

Supporting Information

Proposal of Spin Crossover as A Reversible Switch of Catalytic Activity for Oxygen Evolution Reaction in Two Dimensional Metal-Organic Frameworks

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Stability under electrochemical conditions

The formation energy (E_f) and the dissolution potential (U_{diss})¹⁻³ are defined as:

$$E_f = (E_{total} - E_{substrate} - 2E_{Co})/2$$

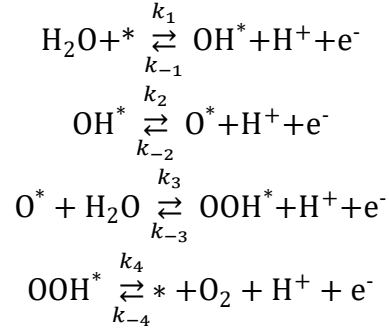
$$U_{diss} = U_{diss}(bulk) - E_f/ne$$

where E_{Co} is the total energy of the Co atom in its most stable bulk structure, E_{total} and $E_{substrate}$ are the energies of Co(TCSA) system and its substrate. $U_{diss}(bulk)$ and n are the standard dissolution potential of bulk metal and the number of electrons involved in the dissolution, respectively. Accordingly, systems with $E_f < 0$ eV are considered to be thermodynamically stable, and materials with $U_{diss} > 0$ V vs SHE are evaluated as electrochemically stable. In our calculation, E_{Co} is -7.04 eV, similar to the previous study. Meanwhile, the E_f are -2.86V and -3.24V to the HS and LS states, respectively.

Microkinetic Model

The current density was simulated by the microkinetic model developed by Hansen et

al.⁴. The OER steps adhere to the following equations:



where k_i and k_{-i} are the forward and backward reaction rate constants, respectively. For an electrochemical step, the equilibrium constant could be calculated by

$$K_i = \exp\left(-\frac{e(U - U_i)}{k_B T}\right)$$

where U_i is the reversible potential, and the rate constant k_i can be expressed as:

$$k_i = A_i \exp\left(-\frac{E_{a,i}}{k_B T}\right) \exp\left(-\frac{e\beta_i(U - U_i)}{k_B T}\right)$$

where $E_{a,i}$ is the activation free energy at the reversible potential of the step, the pre-factor A_i is set to 1×10^9 , k_B is the Boltzmann constant, the temperature T is 298.15 K and β_i is set to be 0.5. According to previous study, the activation free energy is generally small and calculated by 0.26 eV as usual.^{5,6}

Constant potential method

This method implements VASPsol to model electrochemical electrode/solution interface and establish the relationship between charge and electrode potential⁷.

$$U_q(\text{V/SHE}) = -4.6 - \phi_q(f)/e\text{V}$$

where $\phi_q(f)$ is the work function of charge system and 4.6 V is the work function of H_2/H^+ couple under standard conditions⁸⁻¹⁰.

At the fixed applied potential, the electrode potential referenced to SHE scale is

changed by pH values. The relationship is given by

$$U_{\text{RHE}} = U_{\text{SHE}} + k_{\text{B}}T \ln(10)\text{pH}/e$$

Therefore, by adjusting the charge numbers of the system, the energies under specific potentials could be calculated.

According to Neurock methods,¹¹ the potential-dependent charge system energy could be corrected by

$$E_{\text{free}}(U) = E_{\text{DFT}} + \int_0^q \langle \overline{V}_{\text{tot}}(Q) \rangle dQ - q\phi_q(f)$$

where $\langle \overline{V}_{\text{tot}}(Q) \rangle$ refers to the average potential in the cell.

The total free energy values (E_{free}) and the electric potential (U) could be fitted to a quadratic function form (**Figure S5**), consistent with a capacitor created by the charged-slab/background-charge system, written as

$$E(U) = -\frac{1}{2}C(U - U_0)^2 + E_0$$

where U_0 is the potential of zero charge (U_{PZC}), E_0 is the energy at the PZC, and C is the capacitance of the surface. From the quadratic functions, the potential-dependent energy at any electrode potential could be provided.

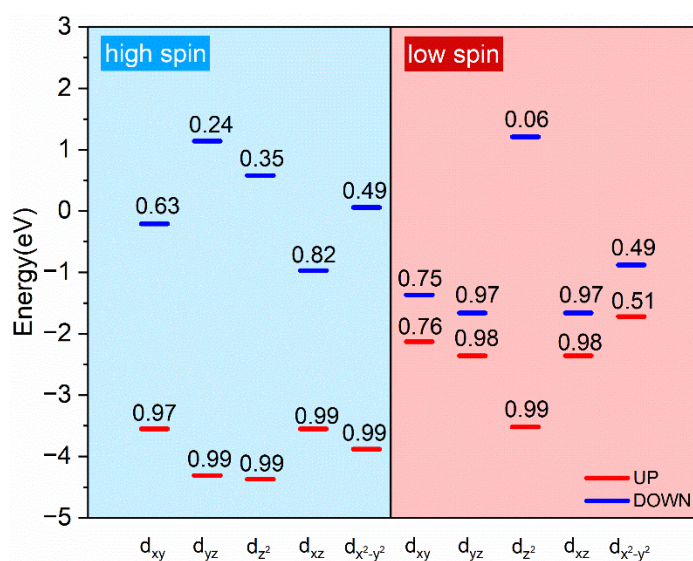


Fig. S1 Energy diagrams of the calculated band centers of d orbitals for the HS state and LS state with PBE+U method, respectively. The number denotes the occupation of spin-up and spin-down orbitals. Red and blue short bars denote the band center with spin-up and spin-down, respectively.

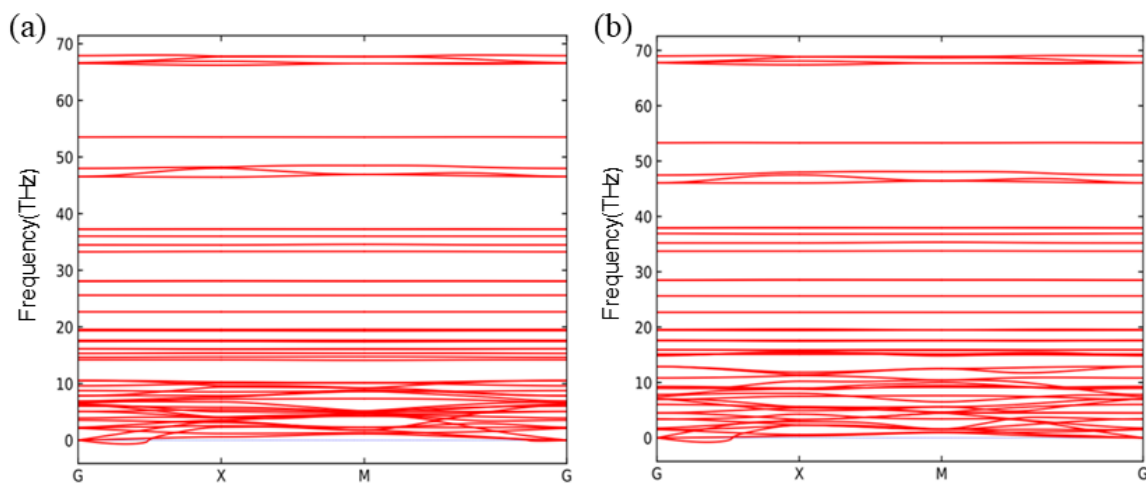


Fig. S2 Phonon band structures of (a) the LS state and (b) the HS state in Co(TCSA), respectively.

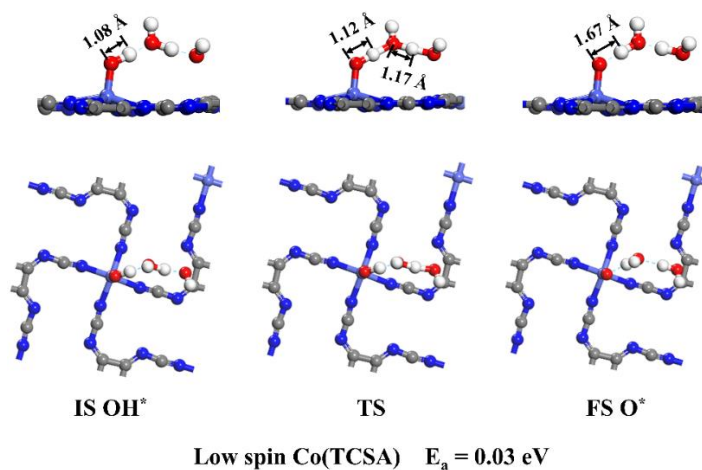


Fig. S3 Schematic of the formation of O* species on the Co(TCSA) in the LS state

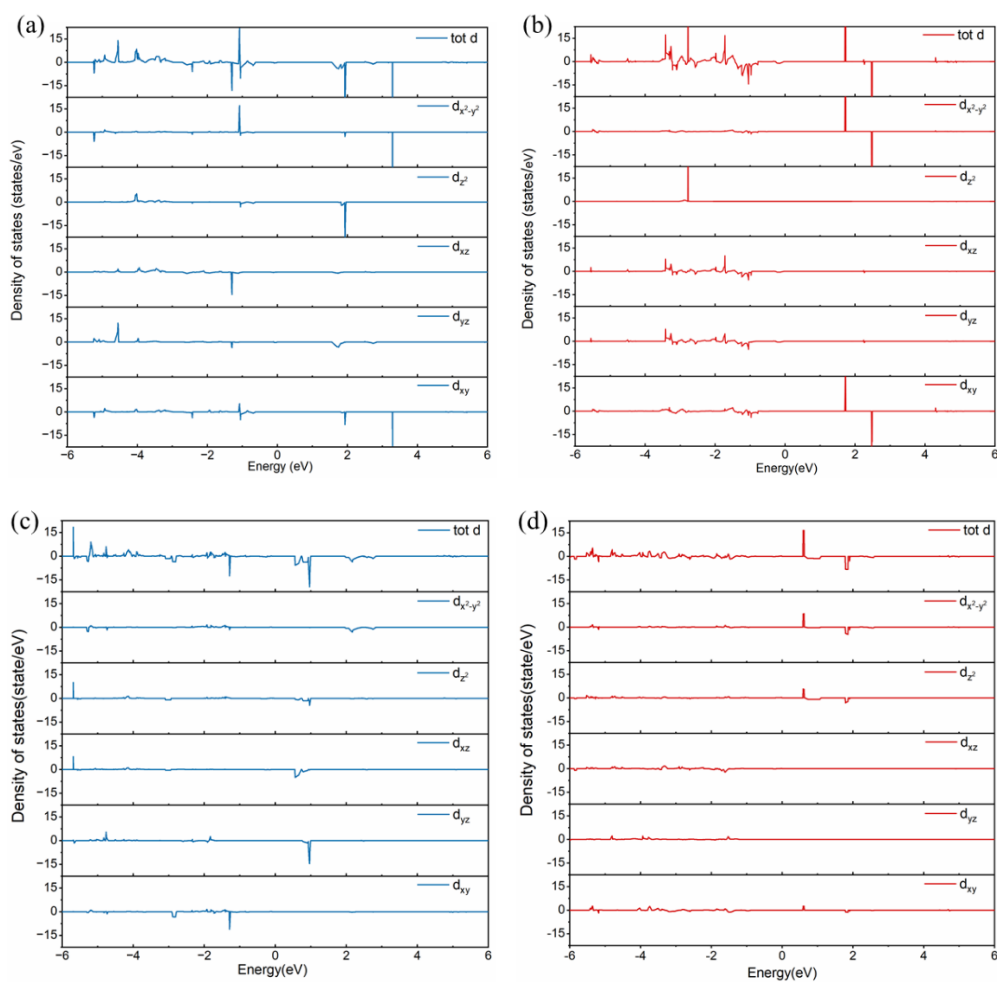


Fig. S4 The projected density of states (PDOS) for (a) the HS state and (b) the LS state, respectively. While (c) and (d) are those with HO* intermediates. The blue lines and red lines represent the HS and LS states, respectively.

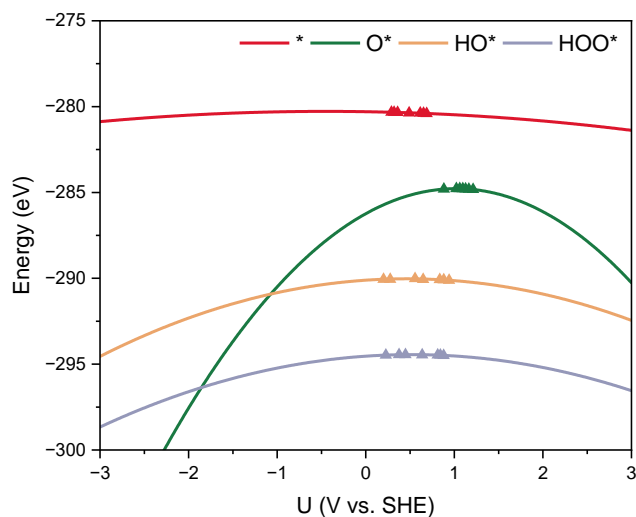


Fig. S5 Total energies of bare (red), HOO* (blue), O* (green), and HO* (yellow) as a function of applied potential U . Calculated total energies (triangle) and polynomial fits (solid lines) are shown.

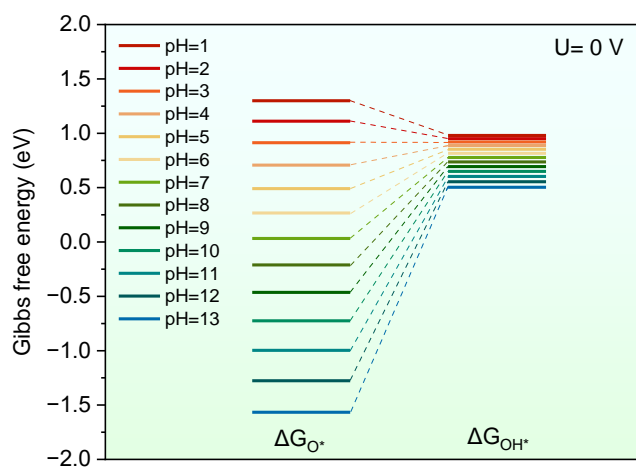


Fig. S6 The pH-dependent Gibbs free energy of O* and OH* on the LS state under CPM.

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