Supplementary Information

Design principle for anode stable solid-state electrolytes

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Supporting note 1. Screened compositional spaces:

To enumerate all possible Li(Na) metal oxide perovskites (Li(Na)-PRX) with prototype formula being $\mathrm{Li}_x(\mathrm{A},\mathrm{Vac})_{1-x}(M_1M_2)_1O_3$, where A and M_1, M_2 are cations of different sizes. We focus on a subset of the broader perovskite family where these A sites, including mixture of Li^+ with Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Sc^{3+}, In^{3+}, Y^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Er^{3+}, Eu^{3+}, Dy^{3+}, represent a screening of alkali and alkaline earth metals, as well as some lanthanides and transition metals, offering a range of ionic radii and charge states to tune the properties of the perovskite. The M_1, M_2 species, which include Mg^{2+}, Zn^{2+}, Ca^{2+}, Sc^{3+}, In^{3+}, Ga^{3+}, Al^{3+}, Ge^{4+}, Ti^{4+}, Sn^{4+}, Zr^{4+}, Hf^{4+}, Nb^{5+}, Sb^{5+}, Ta^{5+}, Mo^{6+}, W^{6+}, Te^{6+}, are primarily transition metals and metalloids. These elements typically have smaller ionic radii compared to the A species and occupy the octahedral sites in the perovskite structure. The overall structure of Li(Na) disordered rocksalt-type metal oxides (Li(Na)-DRX) materials with the prototype formula of Li being $\mathrm{Li}_{1+x+\delta}(M_1M_2)_{1-x}O_2$ is derived from the perovskite architecture by the choice of cations and the stoichiometry. For Li(Na) metal halides (Li(Na)-MH), we consider the following metal species M: Mg^{2+}, Ca^{2+}, Zn^{2+}, La^{3+}, Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Y^{3+}, Ge^{4+}, Hf^{4+}, Zr^{4+}, Ti^{4+}, Sn^{4+}, Nb^{5+}, Ta^{5+}, Sb^{5+}. Overall, we have examined of 16,644 compositions across three typical structures: 3,846 compositions for Li(Na)-PRX, 1,238 compositions for Li(Na)-DRX and 11,560 compositions for Li(Na)-MH, respectively.

Table S1. The chemical potentials for all elements in facets of phase diagram for Li-Zn-O and Na-Zn-O systems.

Facets	$\mu_{Li/Na}$ (eV/atom)	μ_{Zn} (eV/atom)	μ_{O} (eV/atom)
$Li_{10}Zn_4O_9$-Li_6ZnO_4-Zn	-3.220	-1.260	-8.582
Li_6ZnO_4-Li_2O-Zn	-3.078	-1.260	-8.794
Li_2O-Zn-$LiZn_3$	-2.593	-1.260	-9.764
Li_2O-$LiZn_3$-LiZn	-2.223	-1.383	-10.505
Li_2O-LiZn-Li	-1.909	-1.697	-11.132
$Na_{10}Zn_4O_9$-Na_6ZnO_4-$NaZn_{13}$	-1.579	-1.298	-8.821
Na_6ZnO_4-Na_2O-$NaZn_{13}$	-1.444	-1.308	-9.021
Na_2O-$NaZn_{13}$-Na	-1.323	-1.318	-9.264

Table S2. The formation energy of competing phases in phase diagram of Li-Zn-O and Na-Zn-O.

Competing phases	Formation energy (eV/atom)	Competing phases	Formation energy (eV/atom)
$Li_{10}Zn_4O_9$	-1.992	$Na_{10}Zn_4O_9$	-1.634
Li_6ZnO_4	-2.036	Na_6ZnO_4	-1.552
Li_2O	-2.062	Na_2O	-1.439
$LiZn_3$	-0.171	$NaZn_{13}$	-0.054
LiZn	-0.219		

Table S3. The chemical potentials for all elements in facets of phase diagram for Li-Sb-Br and Na-Sb-Br.

Facets	$\mu_{Li/Na}$ (eV/atom)	μ_{Sb} (eV/atom)	μ_{Br} (eV/atom)
Sb-LiBr-Li_2Sb	-2.865	-4.129	-4.353
Li_3Sb -LiBr -Li_2Sb	-2.717	-4.425	-4.501
Li_3Sb-LiBr-Li	-1.909	-6.849	-5.355
Sb-NaBr-NaSb	-2.160	-4.129	-4.489
NaSb-NaBr-Na_3Sb	-1.856	-4.433	-4.793
Na_3Sb-NaBr-Na	-1.326	-6.034	-5.326