

A Perspective of TM-N_x (TM=Fe, Co, and x=2, 4) non-PGM Electrocatalysts from First-Principles Calculations

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A major challenge for science and engineering in the current century is the design of sustainable energy production technologies in particular for non-stationary applications that are consistent with a reduction of greenhouse gas emissions. Research and development of high-performance non-PGM fuel cells continue to attract significant interest. However, overcoming the sluggish kinetics of the ORR at the cathode remains challenging. XPS experiments shows evidence for the presence of TM-N_x (TM=Fe, Co; x=1, 4) defect motifs in the pyrolyzed catalyst. However, which TM-N_x defect motifs remain stable under operating conditions remains unclear. Furthermore, it is difficult to correlate defect motifs and catalytic activity directly by means of experimental methods which generally require reference materials for their interpretation such as vibrational spectroscopy and XPS.

A complimentary approach to experimentation is provided by density-functional-theory (DFT) based simulations and calculations that have the ability to capture the heterogeneous bond topologies in these catalysts. This ability also provides these calculations with reliability and predictive power. In this contribution we compare and contrast two different approaches for the assessment of binding geometries and binding energies of ORR intermediates and the stability of selected defect motifs. In the first approach, the TM-N_x defect motifs are embedded in a carbon sheet which is subjected to 2-d periodic boundary conditions and mimics an extended surface (Fig. 1, top). The second approach is based on the modeling of molecular systems that do not possess any periodicity emphasizing the local chemical interactions of the ORR with an implicit aqueous solvent (Fig. 1, bottom).

An important step for advancing the understanding of TM-N_x ORR electrocatalysts is the defect stability under operating conditions. Under open-circuit conditions the formation energies of graphitic TM-N_x defects is predicted to be exothermic, consistent with XPS observations which corroborate the presence of graphitic defects. However, the large differences in formation energies between TM-N₂ and TM-N₄ suggest that the defect abundance likely depends on the potential across the fuel cell. Defining the critical potential (U_{crit}) as the potential where the formation energy for a 2 electron process changes from exothermic to endothermic (Table 1) shows that the abundance of TM-N₂ defects is expected to decrease over time for potentials $U > 0.5$ V well below the equilibrium potential for ORR.

This observation also suggests that catalytic activity changes over time in response to varying potentials across the fuel cell. Previous work on ORR activity predicts that Co-N₂ defect motifs mediate ORR via a single site 2x2e process, while Co-N₄ is predicted to require a dual site 2x2e process.¹ Thus, while Co-N₂ defects are favorable they are expected to be unstable under operating conditions and are mass-transport limited.

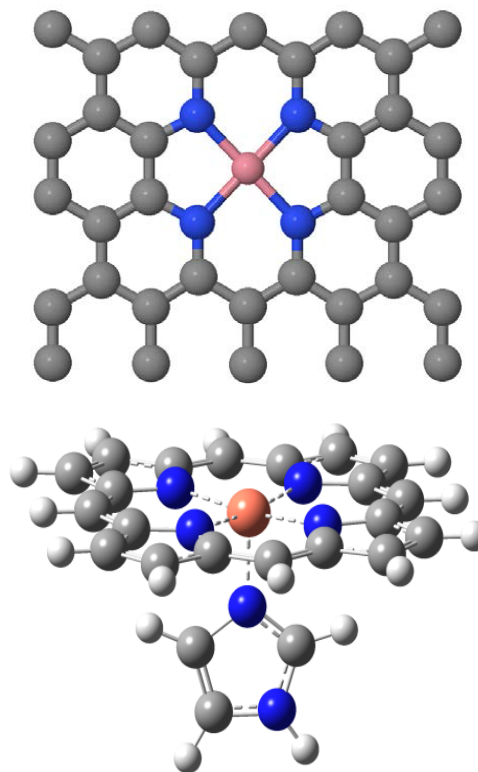


Fig. 1: Example of model systems for the first-principles exploration of TM-N₄ ORR electrocatalysts. Top: extended surface approach. The figure shows the simulation cell which is periodically repeated. Bottom: molecular cluster approach.

	Extended System	
U_{crit} (V)	Fe	Co
TM-N ₂	0.3	0.5
TM-N ₄	1.6	1.8

Table 1: Predicted critical potential of candidate graphitic TM-N_x defect motifs for the first two electron step in ORR.

We will discuss the ramifications of these findings and compare and contrast the results from the two different computational approaches for the prediction of binding geometries and binding energies of ORR intermediates that provide insights into ORR reaction pathway selection and catalyst optimization.

References:

1. S. Kattel, P. Atanassov, B. Kiefer, *J. Phys. Chem. C*, **116**, 8161 (2012).