Supporting Information

Strain-Induced Catalytic Enhancement in Co-BTA and Rh-BTA for Efficient 2e$^-$ Oxygen Reduction: A DFT Study

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Quantitative Analysis of Bonding Interactions via COHP

In this study, the Crystal Orbital Hamilton Population (COHP) analysis was employed to gain insights into the nature of interatomic interactions within the material. COHP offers a quantitative means to assess the bonding or anti-bonding contributions of chemical bonds.[1] By projecting the expectation values of the Hamiltonian operator onto the orbitals of specific atom pairs, COHP analysis reveals the distribution of bonding and anti-bonding states at various energy levels.

Specifically, COHP is achieved by analyzing the orbital information obtained from electronic structure calculations, such as those based on Density Functional Theory. The COHP for each pair of atoms can be expressed as:

$$COHP_{ij}(E) = -\sum_{k} P_{ij}^{k} H_{ij}^{k} \delta(E - E_k)$$

Where P_{ij}^{k} and H_{ij}^{k} represent the crystal orbital overlap and Hamiltonian matrix elements, respectively, and E_k is the corresponding eigenvalue of energy. The integrated COHP (ICOHP) values quantify the total bonding and anti-bonding contributions over the entire energy range.

***d*-band Center Calculation for Transition Metals**

In the present investigation, particular attention was devoted to the position of the *d*-band center of transition metal surfaces, a key factor in understanding their catalytic activities. The *d*-band center refers to the weighted average energy position of the *d*-state electrons in transition metals, significantly influencing surface adsorption properties and catalytic reactions. According to the theory proposed by Hammer and Nørskov, the position of the *d*-band center is intimately related to the electronic structure of adsorption sites on the catalyst surface.[2]

The location of the d-band center is determined by calculating the energy-weighted average of the d-electron states density on the surface. The calculation formula is as follows:

$$\epsilon_d = \frac{\int \epsilon D_d(\epsilon) d_\epsilon}{\int D_d(\epsilon) d_\epsilon}$$

where ϵ represents the energy and $D_d(\epsilon)$ is the density of states function for the *d*-states. The energetic proximity of the *d*-band center to the Fermi level dictates the strength of the interaction between the metal surface and the adsorbed molecules. Typically, the closer the *d*-band center is to the Fermi level, the stronger the interaction with the adsorbate.

Table S1 Free energy of TM-BTA with the adsorption of *OOH.

Type	E_{total} (eV)	G_{corr} (eV)	G_{total} (eV)
Sc	-253.204	0.329	-252.875
Ti	-254.842	0.384	-254.458
V	-254.860	0.363	-254.498
Cr	-255.011	0.319	-254.692
Mn	-253.387	0.334	-253.053
Fe	-250.774	0.333	-250.441
Co	-247.827	0.321	-247.506
Ni	-244.173	0.288	-243.886
Ru	-250.657	0.292	-250.365
Rh	-247.091	0.336	-246.760
Pd	-242.430	0.252	-242.178
Pt	-245.020	0.257	-244.763

Table S2 Values of *d*-Band Centers for Co-BTA and Rh-BTA under varied strain conditions.

Strain	-1.95%	-1.30%	-0.65%	0.00%	+0.65%	+1.30%	+1.95%

Co	-1.846	-1.775	-1.789	-1.746	-1.783	-1.743	-1.735
Rh	-1.713	-1.606	-1.538	-1.457	-1.509	-1.457	-1.464

Table S3 Under different strain conditions, the average bond length (Å) between the metal center atom and the surrounding coordination atoms before and after *OOH adsorption.

Type		-1.95%	-1.30%	-0.65%	0.0%	+0.65%	+1.30%	+1.95%
Sc	N-M	2.092	2.101	2.113	2.121	2.128	2.141	2.151
	N-M(*OOH)	2.204	2.210	2.209	2.237	2.227	2.234	2.241
Ti	N-M	2.003	1.982	1.989	1.996	2.004	2.044	2.029
	N-M(*OOH)	2.049	2.044	2.039	2.047	2.043	2.055	2.063
Cr	N-M	1.942	1.968	1.981	1.993	2.007	2.020	2.035
	N-M(*OOH)	1.967	1.981	1.981	1.987	2.007	2.019	2.033
Mn	N-M	1.894	1.903	1.912	1.920	1.928	1.939	1.949
	N-M(*OOH)	1.925	1.923	1.928	1.935	1.944	1.953	1.965
Fe	N-M	1.847	1.861	1.872	1.879	1.887	1.899	1.909
	N-M(*OOH)	1.892	1.890	1.892	1.898	1.907	1.918	1.929
Co	N-M	1.819	1.827	1.836	1.845	1.855	1.865	1.876
	N-M(*OOH)	1.866	1.867	1.867	1.872	1.881	1.892	1.904
Ni	N-M	1.822	1.830	1.841	1.849	1.858	1.868	1.881
	N-M(*OOH)	1.837	1.845	1.855	1.865	1.874	1.885	1.898
Rh	N-M	1.945	1.953	1.966	1.973	1.985	1.996	2.006
	N-M(*OOH)	1.992	1.991	1.991	1.997	2.008	2.025	2.033
Pd	N-M	1.965	1.974	1.985	1.994	2.002	2.013	2.025
	N-M(*OOH)	1.969	1.978	1.988	1.999	2.009	2.021	2.029
Pt	N-M	1.968	1.976	1.987	1.994	2.002	2.013	2.024
	N-M(*OOH)	1.977	1.982	1.990	1.999	2.010	2.019	2.029

Table S4. The calculated formation energies (ΔE_{form}) of Ni-, Co-, and Rh-BTA.

Type	Ni-BTA	Co-BTA	Rh-BTA
ΔE_{form} (eV)	-4.246	-4.956	-4.478

The corresponding formation energy calculation formula is stated as follows:

$$\Delta E_{form} = E_{TM-BTA} - E_{BTA} + 2E_{H_2} - \mu_{TM}^{0}$$

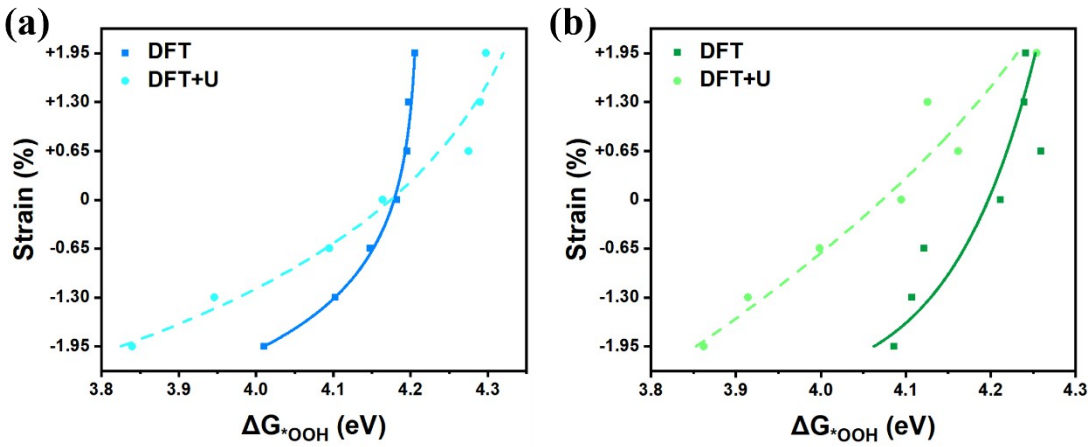

Fig. S1. Plot of the relationship between ΔG_{*OOH} values and the dependent variable obtained by studying the DFT and DFT+U methods, (a) Co-BTA, (b) Rh-BTA. In view of the fact that Co and Rh are elements of the same main group and have similar properties, the same U value of 3.42 eV was used for correction, and the corresponding U value was taken from Reference 3.

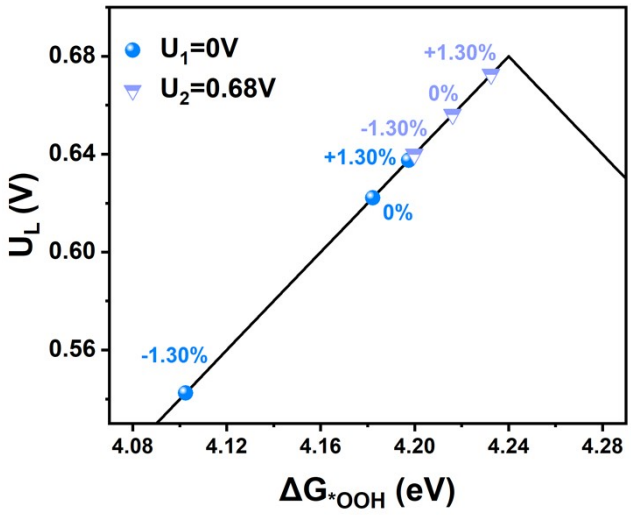

Fig. S2. Trend of the limiting potential of Co-BTA as a function of strain at different electrode potentials.

Modeling Structure:

The structural model consists of two consecutive units in the long chain of TM-BTA, containing 8 nitrogen (N) atoms, 12 carbon (C) atoms, 2 transition metal (TM) atoms, and 12 (H) hydrogen atoms. To avert interlayer interactions stemming from the model's periodicity, a vacuum layer exceeding 15 Å was implemented. Due to the excessive length of the model structure information, we only present the detailed atomic coordinates of Co-BTA and Rh-BTA catalysts below, and the structures of other TM-BTA are consistent with the above two catalysts. The detailed atomic coordinates within the Co-BTA and Rh-BTA structures are presented as follows:

Co-BTA

1.00000000000000

15.3491017285728528 0.0000000000000000 0.0000000000000000

0.0000000000000000 15.0000000000000000 0.0000000000000000

0.0000000000000000 0.0000000000000000 15.0000000000000000

N C Co H

8 12 2 12

94	Direct			
95		0.0895902379050250	0.4991186746333861	0.3865148392397993
96		0.0895887834221885	0.5012397328976045	0.5498835635452040
97		0.4098006943556209	0.4982958718898646	0.3865262809346313
98		0.4098001216528388	0.5004129707827337	0.5498950532058443
99		0.5895902069050261	0.4991186746333861	0.3865148392397993
100		0.5895887444221890	0.5012397328976045	0.5498835635452040
101		0.9098007253556267	0.4982958718898646	0.3865262809346313
102		0.9098000596528411	0.5004129707827337	0.5498950532058443
103		0.1711729500927192	0.5004863898511075	0.5173103360165816
104		0.2496951073533480	0.4983585636293733	0.3716685678086143
105		0.1711732738492757	0.4992387175269557	0.4191008214195861
106		0.2496928267641682	0.5007742693669117	0.5647549011889900
107		0.3282155322063594	0.5000712635554716	0.5173169629724071
108		0.3282172100167997	0.4988248276336688	0.4191075844708111
109		0.6711729500927193	0.5004863898511075	0.5173103360165816
110		0.7496950913533464	0.4983585636293733	0.3716685678086143
111		0.6711732738492757	0.4992387175269557	0.4191008214195861
112		0.7496927947641655	0.5007742693669117	0.5647549011889900
113		0.8282155322063595	0.5000712635554716	0.5173169629724071
114		0.8282172100167997	0.4988248276336688	0.4191075844708111
115		0.4996944040707945	0.4998016422790791	0.4682057959301015
116		0.9996943720707989	0.4998016422790791	0.4682057959301015
117		0.0851034233706787	0.4985115789467765	0.3185155831273289
118		0.0850903367907922	0.5024101604251938	0.6178757992400530
119		0.2496934025220973	0.4973564361431386	0.2988732091262277
120		0.2496922799568755	0.5015350026233641	0.6375557946369916
121		0.4142919573684221	0.4972492176786306	0.3185323861921964
122		0.4142925183019936	0.5011376571367452	0.6178934149446138
123		0.5851034543706779	0.4985115789467765	0.3185155831273289

0.5850903677907910 0.5024101604251938 0.6178757992400530

0.7496934025220974 0.4973564361431386 0.2988732091262277

0.7496922479568729 0.5015350026233641 0.6375557946369916

0.9142918953684170 0.4972492176786306 0.3185323861921964

0.9142925803019987 0.5011376571367452 0.6178934149446138

Rh-BTA

1.00000000000000

15.8723944742817356 0.0000000000000000 0.0000000000000000

0.0000000000000000 15.0000000000000000 0.0000000000000000

0.0000000000000000 0.0000000000000000 15.0000000000000000

N C Rh H

8 12 2 12

Direct

0.0954818285310498 0.4991080770760946 0.3844900472014136

0.0954781254528985 0.5012766839198949 0.5519068476612741

0.4039118509360499 0.4982466549370634 0.3845020481363073

0.4039127928193034 0.5004123177241165 0.5519197348671527

0.5954817975310507 0.4991080770760946 0.3844900472014136

0.5954780864528990 0.5012766839198949 0.5519068476612741

0.9039118819360560 0.4982466549370634 0.3845020481363073

0.9039127308193053 0.5004123177241165 0.5519197348671527

0.1735333118752028 0.5005044316520921 0.5174143176071638

0.2496950440494412 0.4983701250801783 0.3719950909446707

0.1735339421626845 0.4992518411569508 0.4190007811293734

0.2496940220437394 0.5007827031942313 0.5644293280674303

0.3258565912512599 0.5000698454373815 0.5174196332427976

0.3258572071023307 0.4988184955120521 0.4190057418785815

0.6735333118752029	0.5005044316520921	0.5174143176071638
0.7496950280494399	0.4983701250801783	0.3719950909446707
0.6735339421626845	0.4992518411569508	0.4190007811293734
0.7496939900437365	0.5007827031942313	0.5644293280674303
0.8258565912512602	0.5000698454373815	0.5174196332427976
0.8258572071023306	0.4988184955120521	0.4190057418785815
0.4996963121292030	0.4997956539071644	0.4682030661506385
0.9996962801292073	0.4997956539071644	0.4682030661506385
0.0935242602477702	0.4985199849757916	0.3163298219316670
0.0935111106643159	0.5024709240852789	0.6200590122280992
0.2496911484120483	0.4973632388197735	0.2991515852694218
0.2496903188952541	0.5015425345903327	0.6372766798046936
0.4058683034479623	0.4971741864837921	0.3163477184545144
0.4058688899794836	0.5011152784478171	0.6200794394247835
0.5935242912477693	0.4985199849757916	0.3163298219316670
0.5935111416643151	0.5024709240852789	0.6200590122280992
0.7496911484120484	0.4973632388197735	0.2991515852694218
0.7496902868952516	0.5015425345903327	0.6372766798046936
0.9058682414479571	0.4971741864837921	0.3163477184545144
0.9058689519794887	0.5011152784478171	0.6200794394247835

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