# Supporting Information

# for

# Electrochemically and Chemically Stable Electrolyte-Electrode Interfaces for Lithium Iron Phosphate All-Solid-State Batteries with Sulfide Electrolytes

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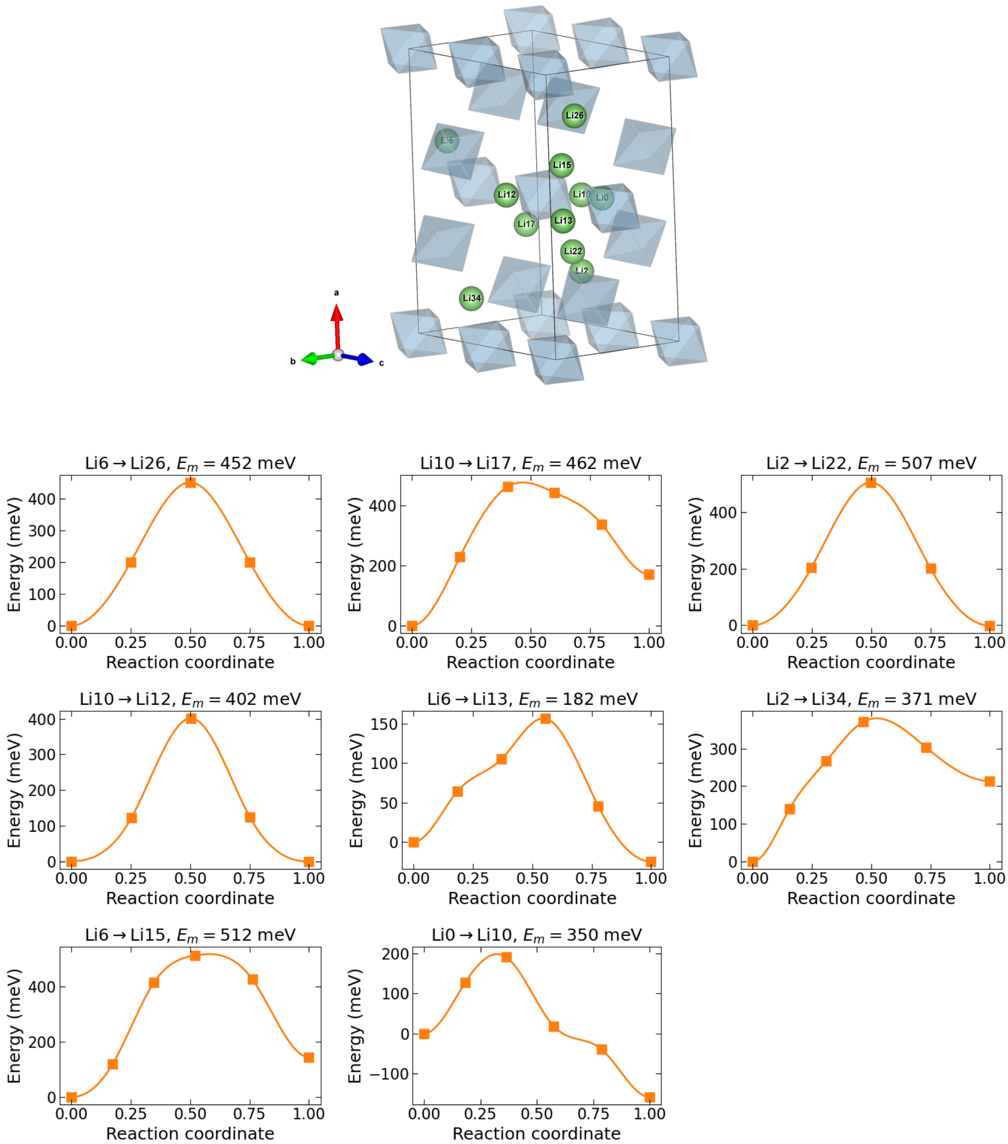


**Figure S1. Crystal structure and Li-ion vacancy migration profiles of $Li_3AlF_6$.**

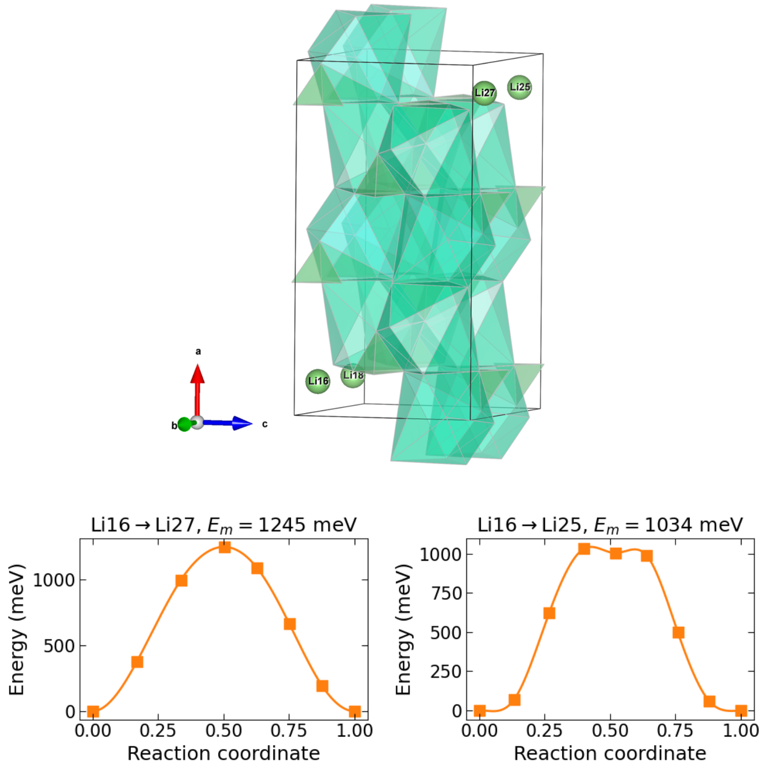


**Figure S2. Crystal structure and Li-ion vacancy migration profiles of $CsLiBeF_4$.**

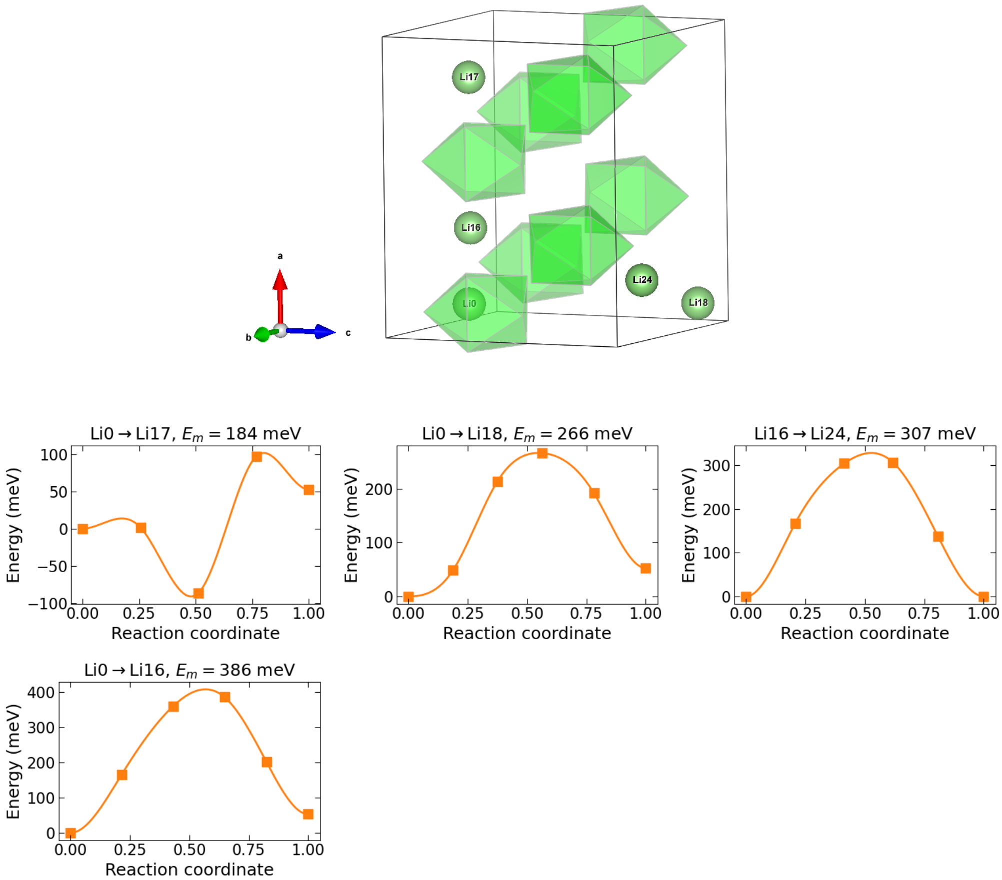


**Figure S3. Crystal structure and Li-ion vacancy migration profiles of $Li_4ZrF_8$.**

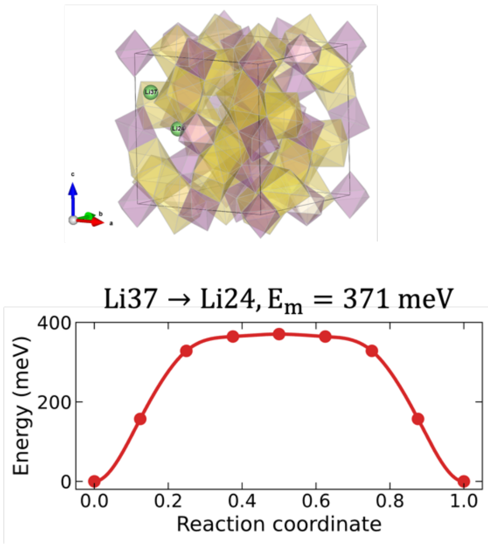


**Figure S4. Crystal structure and Li-ion vacancy migration profiles of $Na_3Li_3Sc_2F_{12}$.**

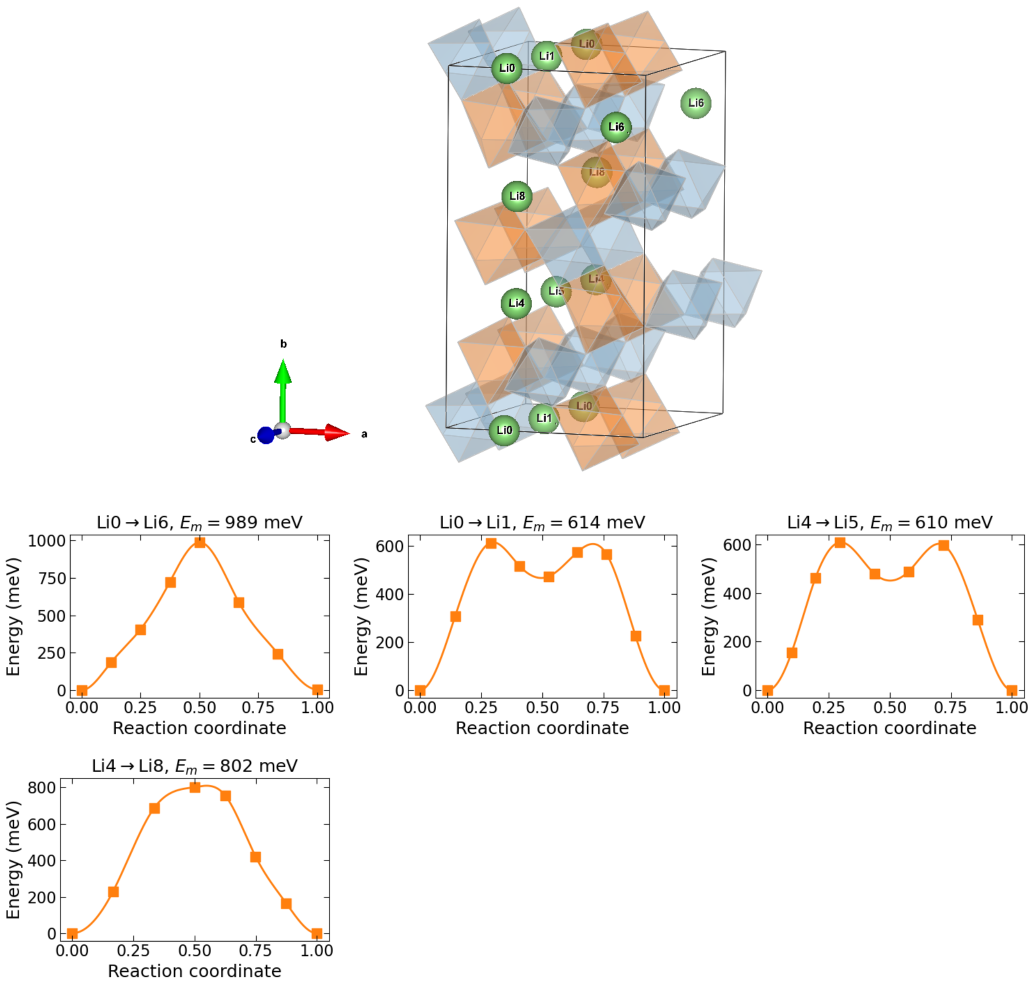


**Figure S5. Crystal structure and Li-ion vacancy migration profiles of $LiMgAlF_6$.**

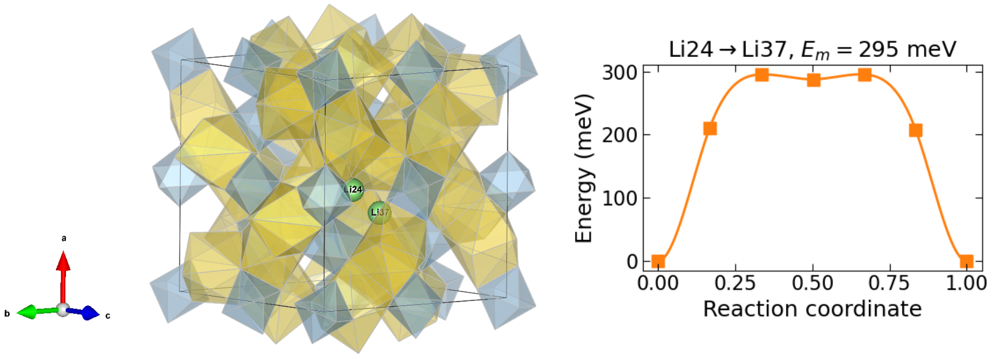


**Figure S6. Crystal structure and Li-ion vacancy migration profiles of $Na_3Li_3Al_2F_7$.**

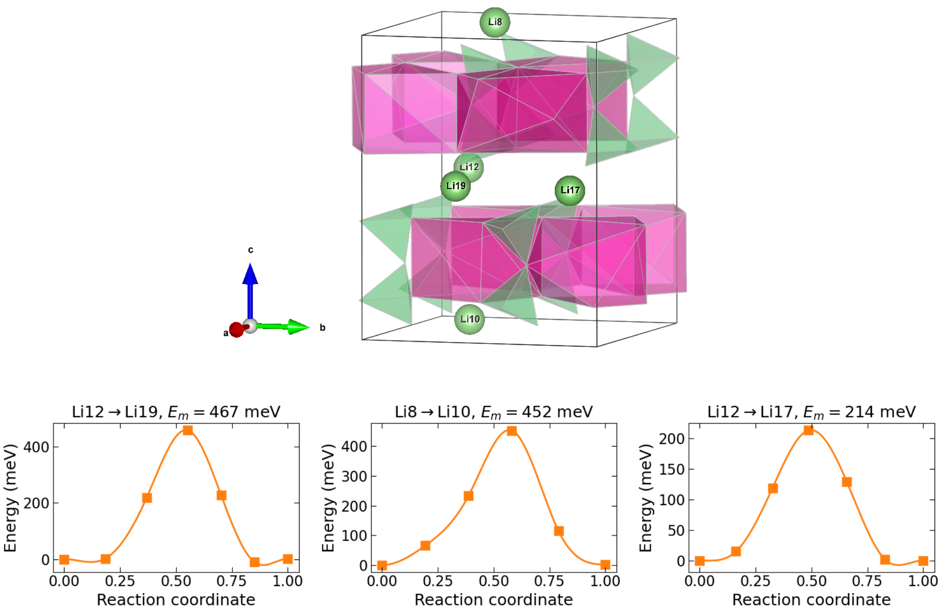


**Figure S7. Crystal structure and Li-ion vacancy migration profiles of $RbLi_2Be_2F_7$.**

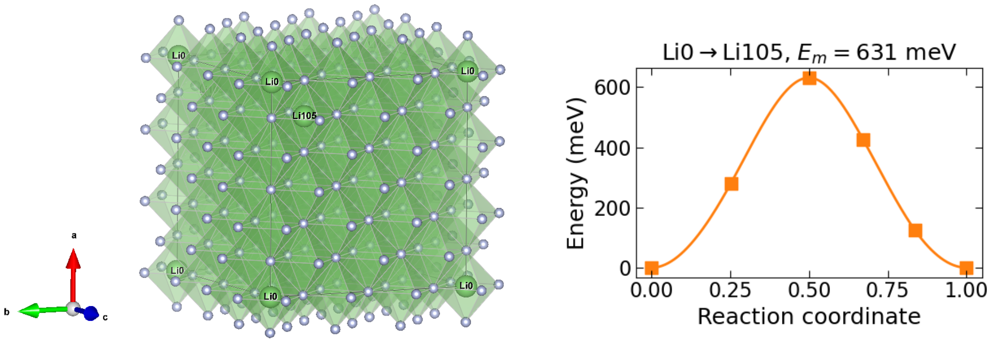


**Figure S8. Crystal structure and Li-ion vacancy migration profiles of LiF.**

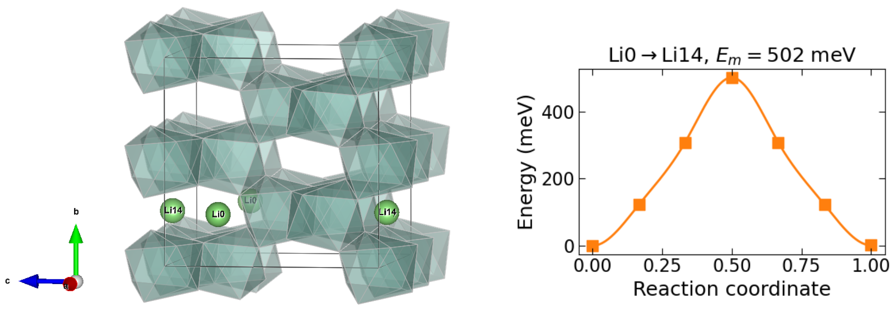


**Figure S9. Crystal structure and Li-ion vacancy migration profiles of $LiYF_4$.**

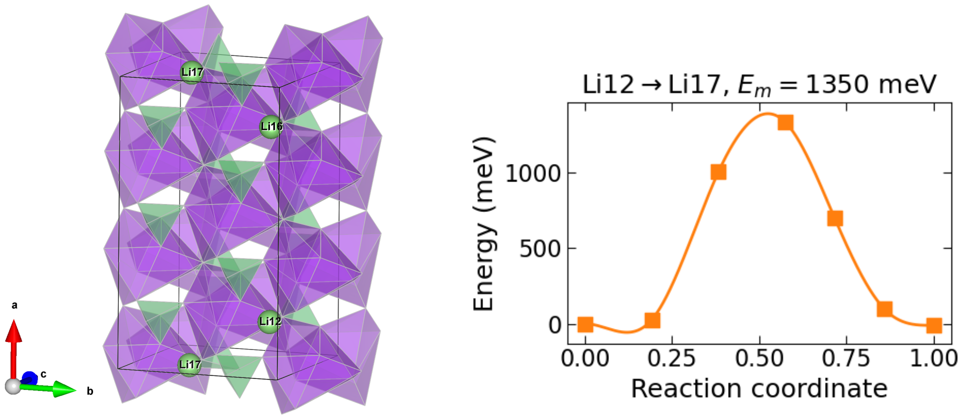


**Figure S10. Crystal structure and Li-ion vacancy migration profiles of $KLiBeF_4$.**

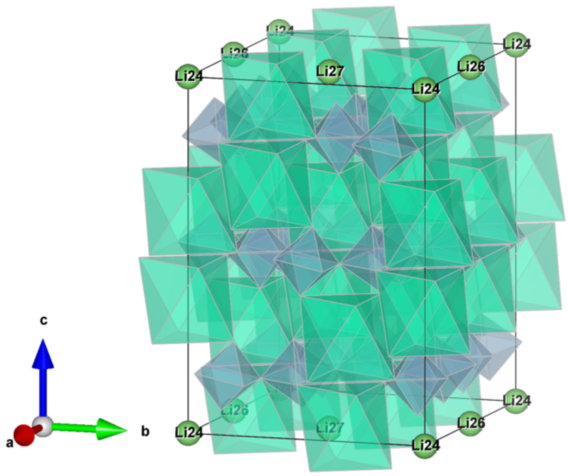


**Figure S11. Crystal structure of $Cs_2LiAl_3F_{12}$.**

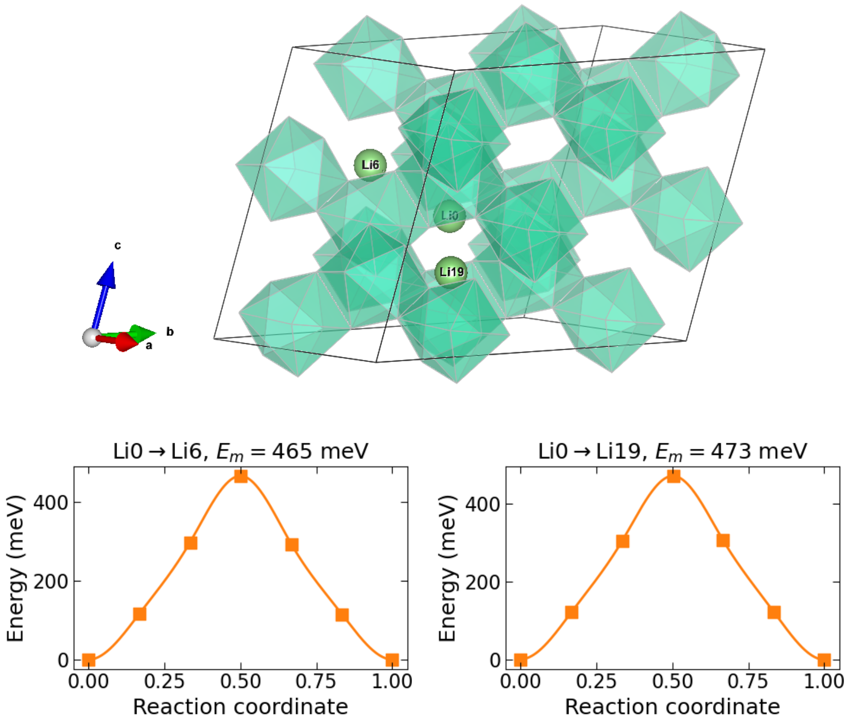


**Figure S12. Crystal structure and Li-ion vacancy migration profiles of $LiLuF_4$.**

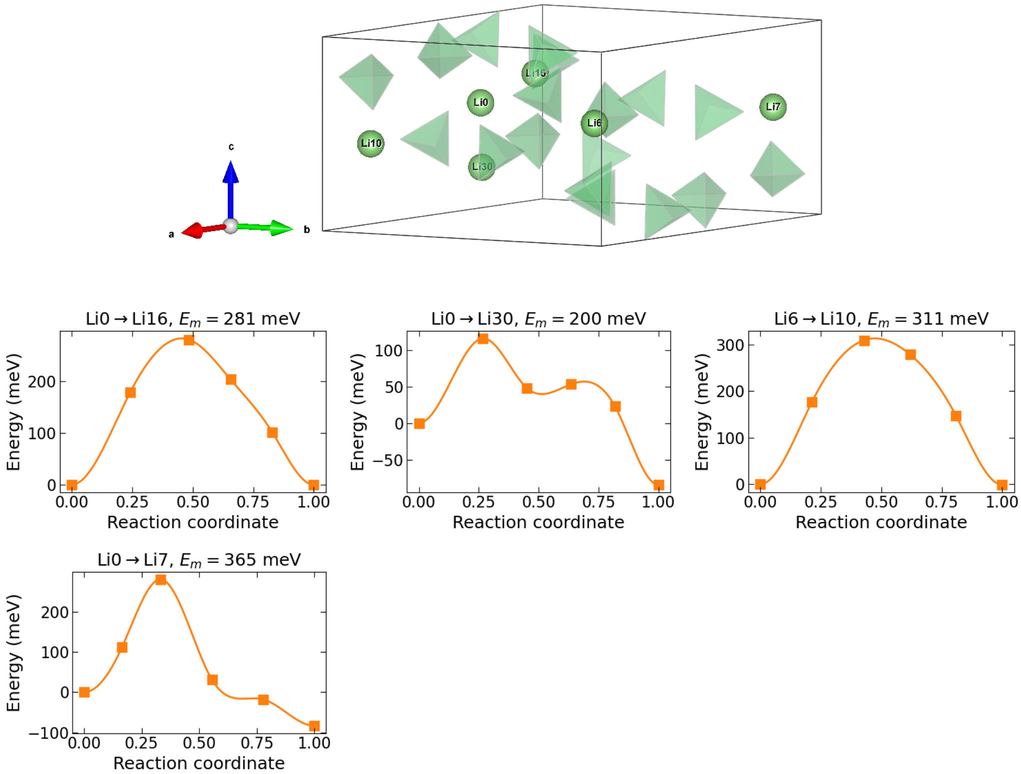


**Figure S13. Crystal structure and Li-ion vacancy migration profiles of $Li_2BeF_4$.**

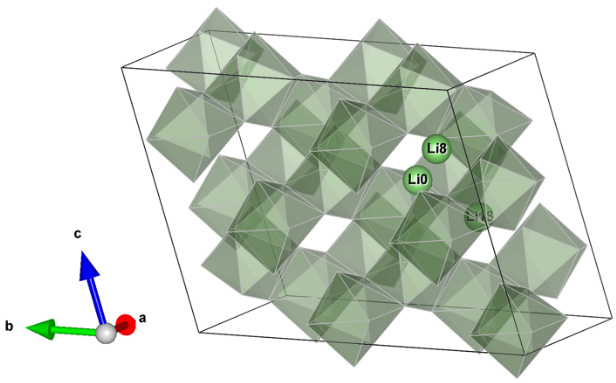


**Figure S14. Crystal structure of $LiErF_4$.**

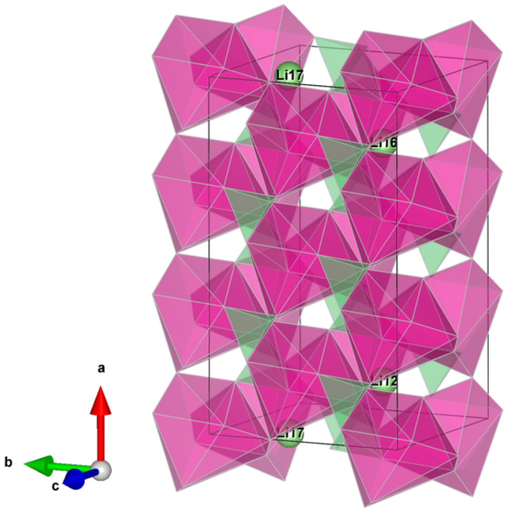


**Figure S15. Crystal structure of $RbLiBeF_4$.**

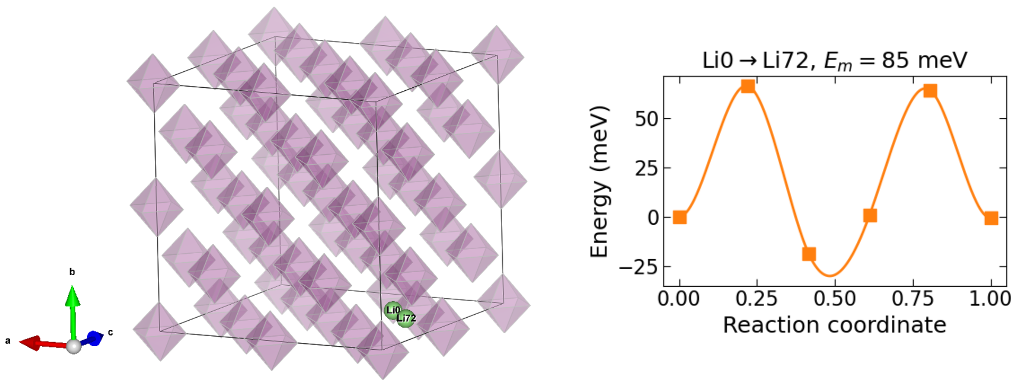


**Figure S16. Crystal structure and Li-ion vacancy migration profiles of $Li_4ScF_7$.**

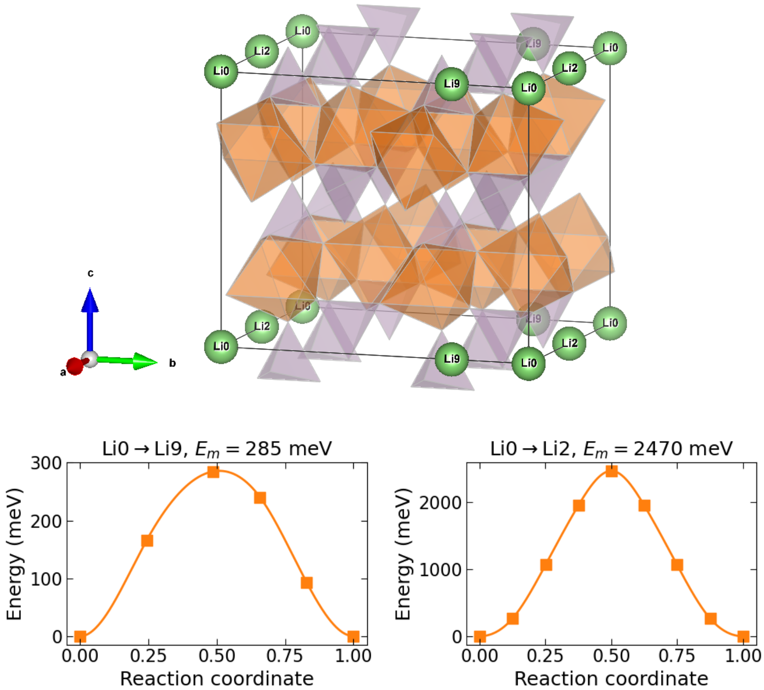


**Figure S17. Crystal structure and Li-ion vacancy migration profiles of $LiMgPO_4$.**

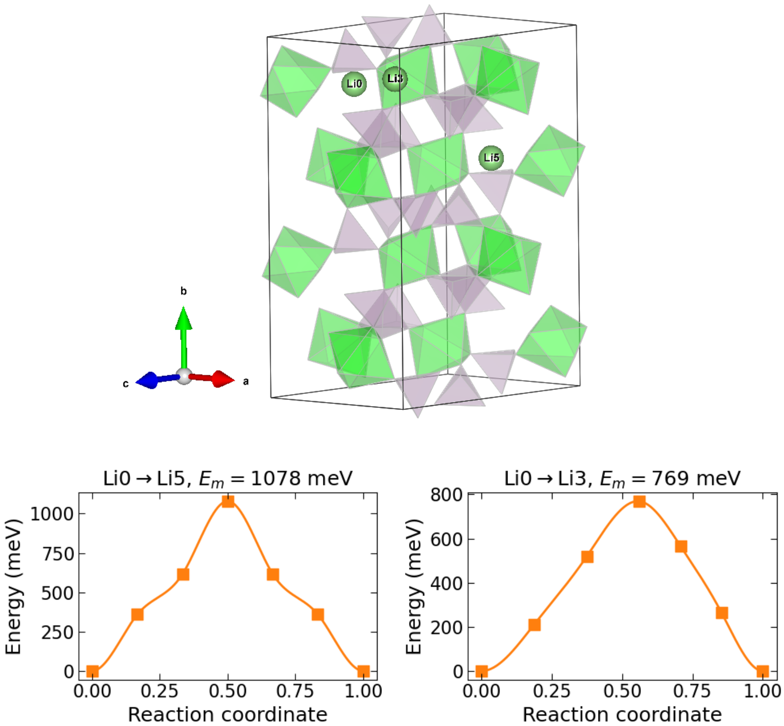


**Figure S18. Crystal structure and Li-ion vacancy migration profiles of $LiZr_2(PO_4)_3$.**

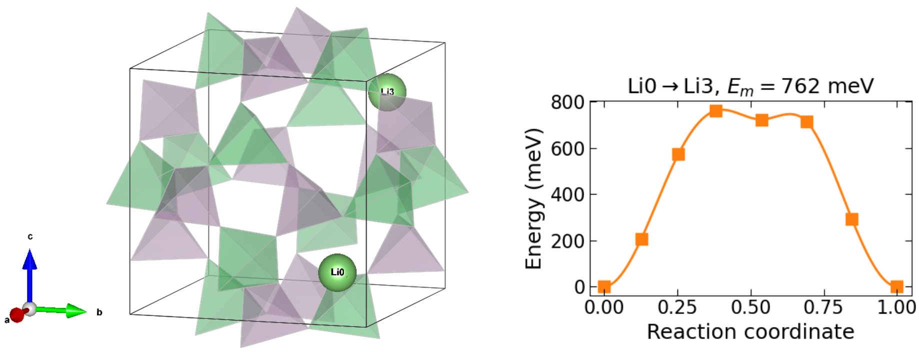


**Figure S19. Crystal structure and Li-ion vacancy migration profiles of $Li_4Be_3P_3BrO_{12}$.**

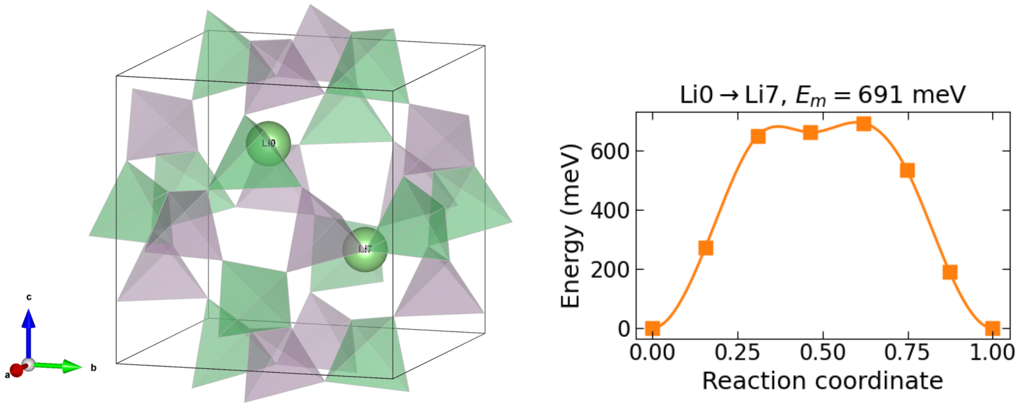


**Figure S20. Crystal structure and Li-ion vacancy migration profiles of $Li_4Be_3P_3ClO_{12}$.**

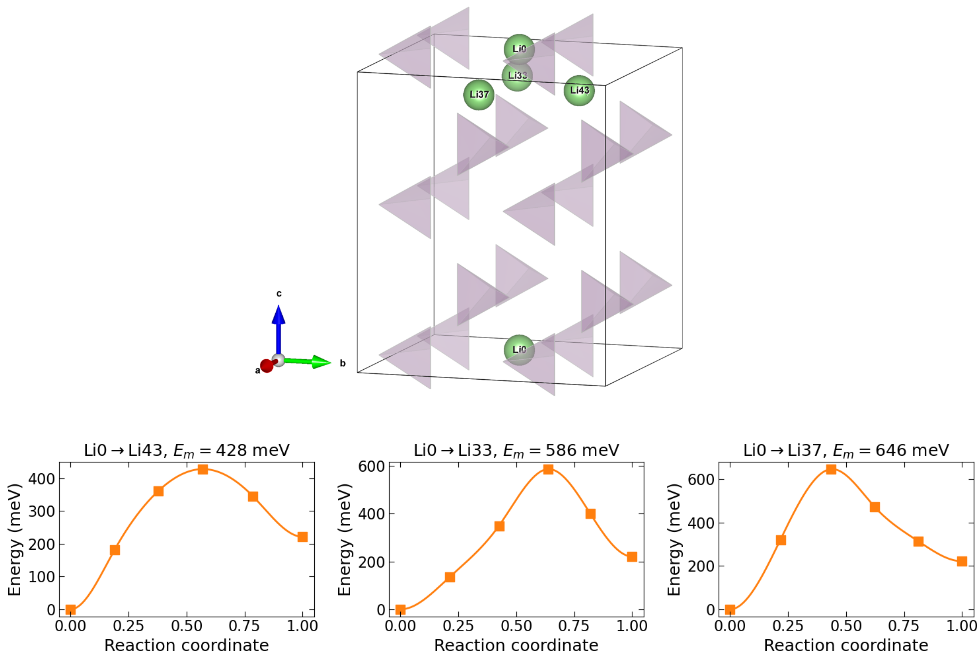


**Figure S21. Crystal structure and Li-ion vacancy migration profiles of $Li_3PO_4$.**

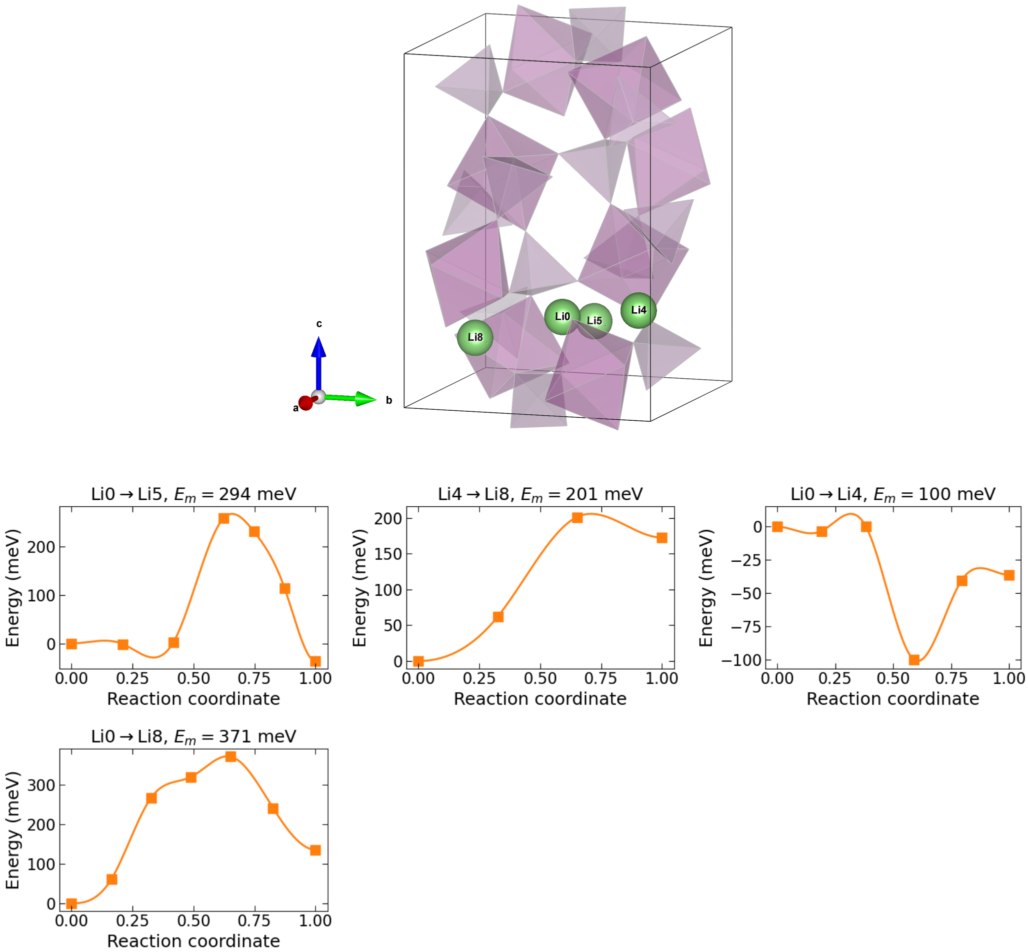


**Figure S22. Crystal structure and Li-ion vacancy migration profiles of $Li_3Sc_2(PO_4)_3$.**

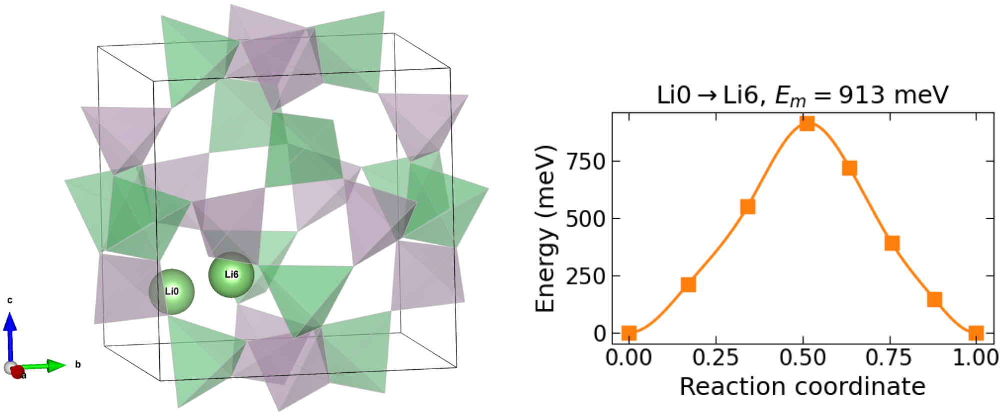


**Figure S23. Crystal structure and Li-ion vacancy migration profiles of $Li_4Be_3P_3IO_{12}$.**

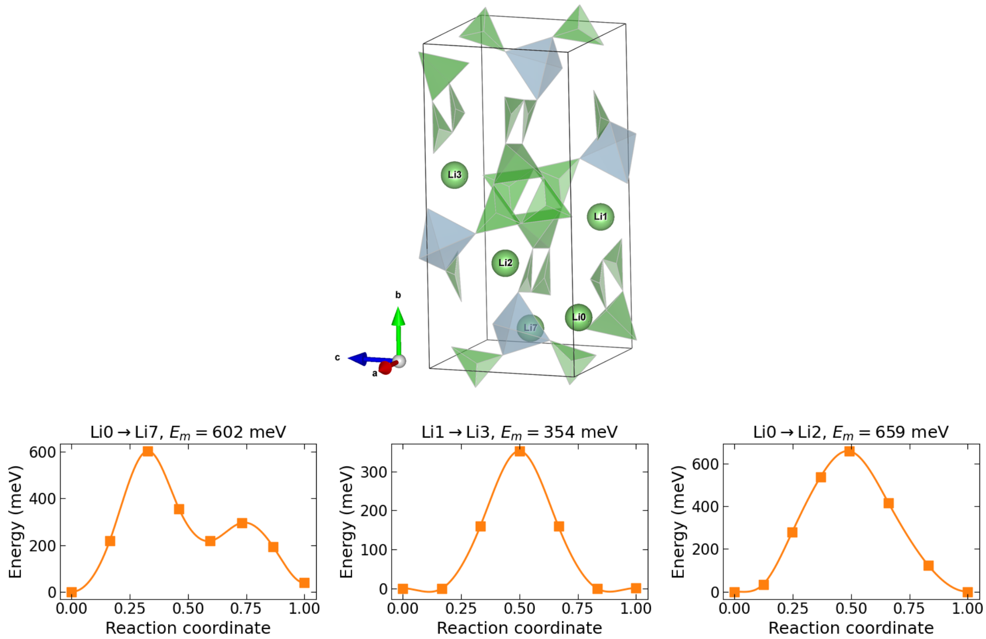


**Figure S24. Crystal structure and Li-ion vacancy migration profiles of $Li_2Al(BO_2)_5$.**

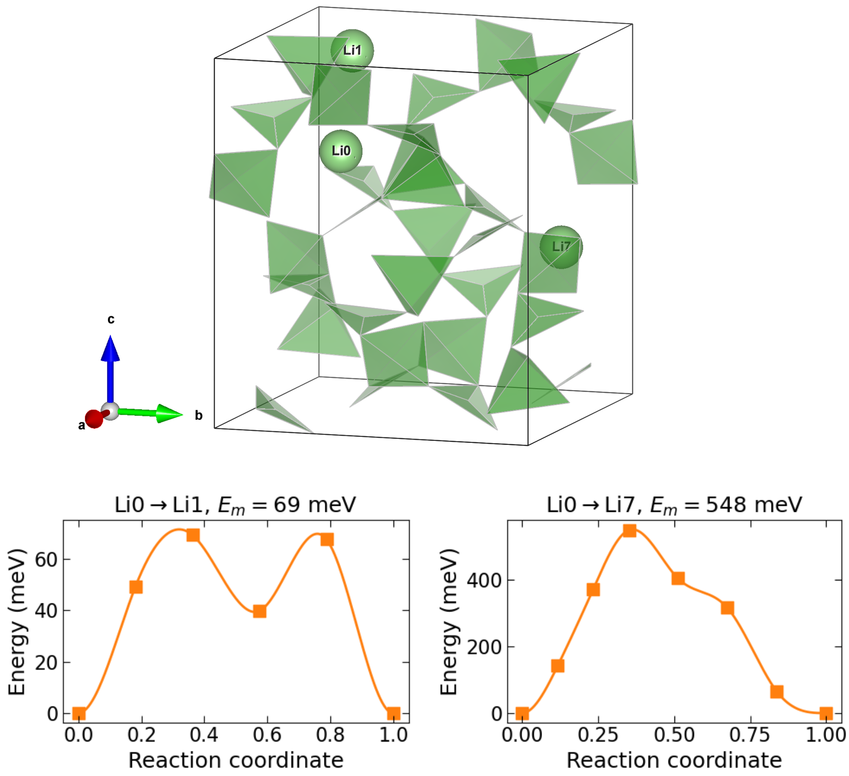


**Figure S25. Crystal structure and Li-ion vacancy migration profiles of $Li_2B_4O_7$.**

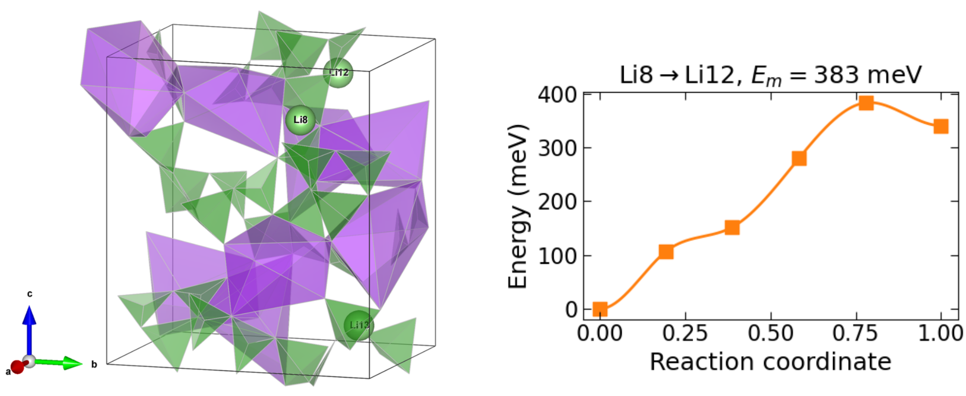


**Figure S26. Crystal structure and Li-ion vacancy migration profiles of $KLiB_4O_7$.**

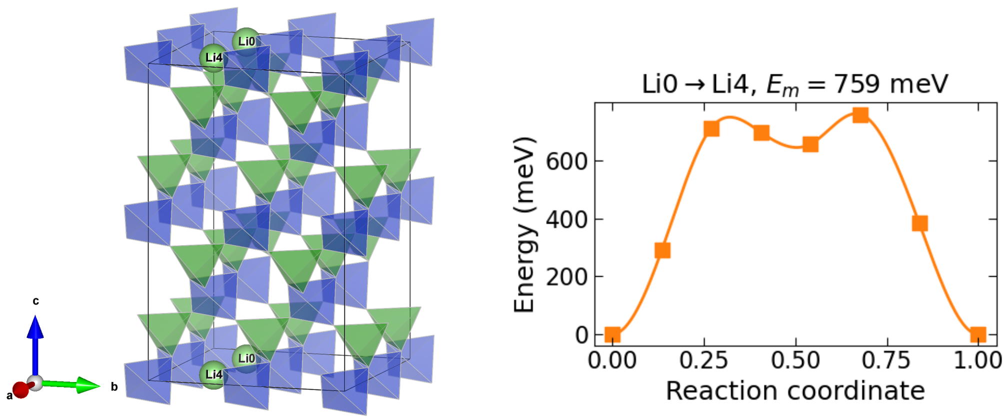


**Figure S27. Crystal structure and Li-ion vacancy migration profiles of $LiSiBO_4$.**

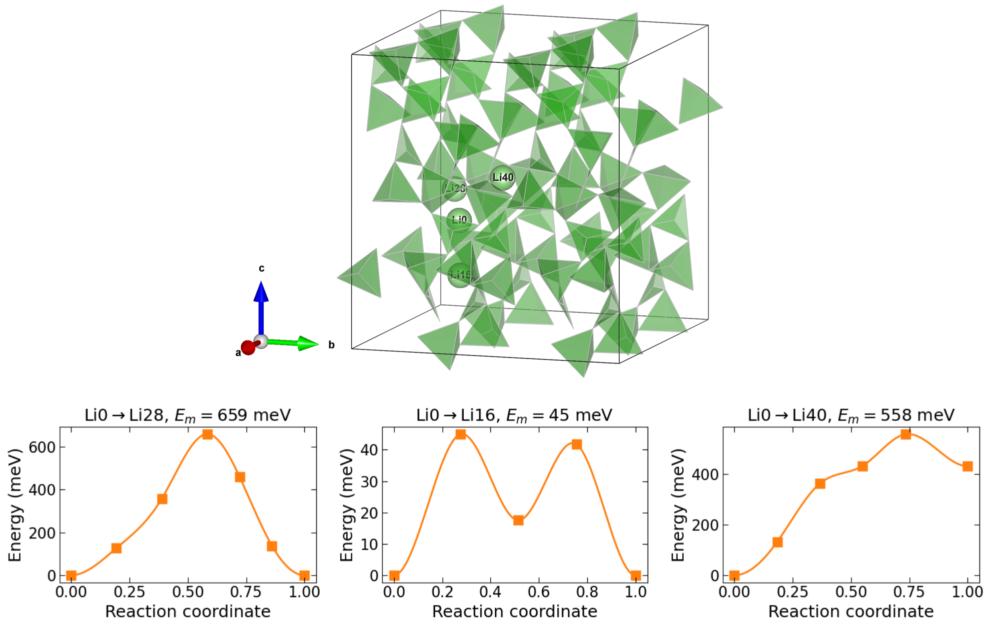


**Figure S28. Crystal structure and Li-ion vacancy migration profiles of $Li_3B_5(HO_5)_2$.**

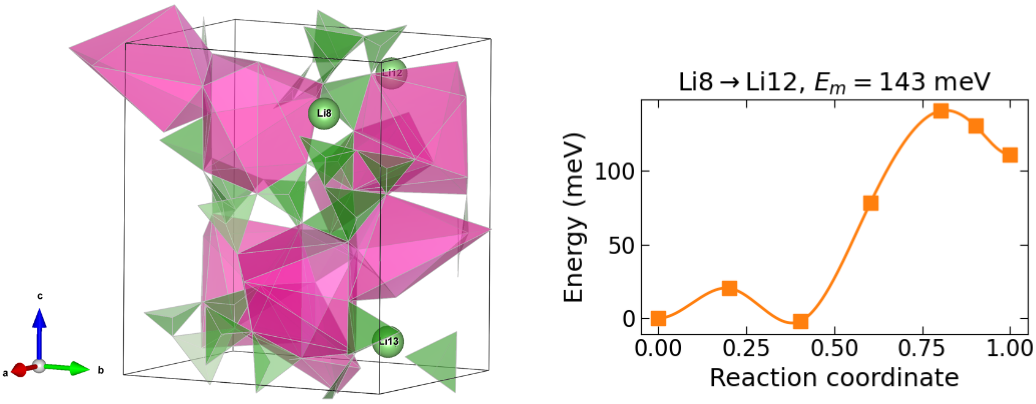


**Figure S29. Crystal structure and Li-ion vacancy migration profiles of $RbLiB_4O_7$.**

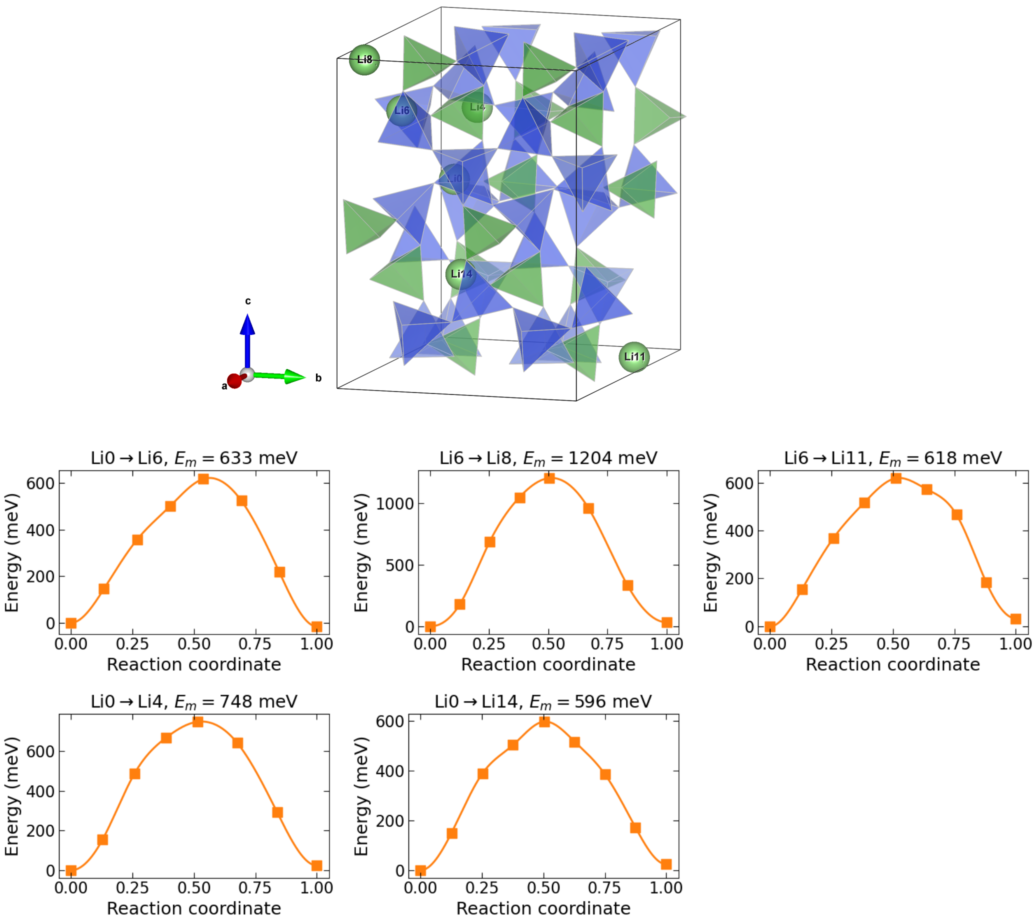


**Figure S30. Crystal structure and Li-ion vacancy migration profiles of $LiSi_2BO_6$.**

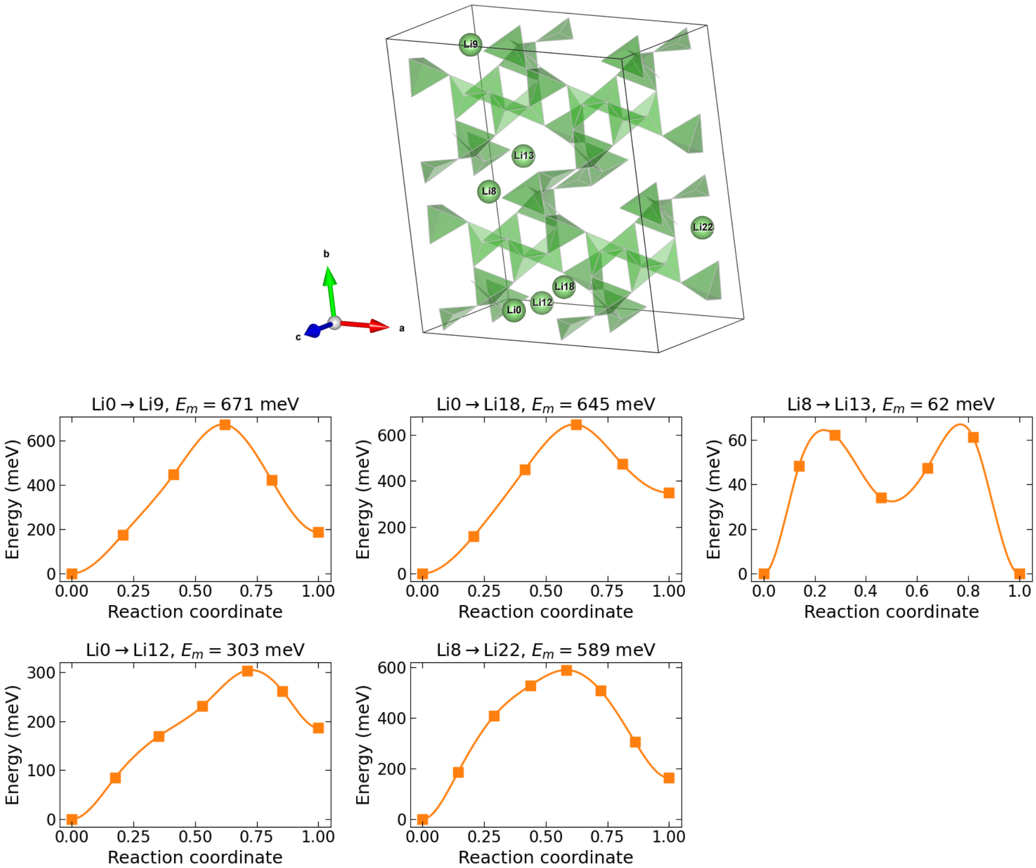


**Figure S31. Crystal structure and Li-ion vacancy migration profiles of $Li_3B_7O_{12}$.**

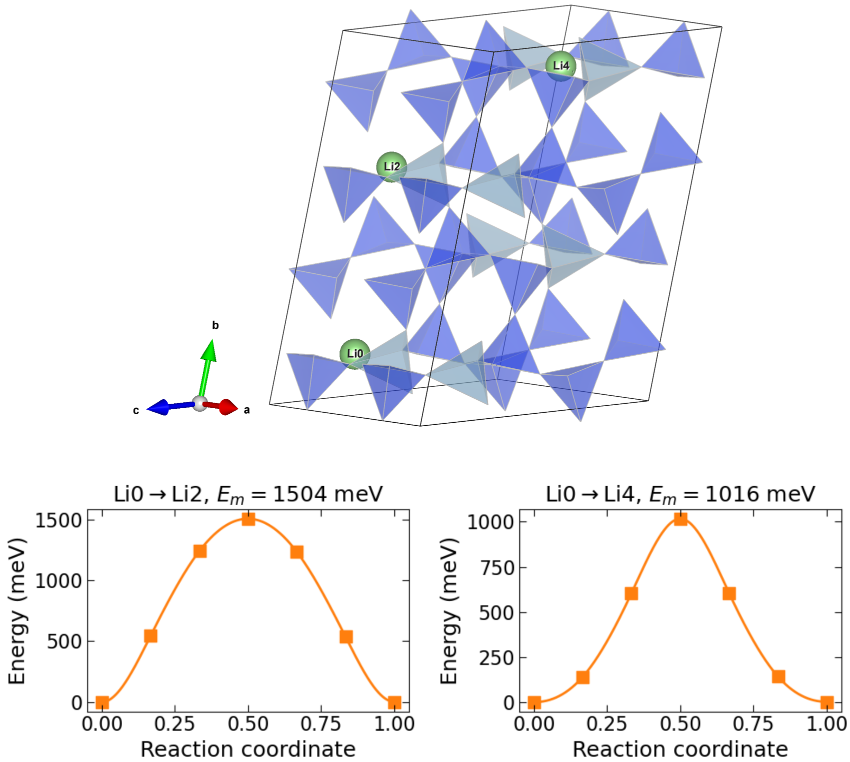


**Figure S32. Crystal structure and Li-ion vacancy migration profiles of $LiAl(Si_2O_5)_2$.**

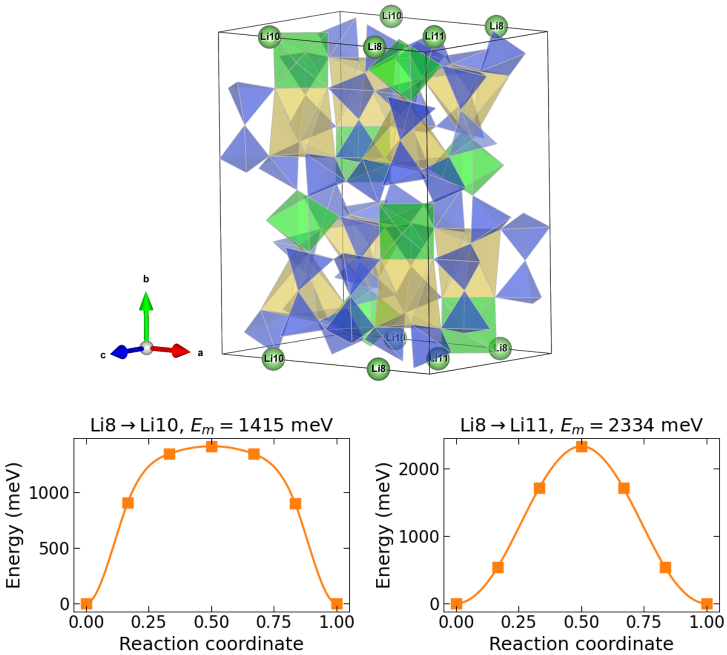


**Figure S33. Crystal structure and Li-ion vacancy migration profiles of $NaLiZr(Si_2O_5)_3$.**

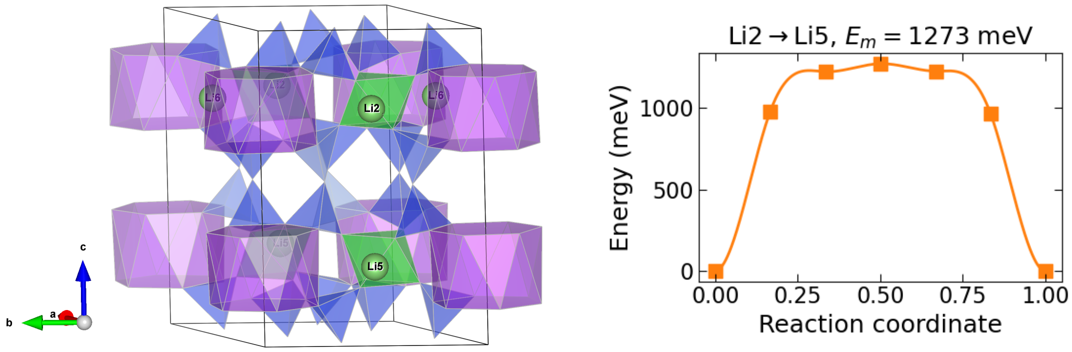


**Figure S34. Crystal structure and Li-ion vacancy migration profiles of $KLi_3Zr_2(Si_2O_5)_6$.**

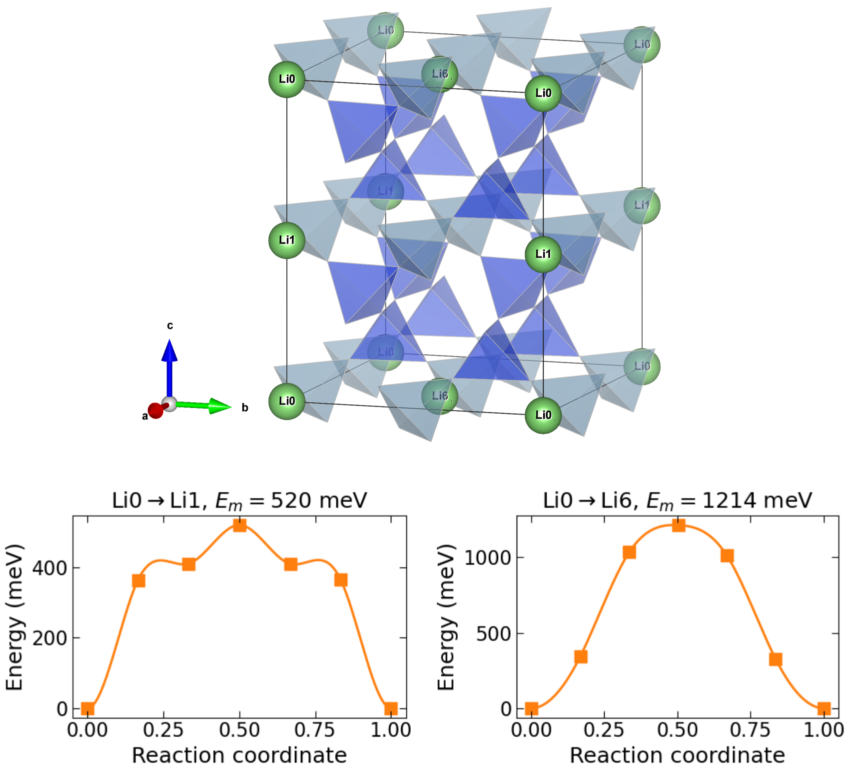


**Figure S35. Crystal structure and Li-ion vacancy migration profiles of $LiAl(SiO_3)_2$.**

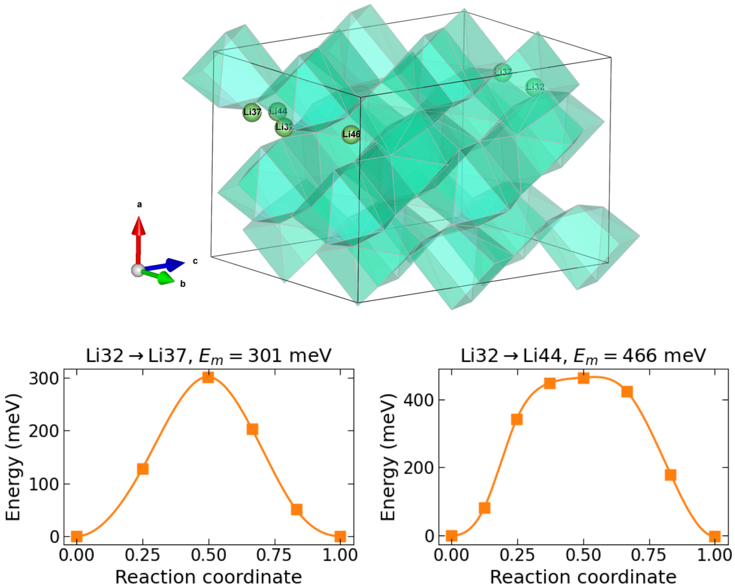


**Figure S36. Crystal structure and Li-ion vacancy migration profiles of $CsLiCl_2$.**

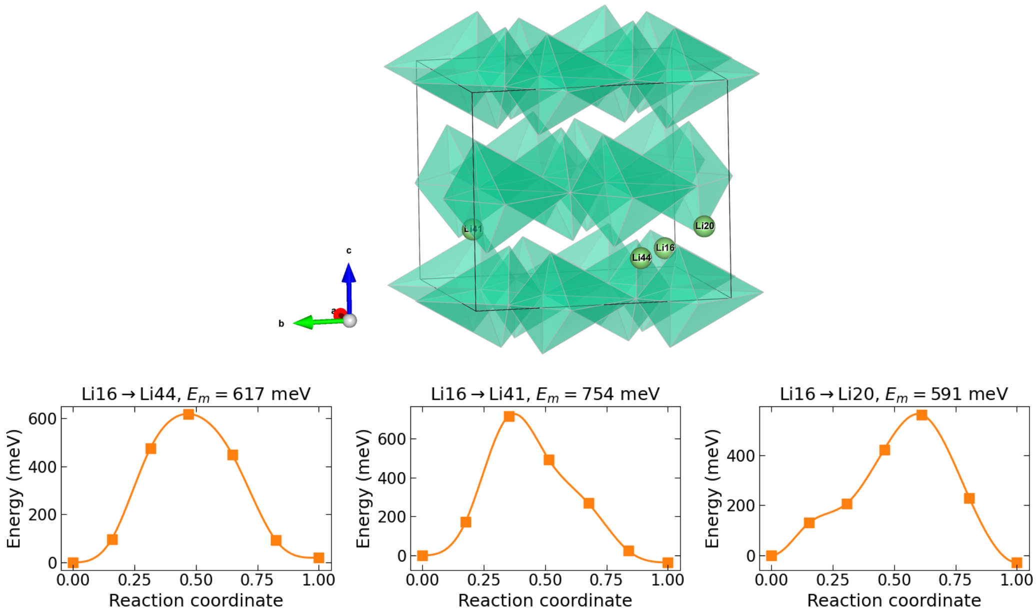


**Figure S37. Crystal structure and Li-ion vacancy migration profiles of $CsLi_2Cl_3$.**

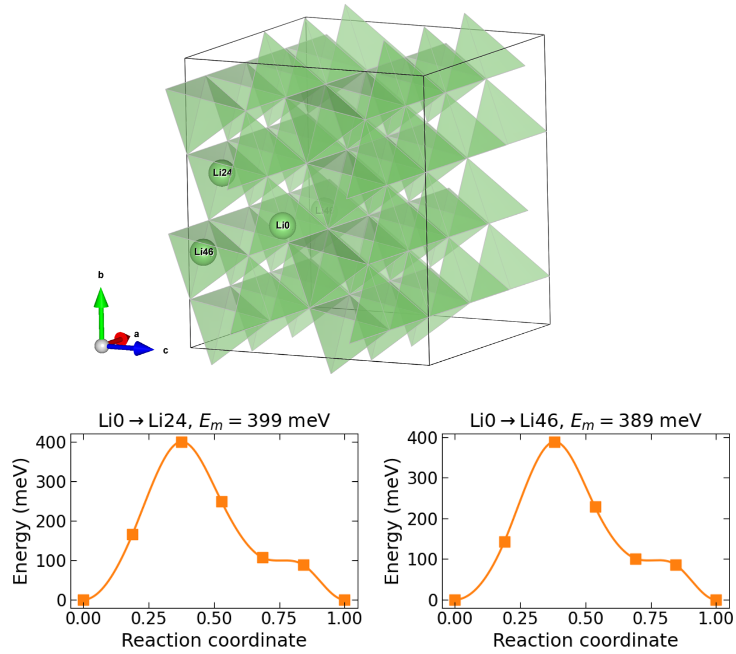


**Figure S38. Crystal structure and Li-ion vacancy migration profiles of LiCl.**

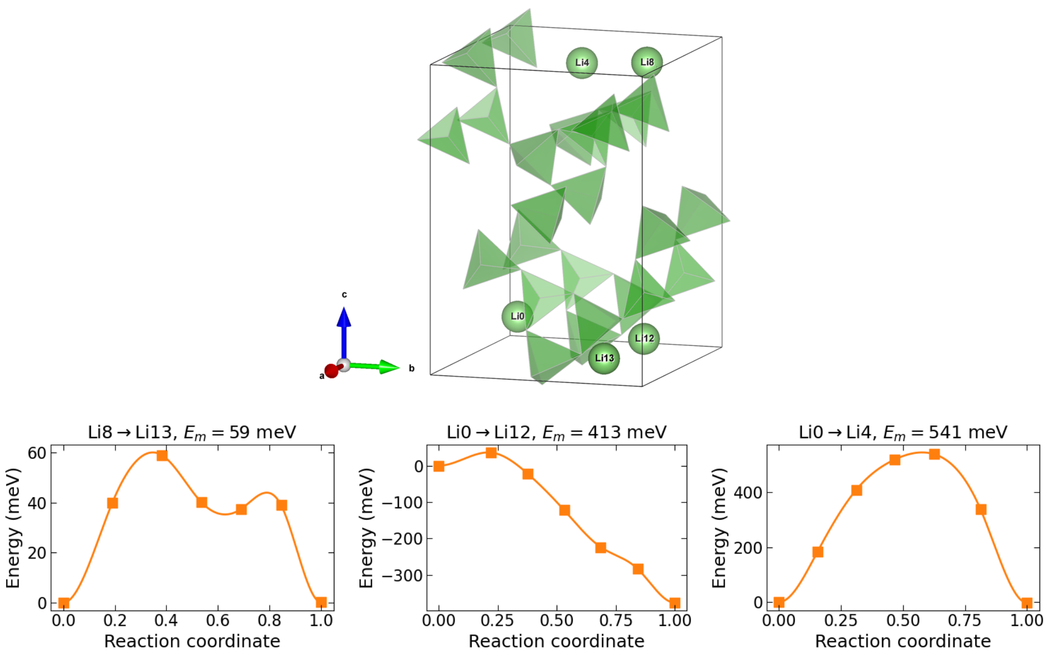


**Figure S39. Crystal structure and Li-ion vacancy migration profiles of $Li_2B_3O_4F_3$.**

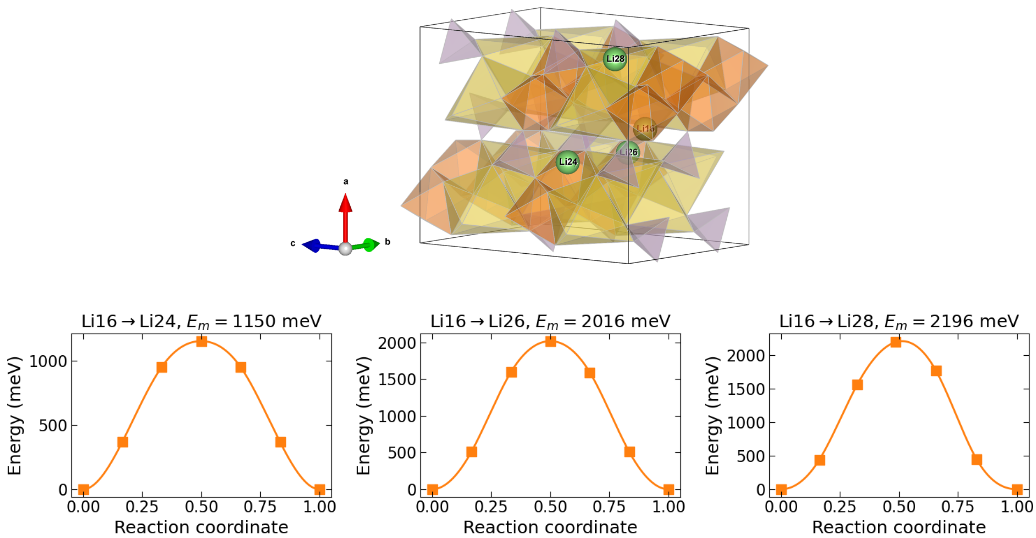


**Figure S40. Crystal structure and Li-ion vacancy migration profiles of $NaLiMgPO_4F$.**

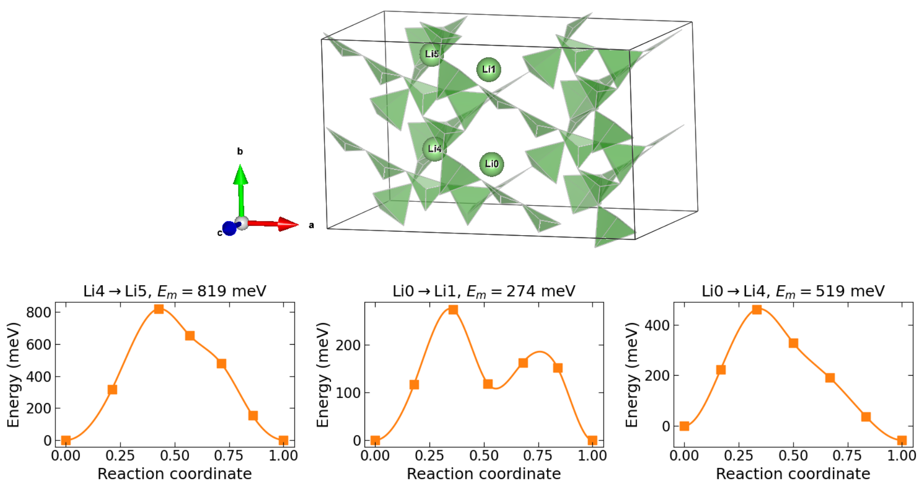


**Figure S41. Crystal structure and Li-ion vacancy migration profiles of $Li_2B_6O_9F_2$.**

**Table S1. Detailed voltages and reactions for redox onsets of various sulfide electrolytes.**

| Formula | Redox Onset | Voltage (V) | Reaction |
|---|---|---|---|
| LSnS | reduction | 1.76 | $Li_4SnS_4 + 2Li \rightarrow 3Li_2S + SnS$ |
| | oxidation | 2.14 | $Li_4SnS_4 \rightarrow 0.333LiS_3 + Li_2SnS_3 + 1.667Li$ |
| LPSI | reduction | 1.71 | $Li_7P_2S_8I + 10Li \rightarrow LiI + 8Li_2S + 2P$ |
| | oxidation | 2.41 | $Li_7P_2S_8I \rightarrow P_2S_7 + SI + 7Li$ |
| LPSC | reduction | 1.71 | $Li_6PS_5Cl + 5Li \rightarrow 5Li_2S + LiCl + P$ |
| | oxidation | 2.13 | $Li_6PS_5Cl \rightarrow Li_3PS_4 + 0.333LiS_3 + LiCl + 1.667Li$ |
| L5.5PSC | reduction | 1.71 | $Li_{5.5}PS_{4.5}Cl_{1.5} + 5Li \rightarrow 4.5Li_2S + 1.5LiCl + P$ |
| | oxidation | 2.13 | $Li_{5.5}PS_{4.5}Cl_{1.5} \rightarrow Li_3PS_4 + 0.1667LiS_3 + 1.5LiCl + 0.8333Li$ |
| LPS | reduction | 1.71 | $Li_3PS_4 + 5Li \rightarrow 4Li_2S + P$ |
| | oxidation | 2.43 | $Li_3PS_4 \rightarrow 0.5P_2S_7 + 0.1667LiS_3 + 2.833Li$ |
| L7PS | reduction | 2.35 | $Li_7P_3S_{11} + 0.2857Li \rightarrow 0.1429P_4S_9 + 2.429Li_3PS_4$ |
| | oxidation | 2.38 | $Li_7P_3S_{11} \rightarrow P_2S_7 + Li_3PS_4 + 4Li$ |
| LGPS | reduction | 1.71 | $Li_{10}Ge(PS_6)_2 + 10Li \rightarrow Li_4GeS_4 + 8Li_2S + 2P$ |
| | oxidation | 2.24 | $Li_{10}Ge(PS_6)_2 \rightarrow 0.1667GeS_{14} + 2Li_3PS_4 + 0.8333GeS_2 + 4Li$ |
| L3.25GPS | reduction | 1.71 | $Li_{3.25}Ge_{0.25}P_{0.75}S_4 + 3.75Li \rightarrow 0.25Li_4GeS_4 + 3Li_2S + 0.75P$ |
| | oxidation | 2.24 | $Li_{3.25}Ge_{0.25}P_{0.75}S_4 \rightarrow 0.04167GeS_{14} + 0.75Li_3PS_4$ $+0.2083GeS_2 + Li$ |
| LSiPSC | reduction | 1.71 | $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3} + 7.2Li$ $\rightarrow 1.74Li_2SiS_3 + 6.48Li_2S + 0.3LiCl + 1.44P$ |
| | oxidation | 2.13 | $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ $\rightarrow 1.44Li_3PS_4 + 1.74Li_2SiS_3 + 0.3LiCl + 0.24LiS_3 + 1.2Li$ |
| L9.6PS | reduction | 1.71 | $Li_{9.6}P_3S_{12} + 14.4Li \rightarrow 12Li_2S + 3P$ |
| | oxidation | 1.71 | $Li_{9.6}P_3S_{12} \rightarrow 3Li_3PS_4 + 0.6Li$ |

**Table S2. Detailed chemical reaction between sulfide electrolytes and $LiFePO_4$/FePO4.**

| Formula | Electrode | Products | $\Delta E$ (meV/atom) |
|---|---|---|---|
| LSnS | LiFePO4 | SnS, FeS, FeS2, Li3PO4 | -159 |
| | FePO4 | SnS, SnS2, FeS2, Li3PO4 | -255 |
| LPSI | LiFePO4 | Li4P2O7, FePS, FeS2, LiI | -136 |
| | FePO4 | PI7, Li4P2O7, FePS, LiPO3, FeS2 | -220 |
| LPSC | LiFePO4 | Li3PO4, FePS, Li4P2O7, FeS2, LiCl | -152 |
| | FePO4 | LiPO3, FePS, Li4P2O7, FeS2, LiCl | -238 |
| L5.5PSC | LiFePO4 | Li3PO4, FePS, Li4P2O7, FeS2, LiCl | -152 |
| | FePO4 | LiPO3, FePS, Li4P2O7, FeS2, LiCl | -216 |
| LPS | LiFePO4 | FePS, Li4P2O7, FeS2 | -141 |
| | FePO4 | FePS, Li4P2O7, LiPO3, FeS2 | -226 |
| L7PS | LiFePO4 | FePS, Li4P2O7, LiPO3, FeS2 | -138 |
| | FePO4 | P4S7, FePS, LiPO3, FeS2 | -218 |
| LGPS | LiFePO4 | Li4P2O7, FePS, Li3PO4, GeS2, FeS2 | -147 |
| | FePO4 | Li4P2O7, FePS, LiPO3, GeS2, FeS2 | -233 |
| L3.25GPS | LiFePO4 | Li4P2O7, FePS, Li3PO4, GeS2, FeS2 | -145 |
| | FePO4 | Li4P2O7, FePS, LiPO3, GeS2, FeS2 | -231 |
| LSiPSC | LiFePO4 | Li4P2O7, FeS2, FePS, LiCl, Li3PO4, SiO2 | -171 |
| | FePO4 | Li4P2O7, FeS2, FePS, LiCl, LiPO3, SiO2 | -266 |
| L9.6PS | LiFePO4 | FePS, Li4P2O7, Li3PO4, FeS2 | -146 |
| | FePO4 | FePS, Li4P2O7, LiPO3, FeS2 | -232 |

**Table S3. Detailed chemical reaction between sulfide electrolytes and $LiFePO_4$ under voltages.**

| Formula | Voltage (V) | Electrode | Products | $\Delta E$ (meV/atom) |
|---|---|---|---|---|
| LSnS | 2 | LiFePO4 | SnS, FeS, FeS2, Li3PO4 | -222 |
| | 2.5 | | Li, SnS2, SnS14, FeS2, Li3PO4 | -271 |
| | 3 | | Li, SnS14, SnS2 | -633 |
| | 3.5 | | Li, SnS14, SnS2 | -1033 |
| | 4 | | Li, SnS14, SnS2 | -1433 |
| LPSI | 2 | LiFePO4 | FeS2, FeS, FeP, Li3PO4, LiI | -227 |
| | 2.5 | | Li, P4S7, Li4P2O7, FePS, PI7, FeS2 | -178 |
| | 3 | | Li, P2S7, SI | -375 |
| | 3.5 | | Li, P2S7, SI | -693 |
| | 4 | | Li, P2S7, SI | -1011 |
| LPSC | 2 | LiFePO4 | FeS2, FeS, FeP, Li3PO4, LiCl | -231 |
| | 2.5 | | Li4P2O7, P2S5, FeS2, LiCl | -218 |
| | 3 | | Li, P2S7, LiCl, LiS4 | -446 |
| | 3.5 | | Li, SCl, P2S7, S | -815 |
| | 4 | | Li, SCl, P2S7, S | -1243 |
| L5.5PSC | 2 | LiFePO4 | FeS2, FeS, FeP, Li3PO4, LiCl | -225 |
| | 2.5 | | Li, P4S7, Li4P2O7, FePS, FeS2, LiCl | -190 |
| | 3 | | Li, P2S7, LiCl, LiS4 | -340 |
| | 3.5 | | Li, PCl5, SCl, P2S7 | -647 |
| | 4 | | Li, PCl5, SCl, P2S7 | -1039 |
| LPS | 2 | LiFePO4 | FeP, FeS2, FeS, Li3PO4 | -230 |
| | 2.5 | | Li, P4S7, Li4P2O7, FePS, FeS2 | -181 |
| | 3 | | Li, P2S7, LiS4 | -328 |
| | 3.5 | | Li, P2S7, S | -624 |
| | 4 | | Li, P2S7, S | -924 |
| L7PS | 2 | LiFePO4 | FeP, FeS2, FeS, Li3PO4 | -235 |
| | 2.5 | | P4S7, Li4P2O7, FePS, FeS2 | -176 |
| | 3 | | Li, P2S7, LiS4 | -295 |
| | 3.5 | | Li, P2S7, S | -543 |
| | 4 | | Li, P2S7, S | -793 |
| LGPS | 2 | LiFePO4 | FeS2, FeS, GeS, FeP, Li3PO4 | -224 |
| | 2.5 | | Li4P2O7, FeS2, GeS2, FePS | -198 |
| | 3 | | Li, P2S7, GeS2, GeS14 | -440 |
| | 3.5 | | Li, GeS14, P2S7, GeS2 | -773 |
| | 4 | | Li, GeS14, P2S7, GeS2 | -1107 |
| L3.25GPS | 2 | LiFePO4 | FeS2, FeS, GeS, FeP, Li3PO4 | -225 |
| | 2.5 | | Li4P2O7, FeS2, GeS2, FePS | -193 |
| | 3 | | Li, P2S7, GeS2, GeS14 | -419 |
| | 3.5 | | Li, GeS14, P2S7, GeS2 | -744 |

| | | | | |
|---|---|---|---|---|
| | 4 | | Li, GeS14, P2S7, GeS2 | -1069 |
| LSiPSC | 2 | LiFePO4 | FeS2, FeS, FeP, Li3PO4, SiO2, LiCl | -238 |
| | 2.5 | | Li, Li4P2O7, P2S5, P2S7, FeS2, SiO2, LiCl | -237 |
| | 3 | | Li, P2S7, SiS14, FeS2, SiCl4, SiS2, SiO2 | -461 |
| | 3.5 | | Li, SiS14, P2S7, SiS2, SiCl4 | -732 |
| | 4 | | Li, SiS14, P2S7, SiS2, SiCl4 | -1047 |
| L9.6PS | 2 | LiFePO4 | FeP, FeS2, FeS, Li3PO4 | -232 |
| | 2.5 | | Li, P4S7, Li4P2O7, FeS2, FePS | -189 |
| | 3 | | Li, P2S7, LiS4 | -380 |
| | 3.5 | | Li, P2S7, S | -695 |
| | 4 | | Li, P2S7, S | -1015 |

**Table S4. Detailed chemical reactions of screened coating candidates (corresponding to the compounds in Table 1, main text) toward LiFePO4, FePO4, and LGPS.**

| Formula | Electrode | Products | $\Delta E$ (meV/atom) |
|---|---|---|---|
| Li3AlF6 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | - | 0 |
| CsLiBeF4 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | Li4GeS4, CsPS3, Li2S, Li2BeF4 | -1 |
| Li4ZrF8 | LiFePO4 | Fe2PO4F, LiZr2(PO4)3, LiF | -7 |
| | FePO4 | LiFePO4F, Li2ZrF6 | -8 |
| | LGPS | ZrS2, Li3PS4, GeS2, LiF | -18 |
| Na3Li3Sc2F12 | LiFePO4 | - | 0 |
| | FePO4 | NaFePO4F, LiFePO4F, ScF3 | -6 |
| | LGPS | Li3PS4, Na2Ge2S5, NaScS2, GeS2, LiF | -15 |
| LiMgAlF6 | LiFePO4 | Fe2PO4F, AlPO4, Li3AlF6, MgF2 | -8 |
| | FePO4 | - | 0 |
| | LGPS | Li3PS4, Li3AlF6, LiAlS2, GeS2, MgF2 | -7 |
| Na3Li3Al2F12 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | Li3AlF6, Li3PS4, Na2GeS3, LiF, LiAlS2 | -1 |
| RbLi2Be2F7 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | Rb3PS4, Li3PS4, Rb2Ge2S5, BeS, Li2BeF4 | -11 |
| LiF | LiFePO4 | - | 0 |
| | FePO4 | LiFePO4F | -12 |
| | LGPS | - | 0 |
| LiYF4 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | - | 0 |
| KLiBeF4 | LiFePO4 | - | 0 |
| | FePO4 | KFePO4F, Li2BeF4, BeF2 | -10 |
| | LGPS | K3PS4, K2GeS3, Li2S, Li2BeF4 | -20 |
| Cs2LiAl3F12 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | Li4GeS4, Li3AlF6, CsPS3, LiAlS2 | -18 |
| LiLuF4 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | - | 0 |

| | | | |
|---|---|---|---|
| Li2BeF4 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | - | 0 |
| LiErF4 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | - | 0 |
| RbLiBeF4 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | Rb2GeS3, Rb3PS4, Li2S, Li2BeF4 | -19 |
| Li4ScF7 | LiFePO4 | - | 0 |
| | FePO4 | LiFePO4F, ScF3 | -9 |
| | LGPS | Li3PS4, LiScS2, GeS2, LiF | -9 |
| LiMgPO4 | LiFePO4 | - | 0 |
| | FePO4 | Li3Fe2(PO4)3, Mg3(PO4)2 | -2 |
| | LGPS | Mg2GeS4, Li3PS4, Li3PO4 | -6 |
| LiZr2(PO4)3 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | Li3PS4, GeS2, ZrS2, Li3PO4 | -11 |
| Li4Be3P3BrO12 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | - | 0 |
| Li4Be3P3ClO12 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | Li3PS4, LiCl, GeS2, Li3PO4, BeO | -1 |
| Li3PO4 | LiFePO4 | - | 0 |
| | FePO4 | Li3Fe2(PO4)3 | -6 |
| | LGPS | - | 0 |
| Li3Sc(PO4)3 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | Li4P2O7, LiScP2O7, GeS2, GeS14, Li3PO4 | -12 |
| Li4Be3P3IO12 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | - | 0 |
| Li2Al(BO2)5 | LiFePO4 | - | 0 |
| | FePO4 | Li3Fe2(PO4)3, FeBO3, AlPO4, Li3B7O12 | -8 |
| | LGPS | - | 0 |
| Li2B4O7 | LiFePO4 | Fe2B2O5, Li3B7O12, Li3PO4 | -5 |
| | FePO4 | FeBO3, Li3Fe2(PO4)3, Li3B7O12 | -8 |
| | LGPS | Li4GeS4, Li3B7O12, Li2S, Li3PO4 | -3 |
| KLiB4O7 | LiFePO4 | K5B19O31, Fe2B2O5, Fe3BO5, Li3PO4, Fe | -8 |

| | | | |
|---|---|---|---|
| | FePO4 | K3Fe2(PO4)3, Fe2O3, Li3PO4, KB5O8 | -20 |
| | LGPS | Li4GeS4, K3PS4, Li3B7O12, Li2S, Li3PO4 | -16 |
| LiSiBO4 | LiFePO4 | Fe2SiO4, Li3B7O12, Li3PO4, SiO2 | -9 |
| | FePO4 | FeBO3, Li3B7O12, Li3PO4, SiO2 | -20 |
| | LGPS | Li3PO4, Li4GeS4, Li3B7O12, SiO2, Li2S | -1 |
| Li3B5(HO5)2 | LiFePO4 | LiB5H2O9, Fe2B2O5, Li3PO4, B(HO)3 | -3 |
| | FePO4 | LiB5H2O9, Li3B7O12, LiFePHO5 | -18 |
| | LGPS | LiH2, Li3B7O12, Li4GeS4, H2S, Li3PO4 | -9 |
| RbLiB4O7 | LiFePO4 | Fe2B2O5, Fe3BO5, Rb5B19O31, Li3PO4, Fe | -7 |
| | FePO4 | FeBO3, Rb5B19O31, Fe2O3, Li3PO4 | -18 |
| | LGPS | Rb3PS4, Rb2GeS3, Li3B7O12, Li2S, Li3PO4 | -18 |
| LiSi2BO6 | LiFePO4 | Fe2SiO4, Li3B7O12, Li3PO4, SiO2 | -7 |
| | FePO4 | FeBO3, Li3B7O12, Li3PO4, SiO2 | -14 |
| | LGPS | - | 0 |
| Li3B7O12 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | - | 0 |
| LiAl(Si2O5)2 | LiFePO4 | - | 0 |
| | FePO4 | Li3Fe2(PO4)3, AlPO4, SiO2, Fe2O3 | -7 |
| | LGPS | - | 0 |
| NaLiZr(Si2O5)3 | LiFePO4 | - | 0 |
| | FePO4 | NaZr2(PO4)3, Na3Fe3(PO4)4, Fe2O3, Li3PO4, SiO2 | -16 |
| | LGPS | Na2ZrS3, Li4GeS4, Li2ZrS3, SiO2, Li3PO4 | -12 |
| KLi3Zr2(Si2O5)6 | LiFePO4 | - | 0 |
| | FePO4 | KZr2(PO4)3, Fe2O3, Li3PO4, SiO2 | -14 |
| | LGPS | Li4GeS4, Li2ZrS3, K3PS4, SiO2, Li3PO4 | -5 |
| LiAl(SiO3)2 | LiFePO4 | - | 0 |
| | FePO4 | AlPO4, SiO2, Fe2O3, Li3PO4 | -10 |
| | LGPS | - | 0 |
| CsLiCl2 | LiFePO4 | - | 0 |
| | FePO4 | Fe2PClO4, Li3Fe2(PO4)3, Cs2FeCl6, CsCl | -1 |
| | LGPS | - | 0 |
| CsLi2Cl3 | LiFePO4 | Fe2PClO4, Li3PO4, CsLiCl2 | -2 |
| | FePO4 | Fe2PClO4, Li3Fe2(PO4)3, CsLiCl2, Cs2FeCl6 | -9 |
| | LGPS | - | 0 |
| LiCl | LiFePO4 | Li3PO4, Fe2PClO4 | -2 |

| | | | |
|---|---|---|---|
| | FePO4 | Li3Fe2(PO4)3, LiFeCl4 | -9 |
| | LGPS | - | 0 |
| Li2B3O4F3 | LiFePO4 | - | 0 |
| | FePO4 | - | 0 |
| | LGPS | Li3PS4, Li5B7S13, Li3B7O12, GeS2, LiF | -5 |
| NaLiMgPO4F | LiFePO4 | - | 0 |
| | FePO4 | Li3PO4, Na3Fe3(PO4)4, Mg2PO4F, MgF2 | -13 |
| | LGPS | Na3PS4, Na2GeS3, Li3PO4, Mg2PO4F, MgS, MgF2 | -18 |
| Li2B6O9F2 | LiFePO4 | - | 0 |
| | FePO4 | LiB6O9F, LiFePO4F | -1 |
| | LGPS | Li3PS4, Li5B7S13, Li3B7O12, GeS2, LiF | -4 |

**Table S5. Detailed chemical reactions of excluded compounds in the last screening step against LiFePO4 and FePO4.**

| Formula | Electrode | Products | $\Delta E$ (meV/atom) |
|---|---|---|---|
| Li6Nd(BO3)3 | LiFePO4 | LiFeBO3, Li3PO4, NdBO3 | -46 |
| | FePO4 | Li3PO4, NdFe3(BO3)4, NdPO4 | -97 |
| KLiDyF5 | LiFePO4 | - | 0 |
| | FePO4 | KFePO4F, LiDyF4 | -29 |
| Li6Ho(BO3)3 | LiFePO4 | Li3PO4, LiFeBO3, HoBO3 | -47 |
| | FePO4 | Li3PO4, HoBO3, Fe2O3, Li3B7O12 | -91 |
| KLiHoF5 | LiFePO4 | - | 0 |
| | FePO4 | KFePO4F, LiHoF4 | -29 |
| CsLiF2 | LiFePO4 | Cs2FeF4, Li3PO4 | -17 |
| | FePO4 | Cs3FeF6, Li3PO4 | -50 |
| Li3AlSiO5 | LiFePO4 | Al2FeO4, Fe2SiO4, LiAlSiO4, Li3PO4 | -26 |
| | FePO4 | LiAlSiO4, Fe2O3, Li3PO4 | -58 |
| LiAlO2 | LiFePO4 | Al2FeO4, Li3PO4 | -24 |
| | FePO4 | Fe2O3, Li3PO4, LiAl5O8 | -51 |
| KLiGdF5 | LiFePO4 | - | 0 |
| | FePO4 | KFePO4F, LiGdF4 | -28 |
| KLiLuF5 | LiFePO4 | - | 0 |
| | FePO4 | KFePO4F, LiLuF4 | -30 |
| LiBO2 | LiFePO4 | Fe2B2O5, Li3B7O12, Li3PO4 | -21 |
| | FePO4 | FeBO3, Li3B7O12, Li3PO4 | -42 |
| KLiTbF5 | LiFePO4 | - | 0 |
| | FePO4 | LiTbF4, KFePO4F | -29 |
| Li6B4O9 | LiFePO4 | Fe2B2O5, Li3B7O12, Li3PO4 | -35 |
| | FePO4 | Li3B7O12, Fe2O3, Li3PO4 | -70 |
| Li3Sc(BO3)2 | LiFePO4 | ScFe2BO5, Li3PO4, ScBO3, Li3B7O12 | -32 |
| | FePO4 | ScFe(BO3)2, Li3PO4 | -63 |
| Li3TaO4 | LiFePO4 | Ta2FeO6, FeO, Li3PO4 | -34 |
| | FePO4 | TaFeO4, Li3PO4 | -92 |
| Li6Y(BO3)3 | LiFePO4 | LiFeBO3, Li3PO4, YBO3 | -47 |
| | FePO4 | Li3PO4, YBO3, Fe2O3, Li3B7O12 | -91 |
| Li3NbO4 | LiFePO4 | Nb2Fe3O8, Li3PO4 | -33 |
| | FePO4 | NbFeO4, Li3PO4 | -86 |
| KLiYF5 | LiFePO4 | - | 0 |
| | FePO4 | KFePO4F, LiYF4 | -28 |
| KLiTmF5 | LiFePO4 | - | 0 |
| | FePO4 | KFePO4F, LiTmF4 | -29 |
| KLiNdF5 | LiFePO4 | - | 0 |

| | | | |
|---|---|---|---|
| | $FePO_4$ | $KFePO_4F$, $LiNdF_4$ | -28 |

**Table S6. Identities of coating candidates corresponding to different databases, including Atomly, ICSD, and MP.**

| Formula | Atomly ID | ICSD ID | MP ID |
|---|---|---|---|
| Li3AlF6 | 0000093303 | 85171 | mp-15254 |
| CsLiBeF4 | 0000020963 | 9434 | mp-18704 |
| Li4ZrF8 | 0000032607 | 80398 | mp-9308 |
| Na3Li2Sc2F12 | 0000101912 | 27007 | mp-14023 |
| LiMgAlF6 | 0000006756 | 5007 | mp-1193222 |
| Na3Li3Al2F12 | 0000105344 | 9923 | mp-6711 |
| RbLi2Be2F7 | 0000010397 | 72 | mp-560518 |
| LiF | 0000057894 | 41409 | mp-1138 |
| LiYF4 | 0000002504 | 96727 | mp-3700 |
| KLiBeF4 | 0000020198 | 2939 | mp-6253 |
| Cs2LiAl3F12 | 0000099318 | 15785 | mp-13634 |
| LiLuF4 | 0000036754 | 152948 | mp-561430 |
| Li2BeF4 | 0000004787 | 14360 | mp-4622 |
| LiErF4 | 3001234939 | — | — |
| RbLiBeF4 | 3001345161 | — | — |
| Li4ScF7 | 3001070431 | — | — |
| LiMgPO4 | 0000083694 | 201138 | mp-9625 |
| LiZr2(PO4)3 | 0000018210 | 91112 | mp-10499 |
| Li4Be3P3BrO12 | 0000114496 | 80472 | mp-554560 |
| Li4Be3P3ClO12 | 0000028543 | 74525 | mp-560894 |
| Li3PO4 | 0000061102 | 10257 | mp-13725 |
| Li3Sc(PO4)3 | 0000110893 | 62301 | mp-6565 |
| Li4Be3P3IO12 | 0000041332 | — | mp-1211168 |
| Li2Al(BO2)5 | 0000125099 | 279578 | mp-557177 |
| Li2B4O7 | 0000030688 | 34670 | mp-4779 |
| KLiB4O7 | 0000088006 | 93601 | mp-6648 |
| LiSiBO4 | 0000088234 | 67536 | mp-8874 |

| | | | |
|---|---|---|---|
| Li3B5(HO5)2 | 0000117025 | 20155 | mp-707105 |
| RbLiB4O7 | 0000005274 | 93602 | mp-6787 |
| LiSi2BO6 | 0000070152 | 90849 | mp-556531 |
| Li3B7O12 | 0000026116 | 68475 | mp-16828 |
| LiAl(Si2O5)2 | 0000063234 | 31283 | mp-6442 |
| NaLiZr(Si2O5)3 | 0000078334 | 100631 | mp-15543 |
| KLi3Zr2(Si2O5)6 | 0000013946 | 89899 | mp-16055 |
| LiAl(SiO3)2 | 0000058662 | — | mp-1222469 |
| CsLiCl2 | 3001483162 | 423634 | mp-1188344 |
| CsLi2Cl3 | 0000045002 | 423635 | mp-1190687 |
| LiCl | 0000122077 | — | mp-1185319 |
| Li2B3O4F3 | 0000028336 | 423661 | mp-1196457 |
| NaLiMgPO4F | 0000087290 | 426199 | mp-1196828 |
| Li2B6O9F2 | 0000054059 | 423435 | mp-1200209 |

## Supporting Note 1. Introduction of Atomly database

The Atomly materials database (URL: atomly.net) is a comprehensive repository of inorganic crystalline compounds, housing the DFT calculated properties of approximately 349,000 materials. This valuable data encompasses essential information such as optimized structures, energy band and density of states, elasticity, and thermodynamic stability. The dataset was meticulously developed through high-throughput DFT runs, utilizing a protocol akin to the one used in the Materials Project. As such, this data is compatible with the Materials Project, adding significant depth to the overall available dataset as it is currently 2.3 times larger. Notably, Atomly features an abundance of newly added structures, primarily composed of transition metal-containing ionic compounds. These structures have been created through element substitution and then screened for their thermodynamic stability by an AI model. Consequently, the dataset is particularly well-suited for electrochemical applications.

## Supporting Note 2. Verification of the Accuracy of BV Analysis

In this study, as an important criterion for preliminarily assessing Li-ion diffusivities, it is essential to quantitatively evaluate the accuracy of bond-valence (BV) method. We compiled a dataset comprising eighteen specific Li-ion migration pathways, with each pathway's migration barrier assessed using both NEB and BV methods. As depicted in Fig. S42, it is evident that BV analysis can reliably yield reasonable migration barriers for Li-ion conductors, with a mean absolute error (MAE) of 115 meV. Additionally, Chen et al. conducted a more comprehensive benchmark on the mobile-ion migration barriers predicted by BV analysis.[1] Their findings align with our predictions as well. Hence, as a low-cost computational approach, BV analysis is a suitable method for the preliminary assessment of the dynamic properties of candidate materials, particularly in the context of high-throughput screening.

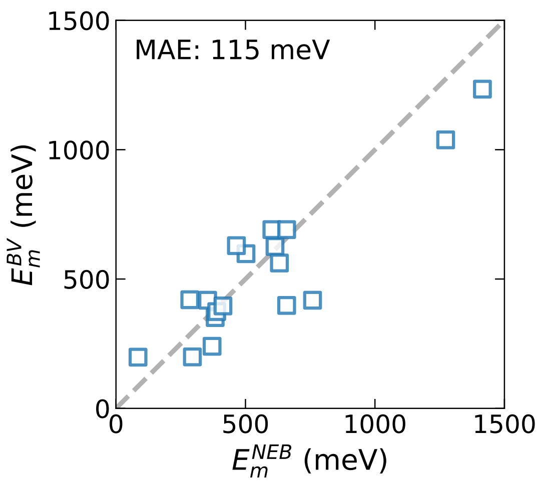


**Figure S42. Comparing Li-ion migration barriers between NEB and BV methods.**

## Supporting Note 3. Potential Passivation

Self-limiting interfacial degradation, i.e., passivation, is another crucial factor in forming a pseudo-stable layer between two contacting materials, as in the case of the Li-LiPON interface. Firstly, we assess the possibility of passivation under the circumstances where sulfide electrolytes come into direct contact with the LFP cathode. Detailed reaction products between sulfide electrolytes and LiFePO4/FePO4 are presented in Table S2 and S3, Supporting Information. It is shown that iron sulfides, such as FeS, FeS2, and FePS, dominate the reaction products. These compounds demonstrate moderate-to-high electronic conductivities, which will enable the continued electrochemical oxidation of sulfide electrolytes. Hence, we predicted that sulfide electrolytes cannot form passivation layers against the LiFePO4 cathode, aligning with recent experimental observations indicating poor interfacial compatibility between Li6PS5Cl and LiFePO4.[2] Additionally, for the fifty-one compounds excluded from being coating candidates solely based upon the consideration of chemical stability in the last screening step, we investigate the possibility of forming passivation layers between them and LiFePO4/FePO4. Two crucial features for passivation are taken into consideration: reaction products cannot contain electronically conducting compounds, and Li-ion conducting materials should dominate the final decomposition products. After investigation, it was found that nineteen compounds simultaneously meet both criteria. Their detailed reactions towards LiFePO4/FePO4 are listed in Table S5. Here, we highlight a promising compound, i.e., Li6B4O9 (ICSD id: 427421), that may form a robust passivation layer against the LiFePO4 cathode, with the chemical reactions of

$$Li_6B_4O_9 + LiFePO_4/FePO4 \rightarrow Fe_2B_2O_5/Fe_2O_3 + Li_3B_7O_{12} + Li_3PO_4$$

where Li-ion containing materials, Li3B7O12 and Li3PO4, dominate the decomposition products, and their potentially high Li-ion diffusivities have been evaluated in Table 1, main text.

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(2) Cronk, A.; Chen, Y.-T.; Deysher, G.; Ham, S.-Y.; Yang, H.; Ridley, P.; Sayahpour, B.; Nguyen, L. H. B.; Oh, J. A. S.; Jang, J.; Tan, D. H. S.; Meng, Y. S. Overcoming the Interfacial Challenges of $LiFePO_4$ in Inorganic All-Solid-State Batteries. *ACS Energy Lett.* **2023**, *8* (1), 827–835. https://doi.org/10.1021/acsenergylett.2c02138.