Supporting Information

The Role of Nitrogen Sources and Hydrogen Adsorption on the Dynamic Stability of Fe-N-C Catalysts in Oxygen Reduction Reaction

Zhou Huang, Fuhua Li, Yongduo Liu, Siguo Chen, Zidong Wei, * and Qing Tang*

*aSchool of Chemistry and Chemical Engineering, Chongqing Key Laboratory of Theoretical and Computational Chemistry, Chongqing University, Chongqing 401331, China

*E-mail: zdwei@cqu.edu.cn; qingtang@cqu.edu.cn
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**Figure S13.** Projected crystal orbital Hamilton population (pCOHP) between the nitrogen atom and hydrogen atom in pyrrolic-type FeN₄ system.
We constructed a Fe–N₄ doped-graphene/water interface (Fe−N−C), added 36 H₂O molecules with a density of 1 g cm⁻³ to the system and introduced an extra hydrogen atom which would decompose into a hydronium and an electron spontaneously to represent the counter charge within the EDL. We performed 5ps with 10000 steps of ab initio molecular dynamics (AIMD) simulation. The changes in energies and temperatures during the AIMD simulation are shown in Figure S1, indicating that the structure is well-equilibrated.

Figure S1. The snapshot structures of pyrrolic-type FeN₄-explicit (a) and pyrrolic-type FeN₄-explicit (b) after 5ps MD simulations; MD energy and temperature profiles for pyrrolic-type FeN₄-explicit (c) and pyrrolic-type FeN₄-explicit (d) during 5 ps AIMD simulations.
To evaluate the dynamic process of iron atom leaching from the surface, an inert helium atom is fixed directly above the Fe atom at a distance of 14.9 Å. Bader charge analysis indicated that the He atom maintains two electrons, which has a negligible effect on the charge of the whole system. Herein, the He atom is just equivalent to the role of a rivet.

Figure S2. Full-size view of Fe–N₄ doped-graphene with 36 explicit water molecules used in our molecular dynamic simulations. Hydrogen bonds are represented by the dashed lines. C: gray; N: blue; Fe: brown; O: red; H: white; He: green.
Figure S3. Illustrations of CV setting in the “slow-growth” method for the reaction of (a) Fe leaching, (b) hydrogen adsorption on Fe and (c) hydrogen adsorption on N.
Figure S4. The Fe 2p XPS spectrum of the FePc molecule and the FePc molecule with nafion.
Figure S5. $^1$H NMR spectra of FePc-with-Nafion and FePc in DMSO-$d_6$. 
Figure S6. Experimental FT-IR spectra of FePc (a), H₂Pc (b) and FePc-with-Nafion (c); Simulated FT-IR spectra of FePc (d), H₂Pc (e) and H-FePc(f).
Figure S7. (a) AIMD simulation snapshots of nitrogen protonation in pyridinic-type FeN$_4$ and pyrrolic-type FeN$_4$ with explicit water. (b) An unconstrained 5 ps AIMD simulation representing the bond lengths of N-H and Fe-H in pyridinic-type FeN$_4$-N-H. (c) Radial Distribution Functions (RDFs) showcasing the Fe-N distance in bare and protonated pyridinic-type FeN$_4$ and pyrrolic-type FeN$_4$ with explicit water at 300 K, within a 5 ps time frame of the AIMD simulation.
**Constant Potential Corrections**

The simulations are done at constant charge [the number of electrons ($N_e$) is fixed], which means that the work functions ($\Phi$) change along the reaction pathway. After the chemisorption of ORR intermediates, there will be some $\Phi$ variations, leading to the potential deviated from the targeted potential $^{1-5}$. The energy difference caused $\Phi$ variations is:

$$\Delta E_{\Phi_1 - \Phi_2} = E_{\Phi_1} - E_{\Phi_2} = \frac{\Delta q \times \Delta \Phi}{2}$$

(1)

The $\Delta q$ and $\Delta \Phi$ are the interfacial charge and work function difference between the states of pristine and adsorbed one. Since the interfacial charge difference is hard to be accurately obtained, we can use the capacitance ($C$) defined in formula (3) to replace $\Delta q$:

$$C = \frac{\Delta q}{\Delta \Phi}$$

(2)

We then substitute the $\Delta q$ in (3) with (4)

$$\Delta E_{\Phi_1 - \Phi_2} = C \times \Delta \Phi^2$$

(3)

We calculate $C$ from the change in the work function as the number of total electrons is varied. For the pyrrolic-type FeN$_4$ surface, the calculated $C$ is 0.72 e/V. We found that the energy variations have little effect (< 0.1 eV). Therefore, we use one $C$ value (0.72 e/V) in our calculation.
Figure S8. Dynamic evolution of bond lengths of Fe-H and O-H, as well as free energy profiles along the reaction coordinate in the pyrrolic-type FeN₄-explicit system, considering the iron protonation process under various potentials.
Figure S9. Dynamic evolution of bond lengths of Fe-H and O-H, as well as free energy profiles along the reaction coordinate in the pyrrolic-type FeN₄-explicit system, considering the nitrogen protonation process under various potentials.
Figure S10. Dynamic evolution of bond lengths of Fe-N(x) along the reaction coordinate in the pyrrolic-type FeN_{x}-xN-xH-explicit system (x = 1, 2), considering the Fe leaching process under various potentials.
Figure S11. Dynamic evolution of bond lengths of Fe-N(x), as well as free energy profiles along the reaction coordinate in the pyridinic-type FeNₓ-Fe-H-explicit system, considering the Fe leaching process under various potentials.
Figure S12. Dynamic evolution of bond lengths of Fe-N(x) along the reaction coordinate in the oxygenated-pyrrolic-type FeN_{x+1}-xN-xH-explicit system (x = 1, 2), considering the Fe leaching process under various potentials.
Figure S13. Projected crystal orbital Hamilton population (pCOHP) between the nitrogen atom and hydrogen atom in pyrrolic-type FeN₄ system: (a) 1H and (b) 2H adsorption at N atoms.

References