

SUPPORTING INFORMATION

Hydrogen and Oxygen Evolution Reactions on Single Atom Catalysts Stabilized by a Covalent Organic Framework

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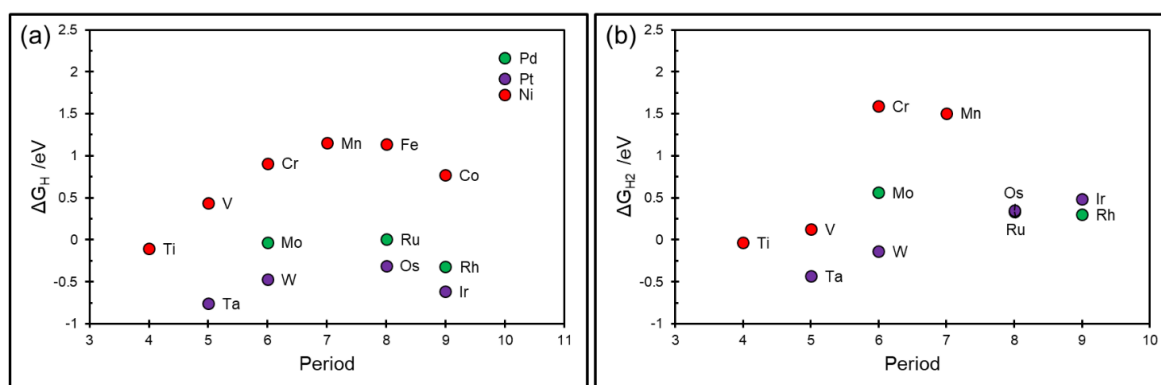
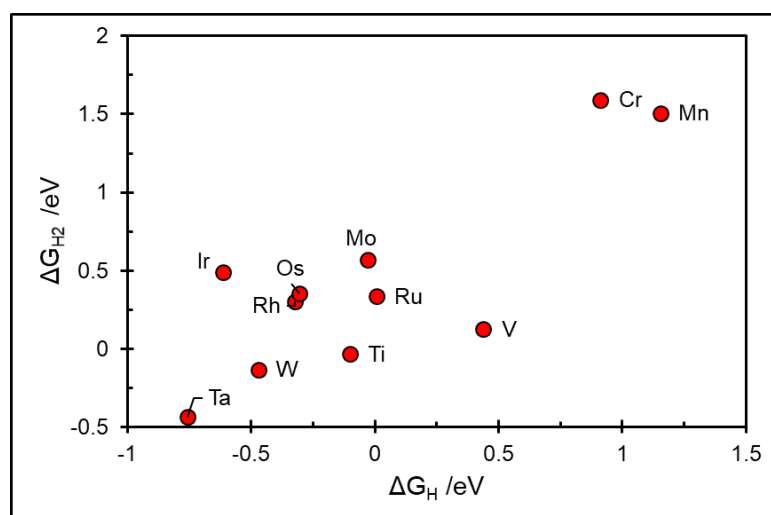


Figure S1: (a) Trend of reactivity to H* vs TM group in the periodic table, (b) Trend of reactivity to H₂* vs TM group in the periodic table.

Figure S2: Gibbs free energy of hydrogen complexes against that of H*.



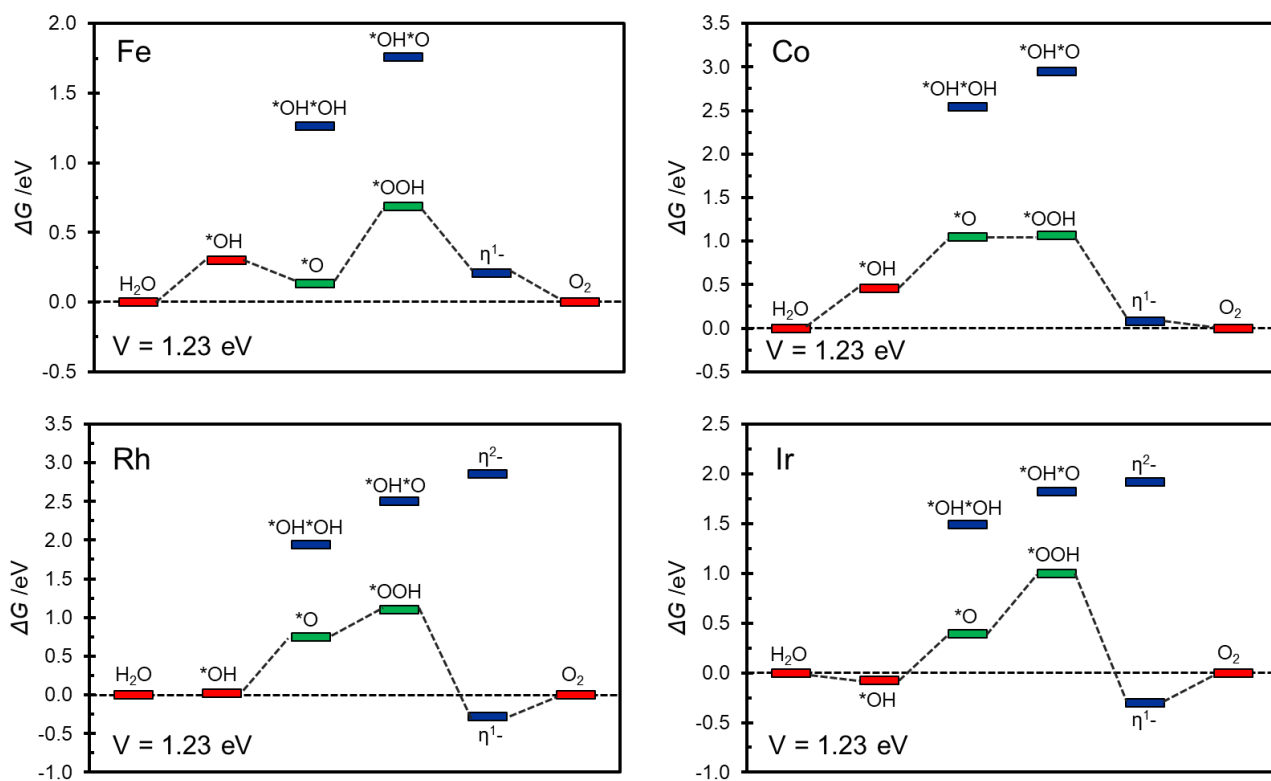


Figure S3: Gibbs Free Energy Profile of Fe, Co, Rh, and Ir SACs.

Table S1: Working entropic contributions of gas phase molecules at $T= 300\text{K}$.

Species	TS / eV
H ₂	0.41
O ₂	0.64
H ₂ O	0.67

Table S2: Calculated Zero-point energy of relevant reaction intermediates.

	ZPE _{OH*}	ZPE _{O*}	ZPE _{OOH*}	ZPE _{η1}	ZPE _{η2}	ZPE _{OH*OH*}	ZPE _{O*OH*}
Mo	0.31	0.06	0.40	0.11	0.14	0.69	0.41
Ru	0.32	0.05	0.42	0.13	0.10	0.69	0.41
Rh	0.32	0.04	0.43	0.13	0.08	0.68	0.39
Average	0.32	0.05	0.41	0.12	0.11	0.69	0.40

The zero point contribution of H* is often small, and typically value is 0.04 eV.¹

Table S3: Comparison of adhesion energies of different TMs on COF, N-doped graphene (4N-Gr) and carbon nitride (C₃N₄).

M	E _{ADH} (COF) /eV	E _{ADH} (4N-Gr) /eV	E _{ADH} (C ₃ N ₄) /eV
Ti	-10.46	-8.50	-6.28
V	-10.13	-7.86	-5.05
Cr	-9.36	-7.20	-3.57
Mn	-8.24	-6.80	-3.36
Fe	-8.93	-7.39	-3.45
Co	-9.27	-7.79	-3.34
Ni	-9.46	-7.78	-3.47
Pd	-8.39	-6.03	-2.24
Pt	-10.58	-7.99	-2.79

Table S4: Gibbs free energies and O-O distances of the most stable oxygen complex intermediates for OER on TM@COF.

M	ΔG /eV	d _{O-O} /Å	Isomer
<i>Ti</i>	1.27	1.46	η^2
<i>V</i>	--	--	--
<i>Cr</i>	4.53	1.29	η^1
<i>Mn</i>	4.71	1.30	η^1
<i>Fe</i>	5.12	1.28	η^1
<i>Co</i>	4.99	1.25	η^1
<i>Ni</i>	--	--	--
<i>Nb</i>	-0.02	2.58	η^2
<i>Mo</i>	0.76	2.55	η^2
<i>Ru</i>	4.38	1.29	η^1
<i>Rh</i>	4.63	1.27	η^1
<i>Pd</i>	--	--	--
<i>Ta</i>	-0.19	2.47	η^2
<i>W</i>	-0.43	2.60	η^2
<i>Os</i>	4.10	2.73	η^2
<i>Ir</i>	4.61	1.28	η^1
<i>Pt</i>	--	--	--

References

- 1 J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *J. Electrochem. Soc.*, 2005, **152**, J23.