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Metal-organic frameworks for the ORR
Thermodynamic and structural considerations

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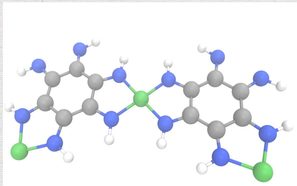
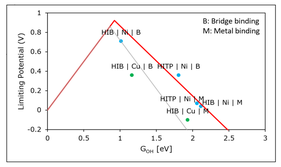
Executive Summary

Motivated by the need for non-precious metal catalysts for the fuel cell oxygen reduction reaction, we investigate M_3(hexaiminobenzene)$_2$ (HAB), motivated by recent experimental proof of its high activity. Density functional theory (DFT) calculations were performed to elucidate the most favorable chemical pathways for Ni and Cu-HAB materials. To elucidate the in-situ structure of Ni-HAB, experimental Raman spectra data was coupled with a normal mode and density functional perturbation theory (DFPT) analysis to aid in the interpretation of the experimental spectra.





Background & Motivation:

Fuel cell devices are a promising alternative to traditional combustion engines due to their clean operation, high efficiencies and non-dependence on carbon based fossil-fuels. To date, the efficacy of this technology has been hindered by the lack of affordable materials that can efficiently catalyze the electrochemical reduction of oxygen to water (the oxygen reduction reaction).

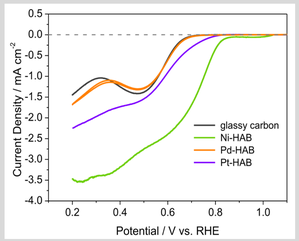


Figure 1. Experimental rotating-disk electrode measurements of ORR activity for various M-HAB catalysts under acidic conditions. Ni-HAB demonstrates substantial activity relative to the other M-HAB systems.

$O_2 + 4(H^+ + e^-) \longrightarrow 2H_2O$

Reaction Mechanism

$* + O_2 + H^+ + e^- \longrightarrow OOH*$

$OOH* + H^+ + e^- \longrightarrow O* + H_2O$

$O* + H^+ + e^- \longrightarrow OH*$

$OH* + H^+ + e^- \longrightarrow * + H_2O$

Figure 2. Overall oxygen reduction reaction (ORR) and reaction mechanism. The ORR proceeds through 3 primary oxygen-based intermediates: *OOH, *O, *OH.

Of particular interest is the class of materials referred to as MOFs (Metal-organic frameworks), which are characterized as crystalline solids composed of both organic and inorganic building blocks. Recent experiments have shown that MOFs of the form NiN_4 with a conjugated graphene-like framework show superb activity for the ORR. Therefore, there is great interest in understanding the identity of the active site and the in-situ structure under operating conditions.

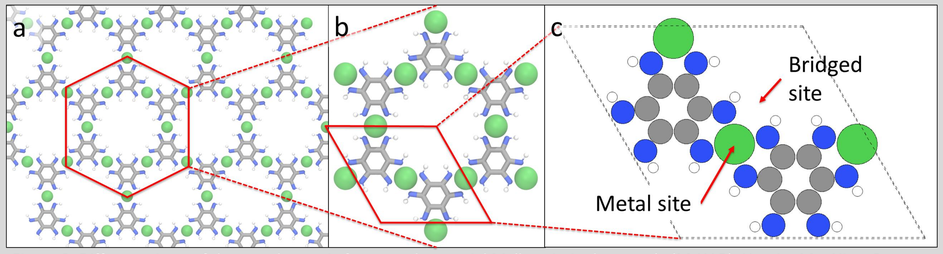


Figure 3. Different views of the metal-organic framework material M_3(hexaiminobenzene)$_2$ (M-HAB). Herein, M ≡ Ni or Cu.
(a) HAB has a unique honeycomb pattern composed of repeating nano-rings
(b) Zoomed-in view of nano-ring, composed of 6 nitrogen-functionalized benzene rings interlinked single-site M atoms
(c) Computational cell used for ab-inito DFT simulations. Atom count: [C: 12, N:12, H:12, M:3]. Metal-ontop and framework-bridged active sites are shown.

Results:

Thermodynamic Analysis of ORR Pathway

The thermodynamic free energy pathway for the ORR was computed via DFT by computing the free energy of adsorption of the relevant intermediates. The free energy diagram (FED) is shown in figure 4 for Ni and Cu-HAB for two key active sites (metal-ontop and framework bridge).

Active Site Trends

- The framework bound active site binds the intermediates species more strongly than the metal coordinated site
- This is advantageous since the metal sites severely under-bind

Metal Cation Trends

- For the bridged active site, Ni binds more strongly compared to Cu

The limiting potential volcano plot, see figure 4(b), shows Ni HAB towards the top of the volcano. This is consistent with the experimental results (see figure 1.). Additionally the bridged vs metal active sites seem to demonstrate different scaling relations.

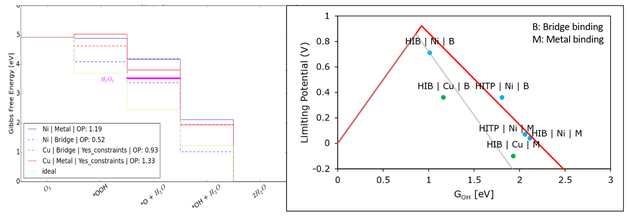


Figure 4. (a) Free energy diagram (FED) along the reaction pathway for the ORR on Ni-HAB and Cu-HAB. The ontop-metal and framework-bridging site are shown. (b) Thermodynamic limiting potential volcano as a function of the *OH binding energy. HITP, a related conjugated graphene MOF material is also shown for comparison.

Elucidating HAB Structure with Raman Spectroscopy

In-situ Raman spectroscopy at variable applied bias was performed. To compliment these studies, the theoretical Raman spectra was computed with DFT at variable degrees of protonation. The resulting experimental and theoretical spectra are shown in figure 5.

The qualitative agreement appears to match more closely between the N_4H_2 species, possibly indicating that the stable form of HAB is partially deprotonated under the conditions of ORR.

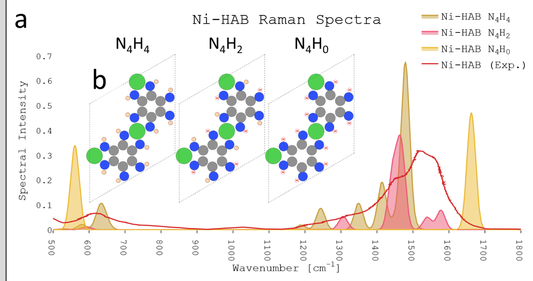


Figure 5. (a) Simulated and experimental Raman spectra for Ni-HAB system at various degrees of protonation. (b) Computational cell of Ni-HAB at various degrees of protonation. Vacant proton sites are marked with a red ⓧ mark while present sites are marked with a H in a solid circle.

Methodology:

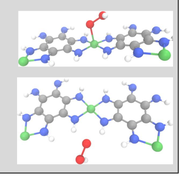
All calculations were performed using plane-wave pseudopotential DFT implemented within the Quantum Espresso code. The exchange correlation was approximated with the BEEF-vdW functional, a plane-wave cutoff of 500 eV was used along with a k-point grid of (3, 3, 1). Spin-polarization was turned on for all calculations.

The thermodynamics of the ORR were computed by carrying out adsorbate calculations of the important ORR intermediates on a HAB slab on two potential active sites (metal-ontop and framework bridged).

The Raman spectra was obtained by computing the normal modes of HAB. The mode intensity was then computed by approximating the highlighted term in the following Raman spectral flux equation.

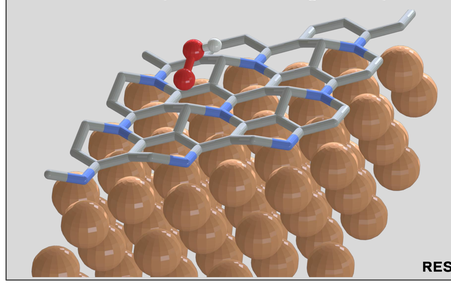
The Raman calculations were performed using the VASP DFT Code with PBE as the exchange-correlation functional.

$$\frac{d\sigma_i}{d\Omega} = \frac{(2\pi\nu_S)^4}{c^4}\left|\hat{e}_S\frac{\partial\tilde{\alpha}}{\partial Q_i}\hat{e}_L\right|^2\frac{h(n_i^b+1)}{8\pi^2\nu_i},$$



Future Work:

- Extend thermodynamic analysis of ORR activity to other transition metals (M = Co, Pd, Pt) M-HAB system
- Include 2nd order effects on Raman spectra:
  - Dispersion effects on vibrational modes
  - HAB Multi-layer effects
- Investigate related chemical motif for ORR
  - N-doped graphene overlayers on transition metals
  - Potentially created during HAB synthesis process



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