

Scaling relation between adsorption energies of oxygen reduction reaction intermediates at defective TiO₂ surfaces

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Enhancing the oxygen reduction reaction is a major topic of electrocatalysis research. The maximal enhancement is achieved, within the thermodynamic argument, by aligning the adsorption free energies of reaction intermediates so that energy barriers along the reaction path are minimized. Full alignment is, however, difficult to realize. This is due to the linear scaling relation between the adsorption energies of intermediates along the reaction path, which has been observed almost universally in electrocatalyst materials including Pt [1]. Thus, finding a way to deviate from this universal relation is an important issue in catalyst design.

Here, we investigate such possibility by studying TiO₂ surfaces modified with substitutional dopants or oxygen vacancies [2]. Defective oxide surfaces can provide various sites for the adsorption including the lattice oxygen and metal sites as well as oxygen vacancies and impurity sites. Thus, the adsorption energies at the oxide surfaces are expected to deviate from the universal scaling because adsorbents can take various adsorbed structures.

Our density functional calculations suggest that the universal scaling is violated on TiO₂ particularly when the adsorbent forms bonding not only with a metal atom but also with a lattice oxygen atom (Figure 1). Most importantly, in this case, the perfect alignment of the adsorption free energies is possibly achieved. This fact suggests that TiO₂ has the potential to surpass conventional catalysts such as Pt in terms of oxygen reduction reaction activity.

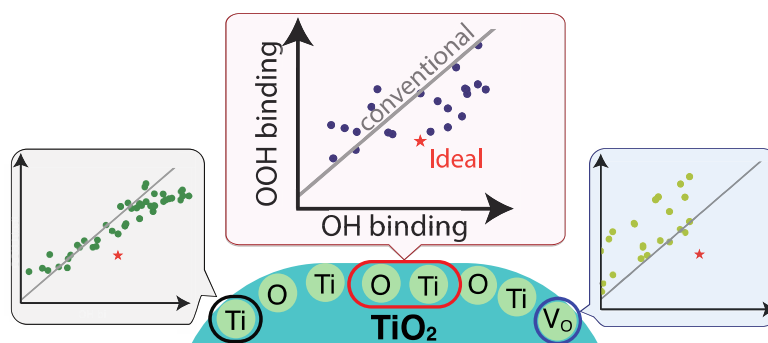


Figure 1. Correlation between adsorption energies of OH and OOH at various sites on TiO₂ surface

References

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