Computational-experimental assessment of transition-metal doping of Co_3O_4 for acidic oxygen evolution reaction with balanced activity and stability

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Table S1 Parameters of doping elements.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronegativity	1.36	1.54	1.63	1.66	1.55	1.83	1.88	1.91	1.9	1.65
Ionic size (Å)	0.745	0.605	0.64	0.615	0.58	0.55	0.545 oct. 0.61 tetra.	0.56	0.73	0.74
$U-J$ (eV)	3.5	4.0	4.0	3.0	3.0	3.1	2.5	4.2	5.0	0.0
Starting magnetic moment (μB)	1.0 oct.	1.5 oct.	2.5 oct.	3.0 oct.	4.0 oct.	5.0 oct.	1.0 oct. 3.0 tetra.	1.0 oct.	1.0 tetra.	0.0 tetra.

Table S2 Lobster input file “lobsterin”.

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basisSet pbeVaspFit2015

# generate many Co–O / metal–metal / O–O pairs automatically up to 3.0 Å
cohpGenerator from 0.1 to 3.0

# write COHP curves and the integrated list
cohp
# (optional) energy window, adjust to your system if needed
COHPstartEnergy -100.0
COHPendEnergy   20

# density of states (optional)
dos
```

Table S3 Calculated formation energy and dissolution potential.

Dopant	Formation energy, E_f (eV)	Standard dissolution potential of bulk metal, U^0_{diss} (V)	Dissolution potential, U_{diss} (V vs. SHE)
Sc	-6.514	-2.08	0.09
Ti	-6.853	-1.63	0.08
V	-4.212	-1.18	-0.34
Cr	-4.090	-0.91	0.45
Mn	-1.977	-1.19	-0.70
Fe	-1.156	-0.45	-0.06
Co (pristine)	0	-0.28	-0.28
Ni	-0.282	-0.26	-0.12
Cu	0.460	0.34	0.11
Zn	0.601	-0.76	-1.06

Tabel S4 ZPE and $T\Delta S$ values.

Phase	ZPE (eV)	$T\Delta S$ (eV)
*	0	0
*O	0.05	0
*OH	0.37	0
*OOH	0.48	0
H_2O (l)	0.57	0.67
H_2 (g)	0.27	0.41

Table S5 Calculated binding energies of the *O, *OH, and *OOH intermediates in doped Co_3O_4.

Dopant	ΔG_{*OH} (eV)	ΔG_{*O} (eV)	ΔG_{*OOH} (eV)	$\Delta G_{*O} - \Delta G_{*OH}$ (eV)	$-\eta$ (V)
Sc	1.19	2.98	4.45	1.79	-0.56
Ti	1.96	3.72	4.89	1.76	-0.53
V	0.15	1.66	3.39	1.51	-0.5
Cr	1.25	2.77	4.36	1.52	-0.36
Mn	0.69	1.74	3.63	1.05	-0.66
Fe	1.14	2.41	3.91	1.27	-0.27
Co (pristine)	0.51	2.3	3.49	1.79	-0.49
Ni	1.39	2.95	4.68	1.56	-0.33
Cu	1.28	2.72	4.57	1.44	-0.62
Zn	0.81	3.06	4.05	2.25	-1.02

Table S6 Oxygen 2p-band center, metal M (dopant and Co) 3d-band center, Co-only 3d-band center, and associated covalency.

Dopant	O 2p-band center, ε_{O-p} (eV)	M (dopant and Co) 3d-band center, ε_{M-d} (eV)	Co 3d-band center, ε_{Co-d} (eV)	Covalency, $\varepsilon_{M-d} - \varepsilon_{O-p}$ (eV)	Covalency, $\varepsilon_{Co-d} - \varepsilon_{O-p}$ (eV)	$-\eta$ (V)
Sc	-5.010	-2.300	-2.280	2.710	2.730	-0.56
Ti	-5.136	-2.253	-2.282	2.882	2.854	-0.53
V	-5.283	-2.355	-2.328	2.928	2.956	-0.5
Cr	-5.191	-2.312	-2.308	2.879	2.883	-0.36
Mn	-4.940	-2.091	-2.047	2.849	2.894	-0.66
Fe	-5.155	-2.389	-2.295	2.766	2.859	-0.27
Co (pristine)	-4.768	-1.984	-1.984	2.784	2.784	-0.49
Ni	-4.970	-2.135	-2.162	2.836	2.809	-0.33
Cu	-4.904	-1.950	-1.973	2.954	2.931	-0.62
Zn	-5.046	-2.514	-2.301	2.532	2.745	-1.02

Table S7 Calculated averaged ICOHP values of O–H bond from the intermediates (*OH and *OOH), Co–O bond from the intermediates (*O, *OH, and *OOH) attached on active Co site, and M–O bonds (M is Co for the pristine sample) of doping element M with its all O neighbors.

Element M	$\mathrm{ICOHP}_{\mathrm{O-H}}$	$\mathrm{ICOHP}_{\mathrm{Co-O}}$	$\mathrm{ICOHP}_{\mathrm{M-O}}$
Sc	-3.793	-1.922	-1.482
Ti	-3.686	-2.032	-2.007
V	-3.807	-2.049	-2.102
Cr	-3.761	-2.034	-1.645
Mn	-3.665	-2.038	-1.383
Fe	-3.699	-2.041	-1.258
Co	-3.796	-1.976	-1.163
Ni	-3.759	-1.964	-1.002
Cu	-3.647	-1.985	-0.802
Zn	-3.884	-1.913	-0.688

Table S8 Calculated averaged bond length of O–H bond from the intermediates (*OH and *OOH), Co–O bond from the intermediates (*O, *OH, and *OOH) attached on the active Co site, and M–O bonds (M is Co for the pristine sample) of the doping element M with all its O neighbors.

Element M	O–H bond (Å)	Co–O bond (Å)	M–O bond (Å)
Sc	1.001	1.764	2.093
Ti	1.010	1.737	1.940
V	1.000	1.730	1.851
Cr	1.008	1.735	1.902
Mn	1.012	1.736	1.902
Fe	1.010	1.735	1.897
Co	1.002	1.752	1.915
Ni	1.003	1.753	1.912
Cu	1.013	1.753	2.004
Zn	0.990	1.766	2.006

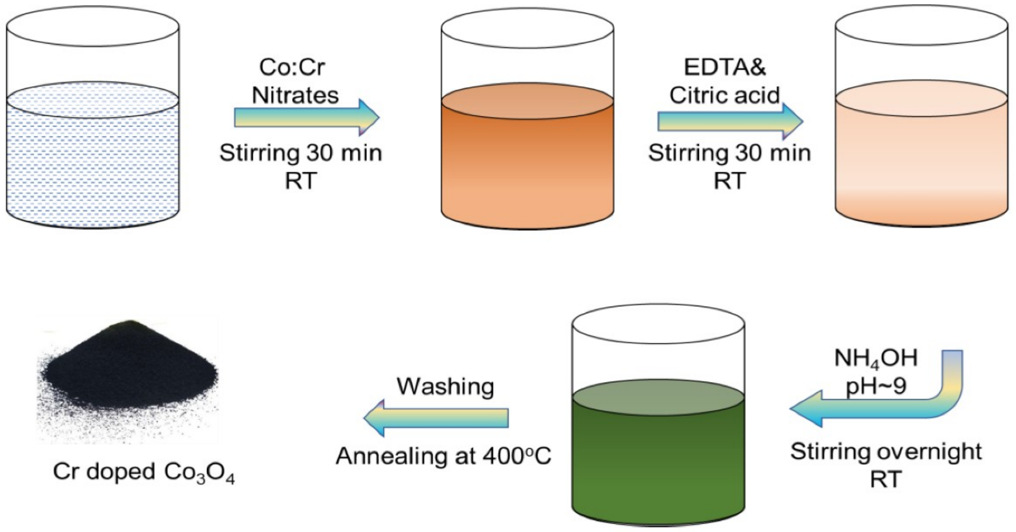

Figure S1 Schematic of the sample synthesis procedures.

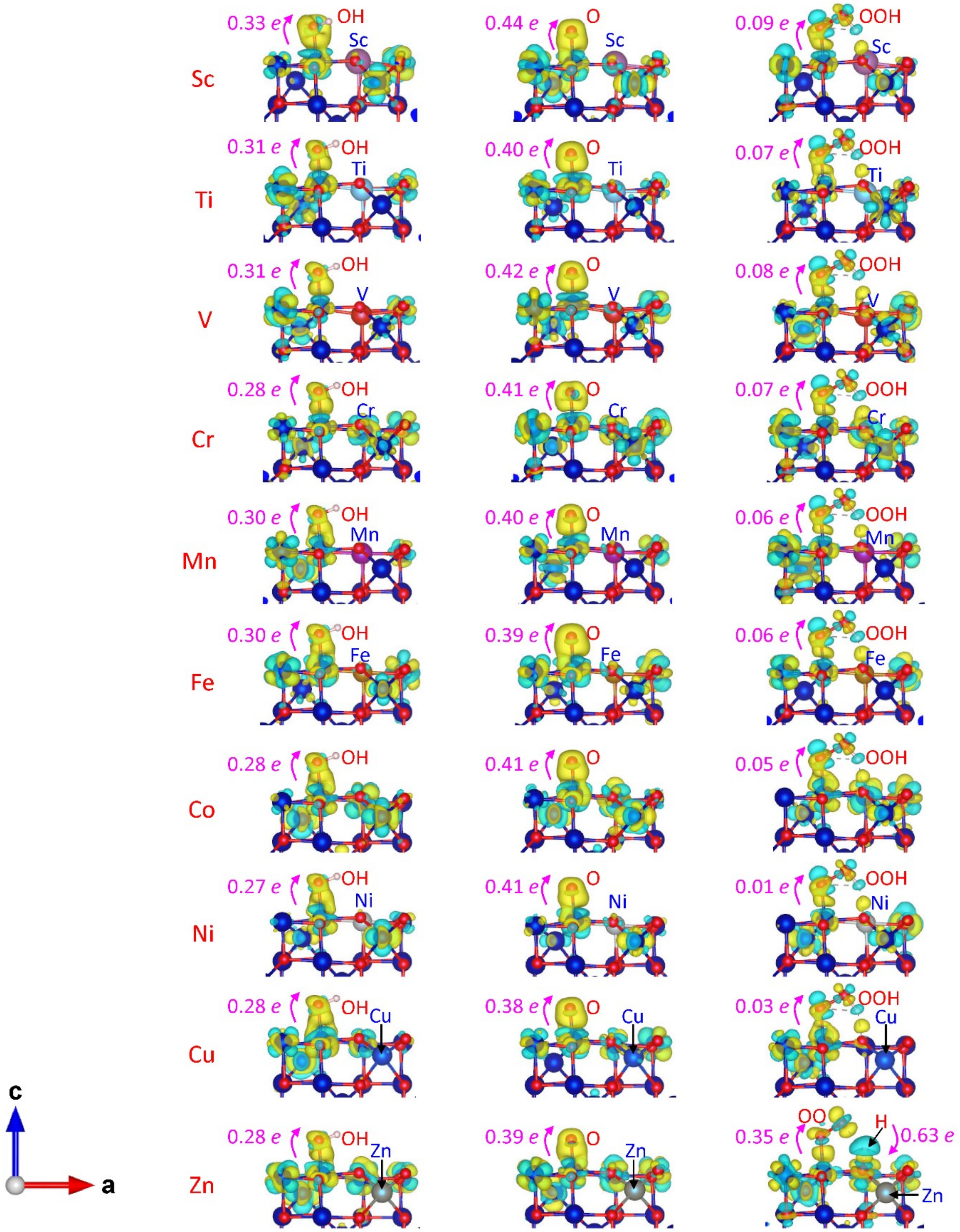

Figure S2 Calculated charge difference of slabs when attached with *OH (left), *O (middle), and *OOH (right) intermediates. The Bader charge transfers are indicated.

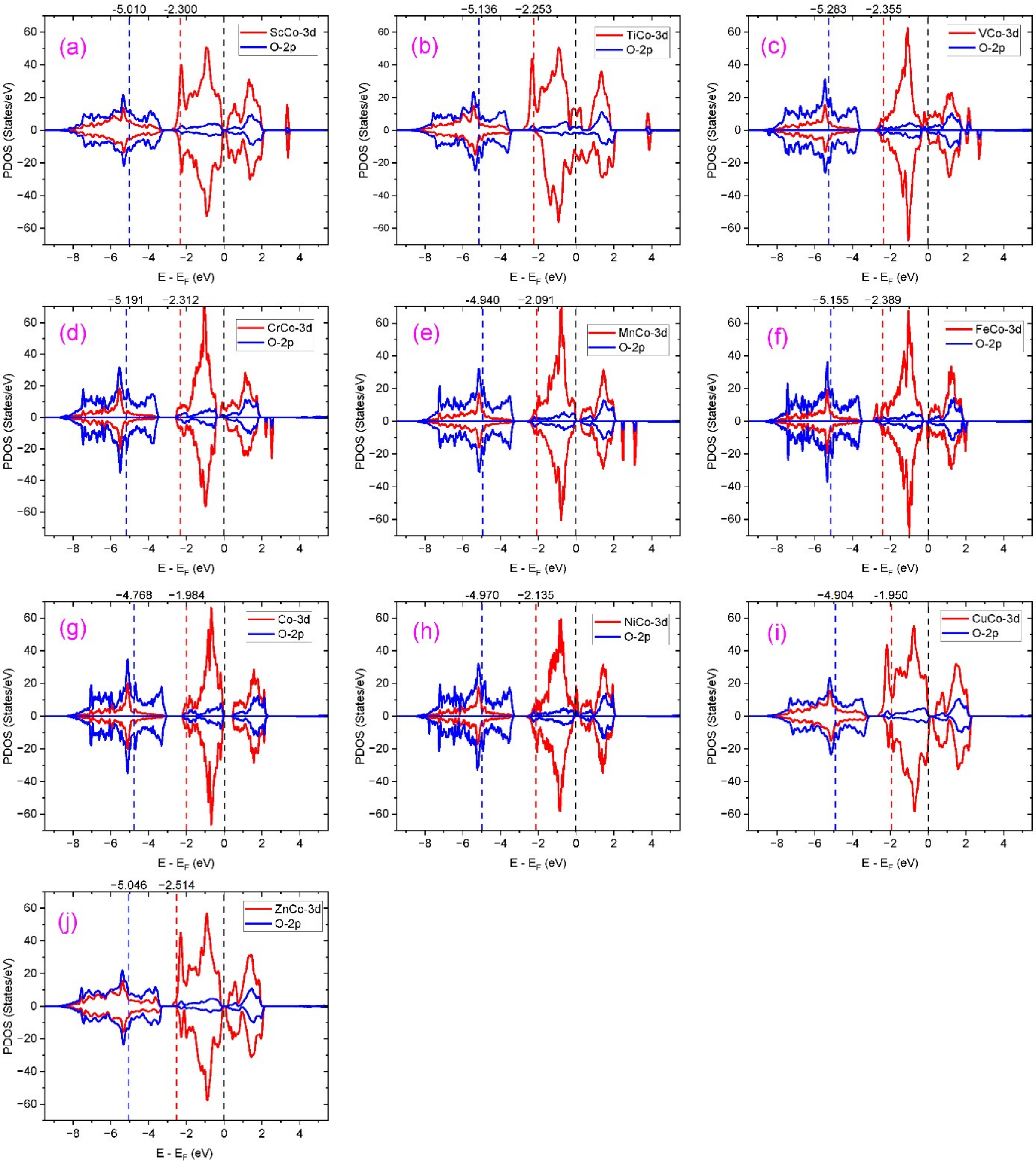

Figure S3 Calculated partial density of states of metal M (both dopant and Co) 3d and oxygen 2p in Co_3O_4 doped with Sc (a), Ti (b), V (c), Cr (d), Mn (e), Fe (f), Co (undoped) (g), Ni (h), Cu (i), and Zn (j). The 3d-band centers of transition metals and the oxygen 2p band centers are marked.

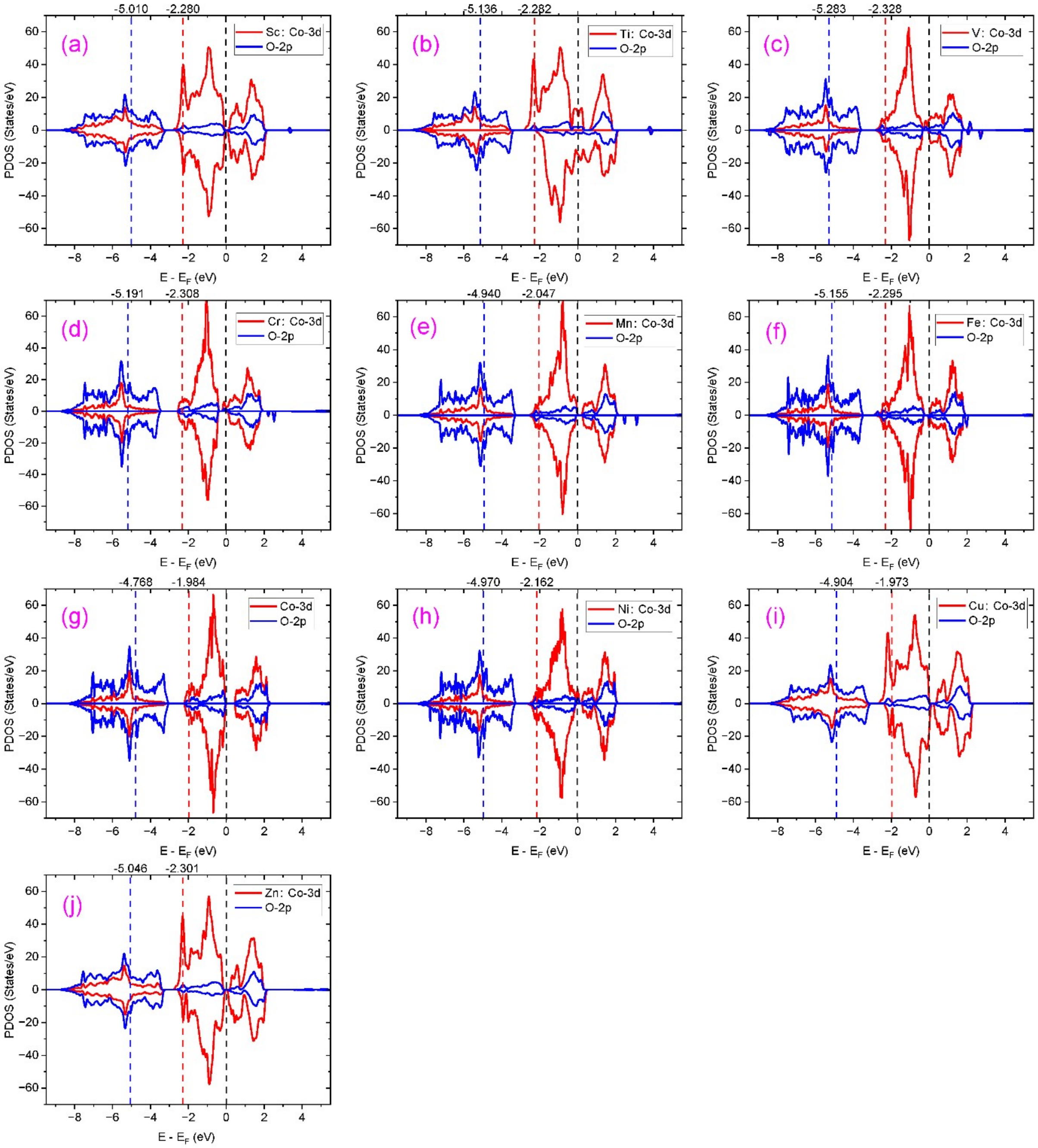

Figure S4 Calculated partial density of states of Co 3d (without dopant M contribution) and oxygen 2p in Co$_3$O$_4$ doped with Sc (a), Ti (b), V (c), Cr (d), Mn (e), Fe (f), Co (undoped) (g), Ni (h), Cu (i), and Zn (j). The 3d-band centers of Co and the oxygen 2p band centers are marked.

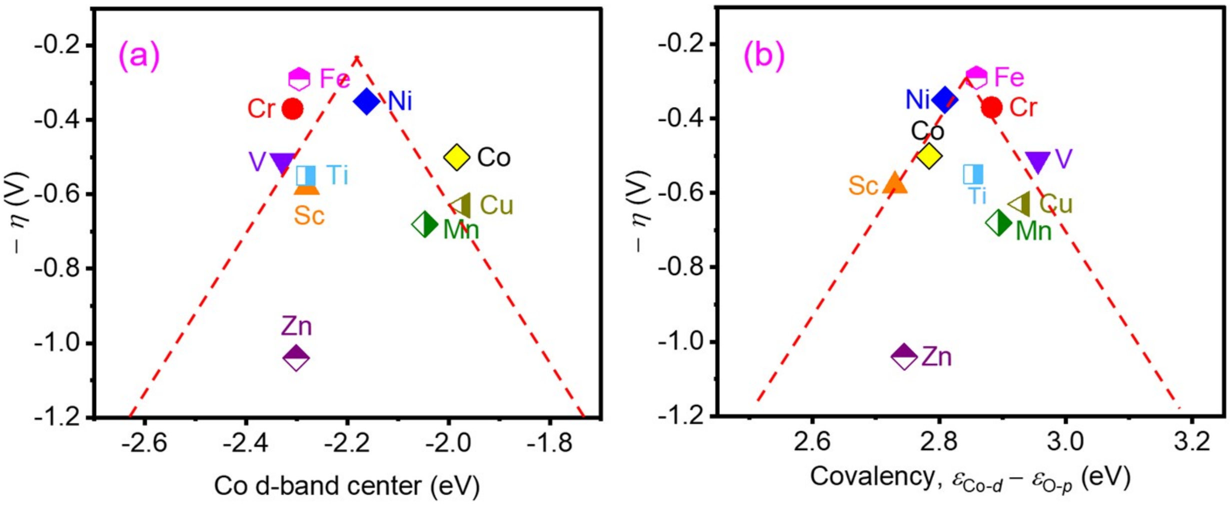

Figure S5 Calculated negative overpotential as a function of Co d-band center (a), covalency between Co only and oxygen (b). Dotted lines guide the eye.

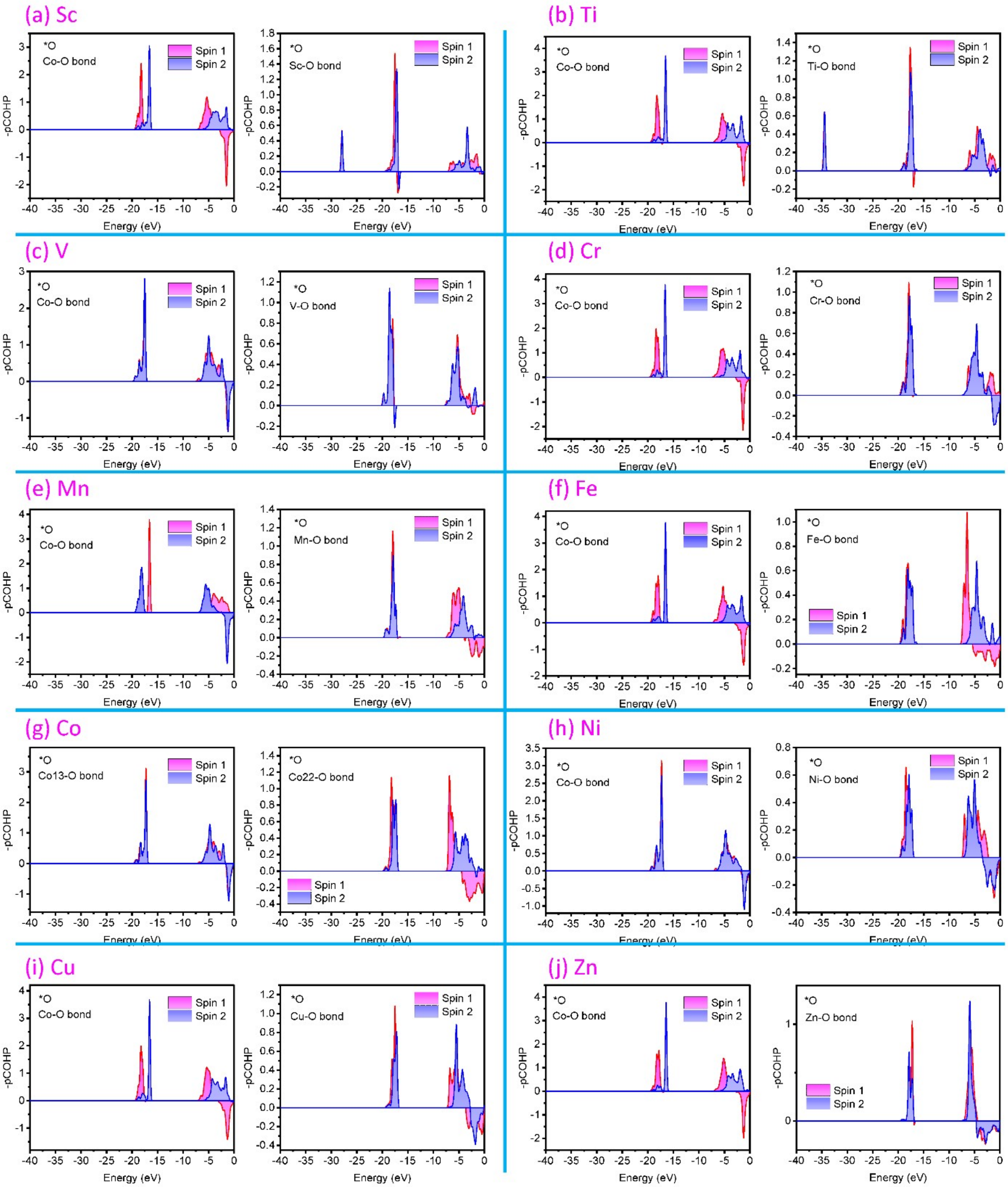

Figure S6 Calculated pCOHP of M-doped slabs with *O intermediate, where Co–O bond is on the active Co site, and M–O bond is the dopant M (or equivalent Co for pristine sample) with one of its neighboring O atoms.

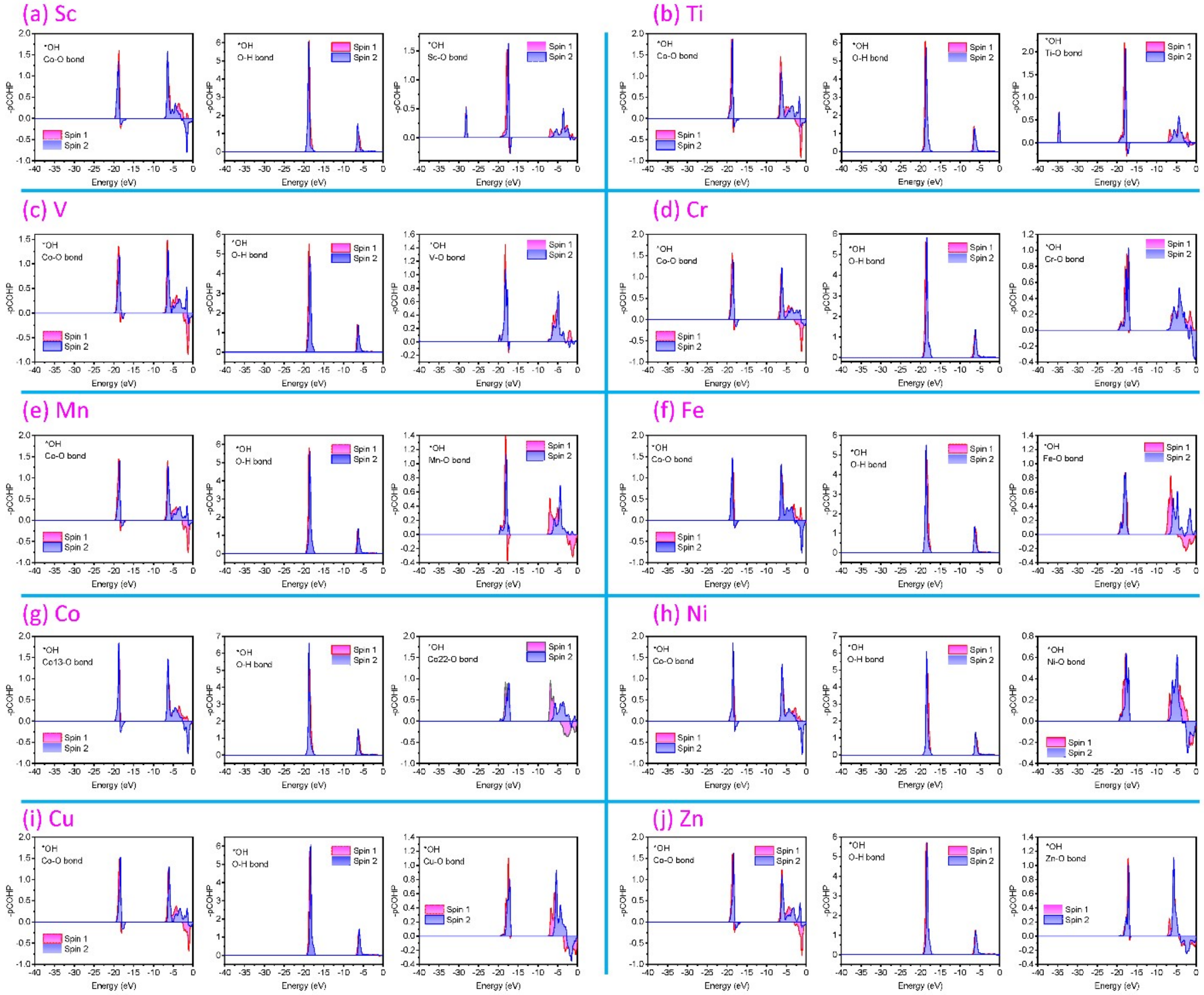

Figure S7 Calculated pCOHP of M-doped slab with *OH intermediate. In each figure (a–j), the pCOHP of the Co–O bond on the active Co site is shown on the left, the O–H bond in the middle, and the M–O bond (or equivalent Co–O for the pristine sample) with one of its neighboring O atoms on the right.

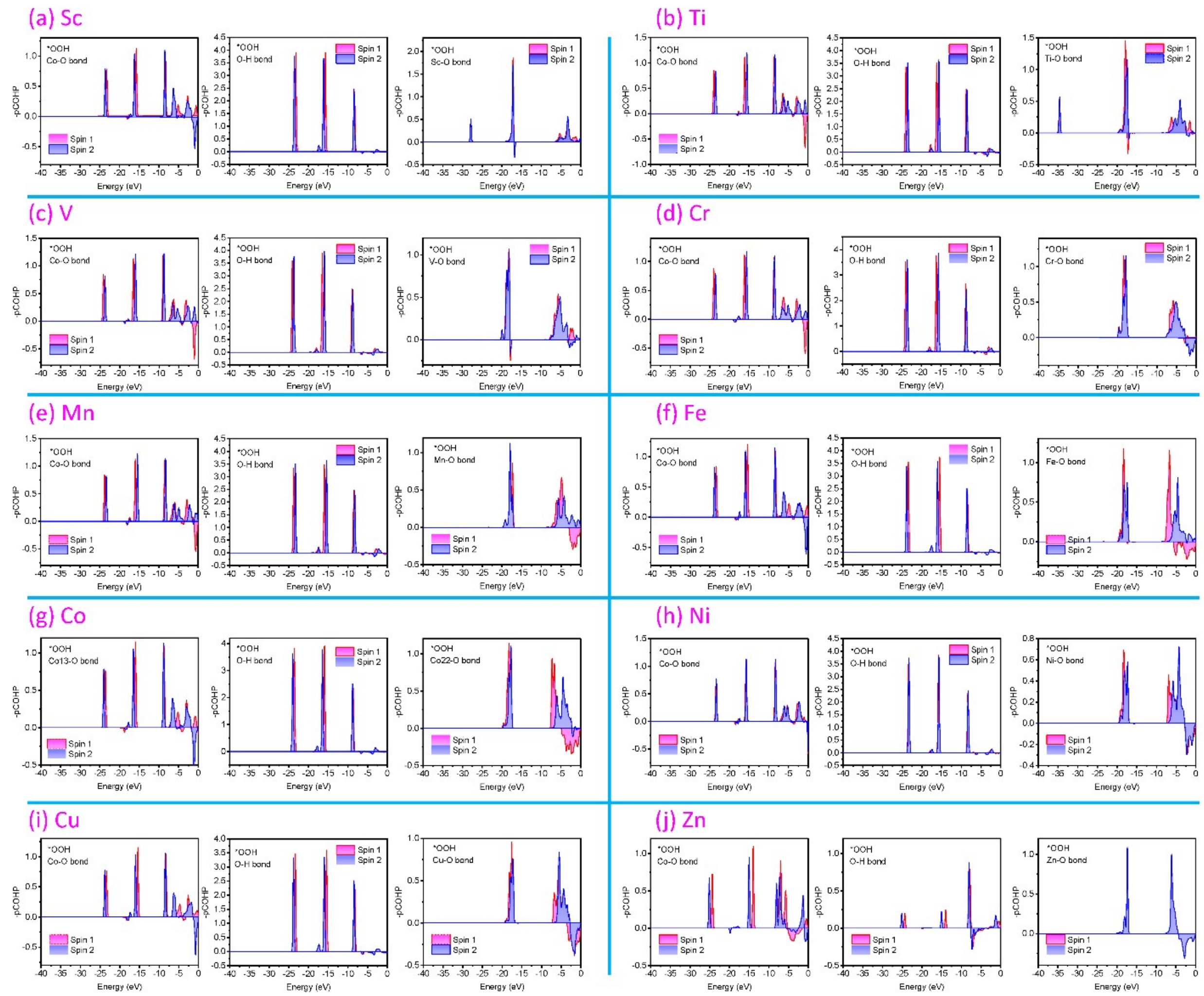

Figure S8 Calculated pCOHP of M-doped slab with *OOH intermediate. In each figure (a–j), the pCOHP of the Co–O bond on the active Co site is shown on the left, the O–H bond in the middle, and the M–O bond (or equivalent Co–O for the pristine sample) with one of its neighboring O atoms on the right.

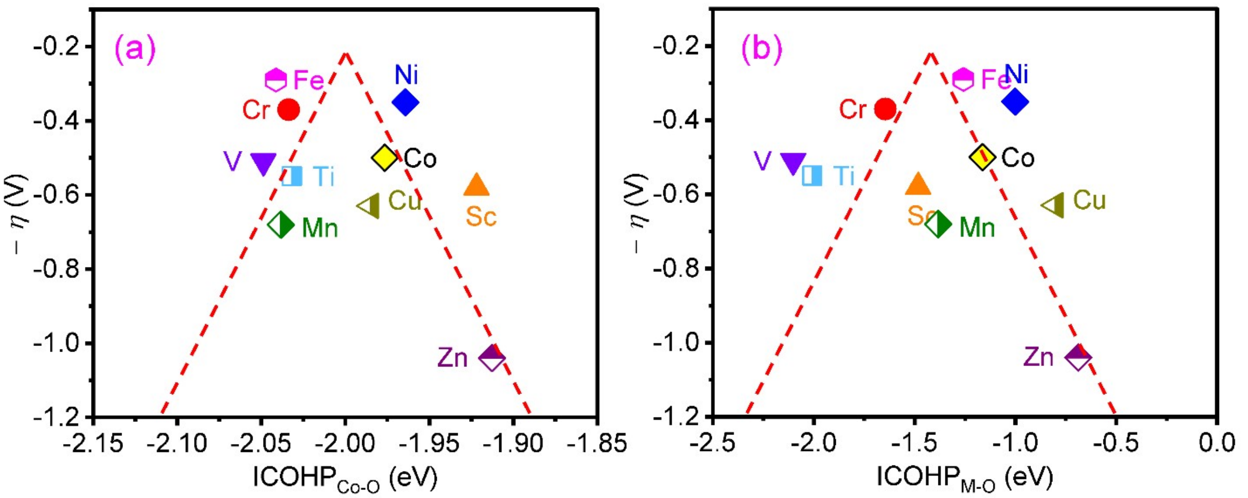

Figure S9 Calculated negative overpotential as a function of ICOHP$_{Co–O}$ (a) and ICOHP$_{M–O}$ (b). Dotted lines guide the eye.

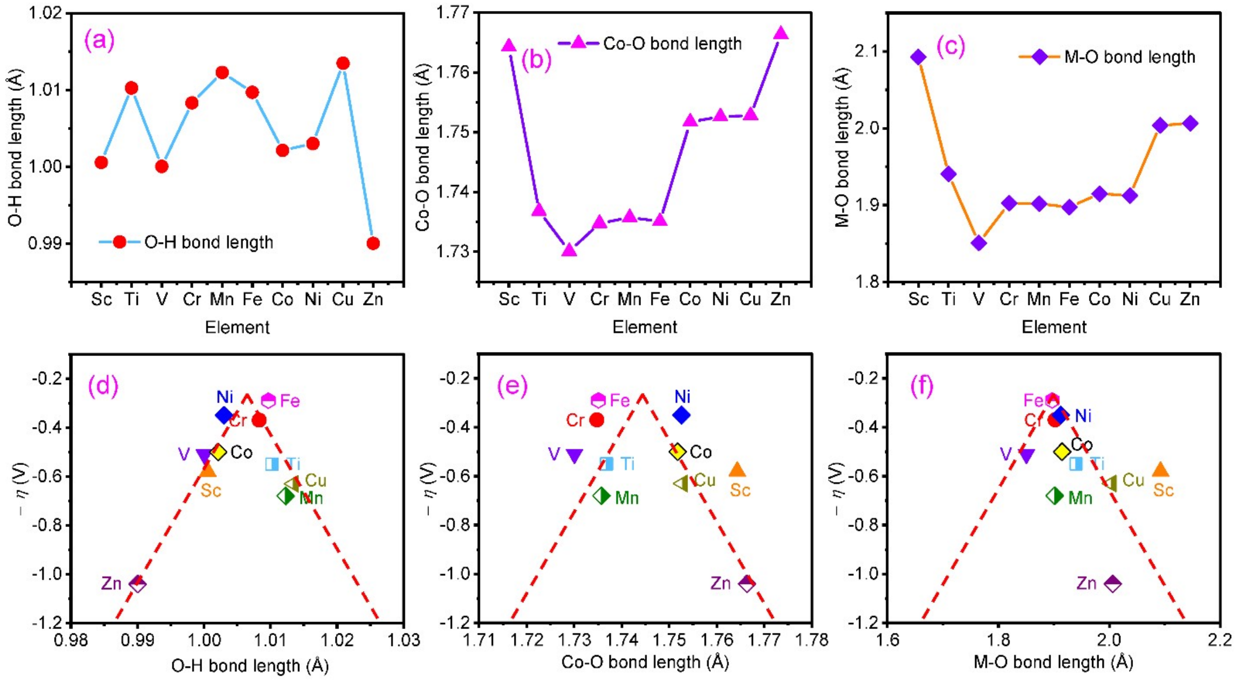

Figure S10 Calculated O–H bond length averaged from *OH and *OOH (a), Co–O bond length averaged from *O, *OH, and *OOH (b), and M–O bond length (M is Co for the pristine sample) averaged from all O neighbors from *O, *OH, and *OOH intermediates. Negative overpotential as a function of their bond length is shown on the bottom row (d–f). Dotted lines guide the eye.

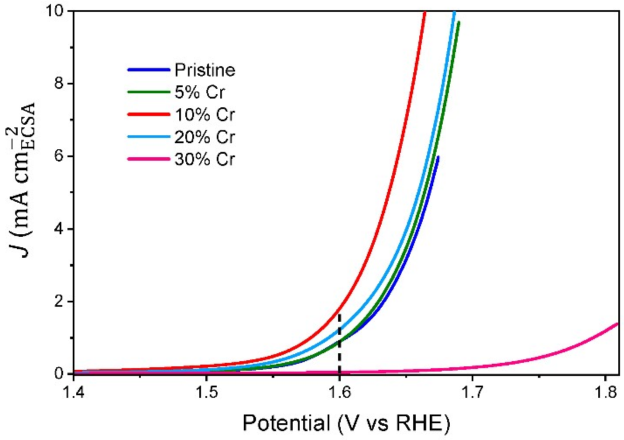

Figure S11 ECSA normalized LSV curves of pristine and Cr-doped Co_3O_4.