

Modeling Non-Precious Metal Catalyst Structures and Their Relationship to ORR Activity

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Non-precious metal catalysts (NPMCs) hold the promise of replacing Pt in proton exchange fuel cell (PEFC) cathodes, leading to a reduction in cost and alleviating materials supply concerns. Despite decades of study, structure-function relations for NPMC active sites, particularly pertaining to oxygen reduction reaction (ORR) activity, are still lacking. Knowledge of these relations would enable targeted synthesis following a rational design principle. The promises of such an approach include increasing the density of stable active site structures with high turnover frequencies leading to more durable, more selective, and more active NPMC materials.

Previously, determination of active site structures and their associated activity has proven rather difficult. This is due to several factors: (1) State-of-the-art NPMCs currently depend on a pyrolysis step¹ that leads to amorphous carbon structures that are hard to characterize experimentally; (2) an exceedingly large number of structures are generated, many of which have varying degrees of ORR activity and overall stability; and (3) there exists doubt over the role that transition metals (TMs) play in NPMC activity. Using density functional theory (DFT) modeling coupled with the computational hydrogen electrode approach², we are working to address these issues by considering ORR pathways on a variety of potential active-site structures with varying chemical compositions.

The use of DFT has previously been applied to NPMC systems, particularly to address N-coordination and the role of TMs in the active site³⁻⁵. These studies have given valuable insights into stability and activity but have not sufficiently considered potential active-site structures at graphene edges. Such edge defects are much more computationally expensive but have been shown to be considerably more stable than their bulk counterparts⁶. Experimental studies indicate that edges may play key role in increasing NPMC ORR activity⁷. Additionally, graphene edges have been shown to have considerably different electronic and magnetic properties, which are likely to have an impact on adsorbate binding energies and thus ORR pathway and activity. Due to these factors, we have focused in this work on graphene edges as potential active-site hosts.

The study of metal and metal oxide catalysts for ORR (and the reverse reaction, oxygen evolution reaction, OER) has led to general scaling laws that have proven powerful for the high-throughput screening of ORR catalysts⁸⁻¹¹. Two such scaling laws include the relation between O-binding energy and OH-binding energy and the relation between OH-binding energy and OOH-binding energy. These scaling laws have been combined to generate an ORR thermodynamic descriptor, in this case, O-binding energy, that roughly indicates how active a given catalyst is likely to be. Often, this is depicted using a Sabatier-principle “volcano plot”.

Herein, we test these scaling relations for graphene-edge N/TM potential active sites that have been deduced through stability constraints in previous work^{6,12}. We

consider several N/TM edge geometries (including 4-N and 3-N coordination), as well as clusters containing a variety of multiple TMs (including mixed-metallic clusters of Fe to Cu). Such mixed-metallic clustering may aid in explaining why catalysts with both Fe and Co are more active than Fe or Co alone. We also consider sites with no TMs and sites next to N/TM complexes to address the role of transition metals in active sites. Over 20 active-site geometries/chemistries are considered.

The calculated stability and potential energy surfaces (PES) for ORR on these sites (see Figure 1), as well as the extrapolated scaling laws are discussed. There is an apparent difference in these scaling laws based on the N-coordination geometry. Our results indicate the potential for ORR/OER activities above those predicted for metals and metal oxides based on the scaling relations.

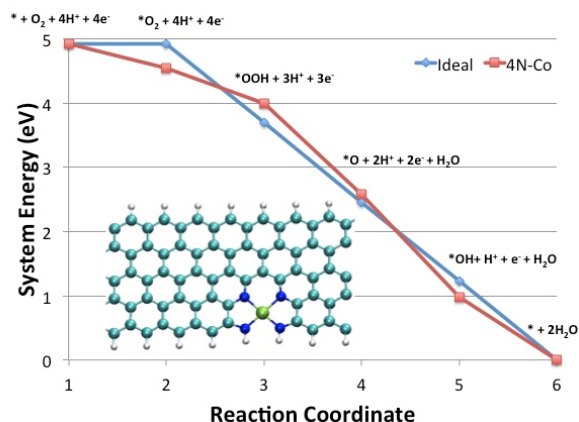


Figure 1: Example PES for a 4N-Co defect at a graphene nanoribbon edge (inset).

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