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Stable Two-Dimensional Materials for Oxygen Reduction and Oxygen Evolution Reactions

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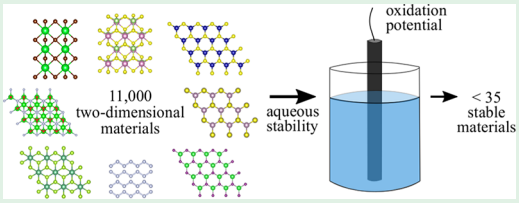
Supporting Information



ABSTRACT: Using density functional theory-predicted energies, we performed a high-throughput screening of more than 11 000 two-dimensional materials from available material databases. We suggest that less than 35 materials are stable under the strongly oxidizing operating conditions of oxygen reduction and/or oxygen evolution reactions in acidic media.

The oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are half-cell electrochemical reactions which hold promise for the integration of renewable energy into our energy systems.[1] While ORR is the cathodic side reaction for the generation of electricity from the hydrogen gas in fuel cells, the OER is the anodic half-cell reaction in aqueous electrolytes for the generation of fuels (such as CO_2 reduction to ethanol and N_2 reduction to ammonia) using renewable electricity. The sluggish kinetics of the OER and ORR occurring on the precious metal-based catalysts is the main bottleneck in the widespread application of these energy technologies.[1] The catalysts currently used for ORR and OER are expensive and scarce and have low stability under relevant acidic reaction conditions. Many materials have been tested for activity in these two reactions, but the best catalysts to date in the acidic media are still platinum and iridium oxide for the ORR and OER, respectively.[1] The search for alternative catalysts is particularly hindered by the harsh operating conditions of strongly acidic media under highly oxidizing potentials.

Recently, 2D materials have emerged as promising candidates for electrochemical reactions.[2] These materials are proving helpful either by providing an active reaction site or by serving as conductive support for single or multiatom catalysts. Many of these 2D materials have known synthetic pathways, and thousands are predicted from computational exfoliation of bulk materials or through combinatorial substitution of already existing materials.[3−5] The stability of these 2D materials under ORR and OER operating conditions has yet to be tested.

In this work, we use density functional theory (DFT)-predicted energies to carry out a high-throughput screening of 2D materials for their stability under ORR and OER operating conditions. We screened all materials from the C2DB,[3] MaterialsCloud,[4] and 2Dmatpedia[5] databases. We find, using reasonable screening criteria, that from more than 11 000 predicted 2D materials, only 21 and 14 are stable under the ORR and OER conditions, respectively.

The 2D materials used in this study are obtained from openly available DFT databases: C2DB, MaterialsCloud, and 2Dmatpedia. The C2DB database is generated by combinatorial substitution of elements in structures of already-synthesized 2D materials.[3] The database has 3712 materials in total, and the materials are tagged for a low, medium, and high thermodynamic and dynamic (inferred from Γ-point phonon frequencies) stability. The MaterialsCloud database has 1036 2D materials which are obtained by topological computational exfoliation of experimental bulk (3D) materials from the Crystallographic Open Database[6] and Inorganic Crystal Structure Database.[4] Only materials with computed exfoliation energy of less than 35 eV/Å^2 were included in the database. The 2Dmatpedia database contains 2940 materials obtained from a top-down exfoliation of existing layered materials and 3409 materials from a bottom-up substitution of existing 2D materials.[5] All together, these databases contain more than 11 000 2D materials.

The aqueous stability of 2D materials under ORR and OER operating conditions is summarized in panels a and b of Figure S1, respectively. The stabilities are tested at a pH of 1 and oxidizing potentials of 0.9 and 1.5 V for ORR and OER, respectively. Only materials with convex hull stability (E_{hull}) ≤ 0.15 eV/atom for decomposition into bulk 3D materials (from the Materials Project Database[7]) are included in Figure S1a,b.

From more than 11 000 total 2D materials in the considered databases, only 130 and 69 materials are found to be potentially stable under the strong oxidizing conditions of ORR and OER in the acidic medium, respectively. These candidate materials are further filtered to remove compounds containing precious and toxic elements (Re, Rh, Ru, Hf, As, Hg, Au, Pt, and Pd) and lanthanides and actinides. This filter reduces the number of materials to 83 and 48 for ORR and OER, respectively.

In a benchmarking study of DFT-predicted aqueous stabilities against experiments, Singh et al.[8] concluded that materials with predicted aqueous decomposition energies of up to 0.20 eV/atom are stable in experiments because of large solid−solid structural reorganization barriers originating from solid-only

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decomposition products. For materials with aqueous phase decomposition products, the stability is observed only for decomposition energies of up to 0.08 eV/atom. Screening of materials through this additional stability filter reduces the number of candidates to 21 and 14 for ORR and OER, respectively. The thermodynamic stability with respect to the convex hull, the aqueous decomposition energy, and the electronic bandgaps (as determined by GGA-DFT) of these filtered compounds are reported in Table 1.

Table 1. Convex Hull Stability (E_{hull}), Aqueous Stability (ΔG_{aq}), and GGA-DFT Predicted Bandgap (E_{gap}^{GGA}) of Filtered Two-Dimensional Materials[a]

composition	E_{hull} (eV/atom)	ΔG_{aq} (eV/atom)	E_{gap}^{GGA} (eV)
	ORR, pH 1, U = 0.9 V		
$Si_2H_2O_5$	0.07	0.01	5.70
$Fe_3P_2(HO)_{16}$	0.10	0.04	2.33
$Pb_3P_2O_8$	0.05	0.05	3.46
$Ti_3H_2O_7$	0.11	0.05	2.83
$AgIO_3$	0.04	0.05	2.27
BiOF	0.05	0.05	3.42
$Sc(IO)_3$	0.03	0.05	3.98
$V_2Pb_3O_8$	0.04	0.06	3.17
$Zr(IO_3)_4$	0.05	0.06	3.30
$PbWO_4$	0.06	0.06	3.57
$FeHO_2$	0.10	0.06	1.91
WH_2O_4	0.13	0.06	1.49
$V_3(H_3O_5)_2$	0.09	0.07	1.23
Bi_2O_3	0.07	0.07	3.02
$Al(OH)_3$	0.10	0.07	4.38
$Cd(IO_3)_2$	0.06	0.07	3.46
$CuH_4(IO_4)_2$	0.11	0.08	0.85
$Al_2Si_2H_4O_9$	0.05	0.08	4.48
GeO_2	0.11	0.11	3.54
$GeBi_2O_5$	0.15	0.15	2.13
$Ge_3Bi_2O_9$	0.15	0.15	3.93
	OER, pH 1, U = 1.5 V		
Ti_2O_7	0.08	0.00	1.20
ZrO_3	0.10	0.00	3.23
NiO_3	0.06	0.00	0.00
$CuHO_2$	0.05	0.01	0.74
AgO_2F	0.02	0.02	0.00
$Pb(BrO_3)_2$	0.05	0.05	3.12
$AgHO_2$	0.10	0.06	0.00
$FeHO_2$	0.10	0.06	1.91
WH_2O_4	0.13	0.06	1.49
$Si_2H_2O_5$	0.07	0.07	5.70
TiO_3	0.09	0.08	2.26
PbO_2	0.10	0.10	1.26
GeO_2	0.11	0.11	3.54
BiO_2	0.12	0.11	0.37

[a]All materials from Materials Project are included in the determination of stabilities.

Under ORR operating conditions, $Si_2H_2O_5$, $Pb_3P_2O_8$, $Ti_3H_2O_7$, $PbWO_4$, $FeHO_2$, WH_2O_4, Bi_2O_3, $CuH_4(IO_4)_2$, and GeO_2 are predicted to decompose to their bulk 3D phases (see Table S1 for decomposition products). Under OER operating conditions, except for $Si_2H_2O_5$ and TiO_3, all materials from Table 1 are predicted to decompose to their respective 3D phases. Note that the aqueous decomposition energies of Ti_2O_7, ZrO_3, and NiO_3 are zero because these materials are obtained from combinatorial substitution in 2Dmatpedia and C2DB databases and do not have more stable 3D phases in the Materials Project.

Interestingly, from filtered stable candidates under ORR operating conditions, no material was found to have a zero electronic bandgap (needed for conductive support), and from filtered stable candidates under OER operating conditions only three candidate materials have zero electronic bandgaps. Because GGA-DFT underpredicts the true electronic gaps,[9] these zero bandgap materials need to be further verified using a higher-level theory. In principle, however, nanostructuring of materials with nonzero bandgaps could nevertheless allow them to perform as electrocatalysts.

We note that our conclusions are similar under alkaline operating conditions (pH 13), where 17 and 15 candidate materials are predicted to be stable for ORR and OER, respectively (see Table S2 for details).

In summary, starting from more than 11 000 predicted 2D materials, we found that only 21 and 14 materials are potentially stable under the operating conditions of ORR and OER, respectively. In particular, we found that no material is a stable conductor under ORR conditions and only NiO_3, AgO_2F, and $AgHO_2$ are stable conductors under OER conditions. This study vastly reduces the search space of 2D materials for electrochemical applications. The suggested materials can be further tested in experiments for their applicability as a catalyst or conductive support.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.9b00876.

Methodology of aqueous stability calculation (PDF)

Aqueous stabilities, GGA-electronic bandgaps, and cif-structure files of all materials (ZIP)

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Notes

The authors declare no competing financial interest.

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