

Fig. 1 a) Variations of formation energies with N atomic number and doping configuration. b) Trend in the theoretical overpotential for the ORR plotted against  $\Delta G^*OH$ .

1. In the double vacancy (DV), as the number of doped N atoms increases, the formation energy  $E_f$  becomes increasingly negative, resulting in Fe-4N defects being the most stable in the Fe-N-C catalyst.
2. The overpotential of the catalyst with double vacancy structure decreases with the incorporation of N atoms. It can be concluded that in the double-vacancy structure, the incorporation of an appropriate number of N atoms and different doping configurations can improve the ORR catalytic performance of the Fe-N coordination structure.

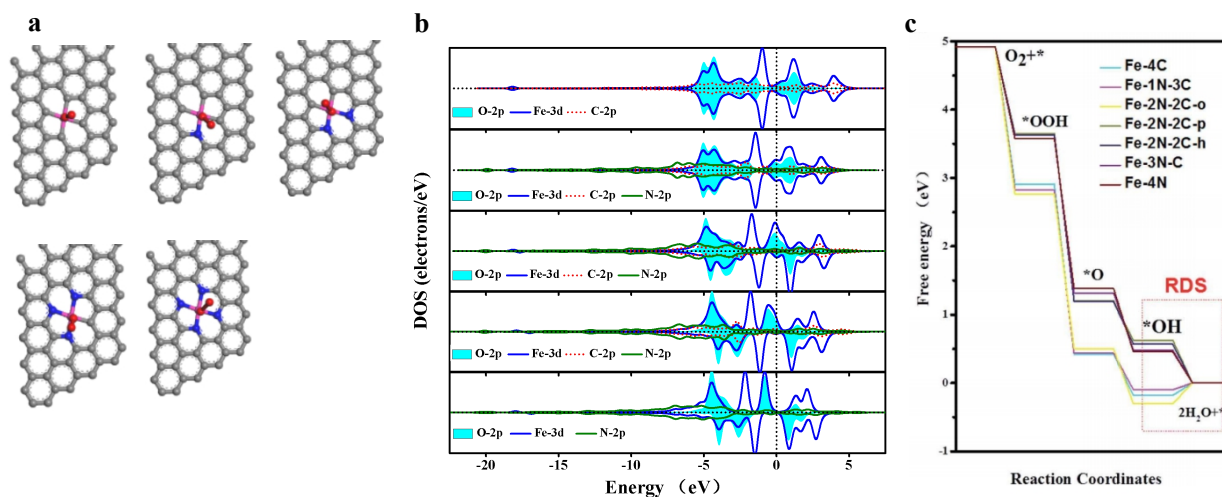


Fig. 2 a) O atoms are adsorbed on Fe-4C sites, Fe-1N-3C sites, Fe-2N-2C site, Fe-3N-C sites and Fe-4N sites. b) DOS diagram of O atoms adsorbed on Fe-N<sub>x</sub> active sites. c) Free energy profiles of Fe-N doped in double vacancy.

3. In the double-vacancy structure, the bond length of the Fe-O bond gradually increases as the number of N atoms increases. The interaction between Fe atoms and O atoms gradually weakens, weakening the strong binding force between oxygen-containing compounds and their surface sites will increase ORR activity.

**Supplementary Table 1.** Comparison of ORR performance between MnO<sub>2</sub>@Mn catalysts and the reported MnO<sub>x</sub>-based catalysts in literatures.

Electrocatalysts	E <sub>onset</sub> (V)	Current density at 0.88 V (mA cm <sup>-1</sup> )	Reference
Fe-N <sub>5</sub> -C	0.93	1.65	This work
Pt/C	0.93	1.54	This work
FePc	0.92	1.04	This work
Fe-N <sub>x</sub> -C-1	0.93	1.53	Ref. 1
Fe-NMP	0.95	1.28	Ref. 2
Czif-Fe(acac) <sub>3</sub> -6	0.925	0.36	Ref. 3
Fe <sub>se</sub> -N-C	0.86	0.58	Ref. 4

### Supplementary References

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