Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2021

Supplementary Information for

Unveiling the Role of Carbon Oxidation in Irreversible Degradation of Atomically-Dispersed FeN_4 Moieties for Proton Exchange Membrane Fuel Cells

Xin Tan,* Hassan A. Tahini, Sean C. Smith*

Integrated Materials Design Laboratory, Department of Applied Mathematics, Research School of Physics, The Australian National University, Canberra, ACT 2601, Australia

Email: Xin.Tan@anu.edu.au, Sean.Smith@anu.edu.au

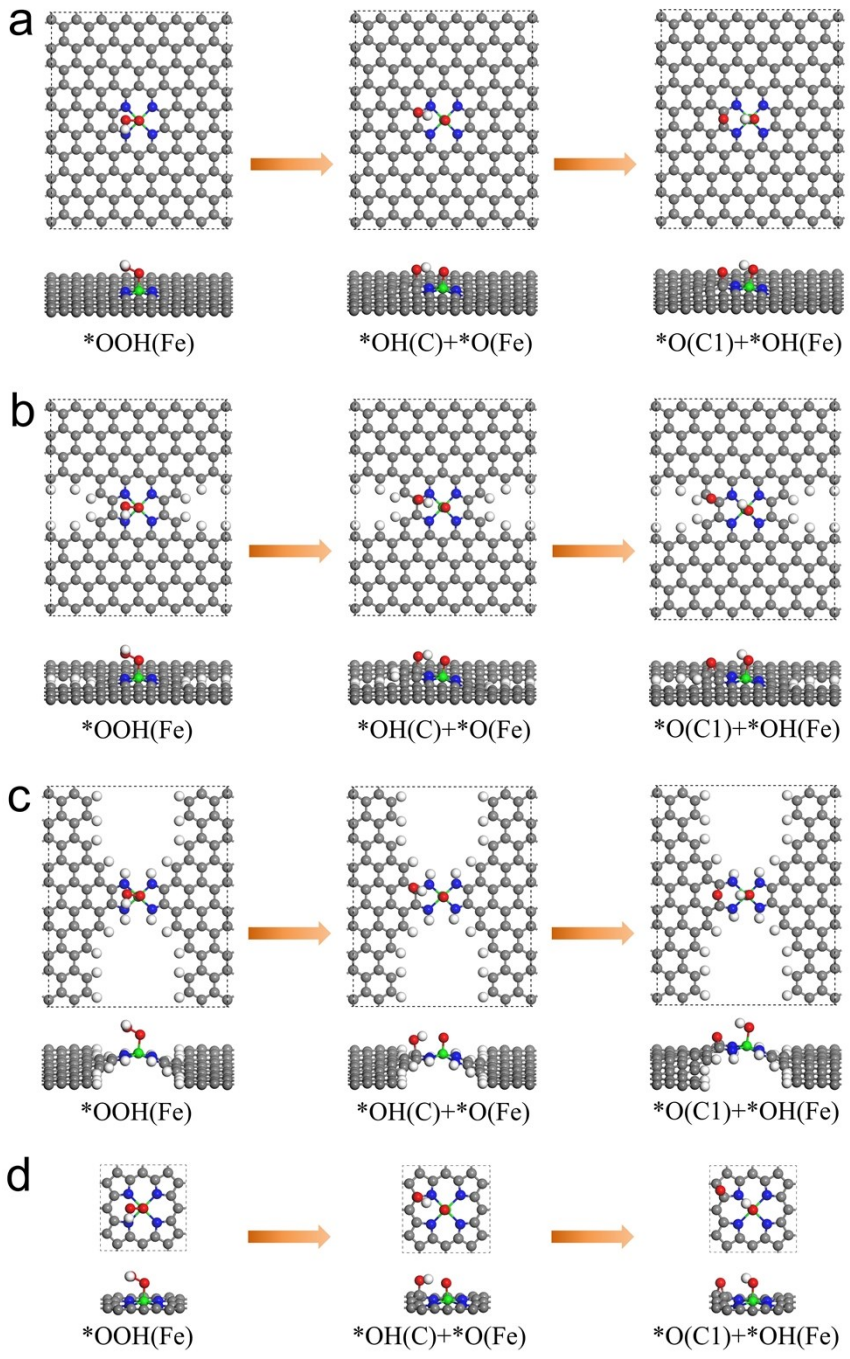
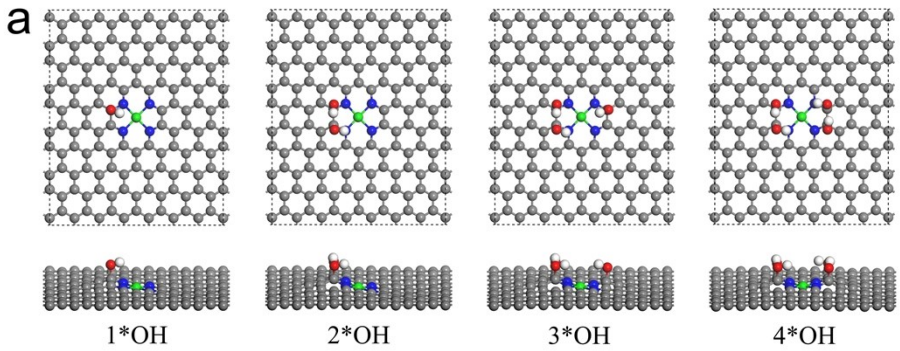
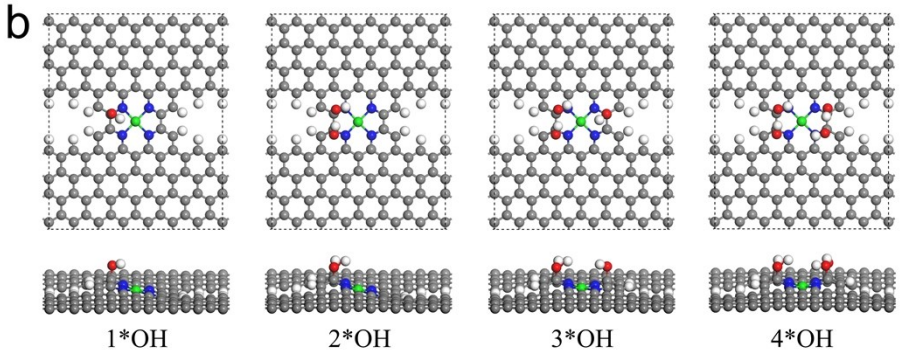
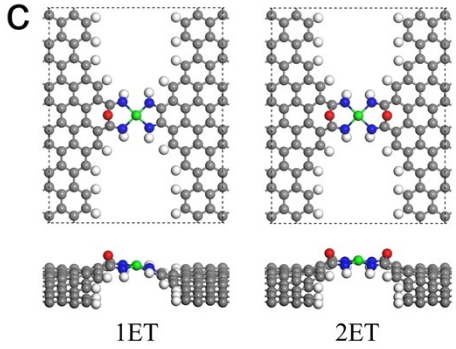
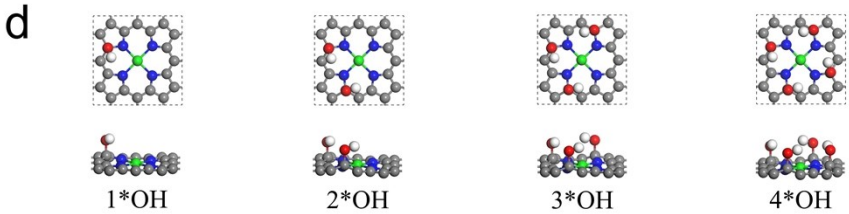


Figure S1. Top (upper) and side (lower) views of atomistic structures of the chemical oxidation of carbon next to FeN_4 moieties through our proposed new carbon oxidation pathway on (a) I-FeN_4C_{10}, (b) H-FeN_4C_{10}, (c) H-FeN_4C_4, and (d) I-FeN_4C_{12}.


a
1*OH
2*OH
3*OH
4*OH


b
1*OH
2*OH
3*OH
4*OH


c
1ET
2ET


d
1*OH
2*OH
3*OH
4*OH

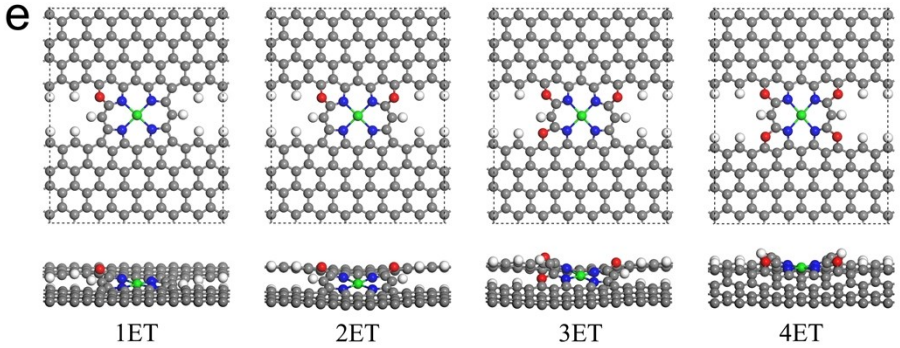

e
1ET
2ET
3ET
4ET

Figure S2. Top (upper) and side (lower) views of atomistic structures of (a) I-FeN_4C_{10}, (b) H-FeN_4C_{10}, (c) H-FeN_4C_4, (d) I-FeN_4C_{12}, and (e) H-FeN_4C_{12} with different depth (coverage of *OH/ET functional groups) of carbon oxidation.

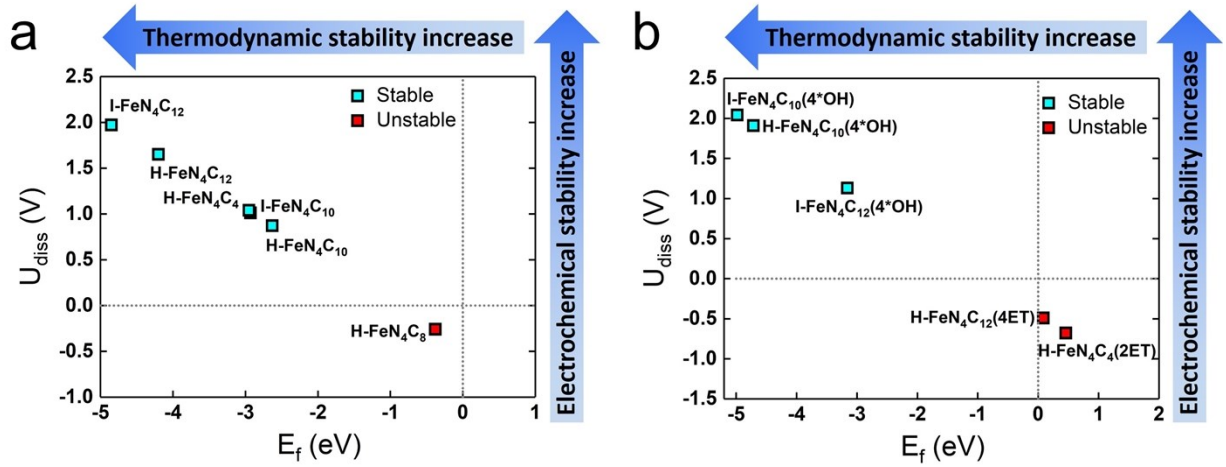


Figure S3. Computed E_f and U_{diss} of Fe atoms for (a) various FeN_4 catalysts and (b) various FeN_4 catalysts with full coverage of *OH/ET functional groups based on DFT(PBE)+U calculations with effective Hubbard-U parameter U-J=3.29 for Fe.[1,2] It is known that PBE often fail to accurately simulate the systems with localized *d* or *f* orbitals. Therefore, we investigated the stability of various FeN_4 catalysts and FeN_4 catalysts with full coverage of *OH/ET functional groups using the DFT(PBE)+U method. The computed E_f and U_{diss} of Fe atoms for various FeN_4 catalysts and FeN_4 catalysts with full coverage of *OH/ET functional groups obtained by DFT(PBE)+U are in good agreement with the PBE results (Figure 2a and 3b), which indicates that the stability of different FeN_4 moiety models would not change when considering the self-interaction corrections.

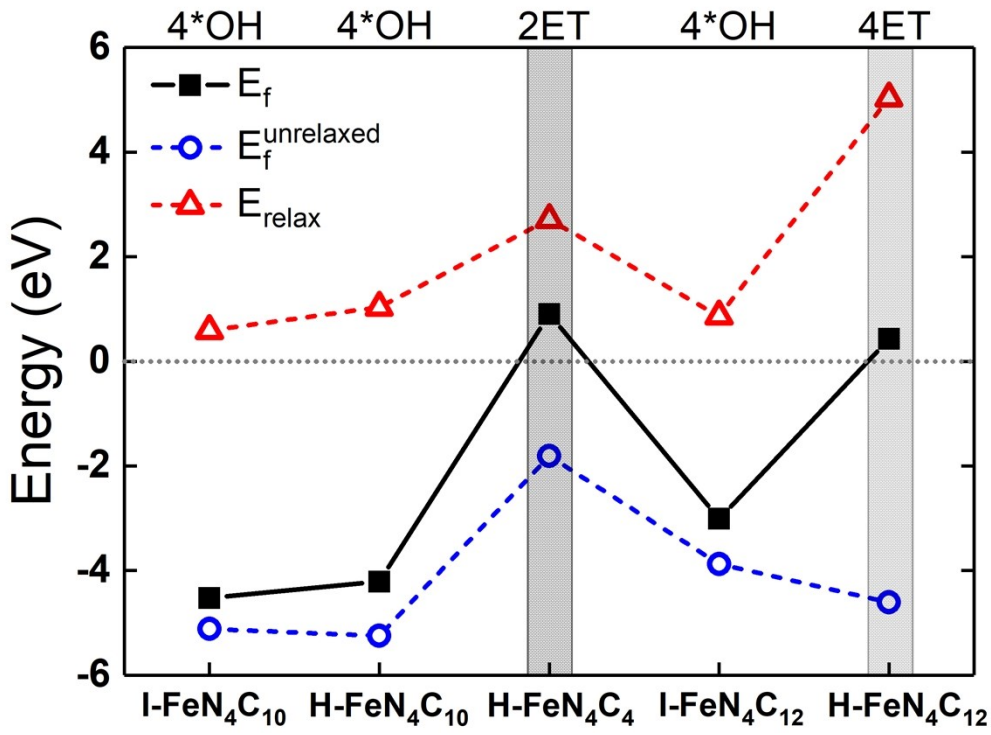


Figure S4. Computed E_f, $E^{unrelaxed}_f$, and E_{relax} of Fe atoms for different FeN_4 catalysts with full coverage of *OH/ET functional groups.

REFERENCES

(1) Xu, H.; Cheng, D.; Cao, D.; Zeng, X. C. A Universal Principle for a Rational Design of Single-Atom Electrocatalysts. *Nat. Catal.* **2018**, *1*, 339–348.

(2) Li, X.; Xi, S.; Sun, L.; Dou, S.; Huang, Z.; Su, T.; Wang, X. Isolated FeN_4 Sites for Efficient Electrocatalytic CO_2 Reduction. *Adv. Sci.* **2020**, *7*, 2001545.□□□□