TM(TM=Fe, Co, Ni)/N/O tri-doped Graphene Heterogeneous Electrocatalysts for Oxygen Reduction Reaction: A Theoretical Insight

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Density functional theory (DFT) is utilized to compute the thermodynamic free energy changes of the elementary reaction steps of the oxygen reduction reaction (ORR) on $\text{TMO}_x\text{N}_{4-x}$ (TM=Fe, Co and Ni; $x=1-3$) single atom catalysts ($\text{TMO}_x\text{N}_{4-x}$ -SACs). Based on thermodynamic stability and catalytic ORR activity, it is found that $\text{CoO}_x\text{N}_{4-x}$ -SACs show relatively good stability and activity. Furthermore, the final reduction reaction step ($\text{OH}^* + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O} + *$) with the largest ΔG value towards five different $\text{CoO}_x\text{N}_{4-x}$ -SACs is the potential-determining step (PDS). All calculated results suggest that the theoretical overpotential of CoO_2N_2 -opp is much close to that of Pt (111), implying the optimal electrocatalytic ORR activity among $\text{TMO}_x\text{N}_{4-x}$ -SACs. Furthermore, electronic structure analysis reveals that the d -band center of Co for CoO_2N_2 -opp is located rather far away from the Fermi level (set as zero) and binding states of adsorbed are reduced and the antibinding states of adsorbed OH^* fragments are increased, compared with that of other $\text{CoO}_x\text{N}_{4-x}$ -SACs. In conclusion, the introduction of N and O can effectively modify d -band of active metal center and adsorption of oxygen-contained intermediates, thus tune ORR activity.

Keywords: density functional theory, oxygen reduction reaction, single atom catalysts

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