}-\text{X})}(\text{\AA})$	$\text{Eb}_{(\text{Li}-\text{XO}_4)}(\text{eV})$
$(\text{AlO}_4)^{5-}$	1.78	2.21	2.49	−5.28
$(\text{SiO}_4)^{4-}$	1.64	3.21	2.43	−5.91
$(\text{GaO}_4)^{5-}$	1.83	1.80	2.43	−5.22
$(\text{GeO}_4)^{4-}$	1.77	2.36	2.47	−5.46

results of the X–O distance, X–O dissociation energy, and Li–X distance in the Li– XO_4 configuration, the substitution of $(\text{Al}/\text{Ga})^{3+}$ with $(\text{Si}/\text{Ge})^{4+}$ within the XO_4 tetrahedrons makes the X–O bonds have a shorter and stronger bonding interaction. This variation in the bonding interaction and the volume of XO_4 tetrahedrons is reflected in the distortion of LiO_y polyhedra in $\text{Li}_{5-x}\text{M}_{1-x}\text{M}'_x\text{O}_4$. The binding energy between Li and (XO_4) units shows a difference of 0.63 eV between Li– AlO_4 and Li– SiO_4 and 0.24 eV between Li– GaO_4 and Li– GeO_4 . The non-uniform bonding interaction for different Li– XO_4 may modify the overall potential energy surface. Therefore, in LAO and LGaO, Li-ions occupy a much more uniform potential energy surface and LiO_y polyhedra, and the energy barrier is relatively high. In the substituted LASO and LGaGeO compounds, the mixing of these XO_4 groups with varied LiO_y polyhedra and bonding interaction of $\text{Eb}_{(\text{Li}-\text{XO}_4)}$ may result in lower barriers and transition of the Li-migration pattern.

To further identify the migration barriers of Li-ions in α - and β -LAO, we then calculate the Li migration process through the CI-NEB method. The ionic conductivity of LAO stems from the diffusion of point defects, including the Li vacancy and Li interstitial.²² For α -LAO (Figure 7a), we evaluate a 3D diffusion path, including intra- and inter-SSR, as shown in the insets of Figure 7a. Along the Li vacancy path, the migrating Li will pass through Li1, Li2, and Li3, and the vacancy migration barrier is calculated to be as high as 0.75 eV in the $\text{Li2} \rightarrow \text{Li3}$ path. Along the Li interstitial path, the migrating Li interstitial will pass I1, I2, Li4, and I3, where the Li interstitial site (I1 or I2) migrates to the lattice site (Li4), meanwhile lattice Li migrates to the interstitial site (I3). Li interstitial migration barriers in the paths: $\text{I1} \rightarrow \text{I2}$ and $\text{Li4} \rightarrow \text{I3}$ are 0.30 and 0.38 eV, respectively, which are substantially lower than that of Li vacancy diffusion. For β -LAO (Figure 7b), we also check one 3D diffusion path, where $\text{Li1}'$ and $\text{Li2}'$ are at the same diffusion channel (i.e., along the *a*-axis direction) but $\text{Li3}'$ is at the adjacent diffusion channel. We find that the Li vacancy migration barrier in the path: $\text{Li1}' \rightarrow \text{Li2}'$ (0.35 eV) is much lower than that in the path: $\text{Li2}' \rightarrow \text{Li3}'$ (0.63 eV) and Li interstitial migration barrier in the path: $\text{Li1}' \rightarrow \text{I1}' \rightarrow \text{Li2}'$ (0.34 eV) is also lower than that in the path: $\text{I2}' \rightarrow \text{Li3}' \rightarrow \text{I3}'$ (0.40 eV), suggesting *a*-axis direction diffusion is more favorable. The different migration barriers further demonstrate that Li diffusion in LAO is highly anisotropic; for example, in β -LAO, it is easier along the *a*-axis direction but harder along the *b*-axis direction. Therefore, based on the CI-NEB calculations, we conclude that the overall 3D migration barrier in α -LAO is about 0.38 eV, and from eqs 2 and 3, the diffusion coefficient and ionic conductivity at room temperature (300 K) are $2.83 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and $9.12 \times 10^{-4} \text{ S cm}^{-1}$, respectively. The overall 3D migration barrier in β -LAO is about 0.40 eV and the diffusion coefficient and ionic conductivity at room temperature are $1.31 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and $4.28 \times 10^{-4} \text{ S cm}^{-1}$, respectively. The ionic conductivity of Li ions in LAO has a magnitude equal to that of the LLZO,³⁸

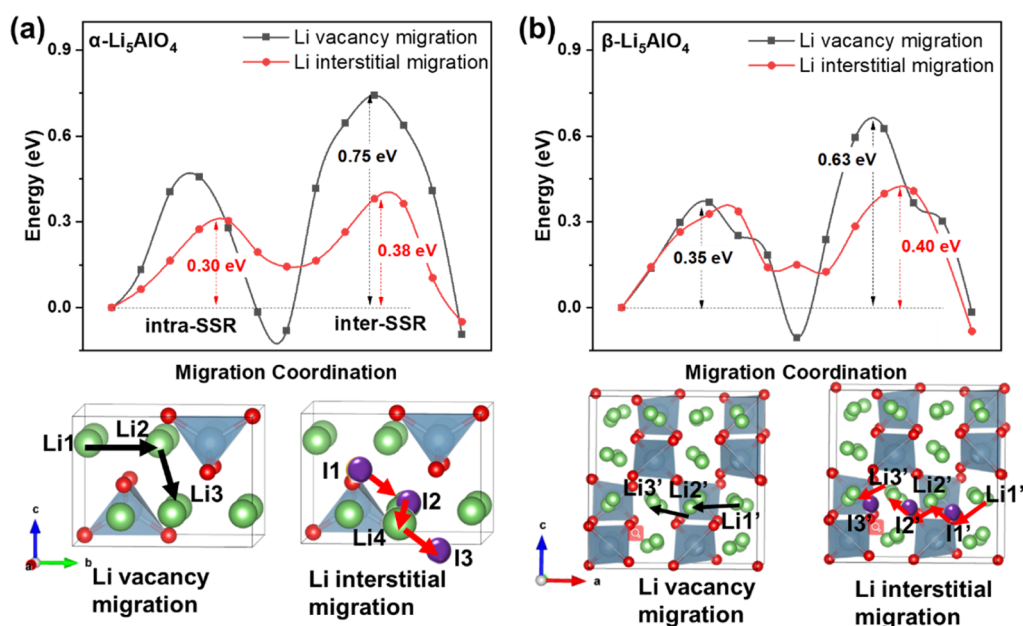


Figure 7. (a,b) Energy profiles and configurations of Li direct hopping via vacancy and Li interstitial migration via interstitial sites, respectively. The tetrahedrons represent the AlO_4 units.

implying a good performance of the battery when using LAO SSE. Overall, the interstitial migration in LAO is more favorable for Li diffusion. This may be rationalized by the brief appearance of Li vacancies and the stable coordination environment maintained during the Li interstitial migration. Therefore, the introduction of lithium interstitial defects is crucial to high conductivity, and fortunately that a large Li-interstitial defect concentration is possible in $\text{Li}_{5+x}\text{Al}_{1-x}\text{Zn}_x\text{O}_4$, potentially allowing it to exceed the conductivity of LAO. Therefore, we can anticipate that LAO-based family SSE materials, with their high ionic conductivity and electrochemical stability, will profoundly improve the overall electrochemical performance of solid-state batteries.

4. CONCLUSIONS

In summary, we have applied the first-principles-based DFT methods to explore the phase structure, defect chemistry, electrochemical properties, and Li-ion conduction of α - and β -LAO to overcome the key challenge of combining stability with high Li-ion conductivity. We have identified LAO as an oxide class of SSE for ASSLBs. The electrochemical stability window of LAO is found to be [0.01–3.20 V] versus Li^+/Li . The LAO forms a stable interface with relatively high-voltage LiCoO_2 and forms SEI-like interfacial phases with LiNiO_2 , LiMnO_2 , LiMn_2O_4 , and LiFePO_4 cathodes. The Li interstitial migration has a migration barrier in α -LAO as low as 0.38 eV. In β -LAO, there are migration barriers of 0.34 eV for 1D diffusion and 0.40 eV for 3D diffusion. Si (or Ge) substitution at Al (or Ga) sites improves its Li-ion mobility but reduces the electrochemical stability window slightly. The calculated Li-ion diffusion coefficients (Li-ion conductivities) for α - and β -LAO at room temperature are about $2.83 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ ($9.12 \times 10^{-4} \text{ S cm}^{-1}$) and $1.31 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ ($4.28 \times 10^{-4} \text{ S cm}^{-1}$), respectively. Indeed, an important reason for this good conductivity is the arrangement of $(\text{Li}/\text{Al})\text{O}_4$ units in α - and β -LAO structures, which allows considerable energy minimum sites for Li-ions and a percolating network of Li-ion diffusion. Overall, LAO is a potential candidate for SSE materials that can balance the stability and ionic conductivity and therefore deserves further experimental examination.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.1c19922>.

Structural parameters and crystal structure of α - and β -LAO; TDOS of LAO and LGaO; voltage profile and phase equilibria of LaSiO , LGaO, and LGaGeO ; mixing reactions with cathodes and SSE materials; mixing reaction between SSE materials and H_2O or CO_2 ; and original Li-ion diffusion path as recommended by BVSE (PDF)

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Notes

The authors declare no competing financial interest.

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