# Supporting Information

**Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analyses Based on First Principles Calculations**

Yizhou Zhu [1], Xingfeng He [1], Yifei Mo [1,2] *

[1] Department of Materials Science and Engineering,

[2] University of Maryland Energy Research Center,

University of Maryland, College Park, MD 20742

*Email: yfmo@umd.edu

## 1. Materials systems

**Table S1.** Crystal structures and phase equilibria of solid electrolyte materials

| Composition | Acronym | Structure used | E above hull (meV/atom) | Phase equilibria |
|---|---|---|---|---|
| $Li_{10}GeP_2S_{12}$ | LGPS | mp-696138[1] | 21 | $Li_3PS_4$, $Li_4GeS_4$ |
| $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ | | - | - | $Li_3PS_4$, $Li_4GeS_4$ |
| $Li_3PS_4$ | | [2] | 0 | $Li_3PS_4$ |
| $Li_4GeS_4$ | | mp-30249[3] | 0 | $Li_4GeS_4$ |
| $Li_7P_3S_{11}$ | | mp-641703[4] | 22 | $Li_3PS_4$, $P_2S_5$ |
| $Li_6PS_5Cl$ | | [5] | 83 | $Li_3PS_4$, $Li_2S$, LiCl |
| $Li_7P_2S_8I$ | | - | - | $Li_3PS_4$, LiI |
| $Li_2PO_2N$ | LiPON | [6] | 0 | $Li_2PO_2N$ |
| $Li_7La_3Zr_2O_{12}$ | LLZO | [7] | 7 | $Li_2O$, $La_2O_3$, $Li_6Zr_2O_7$ |
| $Li_{0.33}La_{0.56}TiO_3$ | LLTO | [8] | 68 | $TiO_2$, $Li_4Ti_5O_{12}$, $La_2Ti_2O_7$ |
| $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ | LATP | [9] | 29 | $LiTi_2(PO_4)_3$, $Li_3PO_4$, $AlPO_4$ |
| $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ | LAGP | - | - | $AlPO_4$, $Ge_5O(PO_4)_6$, $GeO_2$, $Li_4P_2O_7$ |
| $Li_{3.5}Zn_{0.25}GeO_4$ | LISICON | [10] | 34 | $Li_2ZnGeO_4$, $Li_4GeO_4$ |

The crystal structures and the phase equilibria of the commonly used solid electrolyte materials investigated in this study are summarized in Table S1. The energies of most materials in this study were obtained from the MP database.[11] The materials that were not included in MP database were calculated on the basis of the experimentally determined structures. For the structures with disordered site occupancies, we sampled 50-60 different configurations using the same method in the previous studies[12-13] and chose the configuration with the lowest energy as the ground state structure. For example, the ground state structure of $Li_{0.33}La_{0.56}TiO_3$ (LLTO) material was ordered from the experimental structure determined in ref. [8]. The $Li_3PS_4$ phase based on the $Pmn2_1$ $\gamma$ phase[2] was determined to have the lowest energy among its polymorphs and was added into the phase diagrams including Li-P-S compositions.

For the materials with a non-zero energy above hull, we evaluated the electrochemical window of the material by reducing the energy above hull to zero. These solid electrolyte materials may be entropically stabilized by the disordering of Li and other ions as in the LGPS.[12]

For those materials, such as $Li_{3.25}Ge_{0.25}P_{0.75}S_4$, $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ and $Li_7P_2S_8I$, that have no experimentally determined structures from the ICSD database, the materials entries were constructed as the phase equilibria at the given composition with a zero energy above hull. There

is no experimentally determined crystal structure available for the LiPON material systems, which are typically amorphous with a range of compositions. We used the crystalline structure of $Li_2PO_2N$ reported in Ref. [6] as the representative of the LiPON materials systems.

## 2. Calculated plateaus for the lithiation and delithiation of solid electrolyte materials.

**Table S2.** Calculated plateaus for the lithiation and delithiation of solid electrolyte materials.

(a) $Li_{10}GeP_2S_{12}$

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.28 | -0.28 | 23.75 | $Li_2S$, $Li_{15}Ge_4$, $Li_3P$ |
| 0.45 | -0.45 | 22.25 | $Li_9Ge_4$, $Li_2S$, $Li_3P$ |
| 0.56 | -0.56 | 21 | $Li_3P$, $Li_2S$, LiGe |
| 0.87 | -0.87 | 20 | $Li_3P$, $Li_2S$, Ge |
| 0.93 | -0.93 | 16 | $Li_2S$, LiP, Ge |
| 1.17 | -1.17 | 14.86 | $Li_3P_7$, $Li_2S$, Ge |
| 1.30 | -1.30 | 14.29 | Ge, $Li_2S$, $LiP_7$ |
| 1.62 | -1.62 | 14 | $Li_2S$, P, Ge |
| 1.71 | -1.71 | 10 | $Li_4GeS_4$, P, $Li_2S$ |
| | | 0 | $Li_{10}GeP_2S_{12}$ |
| 2.14 | -2.14 | -4 | $GeS_2$, $Li_3PS_4$, S |
| 2.31 | -2.31 | -10 | $P_2S_5$, $GeS_2$, S |

(b) $Li_{3.25}Ge_{0.25}P_{0.75}S_4$

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.28 | -0.28 | 23.75 | $Li_2S$, $Li_{15}Ge_4$, $Li_3P$ |
| 0.45 | -0.45 | 22.25 | $Li_9Ge_4$, $Li_2S$, $Li_3P$ |
| 0.56 | -0.56 | 21 | $Li_3P$, $Li_2S$, LiGe |
| 0.87 | -0.87 | 20 | $Li_3P$, $Li_2S$, Ge |
| 0.93 | -0.93 | 16 | $Li_2S$, LiP, Ge |
| 1.17 | -1.17 | 14.86 | $Li_3P_7$, $Li_2S$, Ge |
| 1.30 | -1.30 | 14.29 | Ge, $Li_2S$, $LiP_7$ |
| 1.62 | -1.62 | 14 | $Li_2S$, P, Ge |
| 1.71 | -1.71 | 10 | $Li_4GeS_4$, P, $Li_2S$ |
| | | 0 | $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ |
| 2.14 | -2.14 | -4 | $GeS_2$, $Li_3PS_4$, S |
| 2.31 | -2.31 | -10 | $P_2S_5$, $GeS_2$, S |

(c) $Li_3PS_4$

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.87 | -0.87 | 8 | $Li_3P$, $Li_2S$ |
| 0.93 | -0.93 | 6 | LiP, $Li_2S$ |
| 1.17 | -1.17 | 5.43 | $Li_3P_7$, $Li_2S$ |
| 1.30 | -1.30 | 5.14 | $LiP_7$, $Li_2S$ |
| 1.71 | -1.71 | 5 | P, $Li_2S$ |
| | | 0 | $Li_3PS_4$ |
| 2.31 | -2.31 | -3 | $P_2S_5$, S |

(d) $Li_4GeS_4$

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.28 | -0.28 | 7.75 | $Li_2S$, $Li_{15}Ge_4$ |
| 0.45 | -0.45 | 6.25 | $Li_9Ge_4$, $Li_2S$ |
| 0.56 | -0.56 | 5 | $Li_2S$, LiGe |
| 1.62 | -1.62 | 4 | $Li_2S$, Ge |
| | | 0 | $Li_4GeS_4$ |
| 2.14 | -2.14 | -4 | $GeS_2$, S |

(e) $Li_7P_3S_{11}$

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.87 | -0.87 | 24 | $Li_3P$, $Li_2S$ |
| 0.93 | -0.93 | 18 | LiP, $Li_2S$ |
| 1.17 | -1.17 | 16.29 | $Li_3P_7$, $Li_2S$ |
| 1.30 | -1.30 | 15.43 | $LiP_7$, $Li_2S$ |
| 1.71 | -1.71 | 15 | P, $Li_2S$ |
| 2.03 | -2.03 | 1.25 | $Li_3PS_4$, P |
| 2.15 | -2.15 | 1.08 | $Li_3PS_4$, $P_4S_3$ |
| 2.24 | -2.24 | 0.67 | $Li_3PS_4$, $P_4S_7$ |
| 2.28 | -2.28 | 0.29 | $Li_3PS_4$, $P_4S_9$ |
| | | 0 | $Li_7P_3S_{11}$ |
| 2.31 | -2.31 | -7 | $P_2S_5$, S |

(f) $Li_6PS_5Cl$

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.87 | -0.87 | 8 | $Li_3P$, $Li_2S$, LiCl |
| 0.93 | -0.93 | 6 | LiP, $Li_2S$, LiCl |
| 1.17 | -1.17 | 5.43 | $Li_3P_7$, $Li_2S$, LiCl |
| 1.30 | -1.30 | 5.14 | $LiP_7$, $Li_2S$, LiCl |
| 1.71 | -1.71 | 5 | P, $Li_2S$, LiCl |
| | | 0 | $Li_6PS_5Cl$ |
| 2.01 | -2.01 | -2 | $Li_3PS_4$, S, LiCl |
| 2.31 | -2.31 | -5 | $P_2S_5$, S, LiCl |
| 2.88 | -2.88 | -6 | $P_2S_5$, S, $PCl_3$ |

(g) $Li_7P_2S_8I$

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.87 | -0.87 | 16 | $Li_3P$, $Li_2S$, LiI |
| 0.93 | -0.93 | 12 | LiP, $Li_2S$, LiI |
| 1.17 | -1.17 | 10.86 | $Li_3P_7$, $Li_2S$, LiI |
| 1.30 | -1.30 | 10.29 | $LiP_7$, $Li_2S$, LiI |
| 1.71 | -1.71 | 10 | P, $Li_2S$, LiI |
| | | 0 | $Li_7P_2S_8I$ |
| 2.31 | -2.31 | -6 | $P_2S_5$, S, LiI |
| 2.47 | -2.47 | -7 | $P_2S_5$, S, I |

(h) LiPON

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.01 | -0.01 | 8 | $Li_3P$, $Li_3N$, $Li_2O$ |
| 0.61 | -0.61 | 6 | $Li_3P$, $Li_7PN_4$, $Li_2O$ |
| 0.68 | -0.68 | 4 | $Li_3P$, $LiPN_2$, $Li_2O$ |
| | | 0 | $Li_2PO_2N$ |
| 2.63 | -2.63 | -0.86 | $P_3N_5$, $Li_4P_2O_7$, $N_2$ |
| 2.75 | -2.75 | -0.92 | $P_4ON_6$, $Li_4P_2O_7$, $N_2$ |
| 2.77 | -2.77 | -1.36 | $P_4ON_6$, $LiPO_3$, $N_2$ |
| 3.05 | -3.05 | -1.50 | PON, $LiPO_3$, $N_2$ |
| 3.63 | -3.63 | -2 | PON, $P_2O_5$, $N_2$ |

(i) LLZO

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.004 | 0.004 | 8 | Zr, $La_2O_3$, $Li_2O$ |
| 0.048 | -0.048 | 6.67 | $Zr_3O$, $La_2O_3$, $Li_2O$ |
| | | 0 | $Li_7La_3Zr_2O_{12}$ |
| 2.91 | -2.91 | -0.50 | $Li_2O_2$, $La_2O_3$, $Li_6Zr_2O_7$ |
| 3.17 | -3.17 | -3.50 | $Li_2O_2$, $La_2O_3$, $La_2Zr_2O_7$ |
| 3.30 | -3.30 | -7 | $O_2$, $La_2O_3$, $La_2Zr_2O_7$ |

(j) LLTO

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.018 | -0.018 | 3.67 | $Ti_6O$, $La_2O_3$, $Li_2O$ |
| 0.12 | -0.12 | 3.33 | $Ti_3O$, $La_2O_3$, $Li_2O$ |
| 0.29 | -0.29 | 1.67 | $Ti_3O$, $La_2O_3$, $Li_4TiO_4$ |
| 0.37 | -0.37 | 1.57 | $Ti_2O$, $La_2O_3$, $Li_4TiO_4$ |
| 0.46 | -0.46 | 0.92 | $LiTiO_2$, $La_2O_3$, $Li_4TiO_4$ |
| 0.50 | -0.50 | 0.64 | $LiTiO_2$, $La_2TiO_5$, $Li_4TiO_4$ |
| 1.12 | -1.12 | 0.56 | $LiTiO_2$, $La_2TiO_5$, $Li_2TiO_3$ |
| 1.14 | -1.14 | 0.28 | $LiTi_2O_4$, $La_2TiO_5$, $Li_2TiO_3$ |
| 1.63 | -1.63 | 0.14 | $LiTi_2O_4$, $La_2Ti_2O_7$, $Li_2TiO_3$ |
| 1.749 | -1.749 | 0.09 | $Li_{7/6}Ti_{11/6}O_4$, $La_2Ti_2O_7$, $Li_2TiO_3$ |
| 1.752 | -1.752 | 0.01 | $Li_{7/6}Ti_{11/6}O_4$, $La_2Ti_2O_7$, $Li_4Ti_5O_{12}$ |
| | | 0 | $Li_{0.33}La_{0.56}TiO_3$ |
| 3.71 | -3.71 | -0.33 | $O_2$, $La_2Ti_2O_7$, $TiO_2$ |

(k) LATP

| Potential $\phi$ ref to Li/$Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.026 | -0.026 | 30.30 | $Ti_3P$, TiAl, $Li_3P$, $Li_2O$ |
| 0.082 | -0.082 | 29.60 | $Ti_2P$, TiAl, $Li_3P$, $Li_2O$ |
| 0.088 | -0.088 | 29.38 | $Ti_2P$, $TiAl_2$, $Li_3P$, $Li_2O$ |
| 0.23 | -0.23 | 28.25 | $Ti_2P$, $Li_5AlO_4$, $Li_3P$, $Li_2O$ |
| 0.69 | -0.69 | 24 | $Li_4TiO_4$, $Li_5AlO_4$, $Li_3P$, $Li_2O$ |
| 0.75 | -0.75 | 16 | $Li_4TiO_4$, $Li_5AlO_4$, $Li_3P$, $Li_3PO_4$ |
| 0.79 | -0.79 | 14.80 | $Li_4TiO_4$, $LiAlO_2$, $Li_3P$, $Li_3PO_4$ |
| 0.86 | -0.86 | 8.33 | $Li_4TiO_4$, $LiAlO_2$, TiP, $Li_3PO_4$ |
| 1.49 | -1.49 | 7.33 | $Li_2TiO_3$, $LiAlO_2$, TiP, $Li_3PO_4$ |
| 1.55 | -1.55 | 6.52 | $LiTi_2O_4$, $LiAlO_2$, TiP, $Li_3PO_4$ |
| 1.71 | -1.71 | 6.35 | $LiTi_2O_4$, $LiAl_5O_8$, TiP, $Li_3PO_4$ |
| 1.84 | -1.84 | 5.82 | $TiO_2$, $LiAl_5O_8$, TiP, $Li_3PO_4$ |
| 1.94 | -1.94 | 5.43 | $TiO_2$, $LiAl_5O_8$, $TiP_2$, $Li_3PO_4$ |
| 1.98 | -1.98 | 4.76 | $TiO_2$, $AlPO_4$, $TiP_2$, $Li_3PO_4$ |
| 2.12 | -2.12 | 4.25 | $TiO_2$, $AlPO_4$, P, $Li_3PO_4$ |
| 2.17 | -2.17 | 2.13 | $LiTiPO_5$, $AlPO_4$, P, $Li_3PO_4$ |
| | | 0 | $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ |
| 4.21 | -4.21 | -0.15 | $LiTi_2(PO_4)_3$, $AlPO_4$, $Li_4P_2O_7$, $O_2$ |
| 4.33 | -4.33 | -0.60 | $LiTi_2(PO_4)_3$, $AlPO_4$, $TiP_2O_7$, $O_2$ |
| 4.66 | -4.66 | -1.30 | $Ti_5P_4O_{20}$, $AlPO_4$, $TiP_2O_7$, $O_2$ |

(l) LAGP

| Potential $\phi$ ref to Li/$Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.06 | -0.06 | 38.25 | $Li_2O$, $Li_{15}Ge_4$, $Li_3P$, $Li_9Al_4$ |
| 0.28 | -0.28 | 35.63 | $Li_2O$, $Li_{15}Ge_4$, $Li_3P$, $Li_5AlO_4$ |
| 0.45 | -0.45 | 33.38 | $Li_2O$, $Li_9Ge_4$, $Li_3P$, $Li_5AlO_4$ |
| 0.56 | -0.56 | 31.50 | $Li_2O$, LiGe, $Li_3P$, $Li_5AlO_4$ |
| 0.69 | -0.69 | 30 | $Li_2O$, Ge, $Li_3P$, $Li_5AlO_4$ |
| 0.75 | -0.75 | 10 | $Li_3PO_4$, Ge, $Li_3P$, $Li_5AlO_4$ |
| 0.87 | -0.87 | 8 | $Li_3PO_4$, Ge, $Li_3P$, $LiAlO_2$ |
| 0.93 | -0.93 | 7.50 | $Li_3PO_4$, Ge, LiP, $LiAlO_2$ |
| 1.17 | -1.17 | 7.36 | $Li_3PO_4$, Ge, $Li_3P_7$, $LiAlO_2$ |
| 1.30 | -1.30 | 7.29 | $Li_3PO_4$, Ge, $LiP_7$, $LiAlO_2$ |
| 1.49 | -1.49 | 7.25 | $Li_3PO_4$, Ge, P, $LiAlO_2$ |
| 1.94 | -1.94 | 7 | $Li_3PO_4$, Ge, P, $LiAl_5O_8$ |
| 2.64 | -2.64 | 6 | $Li_3PO_4$, Ge, $AlPO_4$ |
| 2.70 | -2.70 | 3.50 | Ge, $GeO_2$, $Li_4P_2O_7$, $AlPO_4$ |
| | | 0 | $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ |
| 4.27 | -4.27 | -0.10 | $Ge_5O(PO_4)_6$, $O_2$, $Li_4P_2O_7$, $AlPO_4$ |
| 4.31 | -4.31 | -1.50 | $Ge_5O(PO_4)_6$, $O_2$, $GeP_2O_7$, $AlPO_4$ |

(m) LISICON

| | | | |
|---|---|---|---|
| 0.18 | -0.18 | 8.50 | $Li_2O$, $Li_{15}Ge_4$, LiZn |
| 0.28 | -0.28 | 7.85 | $Li_2O$, $Li_{15}Ge_4$, $Li_8Zn_2Ge_3$ |
| 0.42 | -0.42 | 6.91 | $Li_2O$, $Li_9Ge_4$, $Li_8Zn_2Ge_3$ |
| 0.45 | -0.45 | 6.69 | $Li_2O$, $Li_9Ge_4$, $Li_2ZnGe$ |
| 0.56 | -0.56 | 5.75 | $Li_2O$, LiGe, $Li_2ZnGe$ |
| 0.61 | -0.61 | 5 | $Li_2O$, Ge, $Li_2ZnGe$ |
| 0.73 | -0.73 | 4.75 | $Li_2O$, Ge, LiZnGe |
| 1.02 | -1.02 | 4.50 | $Li_2O$, Ge, Zn |
| 1.44 | -1.44 | 0.50 | $Li_4GeO_4$, Zn |
| | | 0 | $Li_{3.5}Zn_{0.25}GeO_4$ |
| 3.39 | -3.39 | -1.50 | $Li_2ZnGeO_4$, $Li_2GeO_3$, $O_2$ |
| 3.84 | -3.84 | -2.40 | $Li_2ZnGeO_4$, $Li_4Ge_5O_{12}$, $O_2$ |
| 3.85 | -3.85 | -2.79 | $Li_2ZnGeO_4$, $Li_2Ge_7O_{15}$, $O_2$ |
| 3.89 | -3.89 | -3.19 | $LiZn_{1.5}Ge_3O_8$, $Li_2Ge_7O_{15}$, $O_2$ |
| 3.98 | -3.98 | -3.33 | $LiZn_{1.5}Ge_3O_8$, $GeO_2$, $O_2$ |
| 4.00 | -4.00 | -3.50 | $Zn_2GeO_4$, $GeO_2$, $O_2$ |

**3. Calculated plateaus for the lithiation and delithiation of coating layer materials.**

**Table S3.** Calculated plateaus for the lithiation and delithiation of coating layer materials.

(a) $Li_4Ti_5O_{12}$

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.018 | -0.018 | 18.33 | $Ti_6O$, $Li_2O$ |
| 0.12 | -0.12 | 16.67 | $Ti_3O$, $Li_2O$ |
| 0.29 | -0.29 | 7.27 | $Ti_3O$, $Li_4TiO_4$ |
| 0.37 | -0.37 | 6.86 | $Ti_2O$, $Li_4TiO_4$ |
| 0.50 | -0.50 | 4 | $LiTiO_2$, $Li_4TiO_4$ |
| 1.12 | -1.12 | 3 | $LiTiO_2$, $Li_2TiO_3$ |
| 1.63 | -1.63 | 1.5 | $LiTi_2O_4$, $Li_2TiO_3$ |
| 1.75 | -1.75 | 1 | $Li_{7/6}Ti_{11/6}O_4$, $Li_2TiO_3$ |
| | | 0 | $Li_4Ti_5O_{12}$ |
| 3.71 | -3.71 | -4 | $O_2$, $TiO_2$ |

(b) $LiNbO_3$

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.55 | -0.55 | 5 | Nb, $Li_2O$ |
| 0.62 | -0.62 | 2 | $LiNbO_2$, $Li_2O$ |
| 0.94 | -0.94 | 1.2 | $LiNbO_2$, $Li_8Nb_2O_9$ |
| 1.74 | -1.74 | 1 | $LiNbO_2$, $Li_3NbO_4$ |
| | | 0 | $LiNbO_3$ |
| 3.88 | -3.88 | -0.67 | $LiNb_3O_8$, $O_2$ |
| 3.92 | -3.92 | -1 | $Nb_2O_5$, $O_2$ |

(c) $Li_2SiO_3$

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.10 | -0.10 | 8.2 | $Li_{21}Si_5$, $Li_2O$ |
| 0.23 | -0.23 | 7.25 | $Li_{13}Si_4$, $Li_2O$ |
| 0.26 | -0.26 | 3.62 | $Li_{13}Si_4$, $Li_8SiO_6$ |
| 0.26 | -0.26 | 1.81 | $Li_{13}Si_4$, $Li_4SiO_4$ |
| 0.37 | -0.37 | 1.43 | $Li_{12}Si_7$, $Li_4SiO_4$ |
| 0.39 | -0.39 | 1.25 | LiSi, $Li_4SiO_4$ |
| 0.76 | -0.76 | 1 | Si, $Li_4SiO_4$ |
| | | 0 | $Li_2SiO_3$ |
| 3.74 | -3.74 | -1 | $Li_2Si_2O_5$, $O_2$ |
| 3.78 | -3.78 | -2 | $SiO_2$, $O_2$ |

(d) $LiTaO_3$

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.35 | -0.35 | 5 | Ta, $Li_2O$ |
| 0.54 | -0.54 | 2 | Ta, $Li_5TaO_5$ |
| 1.18 | -1.18 | 1.25 | Ta, $Li_3TaO_4$ |
| | | 0 | $LiTaO_3$ |
| 3.95 | -3.95 | -0.67 | $LiTa_3O_8$, $O_2$ |
| 4.12 | -4.12 | -1 | $Ta_2O_5$, $O_2$ |

(e) $Li_3PO_4$

| Potential $\phi$ ref to $Li/Li^+$(V) | $\mu_{Li}$ ref to Li metal (eV) | $\Delta n_{Li}$ per formula | Phase equilibria |
|---|---|---|---|
| 0.69 | -0.69 | 8 | $Li_3P$, $Li_2O$ |
| | | 0 | $Li_3PO_4$ |
| 4.21 | -4.21 | -1 | $Li_4P_2O_7$, $O_2$ |
| 4.33 | -4.33 | -2 | $LiPO_3$, $O_2$ |
| 4.99 | -4.99 | -3 | $P_2O_5$, $O_2$ |

**References**


1. Kamaya, N.; Homma, K.; Yamakawa, Y.; Hirayama, M.; Kanno, R.; Yonemura, M.; Kamiyama, T.; Kato, Y.; Hama, S.; Kawamoto, K.; Mitsui, A., A Lithium Superionic Conductor. *Nat. Mater.* **2011,** *10*, 682-686.
2. Homma, K.; Yonemura, M.; Kobayashi, T.; Nagao, M.; Hirayama, M.; Kanno, R., Crystal Structure and Phase Transitions of the Lithium Ionic Conductor Li3PS4. *Solid State Ionics.* **2011,** *182*, 53-58.
3. Murayama, M.; Kanno, R.; Kawamoto, Y.; Kamiyama, T., Structure of the Thio-LISICON, Li4ges4. *Solid State Ionics.* **2002,** *154–155*, 789-794.
4. Yamane, H.; Shibata, M.; Shimane, Y.; Junke, T.; Seino, Y.; Adams, S.; Minami, K.; Hayashi, A.; Tatsumisago, M., Crystal Structure of a Superionic Conductor, Li7P3S11. *Solid State Ionics.* **2007,** *178*, 1163-1167.
5. Deiseroth, H.-J.; Kong, S.-T.; Eckert, H.; Vannahme, J.; Reiner, C.; Zaiß, T.; Schlosser, M., Li6PS5X: A Class of Crystalline Li-Rich Solids with an Unusually High Li+ Mobility. *Angew. Chem. Int. Ed.* **2008,** *47*, 755-758.
6. Senevirathne, K.; Day, C. S.; Gross, M. D.; Lachgar, A.; Holzwarth, N. A. W., A New Crystalline LiPON Electrolyte: Synthesis, Properties, and Electronic Structure. *Solid State Ionics.* **2013,** *233*, 95-101.
7. Awaka, J.; Takashima, A.; Kataoka, K.; Kijima, N.; Idemoto, Y.; Akimoto, J., Crystal Structure of Fast Lithium-Ion-Conducting Cubic Li7La3Zr2O12. *Chem. Lett.* **2011,** *40*, 60-62.
8. Fourquet, J. L.; Duroy, H.; Crosnier-Lopez, M. P., Structural and Microstructural Studies of the Series La2/3−xLi3x□1/3−2xTiO3. *J. Solid State Chem.* **1996,** *127*, 283-294.
9. Dashjav, E.; Tietz, F., Neutron Diffraction Analysis of NASICON-Type Li1+xAlxTi2–xP3O12. *Z. Anorg. Allg. Chem.* **2014,** *640*, 3070-3073.
10. Hong, H. Y. P., Crystal Structure and Ionic Conductivity of Li14Zn(GeO4)4 and Other New Li+ Superionic Conductors. *MRS Bulletin.* **1978,** *13*, 117-124.
11. Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A., Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *APL Materials.* **2013,** *1*, 011002.
12. Mo, Y.; Ong, S. P.; Ceder, G., First Principles Study of the Li10GeP2S12 Lithium Super Ionic Conductor Material. *Chem. Mater.* **2012,** *24*, 15-17.
13. He, X.; Mo, Y., Accelerated Materials Design of Na0.5Bi0.5TiO3 Oxygen Ionic Conductors Based on First Principles Calculations. *Phys. Chem. Chem. Phys.* **2015,** *17*, 18035-18044.