ELECTRONIC STRUCTURE OF NiFe OXYHYDROXIDE ACTIVE SITES: UNDERSTANDING AN EFFECTIVE OXYGEN-EVOLVING CATALYST AT A QUANTUM-MECHANICAL LEVEL

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EXECUTIVE SUMMARY

This project aims to characterize the likely active sites in the oxygen-evolving electrocatalyst NiFe oxyhydroxide at a density–functional theory level. Such a characterization includes understanding the redox chemistry of the catalyst thin film, its metal oxidation states, as well as the nature of the frontier bands in its electronic structure. The work involves edge-terminated Ni and NiFe oxyhydroxide films. Experimental research has shown that terminations of the film are sites at which catalytic intermediates are turned over, going through high Fe oxidation states in the process. These studies describe how the electronic structure responds to the broken periodicity of the film. In addition, Fe has been doped into the film at both the interior and exterior layers. Novel results include the energetic preference for Fe at exterior sites, reliable metal oxidation states, and the characteristic sites expected to be electrocatalytically active.

RESEARCH CHALLENGE

Facilitating the redox chemistry between H_2O and O_2 is essential to the development of renewable energy technologies—particularly that of solar fuel cells. Doing so will require understanding and optimizing efficient and earth-abundant electrocatalysts. NiFe oxyhydroxide is among the most active such oxygen-evolving electrocatalysts. While previous studies have well characterized this material *in operando* [1,2], recent experiments have proven the particularly high activity of Fe dopants at the edges of the material [3] and the highly valent nature of such Fe centers [4]. This project aims to determine the electronic and chemical nature of these particularly active NiFe oxyhydroxide edges using frontier quantum-mechanical simulation techniques. This work, if successful, will allow for experimentalists and computationalists alike to rationally design even better catalysts for the oxygen evolution reaction.

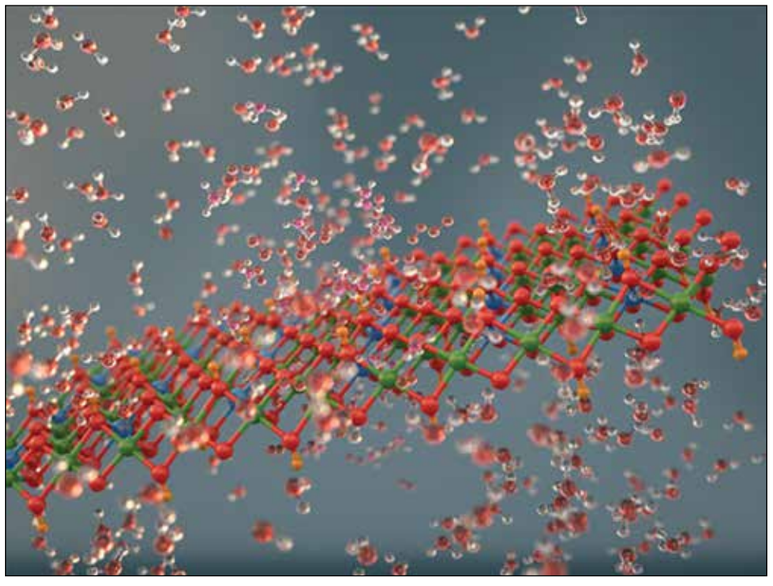

Figure 1: Illustration of a single layer of NiFe oxyhydroxide with 25% Fe doping solvated in water. Ni is shown in green, Fe in blue, O in red, H on the NiFe slab in orange, and H in solution in white.

METHODS & CODES

We performed density–functional theory (DFT) calculations with a hybrid functional for Ni-only and NiFe oxyhydroxide nanowire supercells using Quantum–ESPRESSO [5]. The material's periodicity was broken in one in-plane direction such that the systems contain different interior and exterior metal sites. We probed different degrees of protonation and hydroxylation of Ni and Fe edge sites as a proxy for the different reactive intermediates that appear throughout the progression of the oxygen evolution reaction. We determined metal oxidation states using maximally localized Wannier functions; the catalytic activity of given sites was determined qualitatively by the projected density of states around the Fermi energy.

RESULTS & IMPACT

The methodology described above has been used previously to determine the redox activity, oxidation states, and electronic structure of Ni and NiFe oxyhydroxide bulk materials under open-circuit and operating conditions [1]. With this computational framework in place, we can gain a better understanding of the nature of the purportedly active edge sites, particularly in the doped material. For one, there is a ~ 2 eV energetic preference for Fe to dope an exterior site compared to an interior site. This helps explain experimental evidence that the material's overall catalytic activity is optimized only shortly after introducing Fe dopants to the system [3]. In addition, the projected density of states only shows likely catalytically active Fe oxide motifs when the Fe dopant resides at the material edge. The chemical nature of the material's conduction band minimum likely will determine which sites are most catalytically active. Ongoing calculations and analysis will discern the conditions necessary for achieving high-valent Ni- and Fe-centered reaction intermediates.

WHY BLUE WATERS

This work is enabled by Blue Waters given the considerable computational expense yet high level of parallelizability of hybrid functional DFT calculations. These DFT calculations with hybrid functionals are necessary to compute a qualitatively accurate electronic structure of Ni and NiFe oxyhydroxide. In particular, the modeling of heterogeneous materials interfaces is an important task that can only be done with frontier scientific computing resources such as those of Blue Waters.

Zachary Goldsmith is a fourth-year PhD student who expects to receive his degree in 2019 from the University of Illinois at Urbana-Champaign. He is working under the supervision of Sharon Hammes–Schiffer of Yale University.