

## EFFECT OF MEDIA ON THE ORR ACTIVITY OF NONPRECIOUS METAL MODEL CATALYSTS: AN AB INITIO STUDY

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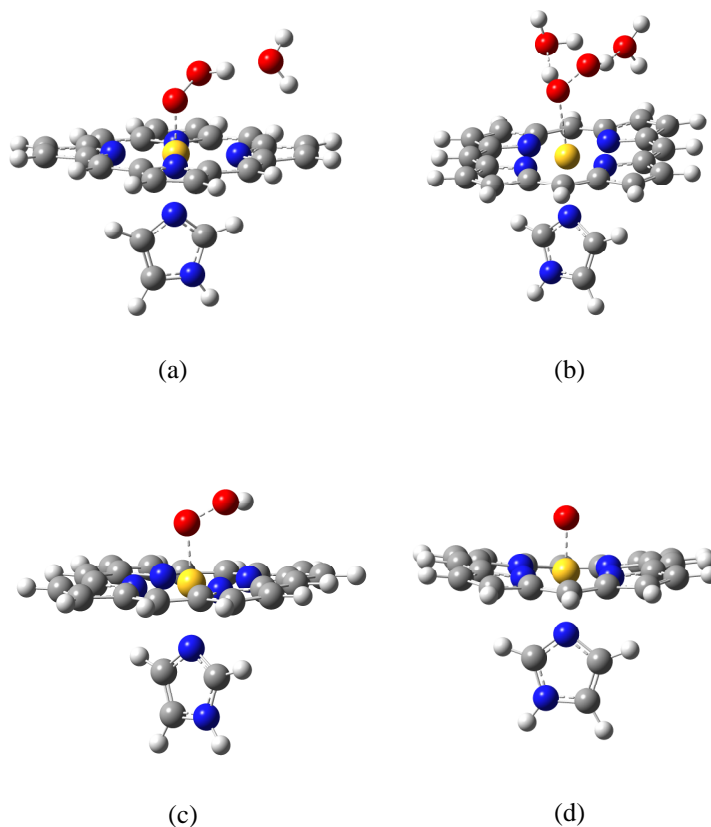
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Non-precious transition metal (NPM) catalysts are attractive for the Oxygen Reduction Reaction (ORR) in fuel cells due to their low cost and high electrochemical activity. (1, 2) Generally, an intrinsic difference in reaction mechanism and catalyst activity has been observed in a change of medium from acidic to alkaline. (3) In this work, Density Functional Theory (DFT) calculations (4) were employed to understand the influence of media on the performance of a series of non-precious transition metal model catalysts (Im)ML<sub>n</sub> (n = 1 or 2) where M = Cu(II), Fe(II), Fe(III), Ni(II), Co(II), Im = imidazole, and L = diaminotriazole (M-N<sub>2</sub>) or porphyrin (M-N<sub>4</sub>). Energy profiles of the ORR mechanism in both acidic and basic media (5) are calculated for all catalysts.

In the acidic medium, \*OOH is firstly formed upon the initial protonation (H<sub>3</sub>O<sup>+</sup> + 1e<sup>-</sup>) of the attached O<sub>2</sub> for all catalysts (Fig. 1). Quickly after, \*H<sub>2</sub>O<sub>2</sub> is generated during the second protonation with one exception, which is the diaminotriazole based Fe(II) catalyst where 2 \*OH is observed instead. In general, porphyrin based catalysts bind to H<sub>2</sub>O<sub>2</sub> less strongly than their diaminotriazole based counterparts. This is in alignment with the energy gap between the LUMO of the catalysts and the HOMO of H<sub>2</sub>O<sub>2</sub> with the larger the gap, the weaker the interaction. In the cases of porphyrin based Cu(II) and Ni(II) catalysts, H<sub>2</sub>O<sub>2</sub> detaches from the catalyst surface as the result of the a very weak interaction between them, which may later require a second active site to facilitate the reduction of H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O in the subsequent protonation steps.

In the alkaline medium, \*OOH is formed in the initial step of H<sub>2</sub>O interacting with the attached O<sub>2</sub> along with a 1e<sup>-</sup> transfer, followed by the generation of \*O and \*OH during the subsequent steps (nH<sub>2</sub>O + ne<sup>-</sup>) (Fig. 1). The ORR activity of the catalysts may strongly depend on their affinity to the intermediate oxygen species. The regeneration of the catalysts relies on their OH<sup>-</sup> affinity with the stronger the OH<sup>-</sup> affinity, the lower the catalytic activity. Compared to the diaminotriazole base catalysts, porphyrin based catalysts may exhibit a weaker OH<sup>-</sup> affinity due to a high electron density on their central metal caused by the additional electron donation from the porphyrin (N<sub>4</sub>).

In summary, our calculations show that not only is the overall kinetics of the ORR in each medium type different, but also distinct mechanisms are observed among the catalysts within the same medium. It is also shown, through the analysis of structural changes and the affinity to the intermediate oxygen species of all the catalysts at each ORR step, that media determine during ORR not only the type of the intermediate species formed, but also the ease of the intermediate species being reduced to H<sub>2</sub>O. The latter is further influenced by a combination of catalysts' central metal, chelating ligands, and how they coordinate, which can be rationalized from the perspective of orbital interactions.



**Figure 1.** Geometries of: (a) (Im)CoL-OOH; (b) (Im)CoL-H<sub>2</sub>O<sub>2</sub> in the acidic medium; and (c) (Im)CoL-OOH; (d) (Im)CoL-O in the basic medium. The different colored spheres represent different atom types in the structures where: grey – carbon, red – oxygen, blue – nitrogen, white – hydrogen, and yellow – Cobalt. L = porphyrin, Im = imidazole.

### Acknowledgement

The authors gratefully acknowledge the financial support from the Department of Energy, EERE, grant no DE-EE 0000459. This grant entitled ‘Development of Novel Non-Pt Group Metal Electrocatalysts for PEM Fuel Cell Applications’ is headed by the Center for Renewable Energy Technology at Northeastern University.

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