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Acid-Stable Oxides for Oxygen Electrocatalysis

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Abstract

Assessing materials' stability under operating conditions is of critical importance to the development of device-oriented electrocatalysts, whereas few efforts have been devoted to this on a large scale. In this work, using the Materials Project data, we explore the aqueous stability of 47,814 non-binary metal oxides under typical oxygen reduction/evolution reaction conditions and identify 68 likely acid-stable candidates for oxygen electrocatalysts. We also construct an "acid-stable periodic table" to guide the search of new acid-stable materials for electrocatalysis.

Electrocatalysis is fundamental to renewable energy applications by facilitating energy conversion between electricity and chemicals.¹ The electrochemical process involving oxygen, such as the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER), however, have become bottlenecks for applications in fuel cells and electrolyzers due to the relatively poor performance of even the best known ORR/OER electrocatalysts. Acid-based devices are more promising in practical applications because of the commercially accessible proton exchange membranes and high current density,^{2,3} but the highly oxidizing and acidic environment severely limits the stability of most materials as catalysts.

To develop an electrocatalyst for practical applications, we need catalysts that are active and stable.³ In the present paper we focus on stability of catalysts under acid condition at potentials relevant to ORR (> 0.6 V vs SHE) and OER (> 1.2 V vs SHE). First ruling out the unstable catalysts may be the most efficient start of a search procedure. We focus on metal oxide catalysts, given that they are the most likely stable candidates under the oxidizing ORR/OER conditions. Hitherto, transition metal binary oxides have been extensively studied experimentally,⁴ but only very few are promising because of low activity and/or instability under operating conditions. The most famous example is the state-of-the-art OER catalyst, IrO₂, which still dissolves at potentials higher than 1.6 V.⁵ The most extensive search for new oxide electrocatalysts so far is by Shinde et al.⁶ who performed an experimental high-throughput screening on the (Mn-Co-Ta-Sb)O_x chemical space to search for acid-stable OER catalyst.

In this work, building on the extensive works constructing computational Pourbaix diagrams,^{7–9} we evaluated the aqueous stability of 47,814 oxides under typical ORR/OER potentials in strong acid based on the data in the Materials Project.¹⁰ Based on a set of stability criteria, we identified 68 acid-stable ternary and quaternary oxides. We further constructed an acid-stable periodic table based on a statistical analysis of compositions of these 68 acid-stable oxides and find that oxides containing the elements of Sb/Ti/Sn/Ge/Mo/W tend to have high corrosion resistance in an acidic and oxidative environment.

Figure 1(a) presents the high-throughput screening workflow we developed to identify acidstable materials for ORR/OER. We began our search among the 47,814 oxides included in the Materials Project database.¹⁰ The aqueous stability of these materials is then computed in the potential range of 0.6 - 1.0 V (vs. SHE) and 1.2 - 2.0 V (vs. SHE) for ORR and OER, respectively, at pH = 0. We note that, in the literature the high-throughput screenings^{11–13} based on aqueous stability often only evaluate the materials' stability at a given potential, which may be insufficient to identify a "truly" stable candidate, since in experiment the catalyst is often cycled over a range of operating potentials at certain pH. Previous benchmark efforts by Singh et al.⁸ have shown that the aqueous stability can be assessed by computing the material's Gibbs free energy difference (ΔG_{pbx}) with respect to the stable domains on the Pourbaix diagram as a function of pH and potential, as illustrated in Figure 1(b). In principle, a stable material should have $\Delta G_{\text{pbx}} = 0$, but it was suggested that a threshold of ΔG_{pbx} of 0.5 eV/atom yields materials with a reasonable stability against corrosion due to self-passivation or the formation of a more stable solid-state phase.⁸ We therefore adopt this criterion in our screening. In addition, we computed the band gap (E_g) of the most promising materials using the screened hybrid Heyd-Scuseria-Ernzerhof (HSE) functional¹⁴ in order to evaluate their electronic properties. We also calculated the energy above the convex hull (E_{hull}), as depicted in Figure 1(c), for these candidates to estimate their phase stability. E_{hull} measures the energy involved in the decomposition reaction from the studied material to the most stable phase in the solid-state phase diagram. The phase diagram was constructed using the energies of relevant compounds obtained from the Materials Project.^{10,15,16}

By applying the aqueous stability criterion of $\Delta G_{pbx} < 0.5$ eV/atom on the 47,814 oxides, we obtained 68 non-binary acid-stable oxides, shown in Table 1 and Table S1. (Table was separated based on the band gap of 1.0 eV due to page limit.) This considerable reduction of potential candidates highlights the importance of aqueous stability evaluation when searching an electrocatalyst for practical application. In Table 1 and Table S1, the smaller ΔG_{pbx}^X (X = ORR/OER), the more stable compounds against aqueous decomposition. We include E_g in the tables to provide an indication of the electronic conductivity, metals ($E_g = 0$) having the best electronic conductivity and the large band gap oxides the lowest. The small gap, semiconducting materials may have a certain electronic conductivity through defects and impurities. The E_{hull} is added in the tables as a proxy of material's synthesizability. A stable phase by definition yields $E_{hull} = 0$ and the higher the E_{hull} , the more unstable this material is and, consequently, the more challenging it might be to synthesize it.

Four of these 68 materials, $M(SbO_3)_2$ (M = Mn/Fe/Co/Ni) have been investigated in experiment as electrocatalysts for OER and the chlorine evolution reaction (CER).^{17,18} It was found in experiment that $M(SbO_3)_2$ (M = Fe/Co/Ni) showed high corrosion resistance under OER and CER operating conditions, which is consistent with our predictions. (Table 1 and Table S1) Close exam-

ination of the aqueous decomposition products of these three acid-stable compounds reveals that the formation of more thermodynamically acid-stable solid phases is mainly responsible for this high corrosion resistance. For example, the formation of FeSbO₄ and antimony oxides (Sb₂O₅ or Sb₃O₈) for Fe(SbO₃)₂ under potentials of 1.2 - 2.0 V at pH = 0, shown in Figure 2(a), prevents its aqueous decomposition because of a higher solid-solid phase transition barrier (1 eV).⁸ Mn(SbO₃)₂ was experimentally observed to exhibit a high dissolution rate at potentials higher than 1.8 V (vs. RHE), which can be attributed to the large Pourbaix decomposition free energy (ΔG_{pbx}), shown in Figure 2(b).

On a side note, we found that some materials (e.g. $Sn(WO_3)_{18}$) are particularly promising as supporting materials as alternatives to carbon-support in Pt/C or for single-atom electrocatalysis because of its wide aqueous stability window and small E_g . Generally, 3*d* transition metal elements (e.g. Mn/Fe/Co/Ni) in compounds serve as the catalytic center for chemical reaction, and we note that the majority compounds identified as possible support materials do not contain these elements, signifying that they are unlikely to be active for ORR/OER by themselves.

As an aid to future design efforts for acid-stable electrocatalyst, we built an "acid-stable period table" reflecting the composition of the 68 stable oxides, shown in Figure 3. We observe that Sb/Ti/Sn/Ge/Mo/W-based oxides have a preference of being stable in strong acid. This insight is of great benefit to search for new stable and active electrocatalyst for ORR and OER using combinatorial chemistry screening or machine learning.^{6,19,20}

Acknowledgement

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Supporting Information Available

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXX

Methods on density functional theory calculations and aqueous stability analysis; Table S1 summarizing the calculated properties of the rest 53 acid-stable oxides

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Table 1: Calculated properties of 15 acid-stable oxides. ΔG_{pbx}^X (X = ORR/OER) (eV/atom) is the maximum Pourbaix decomposition free energy in the potential range of interest. Band gap (eV) was calculated using the HSE functional. MP-ID is material id in the Materials Project database. Materials are sorted by their phase stability, E_{hull} (meV/atom).

Materials	Space group	$E_{\rm hull}$	$\Delta G_{\rm pbx}^{\rm ORR} / \Delta G_{\rm pbx}^{\rm OER}$	Aqueous decomposition products	Band gap	MP-ID
Fe(SbO ₃) ₂	P4 ₂ /mnm	0	0/0.328	$\begin{aligned} & Fe(SbO_3)_2(s) \ (E = 0.6 - 1.0 \ V) \\ & Sb_2O_5(s) + FeSbO_4(s) \ (E = 1.2 - 1.95 \ V) \\ & FeSbO_4(s) + Sb_3O_8(s) \ (E = 1.96 - 2.0 \ V) \end{aligned}$	0	mp-541194
Co(SbO ₃) ₂	P4 ₂ /mnm	0	0.005/0.154	$\begin{split} & Co^{2+} + SbO^+ \ (E=0.6 \ V) \\ & Co(SbO_3)_2(s) \ (E=0.61 \ -1.0, \ 1.2 \ -1.78 \ V) \\ & CoO_2(s) + Sb_2O_5(s) \ (E=1.79 \ -1.95 \ V) \\ & CoO_2(s) + Sb_3O_8(s) \ (E=1.96 \ -2.0 \ V) \end{split}$	0.92	mp-24845
Mn(SbO ₃) ₂	P321	0	0.078/—	$\begin{split} & \text{SbO}^{+} + \text{Mn}^{2+} \ (\text{E} = 0.6 - 0.62 \text{ V}) \\ & \text{SbO}_2(\text{s}) + \text{Mn}^{2+} \ (\text{E} = 0.63 - 0.69 \text{ V}) \\ & \text{Mn}(\text{SbO}_3)_2(\text{s}) \ (\text{E} = 0.7 - 1.0 \text{ V}) \end{split}$	0.78	mp-25043
Mn(SbO ₃) ₂	P4 ₂ /mnm	1	0.124/—	$\begin{split} &SbO^{+} + Mn^{2+} (E = 0.6 - 0.62 \text{ V}) \\ &Mn^{2+} + SbO_{2}(s) (E = 0.63 - 0.69 \text{ V}) \\ &Mn(SbO_{3})_{2}(s) (E = 0.7 - 1.0 \text{ V}) \end{split}$	0	mp-763546
Sn(WO ₃) ₁₈	Pmmn	13	0.247/0.458	$WO_3(s) + SnO_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	0	mp-705699
Sb ₂ Mo ₁₀ O ₃₁	Pma2	17	0.311/—	$\begin{split} Mo_8O_{23}(s) + SbO^+ & (E = 0.6 - 0.61 \text{ V})\\ SbO^+ + MoO_3(s) & (E = 0.62 \text{ V})\\ MoO_3(s) + SbO_2(s) & (E = 0.63 - 0.77 \text{ V})\\ Sb_2O_5(s) + MoO_3(s) & (E = 0.78 - 1.0 \text{ V}) \end{split}$	0	mp-609510
MoWO ₆	P2 ₁ /c	36	0.152/0.150	$ WO_3(s) + Mo_8O_{23}(s) (E = 0.6 - 0.61 V) \\ WO_3(s) + MoO_3(s) (E = 0.62 - 1.0, 1.2 - 2.0 V) $	0.73	mvc-5033
Mn(SbO ₃) ₂	C2/m	43	0.250/—	$\begin{split} & \text{SbO}^{+} + \text{Mn}^{2+} \ (\text{E} = 0.6 - 0.62 \text{ V}) \\ & \text{SbO}_2(\text{s}) + \text{Mn}^{2+} \ (\text{E} = 0.63 - 0.69 \text{ V}) \\ & \text{Mn}(\text{SbO}_3)_2(\text{s}) \ (\text{E} = 0.7 - 1.0 \text{ V}) \end{split}$	0	mp-690561
Ge ₂ MoO ₆	C2/c	62	0.477/—	$\begin{aligned} Mo_8O_{23}(s) + GeO_2(s) & (E = 0.6 - 0.61 \text{ V}) \\ GeO_2(s) + MoO_3(s) & (E = 0.62 - 1.0 \text{ V}) \end{aligned}$	1.00	mp-1043238
Fe(SbO ₃) ₄	P1	82	/0.317	$Sb_2O_5(s) + FeSbO_4(s) (E = 1.2 - 1.95 V)$ $FeSbO_4(s) + Sb_3O_8(s) (E = 1.96 - 2.0 V)$	0	mp-770991
SnSbO ₄	Cmmm	90	0.386/—	$\begin{split} &SnO_2(s) + SbO^+ (E = 0.6 - 0.62 \text{ V}) \\ &SbO_2(s) + SnO_2(s) (E = 0.63 - 0.77 \text{ V}) \\ &Sb_2O_5(s) + SnO_2(s) (E = 0.78 - 1.0 \text{ V}) \end{split}$	0	mp-1218921
CoSbO ₄	Imma	92	—/0.477	$\begin{array}{l} Co(SbO_3)_2(s) + Co^{2+} \left(E = 1.2 - 1.59 \ V \right) \\ Co(SbO_3)_2(s) + CoO_2(s) \left(E = 1.6 - 1.78 \ V \right) \\ Sb_2O_5(s) + CoO_2(s) \left(E = 1.79 - 1.95 \ V \right) \\ CoO_2(s) + Sb_3O_8(s) \left(E = 1.96 - 2.0 \ V \right) \end{array}$	0.94	mp-765886
Hg(SbO ₃) ₂	P4 ₂ /mnm	96	0.289/0.289	$Hg(SbO_3)_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	0	mp-768291
Ge ₂ SbO ₆	C2/c	99	0.373/—	$\begin{split} & \text{SbO}^{+} + \text{GeO}_2(s) \ (\text{E} = 0.6 - 0.62 \ \text{V}) \\ & \text{GeO}_2(s) + \text{SbO}_2(s) \ (\text{E} = 0.63 - 0.77 \ \text{V}) \\ & \text{Sb}_2\text{O}_5(s) + \text{GeO}_2(s) \ (\text{E} = 0.78 - 1.0 \ \text{V}) \end{split}$	0	mp-1042897
Ge ₂ SbO ₆	P2 ₁ /c	114	0.420/—	$\begin{array}{l} GeO_2(s) + SbO^+ \ (E=0.6 - 0.62 \ V) \\ SbO_2(s) + GeO_2(s) \ (E=0.63 - 0.77 \ V) \\ Sb_2O_5(s) + GeO_2(s) \ (E=0.78 - 1.0 \ V) \end{array}$	0	mp-1043019



Figure 1: (a) Computational high-throughput screening workflow for identifying acid-stable oxides for electrocatalysis. Number in parenthesis is the amount of identified candidates. (b) Schematics of the Pourbaix decomposition free energy (ΔG_{pbx}) as a functional of potential at certain pH, where M and N denote two distinct compounds. (c) Illustration of the energy above hull (E_{hull}) for an A-B system, where pink and blue solid circles are stable and unstable phases, respectively. The line connecting the stables phases is the convex hull.



Figure 2: Calculated Pourbaix decomposition free energy ΔG_{pbx} of (a) Fe(SbO₃)₂ and (b) Mn(SbO₃)₂ from the potential 0 - 2.0 V (vs. SHE) at pH = 0. The projection of ΔG_{pbx} onto the potential axis highlights the stable species at the corresponding regions.

Η													He	_	60				
Li 1	Be	Be Acid-Stable Periodic Table											С	Ν	O 68	F	Ne	-	50
Na 1	Mg 2											Al	Si	Ρ	S	CI	Ar	-	40
K 2	Ca 1	Sc 1	Ti 16	V	Cr	Mn 4	Fe 11	Co 2	Ni 1	Cu	Zn 2	Ga 1	Ge 11	As	Se	Br	Kr	-	30
Rb	Sr 2	Y	Zr	Nb	Mo 11	Tc	Ru	Rh	Pd	Ag 1	Cd 1	In	Sn 16	Sb 38	Те	Ι	Xe	-	20
Cs 1	Ba 1		Hf	Та	W 8	Re	Os	lr	Pt	Au	Hg 2	Τİ	Pb 1	Bi 1	Ро	At	Rn	-	10

Figure 3: Frequency at which each element consists in acid-stable oxides. Elements with zero frequency are shaded in gray. Lanthanoids and actinoids are omitted for clarity since no oxide containing these elements was predicted to be stable.



ToC

SUPPORTING INFORMATION Acid-Stable Oxides for Oxygen Electrocatalysis

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Computational Method

Density functional theory calculation

The density functional theory calculations were performed using the Vienna *ab initio* simulation package (VASP) within the projector-augmented wave method.^{1,2} The band gap of 68 identified acid-stable oxides were calculated using the screened hybrid Heyd-Scuseria-Ernzerhof (HSE)^{3,4} functional, with a plane wave energy cutoff of 520 eV and a *k*-point density at least of 50 per Å⁻³. All other energy relevant properties were obtained from the Materials Project via the Materials Project REST API.^{5,6} All data analysis were carried out using the Python Materials Genomics (pymatgen) package.⁷

Aqueous stability analysis

The aqueous stability was evaluated by computing Pourbaix diagram of each material using the Materials Project methods.^{8–10} Here, we briefly summarize the basic ideas and details are directed to the cited references. In the Pourbaix diagram, the stable domains are determined based on the knowledge of all possible equilibrium redox reactions in the chemical composition of interest. The redox reaction for a given material in an aqueous medium is described by:

$$a[\text{Reactants}] + bH_2O \Leftrightarrow c[\text{Products}] + dH^+ + ne^-$$
 (1)

The Gibbs free energy change (ΔG_{rxn}) of this reaction can be computed by the free energy change of the reaction under standard conditions. At equilibrium, the Nernst equation,

$$-nFE' = \Delta G_{\rm rxn} = \Delta G_{\rm rxn}^{\rm o} + RT\ln Q = \Delta G_{\rm rxn}^{\rm o} + RT\ln \frac{(a_{\rm P})^{\rm c} \cdot (a_{\rm H^+})^{\rm d}}{(a_{\rm R})^{\rm a} \cdot (a_{\rm H_2O})^{\rm b}}$$
(2)

is used to relate the cell potential (E') to the Gibbs free energy of the reaction (ΔG_{rxn}) for each possible redox reaction. *T* is the temperature, *F* is the Faraday constant, *R* is the ideal gas constant, a_P , a_R , a_{H_2O} , and a_{H^+} are the activity of the reactants, products, water (= 1) and H⁺. The most stable

species in aqueous solutions can be therefore determined by minimizing ($\Delta G_{rxn} + nFE$) across all possible reactions under certain pH and applied potential. The energy of all compounds and ions studied in are obtained from the Materials Project⁵ via the Materials Application Programming Interface (API).^{6,7} In this work, the aqueous stability of a material was quantitatively measured by its Gibbs free energy difference (ΔG_{pbx}) with respect to the stable domains on the Pourbaix diagram under typical ORR/OER operating conditions.

Table S1: Calculated properties of 53 acid-stable oxides for oxygen electrocatalysis. ΔG_{pbx}^X (X = ORR/OER) (eV/atom) is the maximum aqueous decomposition free energy in the potential range of interest. Band gap (eV) was calculated using the HSE functional. MP-ID is material ID in the Materials Project database. Materials are sorted by their phase stability (*E*_{hull}).

Materials	Space Group	E _{hull}	$\Delta G_{ m pbx}$	Aqueous Decomposition Products	Band Gap	MP-ID
Hg(SbO ₃) ₂	P31m	0	0/0	Hg(SbO ₃) ₂ (s) (E = 0.6 - 1.0, 1.2 - 2.0 V)	1.55	mp-754065
Sb ₂ PbO ₆	₽31m	0	0/0.103	$Sb_2PbO_6(s) (E = 0.6 - 1.0, 1.2 - 1.86 V)$ $Sb_2O_5(s) + PbO_2(s) (E = 1.87 - 1.95 V)$ $Sb_3O_8(s) + PbO_2(s) (E = 1.96 - 2.0 V)$	2.81	mp-20727
Cd(SbO ₃) ₂	P31m	0	0/0	Cd(SbO ₃) ₂ (s) (E = 0.6 - 1.0, 1.2 - 2.0 V)	2.79	mp-8922
BiSbO ₄	C2/c	0	0.005/0.101	$\begin{split} SbO^{+} &+ Bi^{3+} (E = 0.6 \text{ V}) \\ BiSbO_4(s) &(E = 0.61 - 1.0, 1.2 - 1.9 \text{ V}) \\ Bi_2O_5(s) &+ Sb_2O_5(s) &(E = 1.91 - 1.95 \text{ V}) \\ Bi_2O_5(s) &+ Sb_3O_8(s) &(E = 1.96 - 2.0 \text{ V}) \end{split}$	3.53	mp-23018
LiSb ₃ O ₈	P2 ₁ /c	0	0.057/0.108	$\begin{split} Li^{+} &+ SbO^{+} (E = 0.6 - 0.62 \text{ V}) \\ SbO_{2}(s) &+ Li^{+} (E = 0.63 - 0.65 \text{ V}) \\ LiSb_{3}O_{8}(s) (E = 0.66 - 1.0, 1.2 - 1.92 \text{ V}) \\ LiO_{3}(s) &+ Sb_{2}O_{5}(s) (E = 1.93 - 1.95 \text{ V}) \\ Sb_{3}O_{8}(s) &+ LiO_{3}(s) (E = 1.96 - 2.0 \text{ V}) \end{split}$	2.05	mp-29892
KSb ₅ O ₁₃	Ama2	0	0.060/0.069	$\begin{split} & SbO^{+} + K^{+} (E = 0.6 - 0.62 \text{ V}) \\ & K^{+} + SbO_{2}(s) (E = 0.63 - 0.64 \text{ V}) \\ & KSb_{5}O_{13}(s) (E = 0.65 - 1.0, 1.2 - 1.93 \text{ V}) \\ & KO_{3}(s) + Sb_{2}O_{5}(s) (E = 1.94 - 1.95 \text{ V}) \\ & KO_{3}(s) + Sb_{3}O_{8}(s) (E = 1.96 - 2.0 \text{ V}) \end{split}$	1.87	mp-757115
Sc ₂ (MoO ₄) ₃	Pbcn	0	0/0	$Sc_2(MoO_4)_3(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	4.12	mp-19594
Ni(SbO ₃) ₂	P4 ₂ /mnm	0	0.004/0	SbO ⁺ + Ni ²⁺ (E = 0.6 V) Ni(SbO ₃) ₂ (s) (E = 0.61 - 1.0, 1.2 - 2.0 V)	1.33	mp-505271
Fe ₂ (MoO ₄) ₃	Pbcn	0	0.014/0.000	$Fe^{2+} + Mo_8O_{23}(s) (E = 0.6 - 0.61 V)$ $MoO_3(s) + Fe^{2+} (E = 0.62 V)$ $Fe_2(MoO_4)_3(s) (E = 0.63 - 1.0, 1.2 - 2.0 V)$	2.54	mp-31766
Fe ₂ (MoO ₄) ₃	P21/c	0	0.020/0.005	$Fe^{2+} + Mo_8O_{23}(s) (E = 0.6 - 0.61 V)$ $Fe^{2+} + MoO_3(s) (E = 0.62 V)$	2.51	mp-705435

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Materials	Space Group	E _{hull}	$\Delta G_{\rm pbx}$	Aqueous Decomposition Products	Band Gap	MP-ID
				$Fe_2(MoO_4)_3(s) (E = 0.63 - 1.0, 1.2 - 2.0 V)$		
FeSbO ₄	Cmmm	0	0.047/0.000	$Fe^{2+} + Fe(SbO_3)_2(s) (E = 0.6 - 0.69 V)$ FeSbO ₄ (s) (E = 0.7 - 1.0, 1.2 - 2.0 V)	1.74	mp-675127
Sr(SbO ₃) ₂	P31m	0	0.024/—	$Sr^{2+} + SbO^+ (E = 0.6 - 0.61 V)$ $Sr(SbO_3)_2(s) (E = 0.62 - 1.0 V)$	3.7	mp-9126
Ba(SbO ₃) ₂	P31m	0	0.036/—	SbO ⁺ + Ba ²⁺ (E = 0.6 - 0.62 V) Ba ²⁺ + SbO ₂ (s) (E = 0.63 V) Ba(SbO ₃) ₂ (s) (E = 0.64 - 1.0 V)	3.98	mp-9127
Ca(SbO ₃) ₂	P31m	0	0.064/—	$Ca^{2+} + SbO^{+} (E = 0.6 - 0.62 V)$ $SbO_2(s) + Ca^{2+} (E = 0.63 - 0.67 V)$ $Ca(SbO_3)_2(s) (E = 0.68 - 1.0 V)$	3.73	mp-9125
NaSb ₅ O ₁₃	Ama2	0	0.073/—	$Na^{+} + SbO^{+} (E = 0.6 - 0.62 V)$ $Na^{+} + SbO_{2}(s) (E = 0.63 - 0.66 V)$ $NaSb_{5}O_{13}(s) (E = 0.67 - 1.0 V)$	1.89	mp-766341
Ge ₃ Sb ₂ O ₉	P6 ₃ /m	0	0.343/-	$GeO_2(s) + SbO^+ (E = 0.6 - 0.62 V)$ $GeO_2(s) + SbO_2(s) (E = 0.63 - 0.77 V)$ $GeO_2(s) + Sb_2O_5(s) (E = 0.78 - 1.0 V)$	3.87	mp-17708
Ge ₃ (SbO ₃) ₄	I43d	0	0.491/—	$SbO^{+} + GeO_{2}(s) (E = 0.6 - 0.62 V)$ $SbO_{2}(s) + GeO_{2}(s) (E = 0.63 - 0.77 V)$ $Sb_{2}O_{5}(s) + GeO_{2}(s) (E = 0.78 - 1.0 V)$	4.28	mp-1201722
Mn(SbO ₃) ₂	P31m	0	0.119/—	$SbO^{+} + Mn^{2+} (E = 0.6 - 0.62 V)$ $SbO_{2}(s) + Mn^{2+} (E = 0.63 - 0.69 V)$ $Mn(SbO_{3})_{2}(s) (E = 0.7 - 1.0 V)$	1.66	mp-1078318
Zn(SbO ₃) ₂	P4 ₂ /mnm	0	—/0	$Zn(SbO_3)_2(s) (E = 1.2 - 2.0 V)$	1.82	mp-3188
Mg(SbO ₃) ₂	P4 ₂ /mnm	0	—/0	$Mg(SbO_3)_2(s) (E = 1.2 - 2.0 V)$	2.28	mp-3653
GaSbO ₄	Cmmm	0	—/0	$GaSbO_4(s) (E = 1.2 - 2.0 V)$	1.81	mp-1224786
CsSbWO ₆	Ima2	0	—/0.216	$\begin{split} &CsSbWO_6(s) \ (E=1.2\ -\ 1.84\ V)\\ &Sb_2O_5(s)\ +\ WO_3(s)\ +\ Cs_2WO_8(s) \ (E=1.85\ -\ 1.95\ V)\\ &Sb_3O_8(s)\ +\ WO_3(s)\ +\ Cs_2WO_8(s) \ (E=1.96\ -\ 2.0\ V) \end{split}$	3.32	mp-1225944

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-	Materials	Space Group	$E_{\rm hull}$	$\Delta G_{\rm pbx}$	Aqueous Decomposition Products	Band Gap	MP-ID
	KSb ₅ O ₁₃	P2 ₁ /m	0	0.060/0.069	$\begin{split} &SbO^{+} + K^{+} (E = 0.6 - 0.62 \text{ V}) \\ &SbO_{2}(s) + K^{+} (E = 0.63 - 0.64 \text{ V}) \\ &KSb_{5}O_{13}(s) (E = 0.65 - 1.0, 1.2 - 1.93 \text{ V}) \\ &KO_{3}(s) + Sb_{2}O_{5}(s) (E = 1.94 - 1.95 \text{ V}) \\ &Sb_{3}O_{8}(s) + KO_{3}(s) (E = 1.96 - 2.0 \text{ V}) \end{split}$	1.85	mp-1223385
	Fe ₂ (MoO ₄) ₃	P2 ₁	1	0.024/0.009	$Fe^{2+} + Mo_8O_{23}(s) (E = 0.6 - 0.61 V)$ $MoO_3(s) + Fe^{2+} (E = 0.62 V)$ $Fe_2(MoO_4)_3(s) (E = 0.63 - 1.0, 1.2 - 2.0 V)$	2.8	mp-704851
	FeSbO ₄	I41md	8	0.073/0.026	$Fe(SbO_3)_2(s) + Fe^{2+} (E = 0.6 - 0.69 V)$ FeSbO ₄ (s) (E = 0.7 - 1.0, 1.2 - 2.0 V)	1.55	mp-765436
	TiSn ₉ O ₂₀	C2/m	13	0.041/0.041	$TiO_2(s) + SnO_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	2.24	mp-766163
	FeAg(MoO ₄) ₂	P2/c	17	/0.455	$Ag^{+} + Fe_{2}(MoO_{4})_{3}(s) + MoO_{3}(s) (E = 1.2 - 1.53 V)$ $Fe_{2}(MoO_{4})_{3}(s) + MoO_{3}(s) + Ag_{2}O_{3}(s) (E = 1.54 - 2.0 V)$	1.43	mp-1212730
	MoWO ₆	Cm	18	0.083/0.080	$WO_3(s) + Mo_8O_{23}(s) (E = 0.6 - 0.61 V)$ $WO_3(s) + MoO_3(s) (E = 0.62 - 1.0, 1.2 - 2.0 V)$	1.37	mp-1116820
	$Ti(Sn_2O_5)_2$	PĪ	25	0.077/0.077	$SnO_2(s) + TiO_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	2.71	mp-766391
	Ti(GeO ₃) ₂	C2/c	27	0.083/0.083	$TiO_2(s) + GeO_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	4.45	mp-1042864
	Ti(GeO ₃) ₂	P21/c	28	0.084/0.084	$\text{GeO}_2(s) + \text{TiO}_2(s) (\text{E} = 0.6 - 1.0, 1.2 - 2.0 \text{ V})$	4.24	mp-1043032
	Ti ₃ Sn ₇ O ₂₀	Cmmm	36	0.110/0.110	$TiO_2(s) + SnO_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	2.87	mp-765970
	TiSnO ₄	Cmmm	36	0.111/0.111	$TiO_2(s) + SnO_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	2.69	mp-1216649
	Ti ₃ (WO ₆) ₂	P21/c	39	0.135/0.135	$TiO_2(s) + WO_3(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	2.94	mp-776763
	$Ti_2Sn_3O_{10}$	Cmm2	40	0.123/0.123	$TiO_2(s) + SnO_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	2.88	mp-757375
	Sn(GeO ₃) ₂	C2/c	42	0.127/0.127	$\text{GeO}_2(s) + \text{SnO}_2(s) (\text{E} = 0.6 - 1.0, 1.2 - 2.0 \text{ V})$	3.34	mp-1042873
	Sn(GeO ₃) ₂	P21/c	43	0.130/0.130	$\text{SnO}_2(s) + \text{GeO}_2(s) (\text{E} = 0.6 - 1.0, 1.2 - 2.0 \text{ V})$	3.32	mp-1043041
	Ti ₉ SnO ₂₀	C2/m	43	0.131/0.131	$TiO_2(s) + SnO_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	2.87	mp-761148
	TiSnO ₄	Cm	44	0.133/0.133	$SnO_2(s) + TiO_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	2.94	mp-753048

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Materials	Space Group	E _{hull}	$\Delta G_{\rm pbx}$	Aqueous Decomposition Products	Band Gap	MP-ID
FeSbO ₄	I4m2	44	0.182/0.135	$Fe(SbO_3)_2(s) + Fe^{2+} (E = 0.6 - 0.69 V)$ FeSbO ₄ (s) (E = 0.7 - 1.0, 1.2 - 2.0 V)	2.32	mp-1178209
Fe ₂ (MoO ₄) ₃	ΡĪ	45	0.175/0.160	$Fe^{2+} + Mo_8O_{23}(s) (E = 0.6 - 0.61 V)$ MoO ₃ (s) + Fe ²⁺ (E = 0.62 V) Fe ₂ (MoO ₄) ₃ (s) (E = 0.63 - 1.0, 1.2 - 2.0 V)	2.52	mp-1042928
Ti ₄ SnO ₁₀	PĪ	48	0.146/0.146	$SnO_2(s) + TiO_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	2.69	mp-766168
$Ti_3(SnO_5)_2$	Cmm2	49	0.149/0.149	$TiO_2(s) + SnO_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	2.71	mp-759737
Ti ₇ Sn ₃ O ₂₀	Cmmm	53	0.161/0.161	$SnO_2(s) + TiO_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	2.54	mp-761118
TiSnO ₄	I4m2	65	0.198/0.198	$SnO_2(s) + TiO_2(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	3.05	mp-773864
$Sn(WO_4)_2$	P2/c	97	0.356/0.356	$SnO_2(s) + WO_3(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	3.19	mp-1041577
Ge ₃ (WO ₆) ₂	Ia3d	100	0.343/0.343	$\text{GeO}_2(s) + \text{WO}_3(s) (\text{E} = 0.6 - 1.0, 1.2 - 2.0 \text{ V})$	2.96	mvc-4401
Ti(WO ₄) ₂	P2/c	110	0.406/0.406	$TiO_2(s) + WO_3(s) (E = 0.6 - 1.0, 1.2 - 2.0 V)$	2.89	mp-1041486
Zn(SbO ₃) ₂	Pmn2 ₁	115	/0.346	$Zn(SbO_3)_2(s) (E = 1.2 - 2.0 V)$	2.04	mp-1045304
TiFeSbO ₆	P4 ₂ nm	119	0.389/0.358	$Fe^{2+} + TiO_2(s) + Fe(SbO_3)_2(s) (E = 0.6 - 0.69 V)$ FeSbO ₄ (s) + TiO ₂ (s) (E = 0.7 - 2.0 V)	2.13	mp-1216868
Ge ₃ (MoO ₆) ₂	Ia3d	132	0.456/0.454	$Mo_8O_{23}(s) + GeO_2(s) (E = 0.6 - 0.61 V)$ GeO_2(s) + MoO_3(s) (E = 0.62 - 1.0, 1.2 - 2.0 V)	2.44	mvc-4408
Mg(SbO ₃) ₂	Pmn2 ₁	142	/0.426	$Mg(SbO_3)_2(s) (E = 1.2 - 2.0 V)$	2.31	mp-1048765
Sr(SbO ₃) ₂	C2/c	145	0.460/—	$Sr^{2+} + SbO^+ (E = 0.6 - 0.61 V)$ $Sr(SbO_3)_2(s) (E = 0.62 - 1.0 V)$	2.5	mp-675680

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