Breaking the Scaling Relationship of ORR on Carbon-based Single-atom Catalysts Through Building the Local Collaborative Structure

Cehuang Fu[a], Liuxuan Luo[a], Lijun Yang[b], Shuiyun Shen[a], Guanghua Wei[c] and Junliang Zhang*[a]*

AUTHOR ADDRESS

a Institute of Fuel Cells, MOE Key Laboratory of Power & Machinery Engineering, School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai, China.

b MOE Key Laboratory of Mesoscopic Chemistry, Jiangsu Provincial Lab for Nanotechnology, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, China.

c SJTU-Paris Tech Elite Institute of Technology, Shanghai Jiao Tong University, Shanghai, China.

Calculation method

All DFT calculations are carried on by the DMol3 of Material Studio 8.0.[1-2] The electronic exchange and correlation are calculated by the generalized gradient-corrected Perdew-Burke-

Ernzerhof functional method (GGA-PBE).[1-3] Tkatchenko-Scheffler (TS) method is applied in Dispersion-corrected DFT scheme to describe the van der Waals interactions.[4] DFT semi-core pseudopotentials (DSPP) are applied in core treatment. Double numerical plus polarization (DNP) 4.4 basis set is used to calculate the atomic orbital.[5] Spin is unrestricted during calculation. The graphite slab consists of 96 C atoms and sampled by a Monkhorst-Pack grid of 5x4x1. A vacuum slab of 15 Å is applied. The convergence tolerances are 1×10^{-5} Ha, 0.002 Ha/Å, 0.005 Å. The doped structures marked according to doping elements and structural symmetry as Figure S1, for example, PNC-1 represents the situation that the C atom at site 1 is taken the place of by P. The stability is evaluated by:

$$\Delta E_f = E_{structure} - E_{PNC\text{-}1/SNC\text{-}1}$$

where $E_{structure}$ is energy of doped structure and $E_{PNC\text{-}1/SNC\text{-}1}$ is the energy of PNC-1 or SNC-1. The most stable doped structure is used to calculate ORR process further. The distances between doping site and N are listed in Table S1.

The free energy is given as[6-7]:

$$G=E+ZPE-TS-neU$$

where E is the energy of the structure calculated with DFT, ZPE is the zero-point energy which is equal to $\sum(hvi/2)$ (h is the Planck constant and vi is the vibrational frequency), T is the temperature (298.15 K), S is the entropy of the structure, n is the number of electrons transferred in elementary reaction, e is the charge constant and U is the potential. The entropy is calculated by vibrational frequency.[6-7]

H_2 and H_2O are calculated with DFT. $G_{H2O(l)}=G_{H2O(g)}+RT\times In(P/P_0)$ is used to get the energy of H_2O, where R is gas constant, P_0=1 bar and P=0.035 bar. The energy of (H^++e^-) is defined as the half time that of H_2 on the standard condition that U=0 and pH=0. The free energy of O_2 is calculated according to thermodynamic energy of 4.92 eV released by the reaction of $2H_2+O_2\rightarrow 2H_2O$.[6-7] The thermodynamic energy released by the reaction of $H_2+O_2\rightarrow H_2O_2$ is -1.39 eV.

The elementary reactions of $4e^-$ mechanism could be described as followed:

(1) $O_2\rightarrow O_2*$

(2) $O_2*+H^++e^-\rightarrow OOH*$

(3) $OOH*+H^++e^-\rightarrow O*+H_2O$

(4) $O*+H^++e^-\rightarrow OH*$

(5) $OH*+H^++e^-\rightarrow H_2O$

And the elementary reactions of $2e^-$ mechanism could be described as followed:

(1) $O_2\rightarrow O_2*$

(2) $O_2*+H^++e^-\rightarrow OOH*$

(6) $OOH*+H^++e^-\rightarrow H_2O_2$

It is worth mentioned that the processes of $O_2\rightarrow 2O*$ and $O_2*+H^++e^-\rightarrow O*+OH*$ are not considered in our calculation. Cd, Hg are not considered because of their toxicity. Thus, only

structures of M-N_4 (M is one of the transitions metals including Cr, Mn, Fe, Co, Ni, Cu, Zn, Rh, Ru, Rh, Pd, Ag, Ir, Pt, Au) are calculated in our work.

The adsorption energies of intermediate adsorbates (energies of all states in energy diagram of ORR process) are calculated as:

$$\Delta G_{O2*} = G_{O2*} - G_{slab} - G_{O2}$$

$$\Delta G_{OOH*} = G_{OOH*} - G_{slab} - G_{O2} - (G_{H+} + G_{e-})$$

$$\Delta G_{O*} = G_{O*} - G_{slab} - G_{O2} - 2(G_{H+} + G_{e-}) + G_{H2O}$$

$$\Delta G_{OH*} = G_{OH*} - G_{slab} - G_{O2} - 3(G_{H+} + G_{e-}) + G_{H2O}$$

where G_{slab}, G_{O2}, G_{H2O} and $(G_{H+}+G_{e-})$ are free energy of clean slab, O_2 and proton-electron couple. G_{O2*}, G_{OOH*}, G_{O*} and G_{OH*} are the energy of the slab with adsorbates. When the ΔG of elementary reaction is positive, the reaction is considered not to happen thermodynamically. Thus, the onset potential could be evaluated by the max energy released in elementary reaction at 0V:

$$U_{onset} = -(_{max}\Delta G)/e$$

The stability of metal atoms could be evaluated by the dissolution potential by[8]:

$$-eU_{dis} = G_{N4} + G_{metal\text{-}ion} + nG_{e-} - G_{M\text{-}N4}$$

where $G_{metal\text{-}ion} + nG_{e-}$ could be calculated by standard electrode potentials of Table S2.

Table S1. The distance between doped site and metal atom.

Site Number	$D_{M/doped\ site}$(Å)	Site Number	$D_{M/doped\ site}$(Å)	Site Number	$D_{M/doped\ site}$(Å)
1	3.019	9	6.079	17	7.806
2	2.638	10	6.788	18	7.184
3	4.001	11	4.897	19	8.181
4	5.010	12	5.774	20	7.994
5	6.333	13	5.517	21	9.227
6	3.448	14	6.759	22	9.396
7	4.292	15	6.996		
8	4.675	16	8.376		

Table S2. The standard electrode potentials of transition metals.

Reaction	**Potential (E^0)**	**Reaction**	**Potential (E^0)**
$Cr \rightarrow Cr^{3+}+3e^-$	-0.744	$Ru \rightarrow Ru^{2+}+2e^-$	0.455
$Mn \rightarrow Mn^{2+}+2e^-$	-1.185	$Rh \rightarrow Rh^{3+}+3e^-$	0.800
$Fe \rightarrow Fe^{2+}+2e^-$	-0.447	$Pd \rightarrow Pd^{2+}+2e^-$	0.951
$Co \rightarrow Co^{2+}+2e^-$	-0.280	$Ag \rightarrow Ag^{+}+e^-$	0.799
$Ni \rightarrow Ni^{2+}+2e^-$	-0.257	$Ir \rightarrow Ir^{3+}+3e^-$	1.000
$Cu \rightarrow Cu^{2+}+2e^-$	-0.340	$Pt \rightarrow Pt^{2+}+2e^-$	1.180
$Zn \rightarrow Zn^{2+}+2e^-$	-0.762	$Au \rightarrow Au^{+}+e^-$	1.692

Table S3. The dissolution potentials of metal atoms of P-doped M-N_4.

	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ru	Rh	Pd	Ag	Ir	Pt	Au
1	0.78	-0.82	-1.61	-1.97	-2.08	-1.96	-0.76	-1.41	-4.57	-4.20	-1.13	-4.98	-4.73	-2.34
2	1.12	-0.36	-1.17	-1.54	-1.54	-1.56	-0.39	-0.99	-4.15	-3.88	-0.98	-4.56	-4.37	-1.84
3	1.17	-0.35	-1.18	-1.56	-1.76	-1.72	-0.43	-0.82	-4.04	-3.94	-1.14	-4.35	-4.41	-2.00
4	0.78	-0.73	-1.61	-2.04	-2.15	-1.99	-0.81	-1.29	-4.55	-4.36	-1.33	-4.92	-4.84	-2.21
5	0.72	-0.82	-1.68	-2.08	-2.25	-2.04	-0.86	-1.32	-4.54	-4.40	-1.31	-4.89	-4.90	-2.32
6	1.13	-0.25	-1.21	-1.68	-1.68	-1.73	-0.50	-1.19	-4.45	-4.02	-1.40	-4.79	-4.52	-1.73
7	0.83	-0.75	-1.64	-2.06	-2.27	-2.06	-0.79	-1.17	-4.44	-4.39	-1.09	-4.77	-4.85	-2.37
8	0.48	-1.10	-1.92	-2.31	-2.42	-2.25	-1.07	-1.51	-4.75	-4.61	-1.30	-5.13	-5.10	-2.64
9	0.82	-0.72	-1.60	-2.03	-2.20	-1.98	-0.78	-1.19	-4.46	-4.34	-1.24	-4.79	-4.81	-2.17
10	0.67	-0.87	-1.75	-2.19	-2.31	-2.04	-0.91	-1.37	-4.64	-4.42	-1.34	-5.00	-4.93	-2.28
11	0.67	-0.91	-1.83	-2.25	-2.40	-2.14	-0.95	-1.41	-4.66	-4.49	-1.31	-5.02	-5.02	-2.39
12	0.88	-0.66	-1.58	-2.03	-2.16	-1.94	-0.73	-1.19	-4.48	-4.30	-1.22	-4.81	-4.78	-2.07
13	0.82	-0.88	-1.71	-2.14	-2.31	-2.03	-0.77	-1.16	-4.44	-4.29	-1.15	-4.79	-4.82	-2.26
14	0.85	-0.88	-1.65	-2.09	-2.27	-2.00	-0.75	-1.14	-4.43	-4.35	-1.15	-4.76	-4.81	-2.21
15	0.75	-0.94	-1.69	-2.11	-2.27	-2.02	-0.81	-1.24	-4.48	-4.31	-1.20	-4.83	-4.84	-2.31
16	0.76	-0.96	-0.49	-2.11	-2.29	-2.04	-0.82	-1.22	-4.48	-4.34	-0.97	-3.56	-4.85	-2.25
17	0.81	-0.84	-1.66	-2.11	-2.25	-2.00	-0.77	-1.24	-4.52	-4.32	-1.26	-4.85	-4.82	-2.11
18	0.80	-0.85	-1.69	-2.13	-2.29	-2.02	-0.79	-1.22	-4.48	-4.33	-1.20	-3.86	-4.84	-2.20
19	0.80	-0.88	-1.69	-2.11	-2.30	-2.03	-0.80	-1.19	-4.46	-4.33	-0.90	-3.81	-3.74	-2.25
20	0.77	-0.96	-1.73	-2.16	-2.34	-2.06	-0.81	-1.19	-4.47	-4.40	-1.16	-4.56	-3.67	-2.26
21	0.85	-0.92	-1.66	-2.10	-2.27	-2.00	-0.75	-1.15	-4.40	-4.24	-1.16	-4.76	-3.57	-2.16
22	0.77	-0.97	-1.69	-2.12	-2.30	-2.06	-0.80	-1.20	-4.44	-4.36	-0.93	-3.61	-3.55	-2.26

Table S4. The dissolution potentials of metal atoms of S-doped M-N_4.

	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ru	Rh	Pd	Ag	Ir	Pt	Au

1	2.33	0.81	-0.12	-0.54	-0.69	-0.51	0.69	0.09	-3.07	-2.66	0.04	-3.41	-3.14	-0.45
2	2.92	1.40	0.44	0.03	0.14	-0.01	1.33	0.66	-2.51	-2.08	0.50	-2.86	-2.51	-0.51
3	2.63	1.11	0.24	-0.16	-0.31	-0.22	1.02	0.56	-2.67	-2.49	0.27	-2.99	-2.96	-0.29
4	2.18	0.64	-0.26	-0.67	-0.78	-0.62	0.57	0.07	-3.18	-2.95	-0.02	-3.54	-3.43	-0.71
5	1.95	0.40	-0.48	-0.85	-1.03	-0.82	0.36	-0.12	-3.35	-3.16	-0.10	-3.71	-3.69	-0.98
6	3.10	1.68	0.68	0.17	0.29	0.14	1.48	0.59	-2.60	-1.94	0.30	-2.93	-2.43	0.29
7	2.46	0.89	-0.03	-0.47	-0.60	-0.49	0.78	0.38	-2.90	-2.72	0.26	-3.22	-3.18	-0.49
8	1.99	0.45	-0.42	-0.84	-0.98	-0.80	0.39	0.02	-3.26	-3.12	0.00	-3.59	-3.59	-0.94
9	2.09	0.52	-0.38	-0.78	-0.94	-0.71	0.49	0.02	-3.25	-3.08	0.01	-3.60	-3.56	-0.85
10	2.06	0.50	-0.40	-0.81	-0.95	-0.73	0.46	0.00	-3.27	-3.03	-0.05	-3.61	-3.54	-0.85
11	1.92	0.35	-0.59	-0.99	-1.15	-0.90	0.30	-0.17	-3.44	-3.24	-0.12	-3.80	-3.77	-1.01
12	2.20	0.63	-0.29	-0.74	-0.86	-0.63	0.59	0.09	-3.18	-2.97	0.07	-3.40	-3.46	-0.68
13	2.12	0.50	-0.41	-0.86	-1.01	-0.73	0.52	0.12	-3.17	-2.98	0.07	-3.51	-3.51	-0.80
14	2.06	0.44	-0.46	-0.90	-1.06	-0.79	0.76	0.04	-3.24	-3.15	0.04	-3.59	-3.61	-0.92
15	1.98	0.40	1.77	-0.91	-1.08	-0.82	0.40	0.00	-3.26	-3.15	0.01	-3.60	-3.63	-0.98
16	2.01	0.43	-0.46	-0.90	-1.05	-0.79	0.42	-0.02	-3.28	-3.13	0.28	-3.62	-3.63	-0.92
17	2.08	0.50	-0.41	-0.87	-1.00	-0.73	0.49	0.01	-3.27	-3.05	0.00	-3.61	-3.56	-0.83
18	2.04	0.44	-0.47	-0.92	-1.07	-0.79	0.44	0.01	-3.28	-3.10	0.02	-3.62	-3.61	-0.89
19	2.00	0.40	-0.50	-0.94	-1.11	-0.84	0.40	-0.01	-3.29	-3.13	0.02	-1.55	-3.66	-0.94
20	2.01	0.40	-0.50	-0.94	-1.11	-0.83	0.42	0.02	-3.26	-3.11	0.03	-3.60	-1.41	-0.93
21	2.08	0.45	-0.45	-0.90	-1.06	-0.78	0.48	0.06	-3.20	-3.03	0.35	-3.57	-1.31	-0.92
22	2.02	0.40	-0.49	-0.92	-1.09	-0.81	0.42	0.01	-3.24	-2.65	0.29	-1.36	-3.62	-0.95

Table S5. ORR processes on none-doped M-N4 and P/S-doped M-N4(P and S are oxidized by O*). ↓ is used to describe stronger adsorption and ↑ means weaker adsorption.

	O2*	**OOH***	**O***	**OH***
Cr-N_4	-1.092	-1.724	-4.927	-5.063

Cr-PN_4	-0.948 ↑	-1.995 ↓	-4.876 ↑	-5.216 ↓
Cr-SN_4	-0.992 ↑	-1.784 ↓	-4.899 ↑	-5.096 ↓
Mn-N_4	-0.618	-1.314	-3.959	-4.611
Mn-PN_4	-0.543 ↑	-1.549 ↓	-3.913 ↑	-4.794 ↓
Mn-SN_4	-0.602 ↑	-1.426 ↓	-3.945 ↓	-4.733 ↓
Fe-N_4	-0.588	-1.282	-3.407	-4.397
Fe-PN_4	-0.365 ↑	-1.457 ↓	-3.230 ↑	-4.534 ↓
Fe-SN_4	-0.560 ↑	-1.427 ↓	-3.353 ↑	-4.467 ↓
Co-N_4	-0.313	-0.807	-2.159	-3.902
Co-PN_4	-0.194 ↑	-0.979 ↓	-1.941 ↑	-3.867 ↑
Co-SN_4	-0.272 ↑	-0.933 ↓	-2.178 ↓	-3.945 ↓
Ni-N_4	0.065	-0.035	-0.947	-3.017
Ni-N_4P	0.181 ↑	-0.383 ↓	-0.635 ↑	-3.198 ↓
Ni-N_4S	0.164 ↑	-0.092 ↓	-0.702 ↓	-3.126 ↑
Cu-N_4	0.115	-0.105	-0.677	-3.094
Cu-N_4P	0.195 ↑	-0.214 ↓	-0.796 ↓	-3.129 ↓
Cu-N_4S	0.127 ↑	-0.177 ↓	-0.794 ↓	-3.274 ↓
Zn-N_4	0.306	-0.799	-1.424	-4.068
Zn-N_4P	0.763 ↑	-1.219 ↓	-0.750 ↑	-4.080 ↓
Zn-N_4S	0.618 ↓	-1.185 ↓	-0.974 ↑	-4.234 ↓
Ru-N_4	-1.161	-1.727	-4.049	-4.808
Ru-N_4P	-0.920 ↑	-1.841 ↓	-3.999 ↑	-4.806 ↑
Ru-N_4S	-0.995 ↑	-1.703 ↑	-3.915 ↑	-4.750 ↑
Rh-N_4	-0.093	-0.734	-2.105	-3.850
Rh-N_4P	-0.032 ↑	-1.036 ↓	-2.098 ↑	-3.947 ↓
Rh-N_4S	-0.116 ↓	-0.78 ↓	-1.982 ↑	-3.800 ↑
Pd-N_4	0.777	0.291	-0.273	-2.548

Pd-N_4P	0.170 ↓	0.032 ↓	0.026 ↑	-2.636 ↓
Pd-N_4S	0.857 ↑	0.290 ↓	0.053 ↑	-2.446 ↑
Ag-N_4	-0.154	-0.896	-1.371	-3.972
Ag-N_4P	0.193 ↑	-0.754 ↑	-1.349 ↑	-3.642 ↑
Ag-N_4S	0.309 ↑	-0.563 ↑	-0.975 ↑	-3.587 ↑
Ir-N_4	-0.043	-0.669	-2.416	-3.822
Ir-N_4P	-0.037 ↑	-1.046 ↓	-2.570 ↓	-4.041 ↓
Ir-N_4S	0.044 ↑	-0.757 ↓	-2.275 ↑	-3.870 ↓
Pt-N_4	0.116	0.354	-0.293	-2.535
Pt-N_4P	0.185 ↑	0.033 ↓	-0.321 ↓	-2.751 ↓
Pt-N_4S	0.830 ↑	0.136 ↓	-0.231 ↑	-2.563 ↓
Au-N_4	0.579	0.083	-0.238	-2.710
Au-N_4P	0.615 ↑	-0.171 ↓	-0.895 ↓	-2.721 ↓
Au-N_4S	0.680 ↑	0.045 ↓	-0.306 ↓	-2.731 ↓

Table S6. ORR processes on none-doped M-N_4 and P/S-doped M-N_4 without vdW interaction. ↓ is used to describe stronger adsorption and ↑ means weaker adsorption.

	O2*	**OOH***	**O***	**OH***
Cr-N_4	-0.966	-1.567	-4.857	-4.959
Cr-PN_4	-0.813 ↑	-1.815 ↓	-4.785 ↑	-5.094
Cr-SN_4	-0.850 ↑	-1.595 ↓	-4.811 ↑	-4.971
Mn-N_4	-0.435	-1.101	-3.840	-4.453
Mn-PN_4	-0.338 ↑	-1.392 ↓	-3.821 ↑	-4.675 ↓
Mn-SN_4	-0.462	-1.260 ↓	-3.808 ↑	-4.609 ↓
Fe-N_4	-0.450	-1.118	-3.329	-4.279
Fe-PN_4	-0.314 ↑	-1.375 ↓	-3.244 ↑	-4.509 ↓
Fe-SN_4	-0.408 ↑	-1.239 ↓	-3.303 ↑	-4.343 ↓

Co-N_4	-0.174	-0.635	-2.082	-3.783
Co-PN_4	-0.100 ↑	-0.978 ↓	-1.952 ↑	-3.932 ↓
Co-SN_4	-0.122 ↑	-0.745 ↓	-1.844 ↑	-3.823 ↓
Ni-N_4	0.307	0.225	-0.861	-2.838
Ni-N_4P	0.706 ↑	-0.096 ↓	-0.823 ↑	-2.975 ↓
Ni-N_4S	0.805 ↑	0.229 ↑	-0.827 ↑	-2.901 ↓
Cu-N_4	0.330	0.124	-0.490	-3.018
Cu-N_4P	0.445 ↑	-0.055 ↓	-0.353 ↑	-3.078 ↓
Cu-N_4S	0.316 ↓	-0.004 ↓	-1.004 ↓	-3.168 ↓
Zn-N_4	0.353	-0.692	-1.234	-4.077
Zn-N_4P	0.519 ↑	-0.725 ↓	-0.965 ↑	-3.950 ↑
Zn-N_4S	0.389 ↑	-0.739 ↓	-1.189 ↑	-4.109 ↓
Ru-N_4	-1.000	-1.535	-3.947	-4.669
Ru-N_4P	-0.886 ↑	-1.777 ↓	-3.933 ↑	-4.802 ↓
Ru-N_4S	-0.855 ↑	-1.549 ↓	-3.832 ↑	-4.631 ↓
Rh-N_4	-0.110	-0.575	-2.035	-3.730
Rh-N_4P	-0.072 ↑	-0.857 ↓	-2.044 ↓	-3.827 ↓
Rh-N_4S	0.023 ↑	-0.579 ↓	-1.899 ↑	-3.671 ↑
Pd-N_4	0.250	0.452	0.046	-2.464
Pd-N_4P	0.277 ↑	0.218 ↓	0.009 ↓	-2.490 ↓
Pd-N_4S	0.261 ↑	0.482 ↑	0.258 ↑	-2.351 ↑
Ag-N_4	-0.030	-0.766	-1.314	-3.899
Ag-N_4P	0.314 ↑	-0.619 ↑	-0.940 ↑	-3.550 ↑
Ag-N_4S	0.372 ↑	-0.430 ↑	-0.918 ↑	-3.538 ↑
Ir-N_4	0.068	-0.518	-2.367	3.739
Ir-N_4P	0.090 ↑	-0.882 ↓	-2.466 ↓	-3.932 ↓
Ir-N_4S	0.180 ↑	-0.576 ↓	-2.278 ↑	-3.751 ↓

Pt-N_4	0.867	0.532	-0.214	-2.465
Pt-N_4P	0.980 ↑	0.202 ↓	-0.280 ↓	-2.633 ↓
Pt-N_4S	0.972 ↑	0.219 ↓	-0.146 ↑	-2.415 ↑
Au-N_4	0.133	0.241	-0.182	-2.632
Au-N_4P	0.258 ↑	0.152 ↓	-0.666 ↓	-2.484 ↑
Au-N_4S	0.190 ↑	0.216 ↓	-0.126 ↑	-2.650 ↓

Table 7. The Mulliken charges of metal sites on B-doped M-N_4 which is doped by 0~4 B atoms.

	0 B	**1 B**	**2 B**	**3 B**	**4 B**
Cr–N_4	0.459	0.485	0.505	0.540	0.562
Mn-N_4	0.400	0.445	0.487	0.503	0.515
Fe–N_4	0.185	0.228	0.276	0.317	0.361
Co–N_4	0.055	0.092	0.135	0.171	0.203
Ni–N_4	0.081	0.083	0.090	0.119	0.142
Cu–N_4	0.391	0.403	0.422	0.422	0.433
Zn–N_4	0.359	0.381	0.407	0.411	0.424
Ru–N_4	0.452	0.500	0.521	0.543	0.582
Rh–N_4	0.300	0.331	0.361	0.410	0.444
Pd–N_4	0.336	0.370	0.336	0.362	0.375
Ag–N_4	0.457	0.492	0.512	0.525	0.524
Ir-N_4	0.114	0.140	0.167	0.197	0.230
Pt-N_4	0.102	0.091	0.093	0.099	0.125
Au-N_4	0.284	0.273	0.263	0.251	0.247

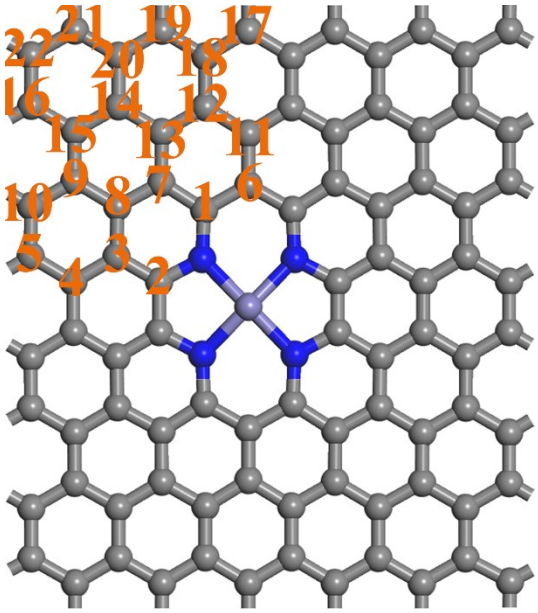

Figure S1. The graphite model used in calculation. Grey, carbon. Blue, nitrogen. Purple, metal atom. Orange number is used to mark doped site.

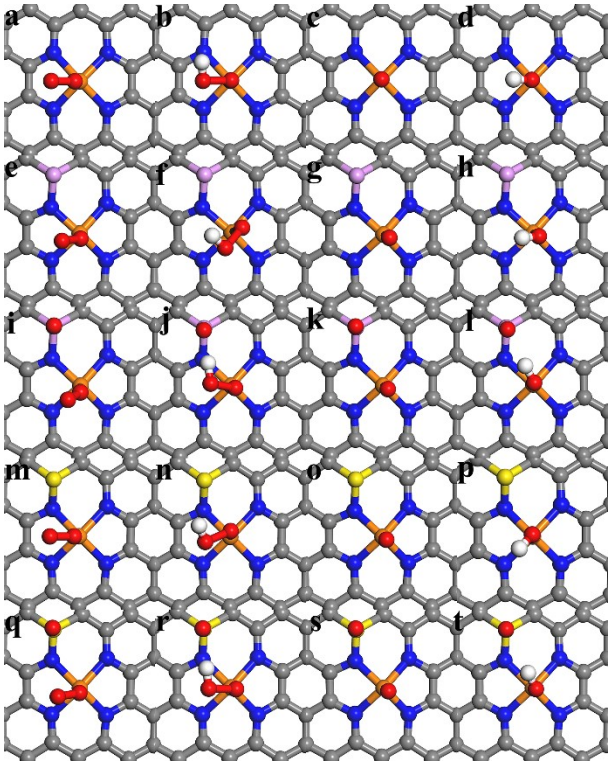

Figure S2. Structures of Cr-N_4 with intermediate adsorbates. (a-d) none-doped Mn-N_4, (e-h) P-doped Mn-N_4 without oxidation, (i-l) P-doped Mn-N_4 with oxidation, (m-p) S-doped Mn-N_4 without oxidation, (q-t) S-doped Mn-N_4 with oxidation. Brown, Cr.

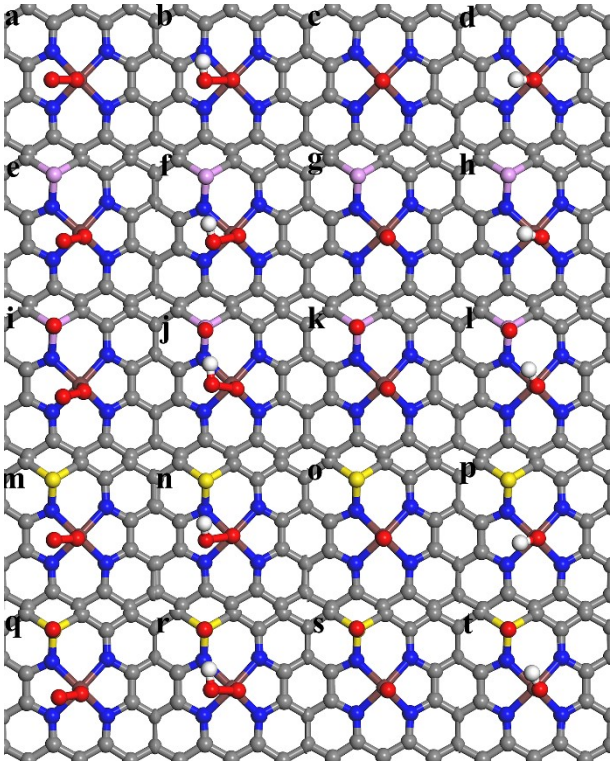

Figure S3. Structures of Mn-N_4 with intermediate adsorbates. (a-d) none-doped Mn-N_4, (e-h) P-doped Mn-N_4 without oxidation, (i-l) P-doped Mn-N_4 with oxidation, (m-p) S-doped Mn-N_4 without oxidation, (q-t) S-doped Mn-N_4 with oxidation. Brown, Cr.

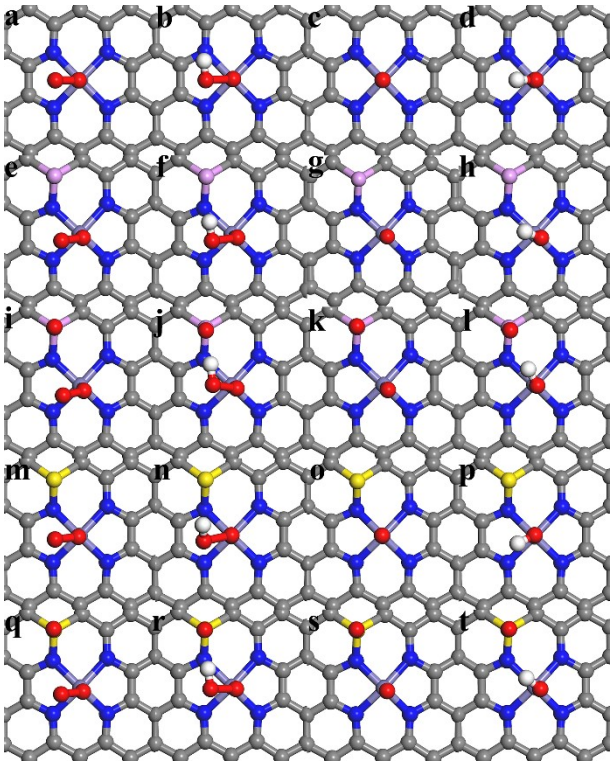

Figure S4. Structures of Fe-N_4 with intermediate adsorbates. (a-d) none-doped Fe-N_4, (e-h) P-doped Fe-N_4 without oxidation, (i-l) P-doped Fe-N_4 with oxidation, (m-p) S-doped Fe-N_4 without oxidation, (q-t) S-doped Fe-N_4 with oxidation. Purple, Fe.

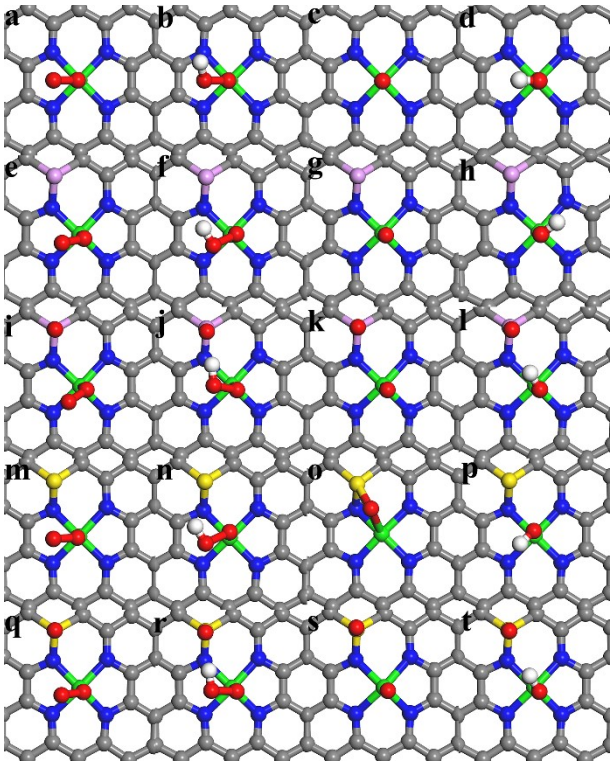

Figure S5. Structures of Co-N_4 with intermediate adsorbates. (a-d) none-doped Co-N_4, (e-h) P-doped Co-N_4 without oxidation, (i-l) P-doped Co-N_4 with oxidation, (m-p) S-doped Co-N_4 without oxidation, (q-t) S-doped Co-N_4 with oxidation.

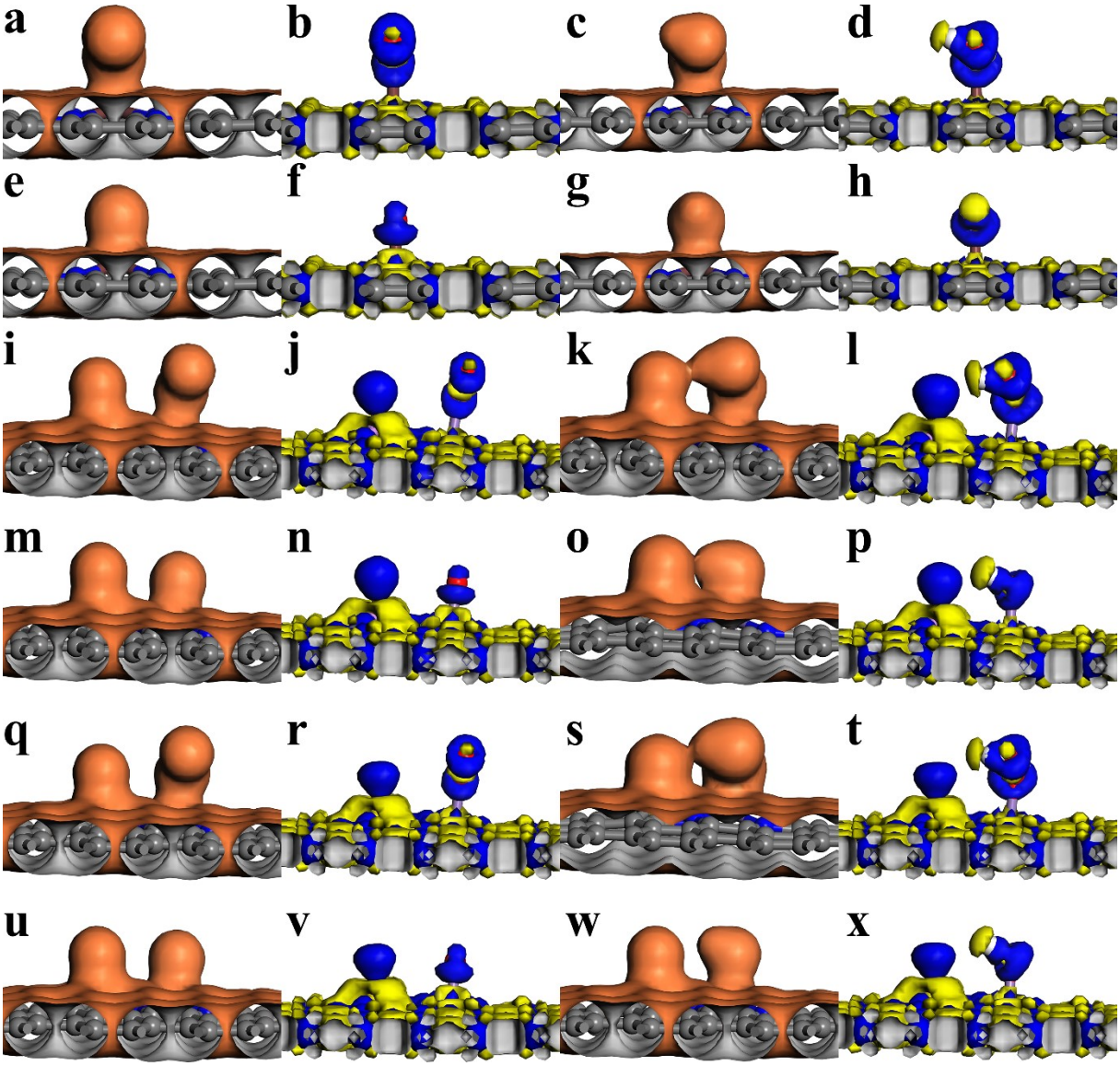

Figure S6. The total and deformation electron density of ORR intermediates (O_2*/OOH*/O*/OH*) on (a-h) non-doped Mn-N_4 (i-p) P-doped Mn-N_4 (q-x) S-doped Mn-N_4. The orange area is total electron density, the blue area is negative electron density and the yellow area is positive electron density. The values of isovalue of total electron and deformation electron density are 0.2 e/Å^3 and 0.06 e/Å^3.

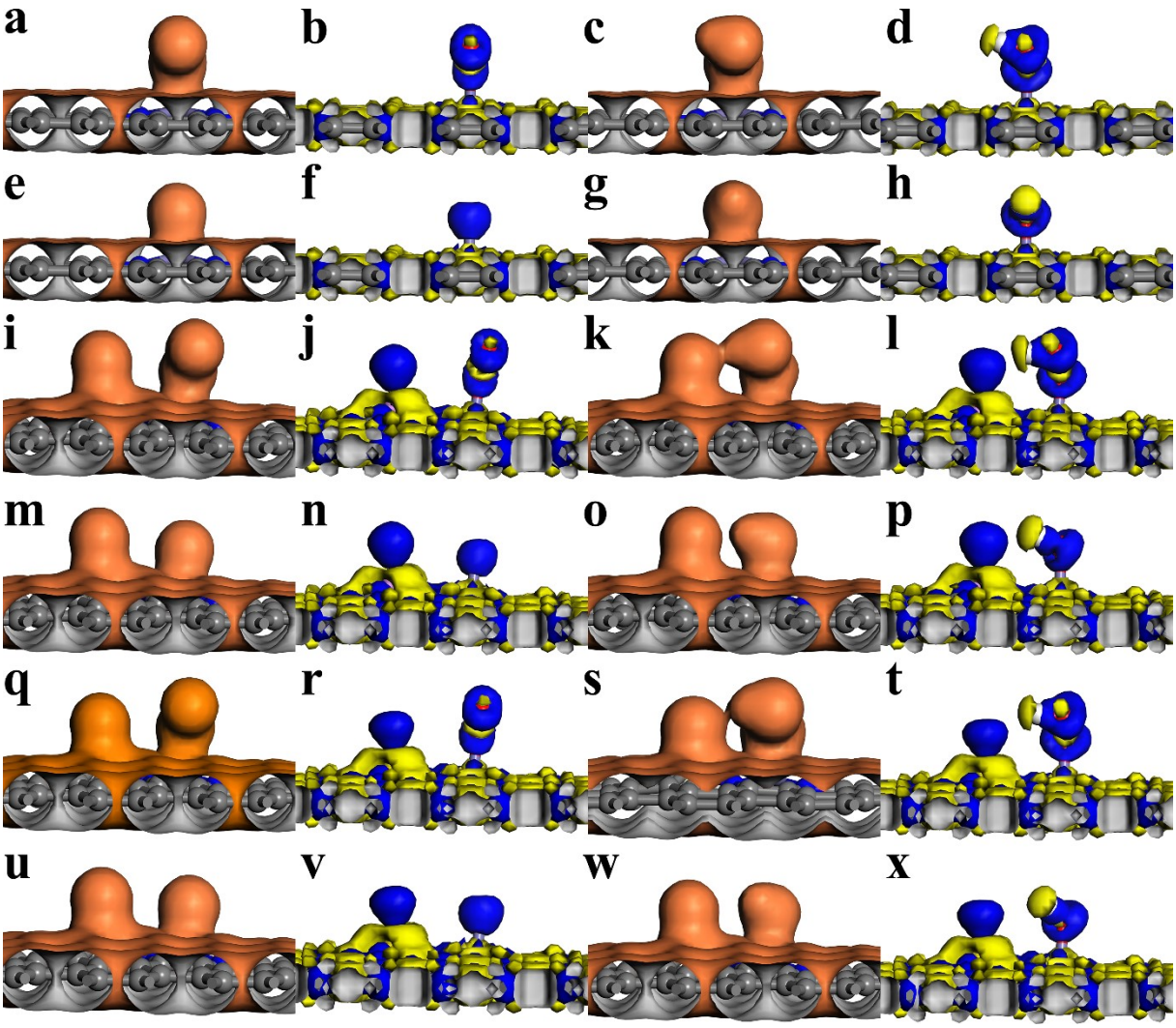

Figure S7. The total and deformation electron density of ORR intermediates (O_2*/OOH*/O*/OH*) on (a-h) non-doped Fe-N_4 (i-p) P-doped Fe-N_4 (q-x) S-doped Fe-N_4.

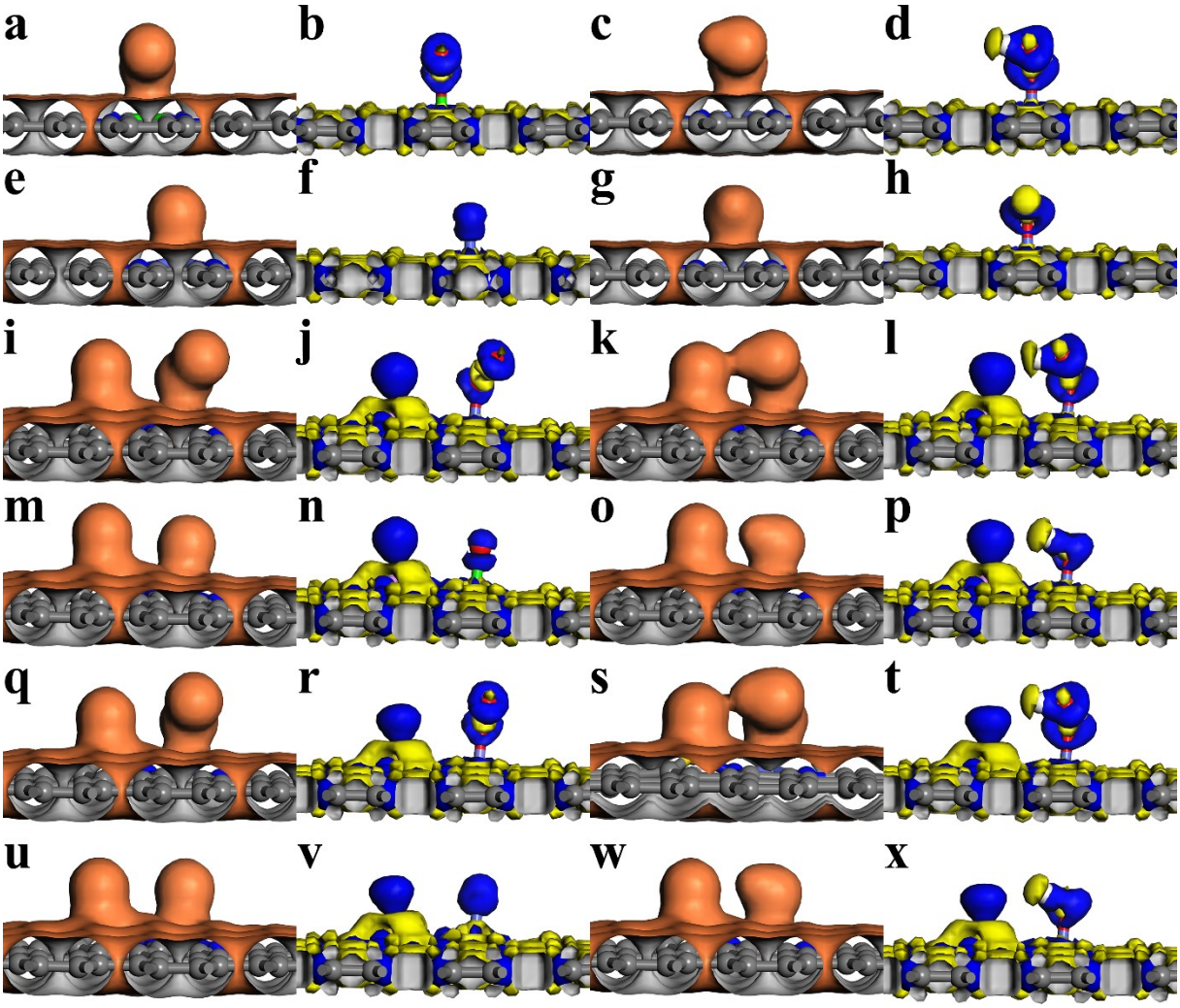

Figure S8. The total and deformation electron density of ORR intermediates (O_2*/OOH*/O*/OH*) on (a-h) non-doped Co-N_4 (i-p) P-doped Co-N_4 (q-x) S-doped Co-N_4.

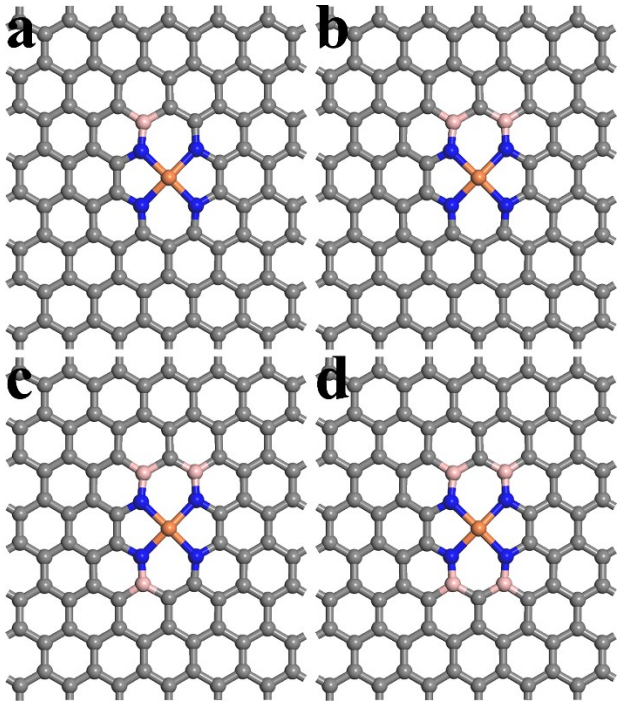

Figure S9. Structures of B doped M-N_4. Pink, B atom. Blue, nitrogen atom. Orange, metal atom. Grey, carbon atom.

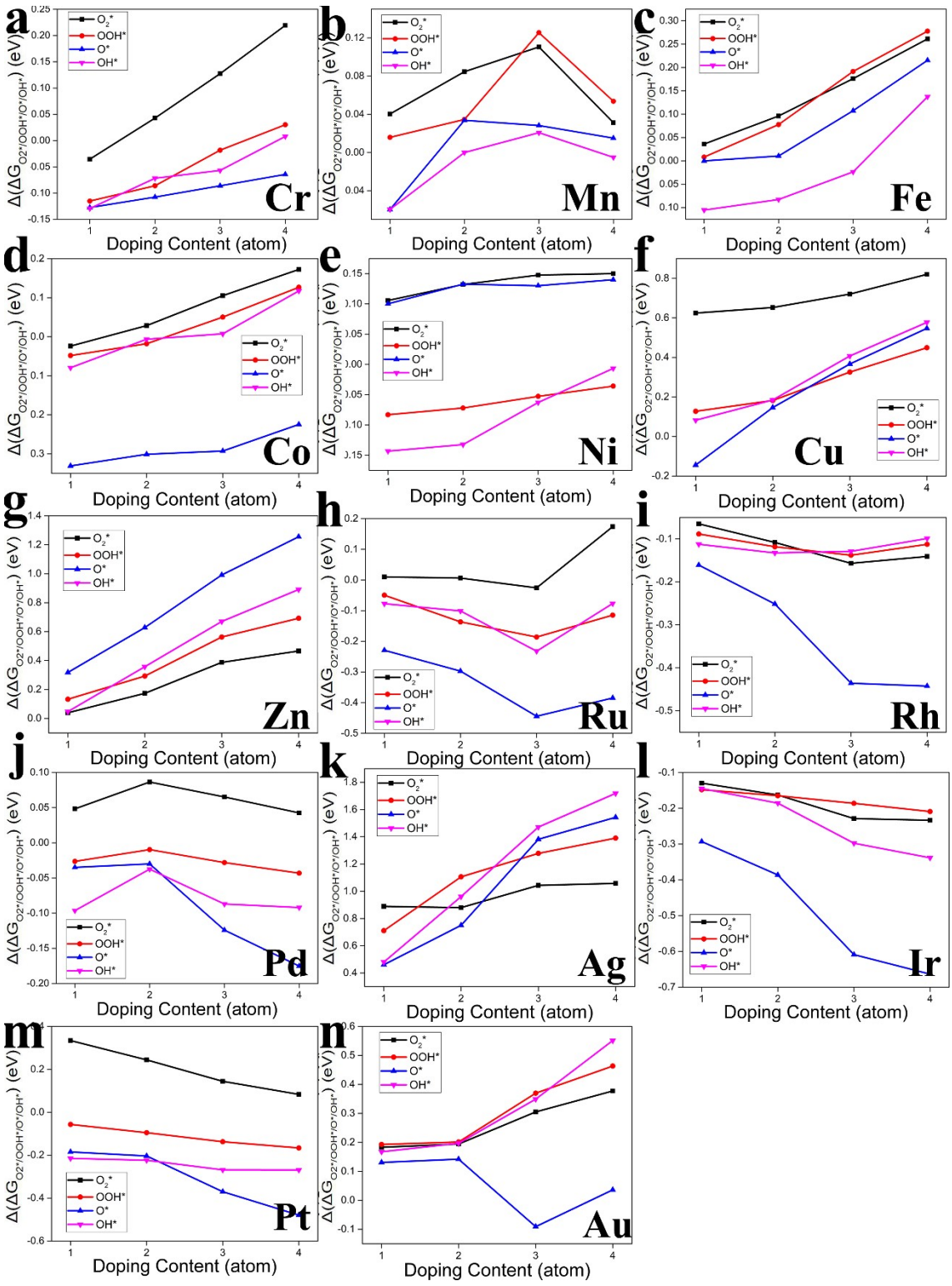
a
Cr
b
Mn
c
Fe
d
Co
e
Ni
f
Cu
g
Zn
h
Ru
i
Rh
j
Pd
k
Ag
l
Ir
m
Pt
n
Au
O2*
OOH*
O*
OH*
Doping Content (atom)
Δ(ΔGO2*/OOH*/O*/OH*) (eV)

Figure 10. The change of adsorption energies after B doping and the energies released in the elementary reactions. For example, $\Delta(\Delta G_{O2*})$ is the difference between ΔG_{O2*} on B-doped M-N_4 and that on non-doped M-N_4.

REFERENCE

[1] Delley, B. An All-electron Numerical Method for Solving the Local Density Functional for Polyatomic Molecules. *J. Chem Phys.*, **1990**, 92, 508.

[2] Delley, B. From Molecules to Solids with the $DMol^3$ Approach. *J. Chem. Phys.*, **2000**, 113, 7756-7764.

[3] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865-3868.

[4] Grimme, S. Semiempirical GGA-type Density Functional Constructed with a Long-range Dispersion Correction *J. Comp. Chem.*, **2006**, 27, 1787.

[5] Hamann, D. R.; Schluter, M.; Chiang, C. Norm-conserving Pseudopotentials. *Phys. Rev. Lett.*, **1979**, 43, 1494-1497.

[6] Hammer, B.; Nørskov, J. K. Why Gold Is the Noblest of All the Metals *Nature*, **1995**, 376, 238.

[7] Nørskov, J. K.; Bligaard, T.; Logadottir, A.; Kitchin, J. R.; Chen, J. G.; Pandelov, S.; Stimming, U. Trends in the Exchange Current for Hydrogen Evolution. *J. Electrochem. Soc.*, **2005**, 152, J23-J26.

[8] X. Guo, J. Gu, S. Lin, S. Zhang, Z. Chen, S. Huang. *J. Am. Chem. Soc.* **2020**, 142, 5709−5721.