Density Functional Theory Study of Oxygen Reduction Reaction on Non-PGM Fe-N_x-C Electrocatalyst

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Electronic Supplementary Information

In alkaline medium, complete O_2 reduction can be summarized by the reactions (1-5)[1]

$$O_2 + 2H_2O + 4e^- \rightarrow {}^*O_2 + 2H_2O + 4e^- \quad (1)$$

$$^*O_2 + 2H_2O + 4e^- \rightarrow {}^*OOH + OH^- + H_2O + 3e^- \quad (2)$$

$$^*OOH + OH^- + H_2O + 3e^- \rightarrow {}^*O + 2(OH^-) + H_2O + 2e^- \quad (3)$$

$$^*O + 2(OH^-) + H_2O + 2e^- \rightarrow {}^*OH + 3(OH^-) + e^- \quad (4)$$

$$^*OH + 3(OH^-) + e^- \rightarrow 4(OH^-) \quad (5)$$

Alternatively, peroxide (OOH^-) can form as a product of reaction (3) and desorb from the catalytic site, requiring a $2 \times 2e^-$ dual site mechanism.[1]

We find that OOH binds strongly to Fe-N_x sites (Table S1). But, OOH^-, which is a closed shell molecule, is expected to bind weakly. Our computations indeed predict a weaker (less favorable) interaction of OOH^- with Fe-N_x sites as compared to OOH (Table S1). Moreover, we

find that O-O bond scission occurs (Figure S1) during the interaction of OOH^- with Fe-N_x sites. One oxygen (*O) remains chemisorbed on Fe-N_x sites and OH^- desorbs, supporting our above proposed ORR mechanism (reaction 3-7). The O-O distances (d_{O-O}) in optimized geometry of OOH^- on Fe-N_4 and Fe-N_2 sites are 2.01Å and 1.97Å, respectively. The comparison of the charged and non-charged peroxide computations shows that ~0.5e reside on OH^- and the remaining charge is distributed over the graphene sheet. Thus, charge localization occurs as expected but is incomplete. Nevertheless, the findings provide a rational for the weaker chemisorption of the anion as compared to the radical. This predicted breaking of the O-O bond in peroxide which is a necessary step for ORR to proceed via a $4e^-$ pathway[2-4] suggests that Fe-N_x sites promote a complete single site $4e^-$ ORR without stable peroxide intermediate formation consistent with the previous predictions on Fe-macrocyclic molecular catalysts.[3, 4] The adsorbed *O undergoes further reduction via the reactions: $*O + H_2O + 2e^- \rightarrow *OH + OH^- + e^- \rightarrow 2(OH^-)$.

Table S1. Binding energies (BEs in eV) of adsorbates, the shortest distance between Fe in graphitic Fe-N_x sites and O of adsorbates (d_{Fe-O} in Å), and the optimized O-O distance (d_{O-O} in Å) in adsorbates.

Sites	adsorbate	BE	dFe-O	dO-O
Fe-N_4	OOH	-1.72	1.77	1.51
	OOH^-	-0.34	1.67	2.01
Fe-N_2	OOH	-2.08	1.71	1.52
	OOH-	-1.50	1.62	1.96

Table S2. DFT calculated total energy (E_{total}) of gas phase species, entropy and ZPE corrections (in eV) to gas phase molecules and adsorbed species. Entropy and ZPE correction of gas phase species are taken from NIST data base.[5]

Gas phase species	E_{total}	TS	ZPE	Adsorbed species	TS	ZPE
H_2	-6.81	0.41	0.27			
O_2	-9.88	0.64	0.18	$*O_2$	0.00	0.14
OOH	-13.27			*OOH	0.00	0.44
O	-1.58			*O	0.00	0.07
OH	-7.74			*OH	0.00	0.35
H_2O_2	-18.17					
H_2O	-14.24	0.67	0.56			

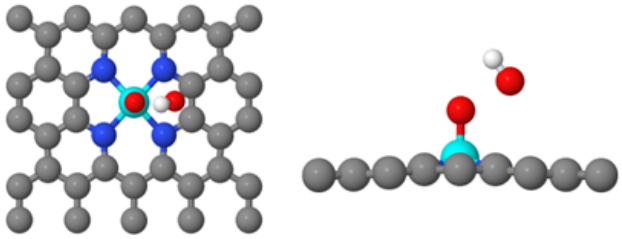

Figure S1. Optimized binding geometry of OOH^- on graphitic Fe-N_4 site. Left panel: top view and right panel: side view. Grey: C, Blue: N, Cyan: Fe, Red: O and White: H atoms, respectively.

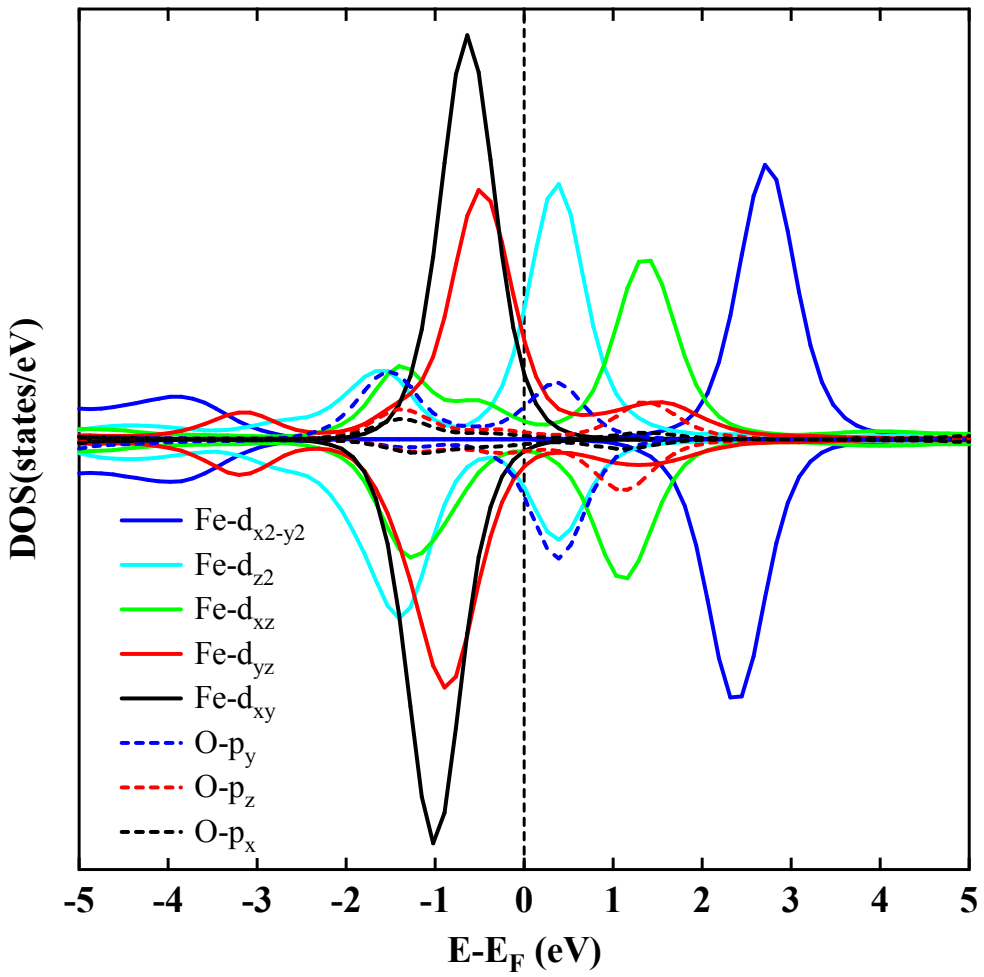

Figure. S2 Electronic density of states (DOS) of O and Fe atoms on optimized on O_2-Fe-N_4 configuration. DOS of O atom that forms direct bond with Fe in end-on O_2-Fe-N_4 configuration is shown.

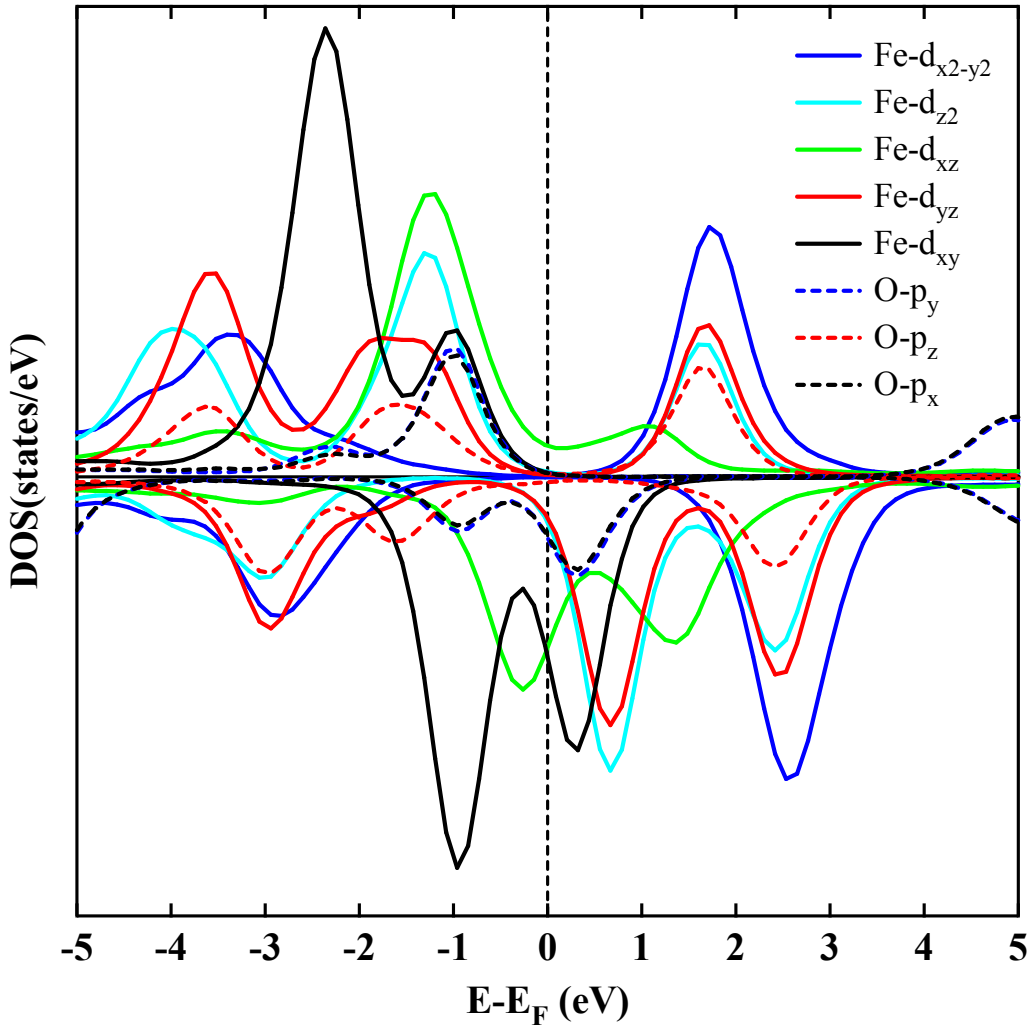

Figure S3. Electronic density of states (DOS) of O and Fe atoms on optimized O_2-Fe-N_2 configuration. Two O atoms remain equidistance from Fe on side-on adsorption of O_2 on Fe-N_2 and have identical DOS. Therefore DOS of only one O atom is shown.

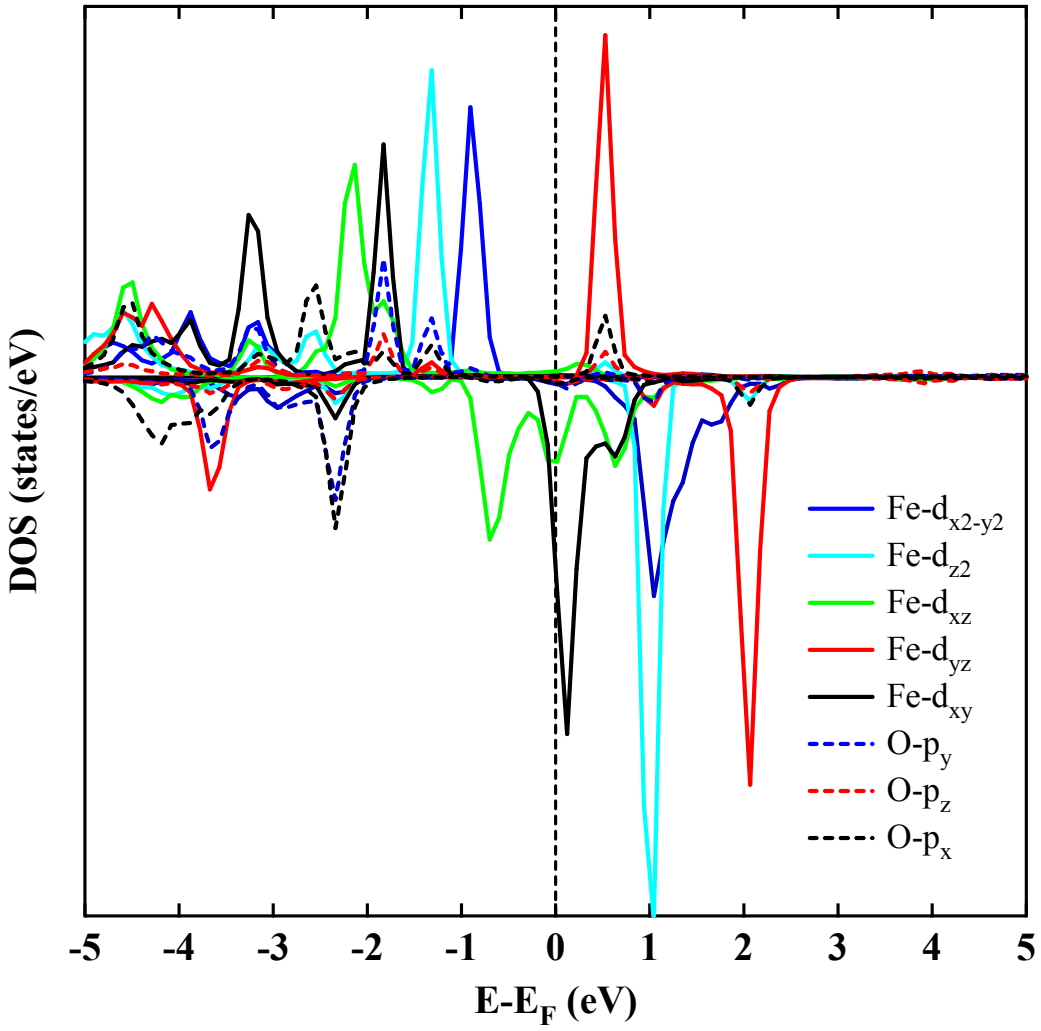

Figure S4. Electronic density of states (DOS) of O and Fe atoms on optimized H_2O_2-Fe-N_4 configuration. Two O atoms remain equidistance from Fe on H_2O_2-Fe-N_4 configuration and have identical DOS. Therefore DOS of only one O atom is shown.

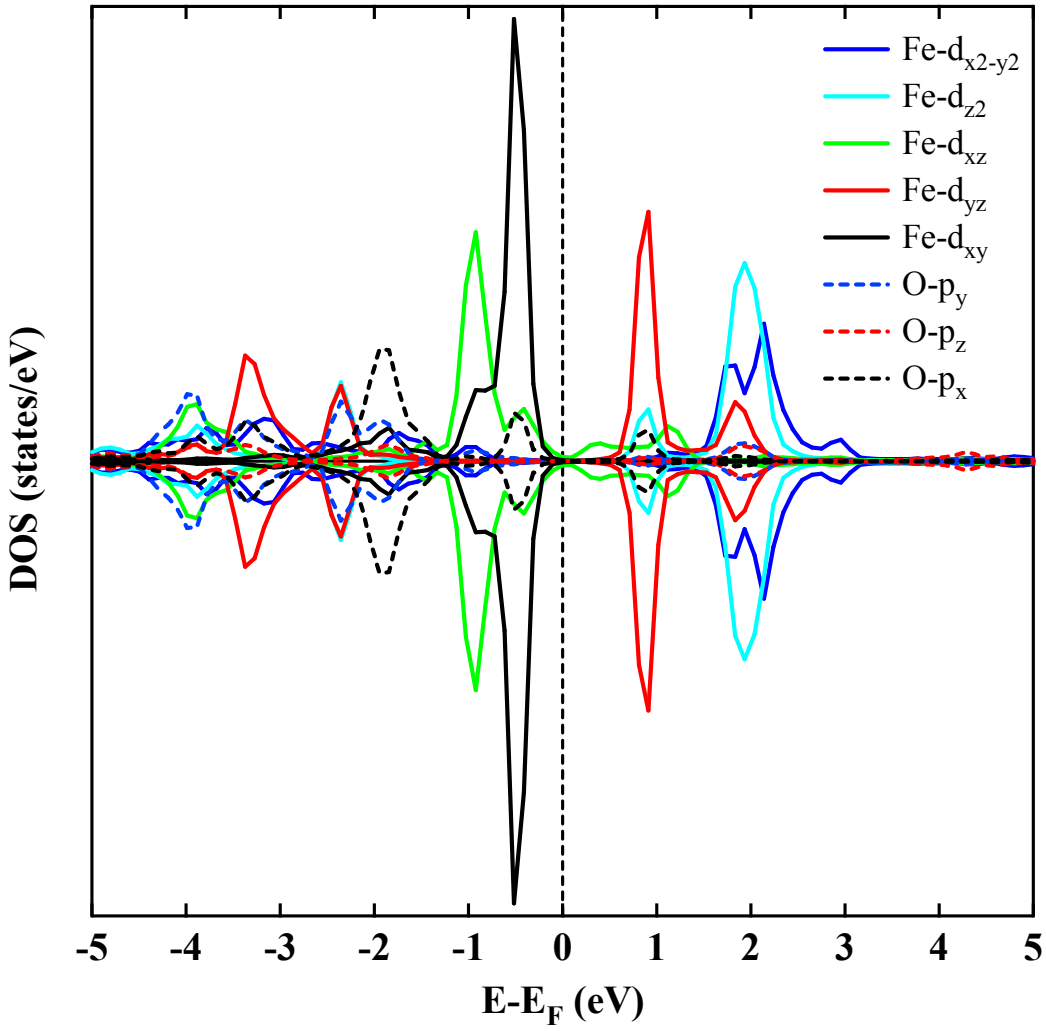

Figure S5. Electronic density of states of adsorbed O and Fe atoms on optimized on H_2O_2-Fe-N_2 configuration. Two O atoms remain equidistance from Fe on H_2O_2-Fe-N_2 configuration and have identical DOS. Therefore DOS of only one O atom is shown.

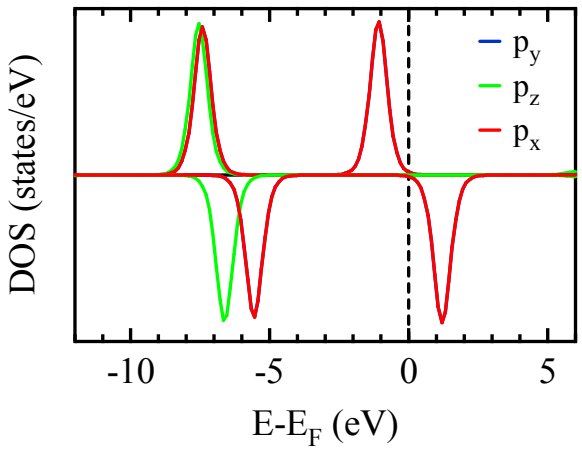

Figure S6. Electronic density of states (DOS) of an oxygen atom in gas phase O_2. Two oxygen atoms in O_2 are degenerate. Therefore DOS of only one O atom is shown in the figure.

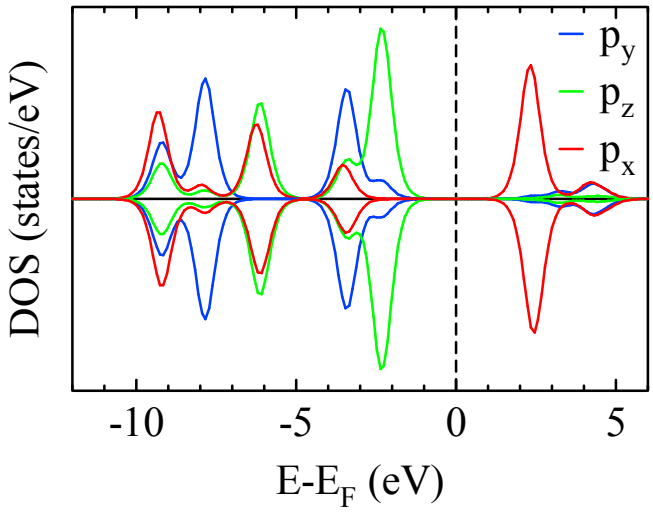

Figure S7. Electronic density of states (DOS) of an oxygen atom in gas phase H_2O_2. Two oxygen atoms in H_2O_2 are degenerate. Therefore DOS of only one O atom is shown in the figure.

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5. http://cccbdb.nist.gov/.