Electronic Supplementary Information (ESI) for

Spin: An Essential Factor in Advancing Oxygen Evolution Reaction

on 2D Fe-MOF

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Table of Contents

- Fig. S1. Electronic configurations for Fe-MOFs at various spin states.
- Fig. S2. PDOS for Fe d orbitals.

Fig. S3. Adsorption energy of oxygen intermediates on 2D Fe-MOF.

Fig. S4. Tendency of bond characteristics between the *O-intermediates and Fe site.

Fig. S5. PDOS for the orbital overlapping between Fe and the adsorbed *OH (a first step).

Fig. S6. PDOS for the orbital overlapping between Fe and the adsorbed *O₂ (a last step).

Table. S1. The estimated oxidation state of Fe cation in 2D Fe-MOF.

Table. S2. Adsorption energy of oxygen intermediates on 2D Fe-MOF.

Table. S3. Bond characteristics between the *O-intermediates and Fe site.

Table. S4. Bond length, bond index, dihedral angle of *O-intermediates and Fe site at HS state.

Table. S5. Gibbs free energy change of *O-intermediates on the 2D Fe-MOF at different potentials.



Scheme S1. Orbital feature of oxygen species in the gas phase as a free molecule, where (a) H_2O and (b) OH are diamagnetic with singlet states while (c) O_2 is paramagnetic with a triplet state.



Fig. S1 Electronic configurations for Fe-MOFs with various initial magnetic moments of 0, 1, 3, and 5 μ_B per Fe unit, illustrating how the spin state can modulate an electronic property, split the d-states as a discrete level and undergo an energy reordering. Herein, LS, MS, and HS represent the low, mid, and high spin states, respectively. The energy differences between the energetically lower state and the middle state are 3.4 eV (too far) for the non-spin case, 1.8 eV (uneven discrete) for the LS case, and ~0.5 eV (evenly distributed) for the MS and HS cases.^{S1} The high spin state results in a stable electronic configuration.



Fig. S2 (a) Schematic diagram of the d-orbital splitting; From left to right, the degenerated d orbitals of a free metal atom and the crystal field splitting of d orbitals in a planar coordination environment.⁵² (b) Spin-polarized PDOS for d-orbitals of Fe atom in this work, which aligns well with the diagram. The PDOS represents that the Fe-d orbital splits into the discrete energy states. The arrow indicates the electron occupation in the spin channel and the horizontal line illustrates the Fermi level, $E_{\rm F}$.



Fig.S3 (a) Overall ICOHP value of oxygen intermediates on 2D Fe-MOF, where the black, blue, green, and red bars indicate the ICOHP at different spin states (the numerical values in Table S3). The ICOHP was used to evaluate the strength of chemical bond interactions between the *O-Fe pair. A higher (more negative) ICOHP value indicates stronger bond interaction, while a lower (less negative) ICOHP value suggests weaker bond interaction. (b) Diagram for the relationship between the O₂ adsorption energy change (ΔE_{ads}^{O2}) and the spin states, where ΔE_{ads}^{O2} decreases as the spin state increases, showing the lowest value at the HS state.



Fig.S4 (a) relationship between the bond length (L_{*O-Fe}) and ICOHP value of the oxygen intermediate and Fe site. (b) tendency of the $*O_2$ -Fe bond and the relevant bond indices at the different spin states (the numerical values in Table S3).



Fig. S5 (a) Spin-polarized PDOS for the orbital overlapping between Fe and the adsorbed *OH and (b) schematic diagram for Fe d and O p orbitals. Here, the d_{x2-y2} and d_{xy} orbitals don't overlap with the *O-p orbitals, however, another three d-orbitals overlap the *O-p orbitals, indicating a selective orbital-dependent interaction. The star marks the state from the adsorbed oxygen intermediate.



Fig. S6 (a) Spin-polarized PDOS for the orbital overlapping between Fe and the adsorbed $*O_2$ and (b) schematic diagram for Fe d and O p orbitals.

Table. S1 the calculated occupation number of 3 d orbitals of Fe cation in Fe-MOF. The occupied d-electrons assigned to Fe cation are in bold, further leading to the high spin state of Fe (III).

	Spin		State				
	channel	3d _{xy}	3d _{yz}	3d _{xz}	3d _{z2}	3d _{x2-y2}	otate
Fe	Up	0.93431	0.96295	0.91040	0.94444	0.98597	High spin
	Down	0.11661	0.02219	0.03025	0.21217	0.17303	Fe (III)

Note: The oxidation state of the Fe cation can be estimated by counting its d-electron number.⁵³⁻⁵⁴ The table contains the results integrated from the PDOS of each d orbital below the E_F (**Fig. S2**). Herein, the estimated occupation numbers are close to 1 for all d orbitals in the spin-up channel, but close to 0 in the spin-down channel. Thus, all five d orbitals in the spin-up channel are occupied, which implies the high spin state of Fe (III).

Table. S2 Adsorption energy (E_{ads}) of oxygen intermediates on 2D Fe-MOF at the different spin states.

Configuration	*OH	*0	*00H	*O ₂
$E^{no-spin}_{ads}$	-3.685	-5.866	-2.596	-2.273
E_{ads}^{LS}	-3.590	-5.041	-2.511	-2.157
E_{ads}^{MS}	-3.514	-4.500	-2.003	-1.404
E_{ads}^{HS}	-3.548	-4.362	-1.964	-1.366

Note: E_{ads} excluding spin provides a large value, while E_{ads} including spin shows a low value. Herein, OH with its sigma bonding is less influenced by the spin state of the Fe active site, while other oxygen intermediates are considerably affected. Importantly, a lower E_{ads} value is preferable for the final decisive step (O₂) of the OER. This arises from the fact that desorption energy, the reverse process of adsorption, serves as an indicator of the reaction product's release from the surface. In particular, the E_{ads} of $*O_2$ decreases as the spin state increases, showing the lowest value of -1.366 eV at the HS state.

	Spin states	*OH	*0	*00H	*O ₂
Geometry		*OH L _{+O-Fe} Fe	*0 <i>D.</i> ₀ Fe		<i>D</i> _{•02}
	no-spin	1.786	1.477	1.749	1.740
gth (Å	LS	1.825	1.670	1.892	1.987
Bond len	MS	1.820	1.641	1.892	2.039
	HS	1.811	1.675	1.890	2.094
ICOHP (eV)	no-spin	-3.283	-6.292	-3.997	-4.032
	LS	-2.888	-4.841	-2.337	-1.942
	MS	-2.633	-4.841	-2.319	-1.699
	HS	-2.624	-4.589	-2.225	-1.605
d index (COBI)	no-spin	0.760	1.477	0.865	0.936
	LS	0.580	0.846	0.361	0.288
	MS	0.400	0.735	0.350	0.265
Bone	HS	0.397	0.730	0.341	0.269

Table. S3. Bond characteristics between the *O-intermediates and Fe site at the different spin states.

Note: The bond length corresponds to a moderate value ICOHP in the presence of the spin, while it is shorter and has a higher ICOHP value in the absence of the spin, which can be less favorable. The bond index can be calculated from the Integrated Crystal Orbital Bond Index (ICOBI); ⁵⁵ e.g. the bond index of $*O_2$ -Fe is 0.269 in the HS state, 3.5 times lower than the non-spin case, suggesting a preferable value for O_2 desorption. Thus, the values for the HS state are highlighted and for further consideration.

		*	*0	*0	*00H	*O ₂
Geometry	Top view:					
~	L(Fe-O ₁)	2.031	2.083	2.114	2.163	2.071
gth (Å	L(Fe-O ₂)	2.031	1.983	2.114	2.032	2.071
nd len	L(Fe-O ₃)	2.031	2.072	2.103	2.029	2.073
Bor	L(Fe-O ₄)	2.031	1.983	2.103	1.987	2.073
31)	Fe-O ₁	0.196	0.185	0.158	0.154	0.221
Bond index (COF	Fe-O ₂	0.196	0.233	0.158	0.206	0.221
	Fe-O₃	0.196	0.193	0.161	0.221	0.222
	Fe-O₄	0.196	0.233	0.161	0.221	0.222
Dihedral angle (⁰)	∠ (*O -Fe-O₁-O₄)	01 90.0 P	*ОН Бе О1 О4 102.7	*0 Fe 01 04 111.0	о ₁ 0 ₂	0 ₂ Fe 0 ₁ 0 ₂ 102.7
	D _{Fe site} (Å)	-	0.389	0.486	0.448	0.389

Table. S4 Bond length (L), bond index (COBI), dihedral angle (\angle), and displacement (D) at the FeO₄ at the HS state.

Note: * indicates a FeO₄ environment. The bond index shows the same value of 0.196 for the Fe-O pair within the pristine one, suggesting the planarity of the present MOF. The change in the bond index after the adsorption implies that significant distortion occurs in the FeO₄. Also, **P** denotes the planarity. One uses the ghost atom for the planar structure to measure the dihedral (torsion) angle. It is also seen that the planarity is not preserved since the angle exceeded > 90° after the adsorption.

Configuratio	$\Delta G^{no-spin}_{U=0V}$	$\Delta G_{U=0V}^{spin}$	$\Delta G_{U=1.23V}^{no-spin}$	$\Delta G_{U=1.23V}^{spin}$	$\Delta G^{no-spin}_{x}$	ΔG^{spin}_{x}
n	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)
H ₂ O + *	0	0	0	0	-	-
*OH	0.244	0.170	-0.986	-1.213	-0.986	-1.213
*0	2.443	1.519	-0.017	-0.941	0.969#	0.272
*00H	4.058	3.239	0.368	-0.451	0.385	0.489#
*+ O ₂	4.920	4.920	0.000	0	-0.368	0.351

Table. S5 Gibbs free energy change (Δ G) of oxygen intermediates on the Fe-MOF at different potentials.

Note: $\Delta G_U \stackrel{spin}{=} 0 V (\Delta G_U^{no-spin})$ indicates the free energy changes at U=0 V, including (excluding) spin. $\Delta G_U \stackrel{spin}{=} 1.23 V (\Delta G_U^{no-spin})$ are the values at the potential of 1.23 V, respectively. Later on, ΔG_x is the difference between the subsequent two energies. *(#) indicates the active site (PDS). The PDS in the non-spin-polarized state is 0.969 eV. Meanwhile, the PDS in the high-spin state shows the lowest value of 0.489 eV among the spin states (e.g., 0.688 eV for the mid-spin state and 0.719 eV for the low-spin state), thus representing the spin-polarized configuration.

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