*Electronic Supplementary Information*

# A general but still unknown characteristic of active oxygen evolution electrocatalysts†

Eleonora Romeo,[a] Francesc Illas,[a,*] and Federico Calle-Vallejo[b,c,*]

[a] Department of Materials Science and Chemical Physics & Institute of Theoretical and Computational Chemistry (IQTCUB), University of Barcelona, C/ Martí i Franquès 1, 08028 Barcelona, Spain.

[b] Nano-Bio Spectroscopy Group and European Theoretical Spectroscopy Facility (ETSF), Department of Polymers and Advanced Materials: Physics, Chemistry and Technology, University of the Basque Country UPV/EHU, Av. Tolosa 72, 20018 San Sebastián, Spain.

[c] IKERBASQUE, Basque Foundation for Science, Plaza de Euskadi 5, 48009 Bilbao, Spain.

*Corresponding authors: FI (francesc.illas@ub.edu) and FCV (federico.calle@ehu.es)

## Table of Contents

## S1. Data collected from the literature

We report in Tables S1 to S3 all the data collected from the literature, grouped by the number of electrochemical steps above 1.23 eV, i.e. $n = 1, 2, 3$. For each material, we specify the family it belongs to, as it is plotted in Figure 1 in the main text, with the relative color: $BaNiO_x$[1] in purple; single atom catalysts (SACs) [2,3] in light green; LSNMR[2] in brown; MO in light blue, $LaMO_3$ and $SrMO_3$[3–5] in red and dark green; $Sr_2MIrO_6$[6] in magenta; $Sr_xNa_yRuO_3$[7] in gray; undoped and doped $TiO_2$[8] in blue; porphyrins[9] in orange; and $MO_2$[4] in black.

The class of materials labelled $BaNiO_x$ includes two Ba-Ni-O phases, $BaNiO_2$ and $BaNiO_{2.78}$, with Ni atoms in square-planar and octahedral coordination, respectively.[1] SACs consist of 26 functionalized graphitic layers with $MN_4$ sites in which M = Cr, Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, Au. We note that there are two types of environments around those sites.[2,3] LSNMR is an acronym describing the double perovskite $La_{1.5}Sr_{0.5}NiMn_{0.5}Ru_{0.5}O_6$, a bifunctional OER/ORR catalyst belonging to the family of doped AA'BB'$O_6$ with different cations in the A and B sublattices, in this particular case La and Sr cations occupy the A and A' positions and Ni, Mn, and Ru cations occupy the B and B' positions.[2] MO are metal monoxides in the rock-salt geometry while $LaMO_3$ and $SrMO_3$ are perovskite oxides ($AMO_3$) with Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Ga and Ge in the M position. [3–5] As part of the perovskite family, we also report $Sr_2MIrO_6$ which is a double perovskite,[6] and $Sr_xNa_yRuO_3$[7] which is a Na-doped ruthenium perovskite. The category "doped $TiO_2$" is composed of rutile $TiO_2$(110) with and without surface doping of V, Nb, Ta, Cr, Mo, W, Mn, Fe, Ru, Ir and Ni.[10] The porphyrin catalysts considered here have Cr, Mn, Fe, Co, Ni and Cu as metal center and -H, -F, -OH, $-NH_2$, $-CH_3$, and $-BH_2$ as ring ligands.[11] Lastly, we considered some dioxide materials, $MO_2$.[6]

**Table S1.** Free adsorption energy of adsorption (in eV) of *O, *OH and *OOH, *ESSI* (in V), a metric for the breaking of the *OOH-*OH scaling relation $\gamma_{OOH/OH}$ (in V), OER overpotential $\eta_{OER}$ for materials with $n = 1$, I and II are 1.23 and 1.60 V vs RHE, respectively.

| Material | family | $\Delta G_O$ | $\Delta G_{OH}$ | $\Delta G_{OOH}$ | *ESSI* | $\gamma_{OOH/OH}$ | $\eta_{OER}$ | $G_{max}(I)$ | $G_{max}(II)$ | span |
|---|---|---|---|---|---|---|---|---|---|---|
| V-$TiO_2$ (6cM) | u/d $TiO_2$ | 2.76 | 0.38 | 3.97 | 1.15 | 0.57 | 1.15 | 1.15 | 0.78 | 8 |
| V-$TiO_2$ (6cM) | u/d $TiO_2$ | 3.40 | 1.02 | 4.56 | 1.15 | 0.54 | 1.15 | 1.15 | 0.78 | 8 |
| V-$TiO_2$ (6cM) | u/d $TiO_2$ | 3.46 | 1.12 | 4.63 | 1.11 | 0.53 | 1.11 | 1.11 | 0.74 | 8 |
| Nb-$TiO_2$ (6cM) | u/d $TiO_2$ | 2.69 | 0.29 | 3.80 | 1.17 | 0.53 | 1.17 | 1.17 | 0.80 | 8 |
| Mo-$TiO_2$ (5cM) | u/d $TiO_2$ | 0.49 | 0.42 | 3.72 | 2.00 | 0.42 | 2.00 | 2.00 | 1.63 | 5 |
| Mo-$TiO_2$ (5cM) | u/d $TiO_2$ | 1.46 | 0.61 | 4.16 | 1.47 | 0.55 | 1.47 | 1.47 | 1.10 | 5 |
| Mo-$TiO_2$ (6cM) | u/d $TiO_2$ | 0.86 | 0.28 | 3.83 | 1.74 | 0.55 | 1.74 | 1.74 | 1.37 | 5 |
| W-$TiO_2$ (5cM) | u/d $TiO_2$ | 0.42 | 0.34 | 3.90 | 2.25 | 0.55 | 2.25 | 2.25 | 1.88 | 5 |
| Ru-$TiO_2$ (5cM) | u/d $TiO_2$ | 2.15 | 1.05 | 4.19 | 0.81 | 0.34 | 0.81 | 0.81 | 0.44 | 5 |
| Mn-F | porphyrins | 1.13 | 0.46 | 3.70 | 1.34 | 0.39 | 1.34 | 1.34 | 0.97 | 5 |
| Mn-$BH_2$ | porphyrins | 1.41 | 0.75 | 3.94 | 1.30 | 0.37 | 1.30 | 1.30 | 0.93 | 5 |
| Fe-H | porphyrins | 1.19 | 0.63 | 3.77 | 1.35 | 0.34 | 1.35 | 1.35 | 0.98 | 5 |
| Fe-F | porphyrins | 1.37 | 0.68 | 3.85 | 1.25 | 0.36 | 1.25 | 1.25 | 0.88 | 5 |
| Fe-$CH_3$ | porphyrins | 1.10 | 0.57 | 3.73 | 1.40 | 0.35 | 1.40 | 1.40 | 1.03 | 5 |
| Fe-$BH_2$ | porphyrins | 1.51 | 0.88 | 4.09 | 1.35 | 0.38 | 1.35 | 0.56 | 0.19 | 5 |
| Co-H | porphyrins | 2.30 | 1.21 | 4.09 | 0.56 | 0.21 | 0.56 | 0.89 | 0.52 | 5 |
| Co-F | porphyrins | 1.97 | 1.04 | 4.09 | 0.89 | 0.30 | 0.89 | 1.07 | 0.70 | 5 |
| Co-OH | porphyrins | 1.65 | 0.88 | 3.95 | 1.07 | 0.31 | 1.07 | 0.70 | 0.33 | 5 |
| Co-$CH_3$ | porphyrins | 2.14 | 1.00 | 4.07 | 0.70 | 0.31 | 0.70 | 1.37 | 1.00 | 5 |
| Co-$NH_2$ | porphyrins | 1.26 | 0.77 | 3.86 | 1.37 | 0.32 | 1.37 | 1.84 | 1.47 | 5 |
| $SrCrO_3$ | $SrMO_3$ | 0.92 | 0.75 | 3.99 | 1.84 | 0.39 | 1.84 | 0.89 | 0.52 | 5 |
| $SrMnO_3$ | $SrMO_3$ | 2.29 | 1.21 | 4.41 | 0.89 | 0.37 | 0.89 | 0.60 | 0.23 | 5 |
| $SrRuO_3$ | $SrMO_3$ | 2.26 | 1.11 | 4.09 | 0.60 | 0.26 | 0.60 | 1.77 | 1.40 | 2 |
| $LaCrO_3$ | $LaMO_3$ | 0.69 | 0.56 | 3.69 | 1.77 | 0.34 | 1.77 | 1.23 | 0.86 | 5 |
| $LaMnO_3$ | $LaMO_3$ | 1.39 | 0.65 | 3.85 | 1.23 | 0.37 | 1.23 | 0.64 | 0.27 | 5 |
| $LaRuO_3$ | $LaMO_3$ | 1.87 | 0.74 | 3.74 | 0.64 | 0.27 | 0.64 | 0.71 | 0.34 | 5 |
| CoO | MO | 1.98 | 0.78 | 3.92 | 0.71 | 0.34 | 0.71 | 0.96 | 0.59 | 5 |
| Mn-FGM | SACs | 1.89 | 0.88 | 4.08 | 0.96 | 0.37 | 0.96 | 0.77 | 0.40 | 5 |
| Fe-FGM | SACs | 2.11 | 1.03 | 4.11 | 0.77 | 0.31 | 0.77 | 0.48 | 0.11 | 8 |
| Co-FGM | SACs | 2.93 | 1.22 | 4.11 | 0.48 | 0.22 | 0.48 | 0.93 | 0.56 | 8 |
| LSNMR@Mn | LSNMR | 3.12 | 0.96 | 4.08 | 0.93 | 0.33 | 0.93 | 0.64 | 0.27 | 5 |
| $PtO_2$ | rutiles | 2.35 | 1.21 | 4.22 | 0.64 | 0.28 | 0.64 | 1.35 | 0.98 | 5 |

**Table S2.** Free adsorption energy of adsorption (in eV) of *O, *OH and *OOH, *ESSI* (in V), a metric for the breaking of the *OOH-*OH scaling relation $\gamma_{OOH/OH}$ (in V), OER overpotential $\eta_{OER}$ for materials with $n = 2$, I and II are 1.23 and 1.60 V vs RHE, respectively.

| material | family | $\Delta G_O$ | $\Delta G_{OH}$ | $\Delta G_{OOH}$ | *ESSI* | $\gamma_{OOH/OH}$ | $\eta_{OER}$ | $G_{max}(I)$ | $G_{max}(II)$ | span |
|---|---|---|---|---|---|---|---|---|---|---|
| $TiO_2$ | u/d $TiO_2$ | 4.60 | 2.07 | 5.08 | 1.07 | 0.28 | 1.30 | 2.14 | 1.40 | 9 |
| V-$TiO_2$ (5cM) | u/d $TiO_2$ | 2.35 | 1.38 | 4.50 | 0.54 | 0.33 | 0.92 | 0.92 | 0.55 | 5 |
| V-$TiO_2$ (5cM) | u/d $TiO_2$ | 3.17 | 1.18 | 4.67 | 0.52 | 0.52 | 0.76 | 1.03 | 0.39 | 6 |
| Nb-$TiO_2$ (5cM) | u/d $TiO_2$ | 2.14 | 0.23 | 3.74 | 0.53 | 0.53 | 0.68 | 1.05 | 0.31 | 6 |
| Nb-$TiO_2$ (6cM) | u/d $TiO_2$ | 2.38 | 0.05 | 3.59 | 0.60 | 0.54 | 1.10 | 1.18 | 0.73 | 3 |
| Ta-$TiO_2$ (6cM) | u/d $TiO_2$ | 2.17 | -0.35 | 3.37 | 0.81 | 0.63 | 1.29 | 1.58 | 0.92 | 3 |
| Ta-$TiO_2$ (6cM) | u/d $TiO_2$ | 2.55 | 0.13 | 3.64 | 0.62 | 0.53 | 1.20 | 1.20 | 0.83 | 8 |
| Cr-$TiO_2$ (5cM) | u/d $TiO_2$ | 2.43 | 1.85 | 4.87 | 0.92 | 0.28 | 1.21 | 1.21 | 0.84 | 5 |
| Cr-$TiO_2$ (6cM) | u/d $TiO_2$ | 2.91 | 1.23 | 4.76 | 0.54 | 0.54 | 0.62 | 1.07 | 0.33 | 6 |
| Cr-$TiO_2$ (6cM) | u/d $TiO_2$ | 4.14 | 1.72 | 5.23 | 0.84 | 0.53 | 1.19 | 1.68 | 0.94 | 9 |
| Cr-$TiO_2$ (6cM) | u/d $TiO_2$ | 3.84 | 1.56 | 5.04 | 0.69 | 0.51 | 1.05 | 1.38 | 0.68 | 9 |
| Mo-$TiO_2$ (6cM) | u/d $TiO_2$ | 2.18 | 0.62 | 4.17 | 0.55 | 0.55 | 0.76 | 1.09 | 0.39 | 6 |
| Mo-$TiO_2$ (6cM) | u/d $TiO_2$ | 2.35 | 0.58 | 4.10 | 0.53 | 0.53 | 0.54 | 1.06 | 0.32 | 6 |
| W-$TiO_2$ (5cM) | u/d $TiO_2$ | -0.33 | -0.23 | 3.16 | 1.40 | 0.47 | 2.26 | 2.79 | 2.05 | 2 |
| W-$TiO_2$ (6cM) | u/d $TiO_2$ | 0.26 | 0.05 | 3.50 | 1.10 | 0.50 | 2.01 | 2.20 | 1.64 | 2 |
| W-$TiO_2$ (6cM) | u/d $TiO_2$ | 1.16 | 0.05 | 3.60 | 0.65 | 0.55 | 1.21 | 1.30 | 0.84 | 2 |
| W-$TiO_2$ (6cM) | u/d $TiO_2$ | 1.46 | 0.21 | 3.71 | 0.52 | 0.52 | 1.02 | 1.04 | 0.65 | 6 |
| Mn-$TiO_2$ (5cM) | u/d $TiO_2$ | 4.22 | 2.06 | 5.07 | 0.88 | 0.28 | 0.93 | 1.76 | 1.02 | 9 |
| Mn-$TiO_2$ (6cM) | u/d $TiO_2$ | 4.20 | 1.94 | 5.09 | 0.87 | 0.35 | 1.03 | 1.74 | 1.00 | 9 |
| Mn-$TiO_2$ (6cM) | u/d $TiO_2$ | 4.50 | 2.01 | 5.07 | 1.02 | 0.30 | 1.26 | 2.04 | 1.30 | 9 |
| Mn-$TiO_2$ (6cM) | u/d $TiO_2$ | 4.48 | 2.01 | 5.10 | 1.01 | 0.32 | 1.24 | 2.02 | 1.28 | 9 |
| Fe-$TiO_2$ (5cM) | u/d $TiO_2$ | 3.73 | 2.10 | 4.95 | 0.64 | 0.20 | 0.87 | 1.27 | 0.53 | 9 |
| Fe-$TiO_2$ (5cM) | u/d $TiO_2$ | 4.31 | 2.16 | 5.10 | 0.93 | 0.24 | 0.93 | 1.85 | 1.11 | 9 |
| Fe-$TiO_2$ (6cM) | u/d $TiO_2$ | 3.98 | 1.55 | 5.06 | 0.76 | 0.53 | 1.20 | 1.52 | 0.83 | 9 |
| Fe-$TiO_2$ (5cM) | u/d $TiO_2$ | 3.88 | 1.50 | 4.94 | 0.71 | 0.49 | 1.15 | 1.42 | 0.78 | 9 |
| Ru-$TiO_2$ (6cM) | u/d $TiO_2$ | 2.98 | 0.49 | 4.53 | 0.79 | 0.79 | 1.26 | 1.58 | 0.89 | 6 |
| Ru-$TiO_2$ (6cM) | u/d $TiO_2$ | 3.83 | 1.42 | 4.96 | 0.69 | 0.54 | 1.18 | 1.37 | 0.81 | 9 |
| Ru-$TiO_2$ (6cM) | u/d $TiO_2$ | 3.90 | 1.47 | 4.95 | 0.72 | 0.51 | 1.20 | 1.44 | 0.83 | 9 |
| Ir-$TiO_2$ (5cM) | u/d $TiO_2$ | 1.81 | 0.61 | 3.68 | 0.33 | 0.31 | 0.64 | 0.65 | 0.27 | 2 |
| Ir-$TiO_2$ (5cM) | u/d $TiO_2$ | 3.45 | 1.75 | 4.68 | 0.50 | 0.24 | 0.52 | 0.99 | 0.25 | 7 |
| Ir-$TiO_2$ (6cM) | u/d $TiO_2$ | 2.72 | 1.13 | 4.64 | 0.53 | 0.53 | 0.69 | 1.05 | 0.32 | 6 |
| Ir-$TiO_2$ (6cM) | u/d $TiO_2$ | 3.78 | 1.44 | 4.94 | 0.66 | 0.52 | 1.11 | 1.32 | 0.74 | 9 |
| Ir-$TiO_2$ (6cM) | u/d $TiO_2$ | 3.64 | 1.35 | 4.86 | 0.59 | 0.53 | 1.06 | 1.18 | 0.69 | 9 |
| Ni-$TiO_2$ (5cM) | u/d $TiO_2$ | 4.55 | 2.03 | 4.80 | 1.05 | 0.16 | 1.29 | 2.09 | 1.35 | 9 |
| Ni-$TiO_2$ (5cM) | u/d $TiO_2$ | 4.59 | 2.39 | 5.12 | 1.06 | 0.14 | 1.16 | 2.13 | 1.39 | 9 |
| Ni-$TiO_2$ (6cM) | u/d $TiO_2$ | 4.27 | 2.03 | 5.31 | 0.91 | 0.41 | 1.01 | 1.81 | 1.07 | 9 |
| Ni-$TiO_2$ (6cM) | u/d $TiO_2$ | 4.57 | 2.08 | 5.08 | 1.06 | 0.27 | 1.26 | 2.11 | 1.37 | 9 |
| Ni-$TiO_2$ (6cM) | u/d $TiO_2$ | 4.47 | 2.04 | 5.06 | 1.01 | 0.28 | 1.20 | 2.01 | 1.27 | 9 |
| Cr-H | porphyrins | 0.85 | 0.26 | 3.53 | 0.81 | 0.41 | 1.45 | 1.61 | 1.08 | 2 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Cr-F | porphyrins | 1.00 | 0.38 | 3.63 | 0.73 | 0.40 | 1.40 | 1.46 | 1.03 | 2 |
| Cr-OH | porphyrins | 0.76 | 0.22 | 3.49 | 0.85 | 0.41 | 1.50 | 1.70 | 1.13 | 2 |
| Cr-$CH_3$ | porphyrins | 0.61 | 0.18 | 3.33 | 0.93 | 0.35 | 1.49 | 1.85 | 1.12 | 2 |
| Cr-$BH_2$ | porphyrins | 0.94 | 0.36 | 3.58 | 0.76 | 0.38 | 1.41 | 1.52 | 1.04 | 2 |
| Cr-$NH_2$ | porphyrins | 0.60 | 0.10 | 3.33 | 0.93 | 0.39 | 1.50 | 1.86 | 1.13 | 2 |
| Mn-H | porphyrins | 0.93 | 0.27 | 3.53 | 0.77 | 0.40 | 1.37 | 1.53 | 1.00 | 2 |
| Mn-OH | porphyrins | 0.74 | 0.23 | 3.51 | 0.86 | 0.41 | 1.54 | 1.72 | 1.17 | 2 |
| Mn-$CH_3$ | porphyrins | 0.74 | 0.18 | 3.39 | 0.86 | 0.38 | 1.42 | 1.72 | 1.05 | 2 |
| Mn-$NH_2$ | porphyrins | 0.46 | -0.05 | 3.18 | 1.00 | 0.39 | 1.49 | 2.00 | 1.26 | 2 |
| Fe-OH | porphyrins | 1.07 | 0.48 | 3.62 | 0.70 | 0.34 | 1.32 | 1.39 | 0.95 | 2 |
| Fe-$NH_2$ | porphyrins | 0.89 | 0.34 | 3.45 | 0.79 | 0.33 | 1.33 | 1.57 | 0.96 | 2 |
| Co-$BH_2$ | porphyrins | 2.47 | 1.24 | 4.29 | 0.30 | 0.30 | 0.59 | 0.60 | 0.22 | 7 |
| Ni-H | porphyrins | 3.66 | 1.82 | 4.85 | 0.60 | 0.29 | 0.61 | 1.20 | 0.46 | 9 |
| Ni-$CH_3$ | porphyrins | 3.82 | 1.84 | 4.60 | 0.68 | 0.15 | 0.75 | 1.36 | 0.62 | 9 |
| Ni-$BH_2$ | porphyrins | 3.85 | 1.93 | 4.78 | 0.70 | 0.20 | 0.70 | 1.39 | 0.65 | 9 |
| Cu-H | porphyrins | 4.12 | 2.07 | 5.07 | 0.83 | 0.27 | 0.84 | 1.66 | 0.92 | 9 |
| Cu-F | porphyrins | 4.15 | 2.04 | 5.01 | 0.85 | 0.26 | 0.88 | 1.69 | 0.95 | 9 |
| Cu-$CH_3$ | porphyrins | 3.76 | 1.83 | 4.89 | 0.65 | 0.30 | 0.70 | 1.30 | 0.56 | 9 |
| Cu-$BH_2$ | porphyrins | 4.61 | 1.78 | 4.99 | 1.08 | 0.37 | 1.61 | 2.15 | 1.41 | 9 |
| Cu-$NH_2$ | porphyrins | 2.69 | 0.92 | 4.48 | 0.55 | 0.55 | 0.56 | 1.10 | 0.36 | 6 |
| $SrScO_3$ | $SrMO_3$ | 5.23 | 2.38 | 5.21 | 1.39 | 0.19 | 1.62 | 2.77 | 2.03 | 9 |
| $SrTiO_3$ | $SrMO_3$ | 3.91 | 1.61 | 4.90 | 0.73 | 0.42 | 1.07 | 1.45 | 0.71 | 9 |
| $SrVO_3$ | $SrMO_3$ | -0.07 | 0.13 | 3.35 | 1.27 | 0.38 | 2.19 | 2.53 | 1.82 | 2 |
| $SrNiO_3$ | $SrMO_3$ | 3.84 | 2.17 | 4.92 | 0.69 | 0.15 | 0.94 | 1.38 | 0.64 | 9 |
| $SrCuO_3$ | $SrMO_3$ | 4.75 | 2.32 | 5.31 | 1.15 | 0.27 | 1.20 | 2.29 | 1.55 | 9 |
| $SrZnO_3$ | $SrMO_3$ | 5.16 | 2.56 | 5.40 | 1.35 | 0.19 | 1.37 | 2.70 | 1.96 | 9 |
| $SrGeO_3$ | $SrMO_3$ | 4.44 | 1.74 | 5.22 | 0.99 | 0.51 | 1.47 | 1.98 | 1.24 | 9 |
| $LaScO_3$ | $LaMO_3$ | 4.80 | 1.82 | 4.88 | 1.17 | 0.30 | 1.75 | 2.34 | 1.60 | 9 |
| $LaTiO_3$ | $LaMO_3$ | -1.82 | -1.16 | 2.23 | 2.14 | 0.47 | 2.82 | 4.28 | 3.54 | 2 |
| $LaVO_3$ | $LaMO_3$ | -0.74 | -0.22 | 2.95 | 1.60 | 0.36 | 2.46 | 3.20 | 2.46 | 2 |
| $LaCoO_3$ | $LaMO_3$ | 2.22 | 1.49 | 4.50 | 0.66 | 0.28 | 1.05 | 1.05 | 0.68 | 5 |
| $LaCuO_3$ | $LaMO_3$ | 4.92 | 2.42 | 5.39 | 1.23 | 0.26 | 1.27 | 2.46 | 1.72 | 9 |
| $LaZnO_3$ | $LaMO_3$ | 5.18 | 2.48 | 5.27 | 1.36 | 0.17 | 1.47 | 2.72 | 1.98 | 9 |
| $LaGaO_3$ | $LaMO_3$ | 4.88 | 1.95 | 5.02 | 1.21 | 0.31 | 1.70 | 2.42 | 1.68 | 9 |
| CaO | MO | 5.38 | 2.32 | 5.04 | 1.46 | 0.13 | 1.83 | 2.92 | 2.18 | 9 |
| ScO | MO | -0.90 | -1.52 | 1.98 | 1.68 | 0.52 | 1.71 | 3.36 | 2.62 | 2 |
| TiO | MO | -1.61 | -1.05 | 2.32 | 2.04 | 0.46 | 2.70 | 4.07 | 3.33 | 2 |
| VO | MO | -0.94 | -0.71 | 2.56 | 1.70 | 0.41 | 2.27 | 3.40 | 2.66 | 2 |
| CrO | MO | 0.22 | -0.13 | 2.90 | 1.12 | 0.29 | 1.45 | 2.24 | 1.50 | 2 |
| MnO | MO | 1.42 | 0.42 | 3.66 | 0.52 | 0.39 | 1.01 | 1.04 | 0.64 | 2 |
| FeO | MO | 1.76 | 0.38 | 3.75 | 0.46 | 0.46 | 0.76 | 0.91 | 0.39 | 6 |
| NiO | MO | 2.49 | 1.03 | 4.12 | 0.32 | 0.32 | 0.40 | 0.63 | 0.03 | 6 |
| CuO | MO | 3.93 | 2.00 | 4.75 | 0.74 | 0.15 | 0.77 | 1.47 | 0.73 | 9 |
| Cr-FGM | SACs | 0.89 | 0.35 | 3.60 | 0.79 | 0.40 | 1.48 | 1.57 | 1.11 | 2 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Ni-FGM | SACs | 4.16 | 2.14 | 4.91 | 0.85 | 0.16 | 0.91 | 1.70 | 0.96 | 9 |
| Cu-FGM | SACs | 4.52 | 2.31 | 5.11 | 1.03 | 0.17 | 1.08 | 2.06 | 1.32 | 9 |
| Ru-FGM | SACs | 1.72 | 0.58 | 3.63 | 0.37 | 0.30 | 0.68 | 0.74 | 0.31 | 2 |
| Rh-FGM | SACs | 2.84 | 1.23 | 4.19 | 0.25 | 0.25 | 0.38 | 0.50 | 0.01 | 6 |
| Pd-FGM | SACs | 4.65 | 2.50 | 5.08 | 1.10 | 0.06 | 1.27 | 2.19 | 1.45 | 9 |
| Ag-FGM | SACs | 4.77 | 2.52 | 5.12 | 1.16 | 0.07 | 1.29 | 2.31 | 1.57 | 9 |
| Ir-FGM | SACs | 2.41 | 1.24 | 4.26 | 0.32 | 0.28 | 0.62 | 0.62 | 0.25 | 5 |
| Pt-FGM | SACs | 4.61 | 2.42 | 5.11 | 1.08 | 0.12 | 1.19 | 2.15 | 1.41 | 9 |
| Au-FGM | SACs | 4.84 | 2.62 | 5.11 | 1.19 | 0.02 | 1.39 | 2.38 | 1.64 | 9 |
| $BaNiO_3$ | $BaNiO_x$ | 3.88 | 1.87 | 4.99 | 0.71 | 0.33 | 0.78 | 1.42 | 0.68 | 9 |
| $BaNiO_{3-d2}$ | $BaNiO_x$ | 3.94 | 1.78 | 5.15 | 0.74 | 0.46 | 0.93 | 1.48 | 0.74 | 9 |
| $Sr_5Na_2Ru_8O_{24}$ | $Sr_xNa_yRuO_3$ | 2.66 | 0.94 | 4.34 | 0.47 | 0.47 | 0.49 | 0.94 | 0.20 | 6 |
| LSNMR@Ni | LSNMR | 3.71 | 1.47 | 4.41 | 0.63 | 0.24 | 1.01 | 1.25 | 0.64 | 9 |
| LSNMR@Ru | LSNMR | 2.27 | 0.54 | 3.89 | 0.45 | 0.45 | 0.50 | 0.89 | 0.15 | 6 |
| $Sr_2NiIrO_6$ | $Sr_2MIrO_6$ | 2.12 | 0.77 | 3.25 | 0.28 | 0.01 | 0.44 | 0.46 | 0.07 | 3 |
| $Sr_2ScIrO_6$ | $Sr_2MIrO_6$ | 1.48 | 0.41 | 3.50 | 0.49 | 0.32 | 0.79 | 0.98 | 0.42 | 2 |
| $Sr_2FeIrO_6$ | $Sr_2MIrO_6$ | 1.51 | 0.30 | 3.50 | 0.47 | 0.37 | 0.75 | 0.95 | 0.38 | 2 |

**Table S3.** Free adsorption energy of adsorption (in eV) of *O, *OH and *OOH, *ESSI* (in V), a metric for the breaking of the *OOH-*OH scaling relation $\gamma_{OOH/OH}$ (in V), OER overpotential $\eta_{OER}$ for materials with $n = 3$, I and II are 1.23 and 1.60 V vs RHE, respectively.

| material | family | $\Delta G_O$ | $\Delta G_{OH}$ | $\Delta G_{OOH}$ | *ESSI* | $\gamma_{OOH/OH}$ | $\eta_{OER}$ | $G_{max}(I)$ | $G_{max}(II)$ | span |
|---|---|---|---|---|---|---|---|---|---|---|
| Nb-$TiO_2$ (5cM) | u/d $TiO_2$ | 1.38 | -0.08 | 3.39 | 0.44 | 0.51 | 0.78 | 1.31 | 0.41 | 3 |
| Nb-$TiO_2$ (6cM) | u/d $TiO_2$ | 2.33 | 0.10 | 3.61 | 0.38 | 0.53 | 1.00 | 1.13 | 0.63 | 3 |
| Ta-$TiO_2$ (5cM) | u/d $TiO_2$ | 1.50 | -0.51 | 3.04 | 0.58 | 0.55 | 0.78 | 1.74 | 0.63 | 3 |
| Ta-$TiO_2$ (5cM) | u/d $TiO_2$ | 1.86 | -0.02 | 3.52 | 0.42 | 0.54 | 0.65 | 1.25 | 0.34 | 3 |
| Ta-$TiO_2$ (6cM) | u/d $TiO_2$ | 2.33 | 0.07 | 3.60 | 0.39 | 0.54 | 1.03 | 1.16 | 0.66 | 3 |
| Cr-$TiO_2$ (5cM) | u/d $TiO_2$ | 3.44 | 1.61 | 5.14 | 0.48 | 0.54 | 0.60 | 1.45 | 0.34 | 7 |
| Mn-$TiO_2$ (5cM) | u/d $TiO_2$ | 3.38 | 1.92 | 4.82 | 0.38 | 0.22 | 0.69 | 1.13 | 0.32 | 7 |
| Fe-$TiO_2$ (6cM) | u/d $TiO_2$ | 3.81 | 1.55 | 5.06 | 0.46 | 0.53 | 1.03 | 1.37 | 0.66 | 7 |
| Ru-$TiO_2$ (5cM) | u/d $TiO_2$ | 3.55 | 1.73 | 5.12 | 0.48 | 0.47 | 0.59 | 1.43 | 0.35 | 7 |
| Ni-F | porphyrins | 3.43 | 1.85 | 4.93 | 0.41 | 0.31 | 0.62 | 1.24 | 0.25 | 7 |
| Ni-OH | porphyrins | 3.21 | 1.58 | 4.78 | 0.36 | 0.37 | 0.40 | 1.09 | 0.03 | 7 |
| Ni-$NH_2$ | porphyrins | 3.10 | 1.32 | 4.46 | 0.26 | 0.34 | 0.55 | 0.77 | 0.18 | 7 |
| Cu-OH | porphyrins | 3.69 | 1.62 | 4.94 | 0.42 | 0.43 | 0.84 | 1.25 | 0.49 | 7 |
| $SrFeO_3$ | $SrMO_3$ | 2.98 | 1.67 | 4.70 | 0.34 | 0.29 | 0.49 | 1.01 | 0.12 | 7 |
| $SrCoO_3$ | $SrMO_3$ | 3.00 | 1.54 | 4.44 | 0.25 | 0.22 | 0.31 | 0.75 | -0.06 | 7 |
| $LaFeO_3$ | $LaMO_3$ | 2.74 | 1.25 | 4.55 | 0.29 | 0.42 | 0.58 | 0.86 | 0.21 | 7 |
| $LaNiO_3$ | $LaMO_3$ | 3.09 | 1.54 | 4.61 | 0.31 | 0.31 | 0.32 | 0.92 | -0.05 | 7 |
| $BaNiO_{3\text{-}d1}$ | $BaNiO_x$ | 3.54 | 1.93 | 5.00 | 0.44 | 0.31 | 0.70 | 1.31 | 0.34 | 7 |
| $BaNiO_2$ | $BaNiO_x$ | 3.46 | 1.85 | 4.78 | 0.36 | 0.24 | 0.62 | 1.09 | 0.26 | 7 |
| $Sr_{7/8}Na_{1/8}RuO_3$ | $Sr_xNa_yRuO_3$ | 3.16 | 1.56 | 4.43 | 0.25 | 0.21 | 0.37 | 0.74 | 0.00 | 7 |
| $Sr_{6/8}Na_{2/8}RuO_3$ | $Sr_xNa_yRuO_3$ | 3.31 | 1.59 | 4.76 | 0.36 | 0.36 | 0.49 | 1.07 | 0.12 | 7 |
| $Sr_7Ru_8O_{24}$ | $Sr_xNa_yRuO_3$ | 3.38 | 1.58 | 5.02 | 0.44 | 0.49 | 0.57 | 1.33 | 0.24 | 7 |
| $Sr_6Na_1Ru_8O_{24}$ | $Sr_xNa_yRuO_3$ | 3.44 | 1.62 | 4.79 | 0.37 | 0.36 | 0.59 | 1.10 | 0.24 | 7 |
| $IrO_2$ | rutiles | 1.65 | 0.29 | 3.45 | 0.31 | 0.35 | 0.57 | 0.94 | 0.20 | 3 |
| $RuO_2$ | rutiles | 2.72 | 1.35 | 4.35 | 0.22 | 0.27 | 0.40 | 0.66 | 0.03 | 7 |
| $MnO_2$ | rutiles | 3.20 | 1.84 | 5.04 | 0.45 | 0.37 | 0.61 | 1.35 | 0.24 | 7 |
| $Sr_2CoIrO_6$ | $Sr_2MIrO_6$ | 1.63 | 0.00 | 3.40 | 0.41 | 0.47 | 0.54 | 1.23 | 0.20 | 3 |

**S2. Free-energy span model**

The potential-dependent free-energy spans are calculated on the basis of the adsorption energies of *O, *OH and *OOH as follows:[10]

$$span_1(U) = \Delta G_{O_2}(U) - \Delta G_{OOH}(U) \quad \text{(S1)}$$

$$span_2(U) = \Delta G_{O_2}(U) - \Delta G_{O}(U) \quad \text{(S2)}$$

$$span_3(U) = \Delta G_{O_2}(U) - \Delta G_{OH}(U) \quad \text{(S3)}$$

$$span_4(U) = \Delta G_{O_2}(U) - \Delta G_{H_2O}(U) \quad \text{(S4)}$$

$$span_5(U) = \Delta G_{OOH}(U) - \Delta G_{O}(U) \quad \text{(S5)}$$

$$span_6 = \Delta G_{OOH}(U) - \Delta G_{OH}(U) \quad \text{(S6)}$$

$$span_7(U) = \Delta G_{OOH}(U) - \Delta G_{H_2O}(U) \quad \text{(S7)}$$

$$span_8(U) = \Delta G_{O}(U) - \Delta G_{OH}(U) \quad \text{(S8)}$$

$$span_9(U) = \Delta G_{O}(U) - \Delta G_{H_2O}(U) \quad \text{(S9)}$$

$$span_{10}(U) = \Delta G_{OH}(U) - \Delta G_{H_2O}(U) \quad \text{(S10)}$$

where $\Delta G_{H_2O} = 0$ at all potentials and $\Delta G_{O_2} = 4.92\ eV$ at 0 V vs RHE. The effect of the potential on the adsorption energies is evaluated by means of the computational hydrogen electrode.[11] The descriptor $G_{max}(\eta)$ is calculated as the largest positive span in Equations S1-S10:

$$G_{max}(\eta) = \max\left(span_i(U)\right) \quad \text{(S11)}$$

## References


1 M. Retuerto, F. Calle-Vallejo, L. Pascual, P. Ferrer, Á. García, J. Torrero, D. Gianolio, J. L. G. Fierro, M. A. Peña, J. A. Alonso and S. Rojas, Role of lattice oxygen content and Ni geometry in the oxygen evolution activity of the Ba-Ni-O system, *J. Power Sources*, 2018, **404**, 56–63.

2 M. Retuerto, F. Calle-Vallejo, L. Pascual, G. Lumbeeck, M. T. Fernandez-Diaz, M. Croft, J. Gopalakrishnan, M. A. Peña, J. Hadermann, M. Greenblatt and S. Rojas, La1.5Sr0.5NiMn0.5Ru0.5O6 Double Perovskite with Enhanced ORR/OER Bifunctional Catalytic Activity, *ACS Appl. Mater. Interfaces*, 2019, **11**, 21454–21464.

3 F. Calle-Vallejo, N. G. Inoglu, H. Y. Su, J. I. Martínez, I. C. Man, M. T. M. Koper, J. R. Kitchin and J. Rossmeisl, Number of outer electrons as descriptor for adsorption processes on transition metals and their oxides, *Chem. Sci.*, 2013, **4**, 1245–1249.

4 I. C. Man, H. Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martínez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov and J. Rossmeisl, Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces, *ChemCatChem*, 2011, **3**, 1159–1165.

5 F. Calle-Vallejo, O. A. Díaz-Morales, M. J. Kolb and M. T. M. Koper, Why is bulk thermochemistry a good descriptor for the electrocatalytic activity of transition metal oxides?, *ACS Catal*, 2015, **5**, 869–873.

6 M. Retuerto, L. Pascual, O. Piqué, P. Kayser, M. A. Salam, M. Mokhtar, J. A. Alonso, M. Peña, F. Calle-Vallejo and S. Rojas, How oxidation state and lattice distortion influence the oxygen evolution activity in acid of iridium double perovskites, *J. Mater. Chem. A*, 2021, **9**, 2980–2990.

7 M. Retuerto, L. Pascual, F. Calle-Vallejo, P. Ferrer, D. Gianolio, A. G. Pereira, Á. García, J. Torrero, M. T. Fernández-Díaz, P. Bencok, M. A. Peña, J. L. G. Fierro and S. Rojas, Na-doped ruthenium perovskite electrocatalysts with improved oxygen evolution activity and durability in acidic media, *Nat. Commun. 2019 10:1*, 2019, **10**, 1–9.

8 M. García-Mota, A. Vojvodic, H. Metiu, I. C. Man, H. Y. Su, J. Rossmeisl and J. K. Nørskov, Tailoring the Activity for Oxygen Evolution Electrocatalysis on Rutile TiO2(110) by Transition-Metal Substitution, *ChemCatChem*, 2011, **3**, 1607–1611.

9 F. Calle-Vallejo, A. Krabbe and J. M. García-Lastra, How covalence breaks adsorption-energy scaling relations and solvation restores them, *Chem. Sci.*, 2016, **8**, 124–130.

10 S. Razzaq and K. S. Exner, Materials Screening by the Descriptor Gmax(η): The Free-Energy Span Model in Electrocatalysis, *ACS Catal.*, 2023, 1740–1758.

11 J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jónsson, Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode, *J. Phys. Chem. B*, 2004, **108**, 17886–17892.