Geometry Adaptive Catalysts to Bypass Scaling Relations in Oxygen Reduction Reaction

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In this computational study we consider electrocatalytic oxygen reduction reaction (ORR). In the ORR scaling relations have been established as the fundamental limitation. The coupling between two key intermediates, OOH and OH, places a constraint on the theoretically achievable overpotential. Accordingly, various strategies have been suggested to avoid the OOH and OH scaling. The two most prominent strategies involve either stabilising the OOH intermediate via hydrogen bonding or avoiding the OOH intermediate via a dissociative mechanism, resulting in O/OH species that scale differently. Nevertheless, both strategies still result in non-zero theoretical overpotential, as shown in Figure 1, and supported with experimental observations.

- With pure OOH – OH scaling, the predicted overpotential is around 0.30 V, closely matching the best experimentaly observed experimental results with half-wave potential of 0.95 V, 0.28 V away from equilibrium potential for oxygen reduction.[1]
- With O/OH – OH scaling, the theoretical prediction limits overpotential to around 0.2 V, closely matching the best experimental result with half-wave potential of 1.05 V, 0.18 V away from equilibrium potential for oxygen reduction.[2]

Inspired by a mechanism in enzyme-catalysed oxygen reduction reaction and our previous research of curvature effect in Metal-Nitrogen-Carbon (M-N-C) catalysts,[3] we propose to use the geometry effect and introduce the concept of Geometry Adaptive Catalysts (GACs). The geometry effect, based on computational research, involves changing catalytic activity by adjusting the adsorption energy of intermediates through the control of catalyst geometry – leading to a new strategy that completely bypasses the scaling relations.[4]

- The bypassing results in observation of theoretical overpotential less than 0.1 V, which, in principle, can approach 0 V.

The concept of GACs can be applied to any reaction limited by the scaling relations as they allow to bypass these limitation. Thus, this work opens many research directions from enhancing the ORR for batteries and fuel cells to P2X applications such as green ammonia synthesis, CO_2 reduction reaction and many others.

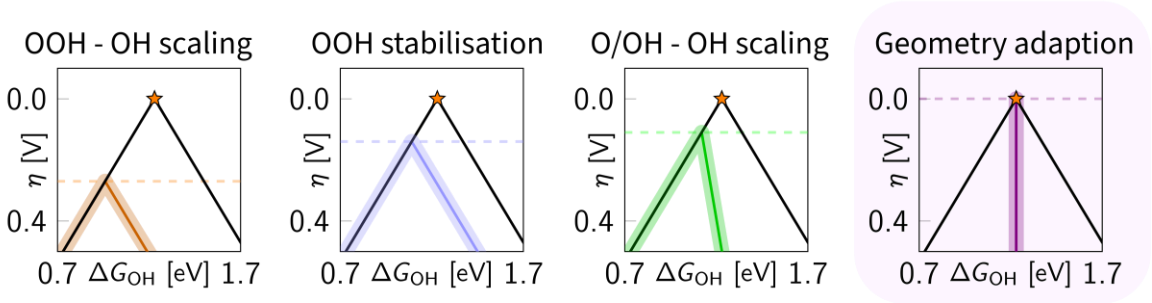

Figure 1: Theoretical overpotential limitations for various strategies to avoid scaling relations.

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References

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