

Supplementary Information

Solid-State Chemistries Stable with High-Energy Cathodes for Lithium-Ion Batteries

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Computation methods.

Using the same scheme as in previous studies,^{1,2} we studied the reaction between two materials, a cathode and a contacting material, as a pseudo-binary with the composition

$$C_{\text{pseudo-binary}}(C_{\text{cathode}}, C_{\text{contacting material}}, x) = xC_{\text{cathode}} + (1-x)C_{\text{contacting material}}$$

where C_{cathode} and $C_{\text{contacting material}}$ are the compositions of the cathode and contacting material, normalized to one atom per formula unit, and x is the molar fraction of the cathode. Similar to the composition, the energy of the pseudo-binary $E_{\text{pseudo-binary}}(\text{cathode}, \text{contacting material}, x)$ is a linear combination of the energies of the cathode and contacting material

$$E_{\text{pseudo-binary}}(\text{cathode}, \text{contacting material}, x) = xE_{\text{cathode}} + (1-x)E_{\text{contacting material}}$$

where E_{cathode} and $E_{\text{contacting material}}$ are the ground state energies of the cathode and the contacting material, respectively. The decomposition energy $\Delta E_{\text{D}}(\text{phase})$ of any phase is given by

$$\Delta E_{\text{D}}(\text{phase}) = E_{\text{eq}}(C) - E(\text{phase})$$

where $E_{\text{eq}}(C)$ is the energy of the phase equilibria and $E(\text{phase})$ is the energy of the phase. The phase equilibria is the combination of phases with minimum total energy for composition C .

Using this equation, the decomposition energy of the pseudo-binary was calculated as

$$\Delta E_{\text{D}}(\text{cathode}, \text{contacting material}, x) =$$

$$E_{\text{eq}}(C_{\text{pseudo-binary}}(C_{\text{cathode}}, C_{\text{contacting material}}, x)) - E_{\text{pseudo-binary}}(\text{cathode}, \text{contacting material}, x)$$

Since $\Delta E_{\text{D}}(\text{cathode}, \text{contacting material}, x)$ includes the decomposition energy of the contacting material or cathode if they are not stable, $\Delta E_{\text{D, mutual}}(\text{cathode}, \text{contacting material}, x)$ was calculated as

$$\Delta E_{\text{D, mutual}}(\text{cathode}, \text{contacting material}, x) =$$

$$\Delta E_{\text{D}}(\text{cathode}, \text{contacting material}, x) - x\Delta E_{\text{D}}(\text{cathode}) - (1-x)\Delta E_{\text{D}}(\text{contacting material})$$

where $\Delta E_{\text{D}}(\text{cathode})$ and $\Delta E_{\text{D}}(\text{contacting material})$ are the decomposition energies of the cathode and the contacting materials to their respective phase equilibria. Finally, the minimum of the $\Delta E_{\text{D, mutual}}(\text{cathode}, \text{contacting material}, x)$ was taken as the decomposition energy E_{d} used throughout the paper. The calculated energies of all phases investigated were obtained from the Materials Project database³. Additional details can be found in previous studies.^{1,2}

Table S1. Lithium ternary oxide compounds stable with LiCoO_2 and $\text{Li}_{0.5}\text{CoO}_2$, stable with LiNiO_2 and $\text{Li}_{0.5}\text{NiO}_2$, stable with LiNiO_2 , $\text{Li}_{0.5}\text{NiO}_2$, and $\text{Li}_{0.25}\text{NiO}_2$, and stable with all of these cathodes.

Stable with LCO and $\text{L}_{0.5}\text{CO}$		Stable with LNO and $\text{L}_{0.5}\text{NO}$		Stable with LNO, $\text{L}_{0.5}\text{NO}$, and $\text{L}_{0.25}\text{NO}$	Stable with all
Li_5IO_6	Li_2GeO_3	Li_5IO_6	Li_2GeO_3	Li_5IO_6	Li_5IO_6
Li_3AsO_4	Li_2PtO_3	Li_3AsO_4	Li_2PtO_3	Li_3AsO_4	Li_3AsO_4
LiClO_4	Li_4WO_5	LiClO_4	Li_4WO_5	LiClO_4	LiClO_4
Li_2SeO_4	LiBO_2	Li_2SeO_4	Li_3NbO_4	Li_2SeO_4	Li_2SeO_4
LiAuO_2	Li_3NbO_4	LiAuO_2	Li_4TeO_5	LiAuO_2	LiAuO_2
LiNO_3	Li_4TeO_5	LiNO_3	Li_3TaO_4	LiNO_3	LiNO_3
Li_2PdO_3	Li_3TaO_4	Li_2PdO_3	$\text{Li}_6\text{B}_4\text{O}_9$	Li_2PdO_3	Li_2PdO_3
LiReO_4	$\text{Li}_6\text{B}_4\text{O}_9$	LiReO_4	Li_2SnO_3	LiReO_4	LiReO_4
Li_2MoO_4	LiTaO_3	Li_2MoO_4		Li_2MoO_4	Li_2MoO_4
Li_2CrO_4	Li_2WO_4	Li_2CrO_4		Li_2CrO_4	Li_2CrO_4
Li_3VO_4	Li_2SnO_3	Li_3VO_4		Li_3VO_4	Li_3VO_4
Li_2CO_3	LiFeO_2	Li_2CO_3		Li_2CO_3	Li_2CO_3
Li_3PO_4	LiNbO_3	Li_3PO_4		Li_3PO_4	Li_3PO_4
Li_2SO_4	LiAl_5O_8	Li_2SO_4		Li_2SO_4	Li_2SO_4
LiGaO_2	$\text{Li}_2\text{B}_4\text{O}_7$	LiGaO_2			
Li_2SiO_3	$\text{Li}_3\text{B}_7\text{O}_{12}$	Li_2SiO_3			
LiCuO_2	$\text{Li}_4\text{Ti}_5\text{O}_{12}$	LiCuO_2			
LiAlO_2	LiSbO_3	LiAlO_2			
Li_2TiO_3	Li_3SbO_4	Li_2TiO_3			
LiBiO_3	Li_2TeO_4	LiBiO_3			

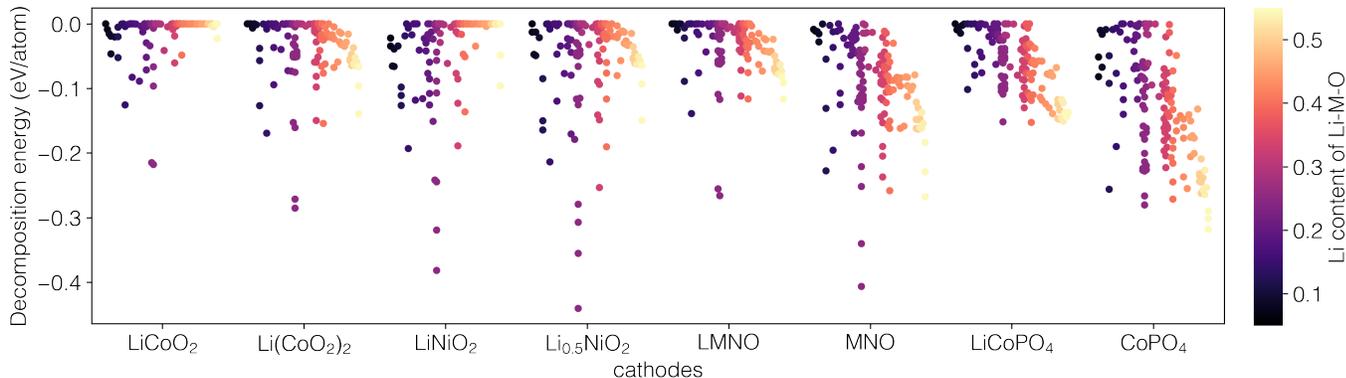


Figure S1. Swarmplot comparing the minimum mutual decomposition energy E_d of all the lithium ternary oxide (Li-M-O) compounds with each of the cathodes. The pseudo-binary of the Li-M-Os and each cathode is denoted by a cluster of points. Within each cluster, a point represents a single Li-M-O compound. The color of the point indicates the lithium content of the composition. In each cluster, points are grouped by their lithium content. Delithiated cathodes tend to react more vigorously with the most lithiated compounds (Li content 0.45-0.5 or greater) than lithiated cathodes. The decomposition energies of LNO cathodes are more negative than the LCO cathodes, which indicates they tend to have slightly larger decomposition energies.

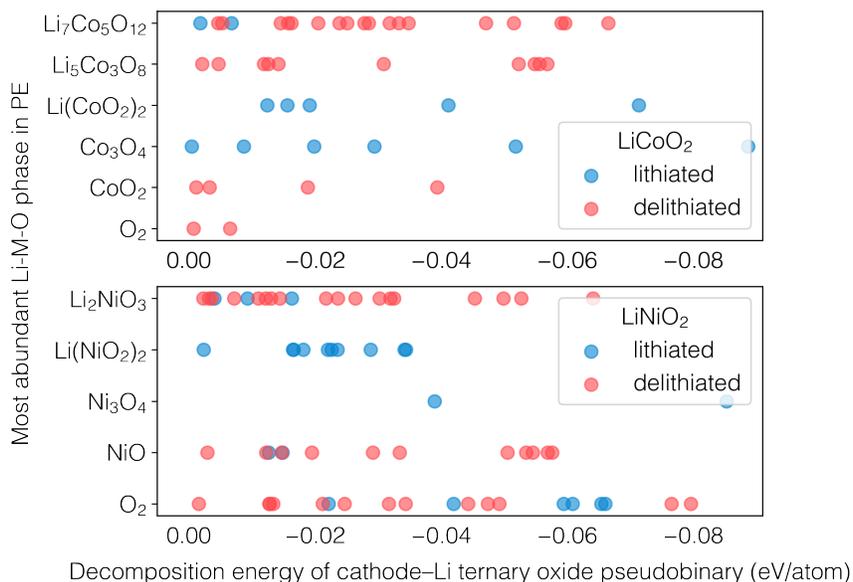


Figure S2. Scatterplots of the most abundant phase in the phase equilibria (y -axis) versus the decomposition energy (x -axis) of pseudo-binaries of the lithium ternary oxides and LCO (top) and LNO (bottom) cathodes. The Li-M-O or M-O phase ($M = \text{Co}$ or Ni) with the largest coefficient in the phase equilibria was considered to be the most abundant phase for that pseudo-binary (normalized to one atom per formula unit). Each point represents a pseudo-binary of a different compound. The pseudo-binaries that are stable were not included.

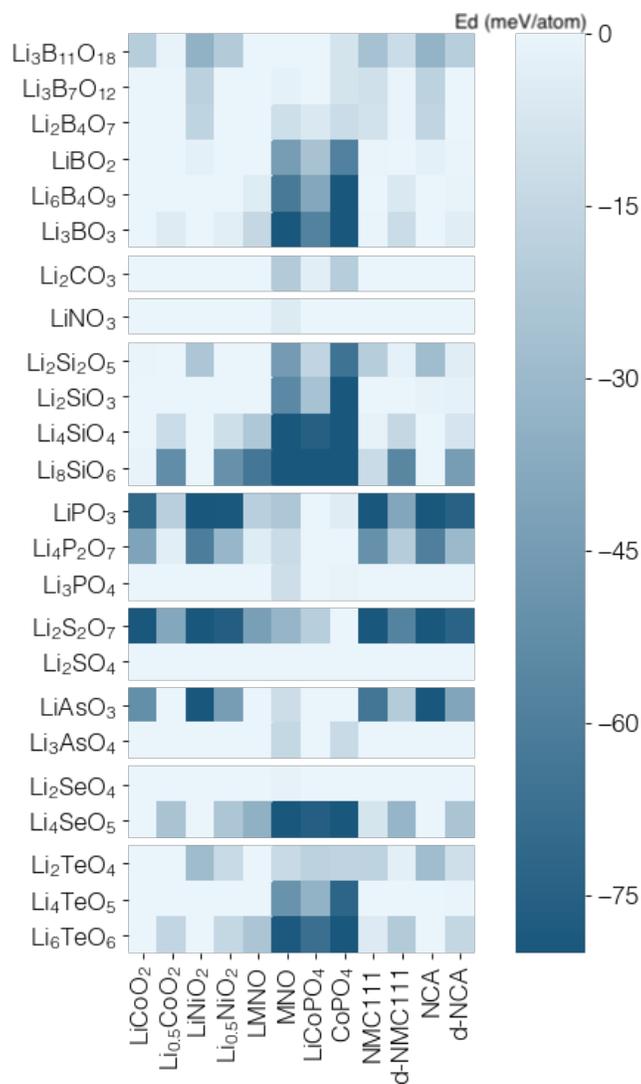


Figure S3. Stability heatmap of lithiated and delithiated (prefix “d-”) NMC111 ($\text{LiMn}_{0.3}\text{Co}_{0.3}\text{Ni}_{0.3}\text{O}_2$) and NCA ($\text{LiAl}_{0.05}\text{Co}_{0.15}\text{Ni}_{0.8}\text{O}_2$) cathodes compared to LNO, LCO, LMNO, and LCP (for lithium ternary nonmetal oxides). The results showed that LNO can be a good proxy to NCA and NMC for thermodynamic stability.

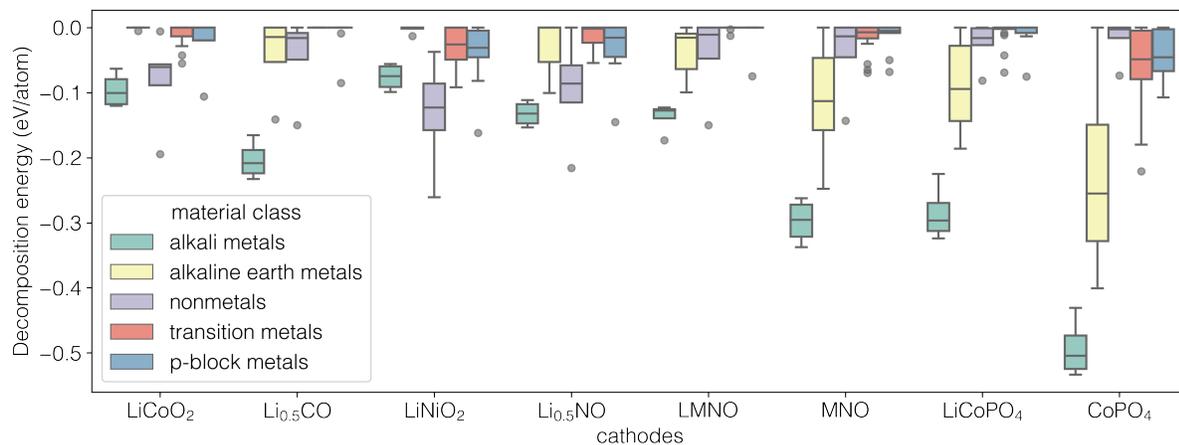


Figure S4. Boxplot comparing the decomposition energies of each of the groups of binary oxides with all the cathodes. Data outside the endpoints are marked individually as grey circles.

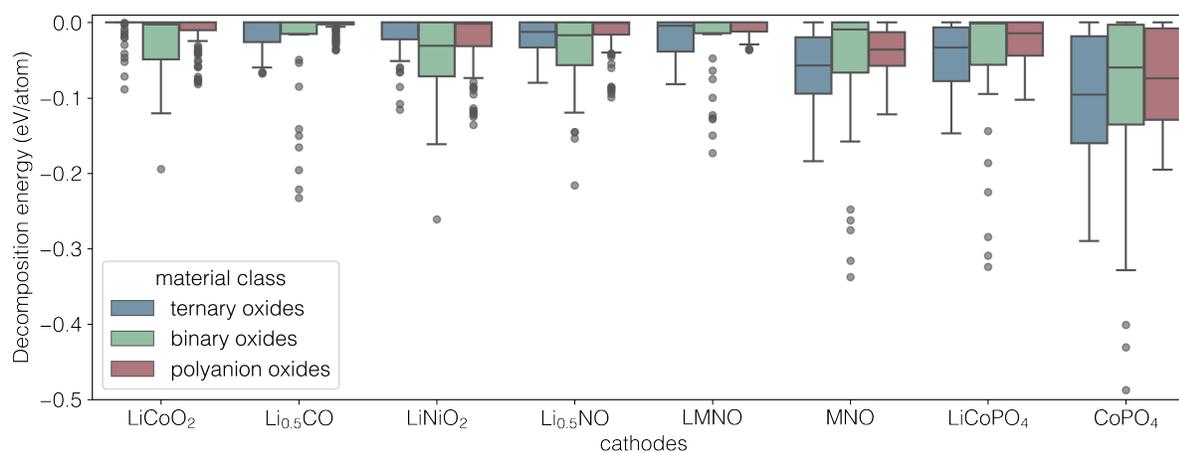


Figure S5. Boxplot of the decomposition energies of the lithium ternary oxides, binary oxides, and polyanion compounds with each of the cathodes. Data outside the endpoints are marked individually as grey circles.

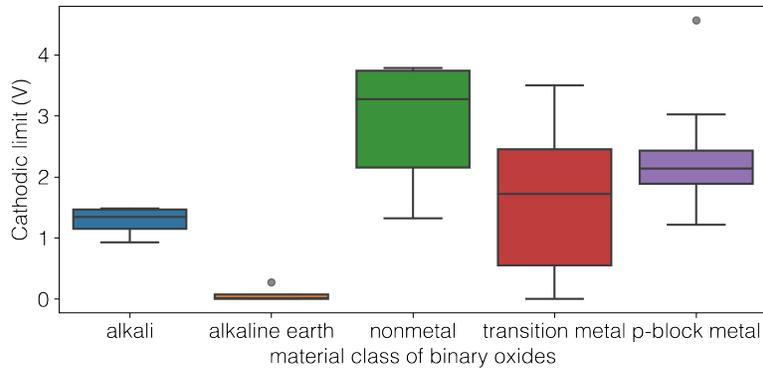


Figure S6. Boxplot of calculated cathodic limits for the classes of binary oxides.

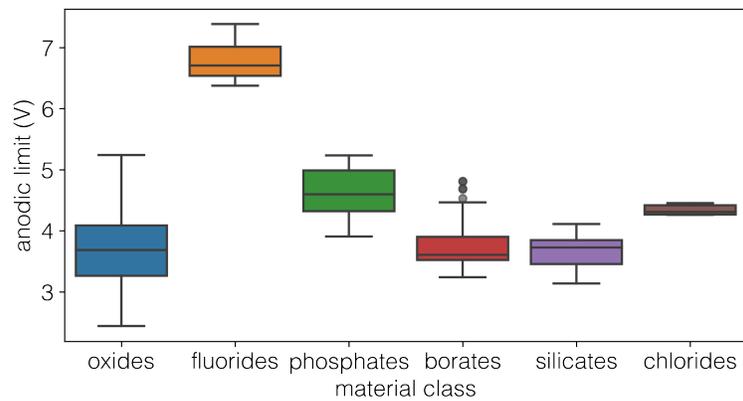


Figure S7. Boxplot of calculated anodic limits for each materials class.

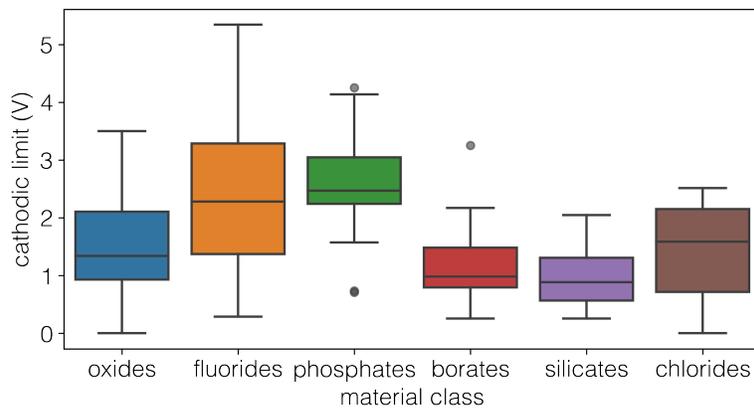


Figure S8. Boxplot of calculated cathodic limits for each materials class.

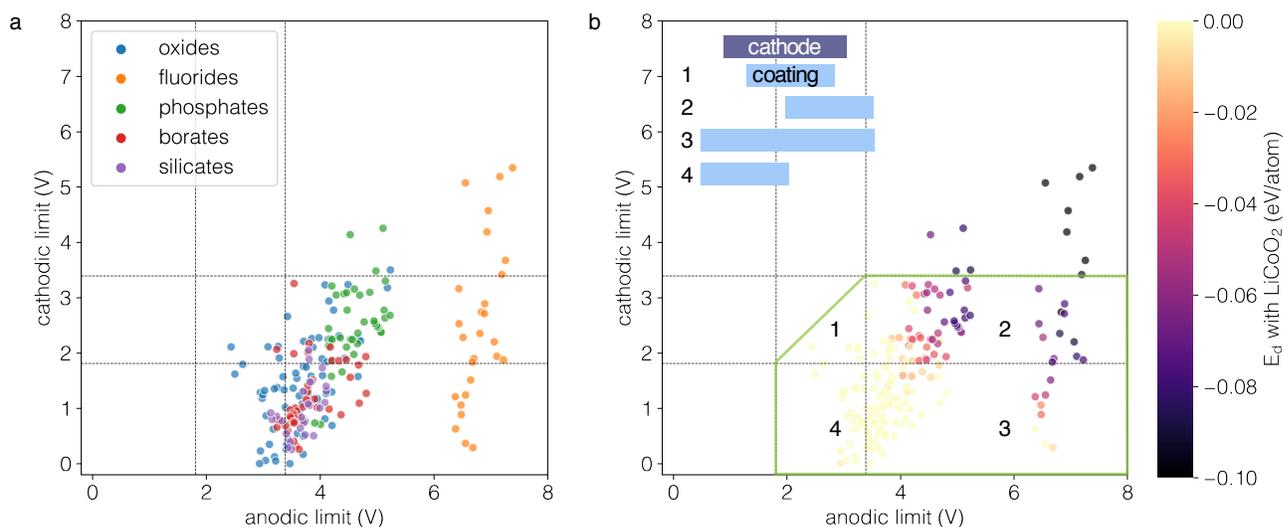


Figure S9. Cathodic vs anodic limits of all lithium-containing materials studied. (a) Colored by materials classes. (b) Colored by decomposition energy with LiCoO_2 . Outlined green area indicates region where there is overlap between the electrochemical window of the cathode and the coating, with the type of overlap specified by the legend. Overlap of the electrochemical windows of the two materials does not necessarily mean the two materials are stable.

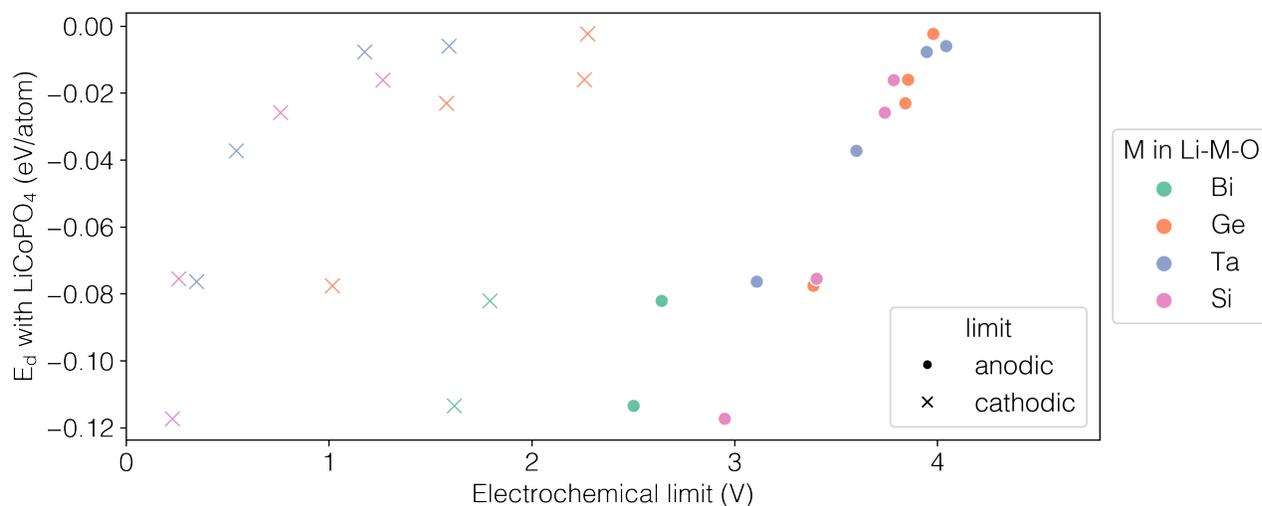


Figure S10. Decomposition energy of LiCoPO_4 with Li-M-O oxides vs the anodic and cathodic limits of the oxides. The materials with higher anodic limit (oxidation limit) in generally exhibit better interface stability.

References

- (1) Zhu, Y.; He, X.; Mo, Y. First Principles Study on Electrochemical and Chemical Stability of Solid Electrolyte–Electrode Interfaces in All-Solid-State Li-Ion Batteries. *J. Mater. Chem. A* **2016**, *4* (9), 3253–3266.
- (2) Zhu, Y.; He, X.; Mo, Y. Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analyses Based on First-Principles Calculations. *ACS Appl. Mater. Interfaces* **2015**, *7* (42), 23685–23693.
- (3) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; et al. Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *APL Mater.* **2013**, *1* (1), 011002.