Tailoring of Fe-N-C Single Atom Catalyst's Coordination Spheres via S-Doping for Oxygen Reduction Reaction Activity: A DFT Study

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Abstract

The modulation of electronic properties of Fe-N-C catalysts via S-atom doping has been identified as a promising approach to enhance their oxygen reduction reaction (ORR) activity. However, influence of S-dopant distance from Fe-site on their ORR activity is poorly explored. Herein, varying the S-dopant distance from the Fe-site in Fe-SAC, four models Fe-N_4-C_y, Fe-N_3-S^1-C_y, Fe-N_4-S^2-C_y, and Fe-N_4-S^3-C_y were considered to examine the S-dopant distance's influence on their ORR activity. The optimization, charge density difference, density of states, electron localized function, and spin polarization for created models were studied using density functional theory. The overpotential for the potential limiting step, formation of *OOH step, was used to measure ORR activity for these models. The Fe-N_4-S^2-C_y structure displayed the lowest overpotential of 0.37 V, making it a good ORR catalysis candidate, as compared to Fe-N_4-C_y (η = 0.41 V), Fe-N_3-S^1-C_y (η = 0.62 V), and Fe-N_4-S^3-C_y (η = 0.65 V). The results showed that the S-atom's electron density affected the metal's d-orbitals depending on the S-Fe distance. When the S atom was close to the FeN_4 core (in second coordination sphere), its effect on Fe's electronic structure was greater, optimizing O_2 adsorption and *OOH formation at the Fe site and improving the ORR activity. However, *OOH formation at the Fe-site was hard when the S-atom was further away (in higher coordination sphere) or close (in first coordination sphere), limiting the active site for additional steps and decreasing ORR activity. This study demonstrates the tailoring of binding energy of ORR intermediates at active site by varying the heteroatom dopant distance from active site to influence the ORR activity of SACs.

References

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