

Functional property of electrodes

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The water splitting and the fuel-cell reactions occurring on the electrode have recently become an important target of modern surface/interface science. Those reactions are known to occur efficiently catalyzed by platinum but novel class of catalysts such as TiO_2 has attracted attention because of technological importance; however, the reason why TiO_2 should play a role as electrocatalyst is not well known. As a step towards the understanding, we applied a thermodynamic approach to the oxygen reduction reaction (ORR), which has been successfully used to explain why existing electrocatalysts are far from ideal. The approach says that at least one of the elementary steps for ORR is an uphill reaction almost unexceptionally; this happens because adsorption energy of O_2H is linearly dependent on that of OH for most existing catalysts. This phenomenological rule implies that those adsorption energies cannot be modified independently of each other to satisfy the ideal condition by changing the catalyst materials. *In addition*, the adsorption energies follow a universal line that does not cross the point of ideal catalyst.

Our first-principles calculation, however, shows that the adsorption energies do not strictly follow a linear relationship on a rutile and

brookite TiO_2 surfaces when a surface Ti atom is doped with various transition metals [1]. That is, there is significant fluctuation in the $E_{\text{ads}}(\text{O}_2\text{H})$ - $E_{\text{ads}}(\text{OH})$ plot, where E_{ads} means the adsorption energy. It is also found that the adsorption energies approach much closer to the ideal point when doped with some transition metals.

The results of the calculation indicate that the universal relationship is exceptionally violated on TiO_2 . They also indicate that, when there is a way to stabilize the dopants at a complex interface although they are not so stable on our model surface that is atomically flat, the dopants may strongly enhance the ORR. We conjecture that such reaction environment may be provided in some part of the real catalyst; we are planning to make it sure by performing an ab initio Monte Carlo simulation.

References

[1] Y. Yamamoto, S. Kasamatsu, and O. Sugino, *submitted*.