

Electronic structure characterization of O₂-evolving catalyst NiFe oxyhydroxide

Zachary K. Goldsmith

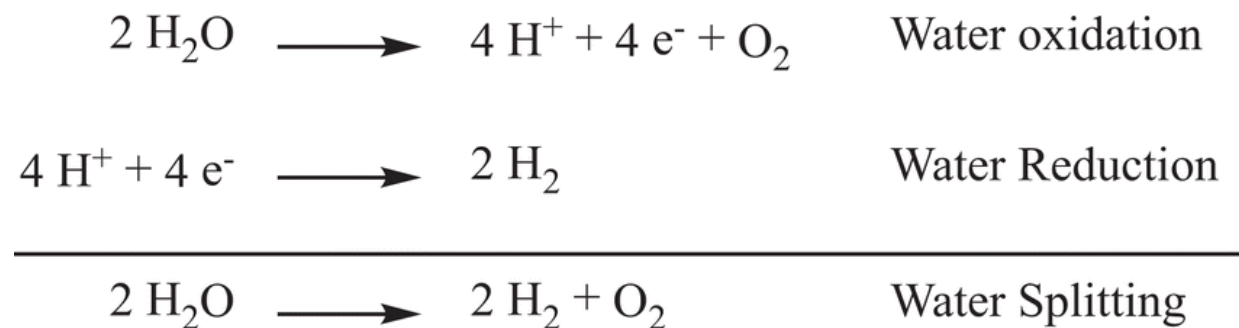
Yale University & University of Illinois at Urbana-Champaign

Blue Waters Symposium 2018, Sunriver, OR

6/5/18

O₂ evolution reaction (OER)

- The (photo)electrolysis of water to O₂ and H₂ is a means for renewable, sustainable energy storage

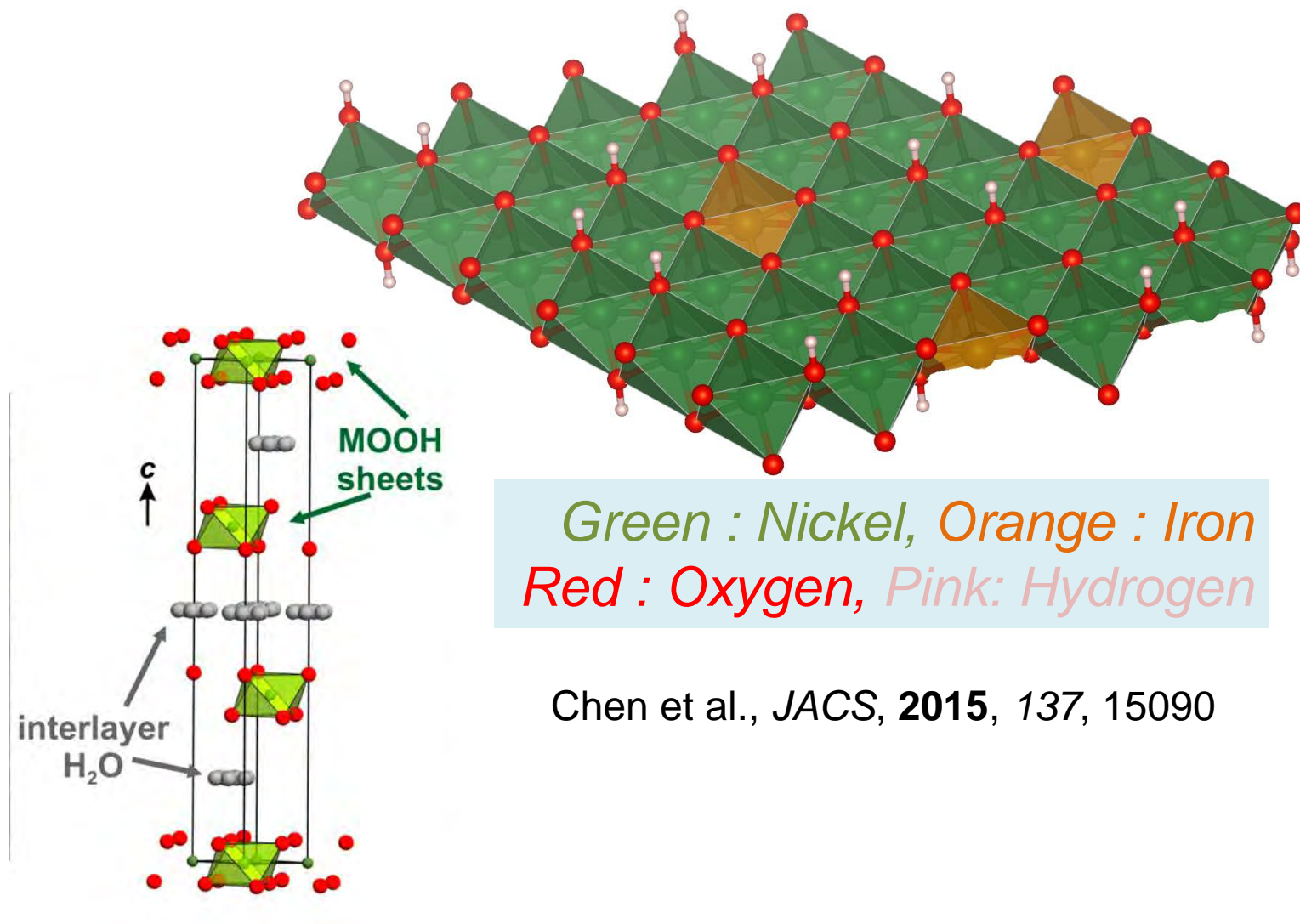


- Application: Storage of (solar) energy in chemical fuel for future use
- Catalysts are required
 - Earth-abundant transition metal oxides and (oxy)hydroxides
 - Goal: high turnover frequency, low overpotential, high selectivity

System of interest



- Layered Fe-doped Ni oxyhydroxide
- Mixed-metal system is more active than each pure oxyhydroxide
- Other metals have been examined in the same framework, e.g., Co, Mn



Chen et al., *JACS*, **2015**, 137, 15090

Trotochaud et al., *JACS*, **2014**, 136, 6744

Ni electrolyzers are old!

Electroanalytical Chemistry and Interfacial Electrochemistry, 60 (1975) 89–96
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EVALUATION OF ELECTROCATALYSTS FOR WATER
ELECTROLYSIS IN ALKALINE SOLUTIONS*

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(Received 13th November 1974)

J. Electroanal. Chem. **1975**, 60, 89–96

J. Electrochem. Soc. **1987**, 134, 377-384

The Catalysis of the Oxygen Evolution Reaction by Iron Impurities in Thin Film Nickel Oxide Electrodes

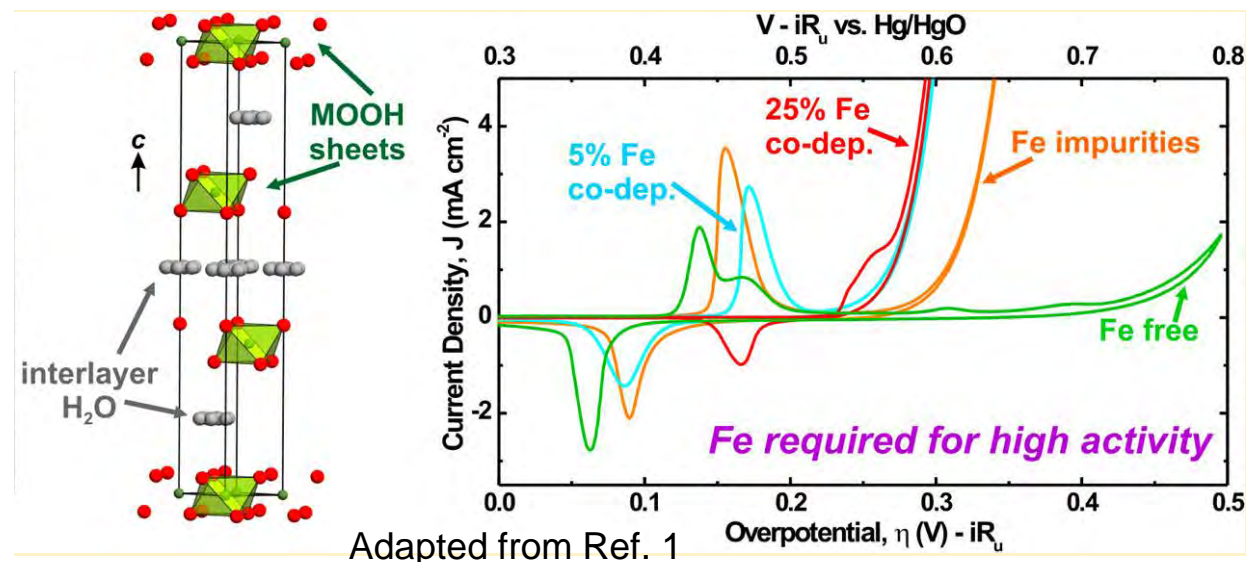
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- Ni has been known to be a catalyst for water splitting since at least the 70s
- Effects of Fe doping first reported in 1987
- New techniques (comp. & expt.) and invigorated interest in renewable energy technologies brings opportunity to revisit the problem and learn more

Recent work on NiFe oxyhydroxides

- $\text{Ni}_{1-x}\text{Fe}_x\text{OOH}$ with $x = 0.25$ is an extremely robust OER catalyst¹



- Bell, Nørskov, and co-workers proposed a mechanism based on an Fe^{3+} active site²
- Ni and Fe oxidation states are very sensitive to the O/OH ligand environment³
- Solvent and ions intercalate (oxy)hydroxide layers and may influence the OER kinetics⁴
- Stahl and coworkers observed Fe^{4+} at catalytic potentials with Mössbauer⁵

1. L. Trotochaud, S. L. Young, J. K. Ramsey, S. W. Boettcher, *JACS*, **2014**, 136, 6744
2. D. Friebel et al., *JACS*, **2015**, 137, 1305
3. J. Conesa, *J. Phys. Chem. C*, **2016**, 120, 18999
4. B. W. Hunter, W. Hieringer, J. R. Winkler, H. B. Gray, A. M. Müller, *EES*, **2016**, 9, 1734
5. Chen et al., *JACS* **2015**, 137, 15090

Objectives

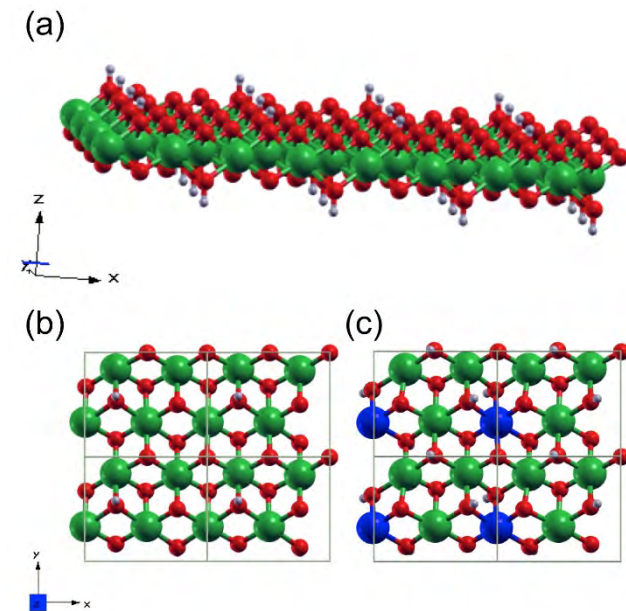
- **Redox behavior** Determine potentials for the proton-coupled oxidations preceding catalysis
- **Oxidation states** Determine how the Ni and Fe oxidation states change upon proton-coupled oxidation
- **Electronic structure** Study Ni and NiFe oxyhydroxides using periodic DFT, compare with spectroscopic results
- **Understand catalysis** Use spectroelectrochemistry and electronic structure calculations to infer the role of Fe in this robust catalyst

Z. K. Goldsmith, A. K. Harshan, J. B. Gerken, M. Vörös, G. Galli, S. S. Stahl, S. Hammes-Schiffer, *Proc. Nat. Acad. U.S.A.* **2017** 14, 3050

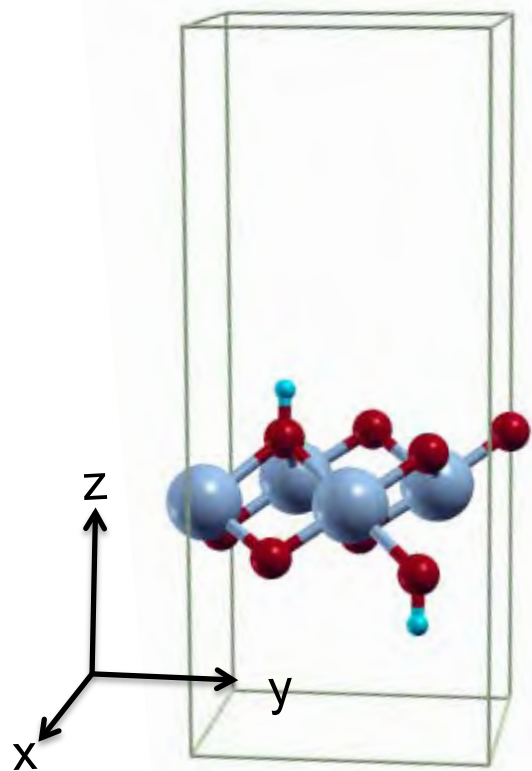
Computational methods

- Periodic, planewave-based DFT calculations using Quantum-ESPRESSO
- Geometry optimizations performed with PBE+U, electronic structure calculations using hybrid functional PBE0
- Proton-coupled oxidation potentials computed using thermodynamic scheme for referencing and cancellation of H_2 and entropic contributions
- Ni and Fe oxidation states determined using magnetization on metal site, integrating spin density over volume around metal site

Pure $Ni_4O_8H_n$				
Structure	Expt. ¹		Calc.	
Values in Å	Ni-O	Ni-O	Ni-O	Ni-O
Ni(OH) ₂	2.06	--	2.03	--
NiOOH	2.07	1.89	2.05	1.91

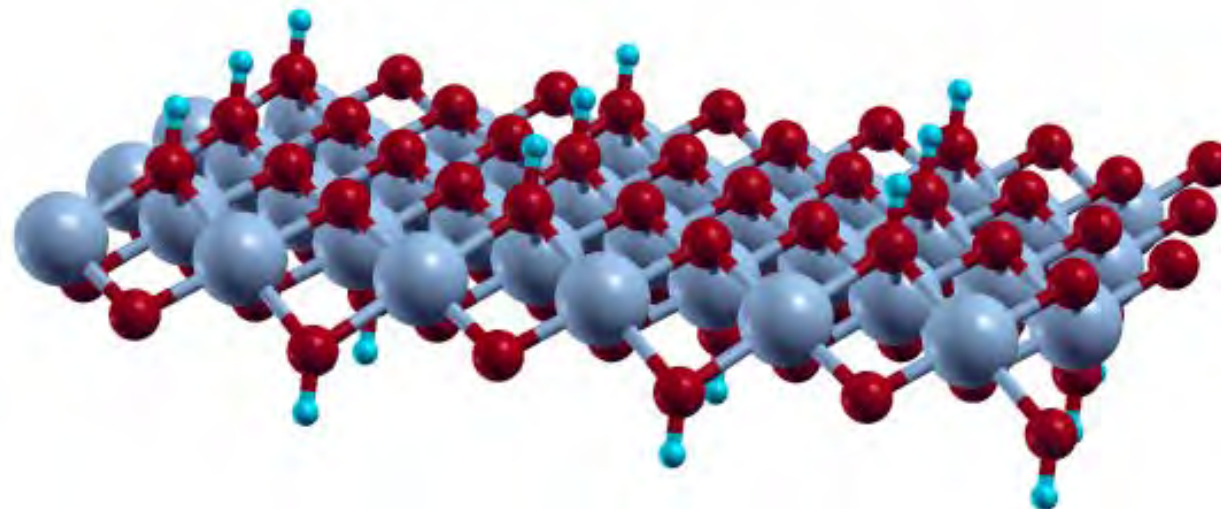


Ni(Fe) model system



$\text{NiOOH}_{0.5}$ single layer unit cell

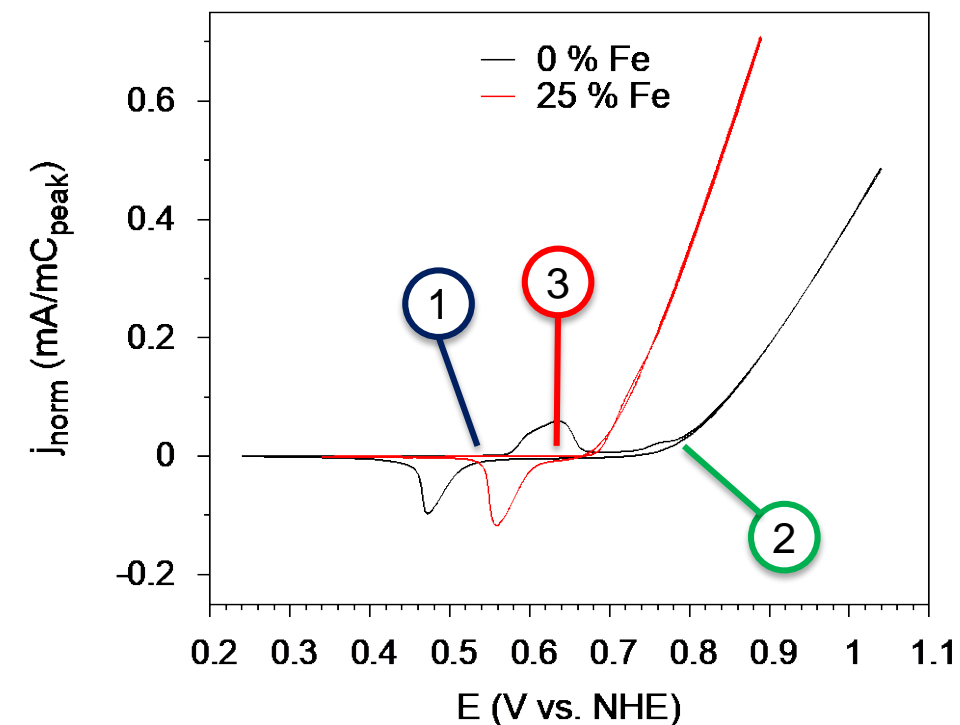
Periodic boundary conditions



2D-periodic slab of $\text{NiOOH}_{0.5}$ ("2H")

- 4 metal sites and 8 O atoms per unit cell
- Hydrogenation levels of $\text{M}_4\text{O}_8\text{H}_n$ for $0 \leq n \leq 8$
- 25% Fe doping: $\text{Ni}_3\text{Fe}_1\text{O}_8\text{H}_n$

Electrochemical behavior

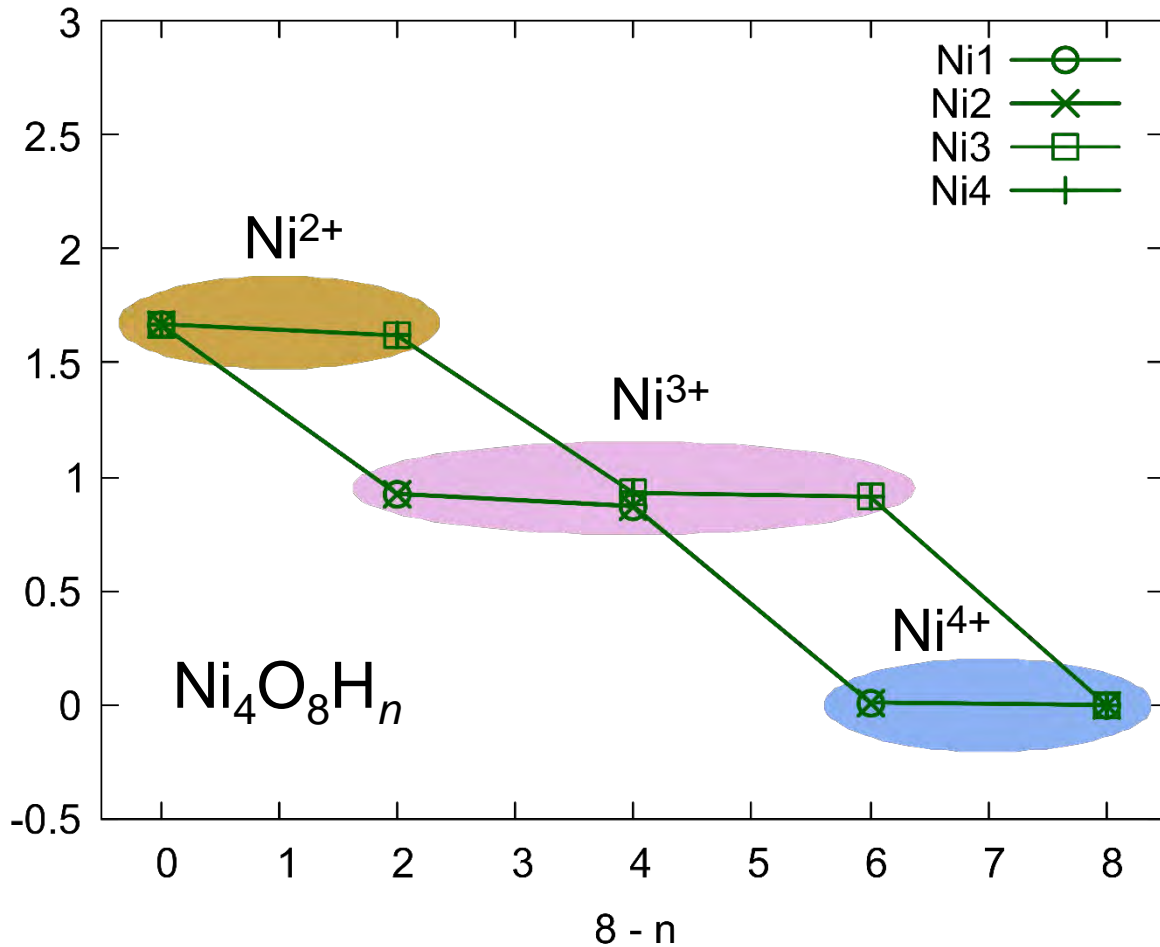


$\text{Ni}_4\text{O}_8\text{H}_n$			$\text{Ni}_3\text{Fe}_1\text{O}_8\text{H}_n$		
Reactant	Products	E	Reactant	Products	E
	$6\text{H} + \text{H}_2$	0.52	8H	$7\text{H} + 0.5 \text{H}_2$	-0.72
8H	$4\text{H} + 2 \text{H}_2$	0.53*		$6\text{H} + 0.5 \text{H}_2$	0.60
	$2\text{H} + 3 \text{H}_2$	0.59		$5\text{H} + 1 \text{H}_2$	0.52
6H	$4\text{H} + \text{H}_2$	0.54		$4\text{H} + 1.5 \text{H}_2$	0.55
4H	$2\text{H} + \text{H}_2$	0.73	7H	$3\text{H} + 2 \text{H}_2$	0.63
2H	$0\text{H} + \text{H}_2$	0.92		$2\text{H} + 2.5 \text{H}_2$	0.60
*Reference				$1\text{H} + 3 \text{H}_2$	0.69
All values in V vs. NHE				$0\text{H} + 3.5 \text{H}_2$	0.73

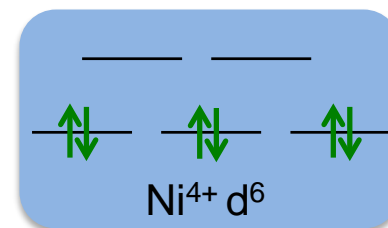
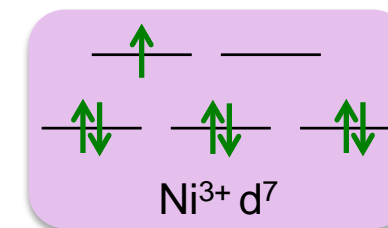
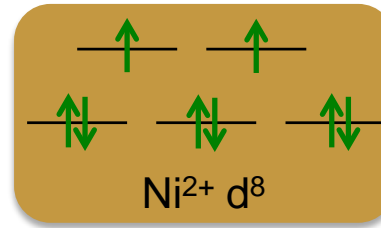
- ① $\text{Ni}^{2+}/\text{Ni}^{3+}$ quasi-reversible wave, reference potential
- ② Oxidation past NiOOH (4H) preceding catalysis
- ③ One oxidation event corresponding to catalytic onset in 25% Fe-doped system

➤ Doped pre-catalyst is the $n = 7$ species

Ni oxidation states, pure Ni



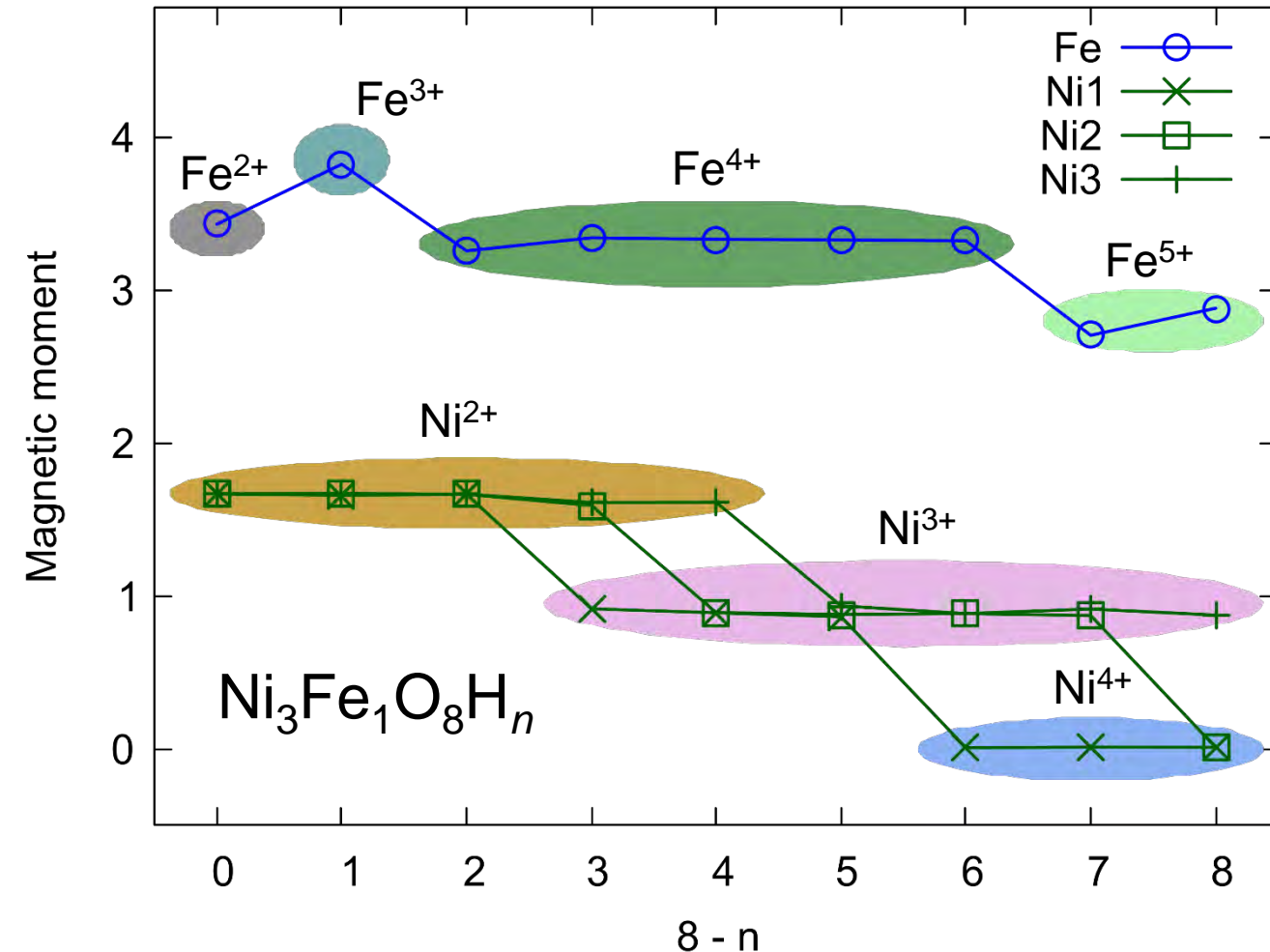
Electronic configurations corresponding to different Ni oxidation states*



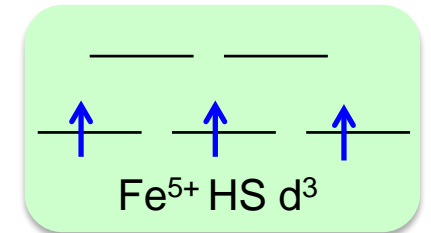
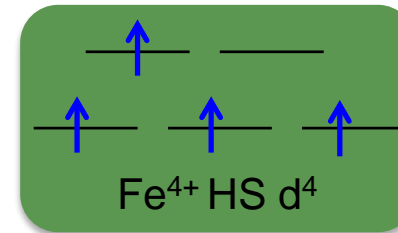
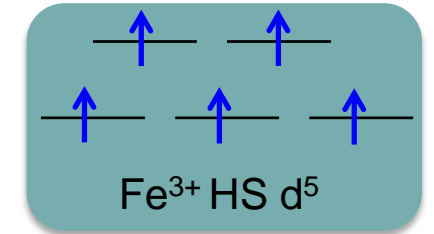
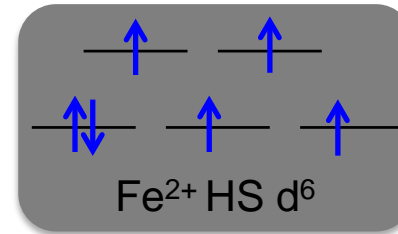
- The magnetism on each Ni site gives a clear probe of oxidation state, based on t_{2g} and e_g occupations
- Proton-coupled oxidation of the slab correspondingly oxidizes Ni sites**

*Idealized picture that ignores Jahn-Teller distortions

Ni and Fe oxidation states, Fe-doped



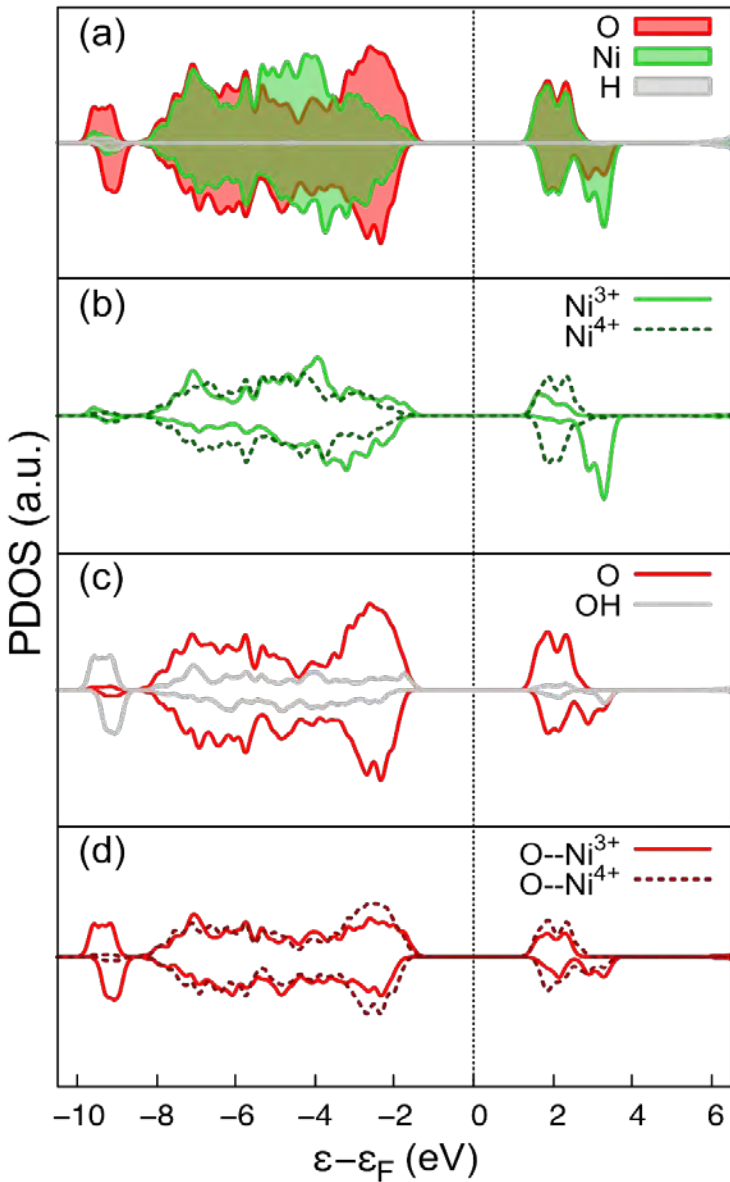
Electronic configurations corresponding to different Fe oxidation states*



- Fe will be oxidized up to 4+ before any Ni oxidation
- **Any oxidation associated with the onset of the OER will yield Fe^{4+}**

*Idealized picture that ignores Jahn-Teller distortions

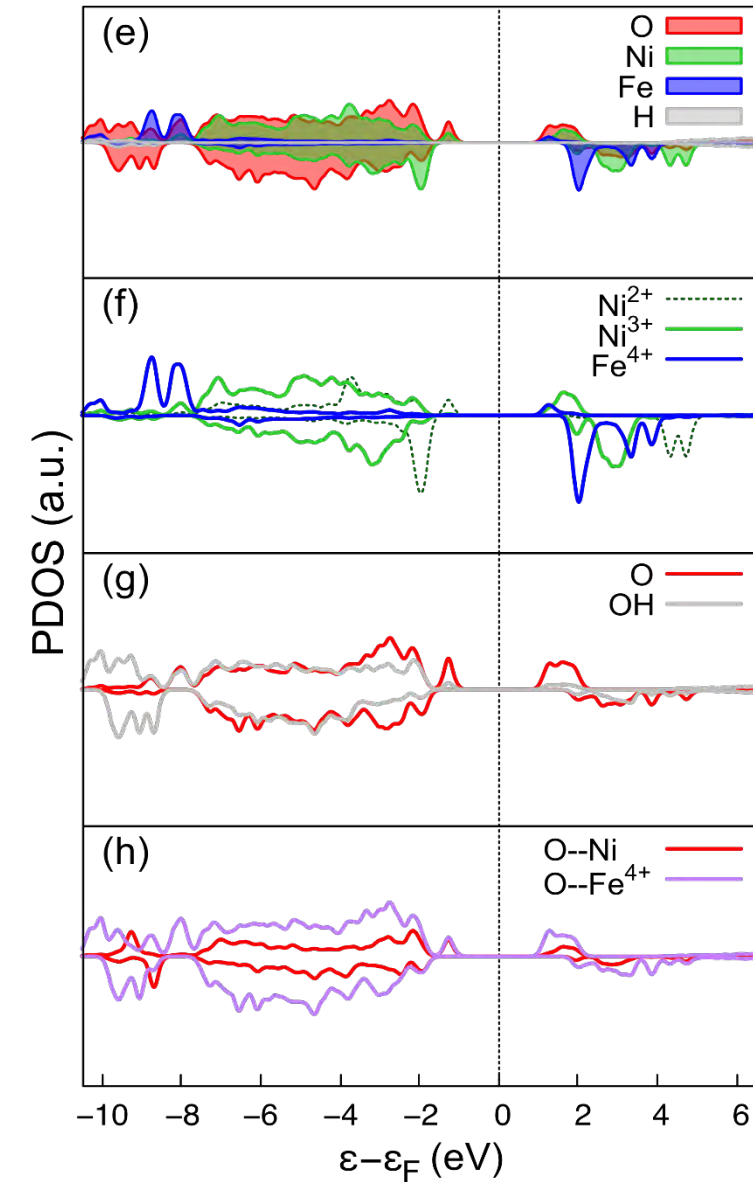
Electronic structure, pure and doped



What are the chemical natures of the frontier electronic states?

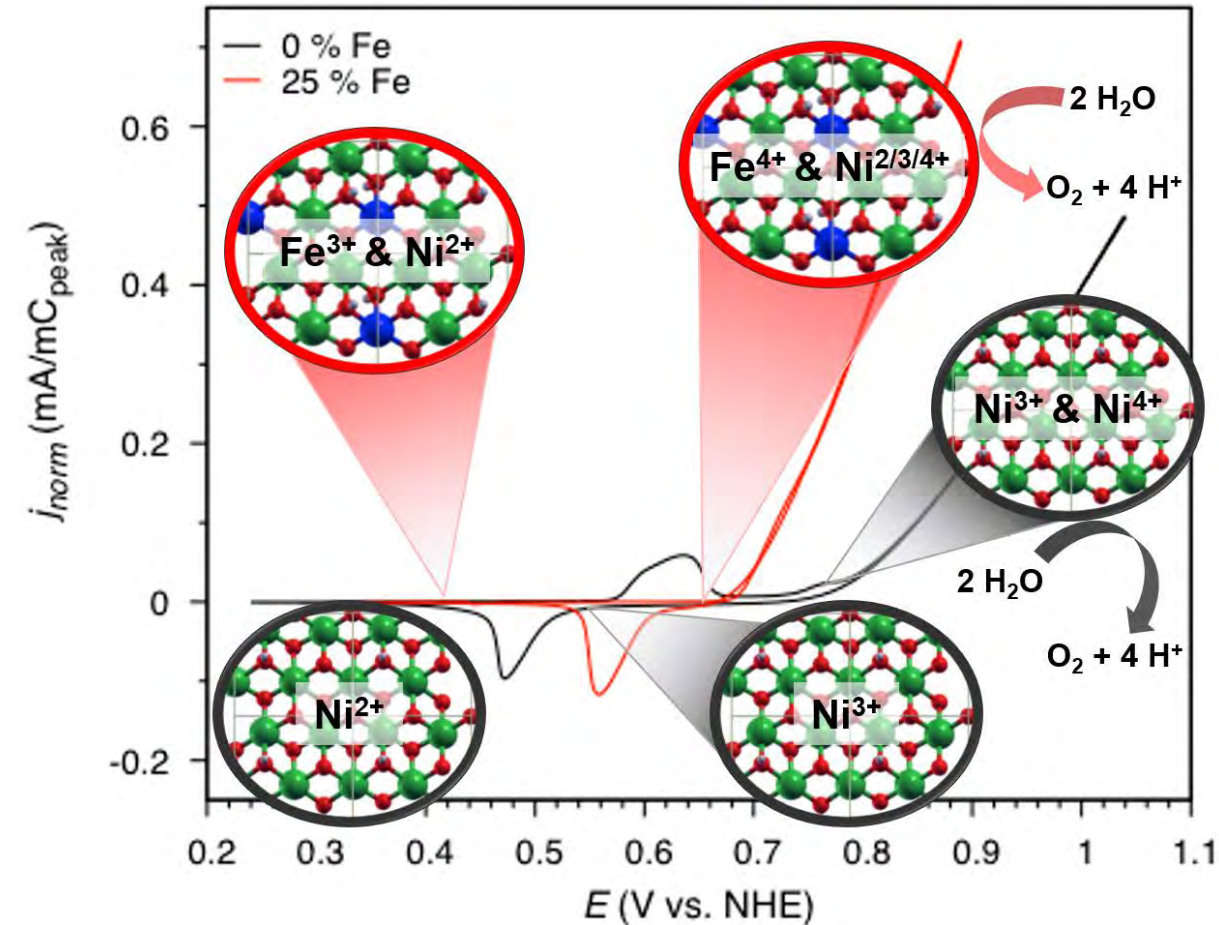
- Oxide motifs at the CBM
- Characteristic Fe to Ni charge transfer across the band gap — Ni²⁺ VBM, Fe⁴⁺ CBM
- Fe⁴⁺ oxide motifs dominate at the CBM

➤ α spin plotted up and β spin plotted down



Summary: Bulk Ni(Fe) oxyhydroxides

- ✓ Calculated proton-coupled redox potentials
- ✓ Identified Ni⁴⁺ and Fe⁴⁺ in pure/doped catalytic species
- ✓ Spectroelectrochemistry to demonstrate redox changes
- ✓ Characterized frontier electronic structure



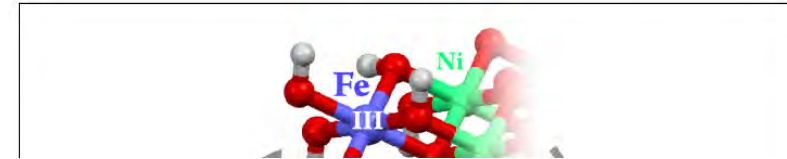
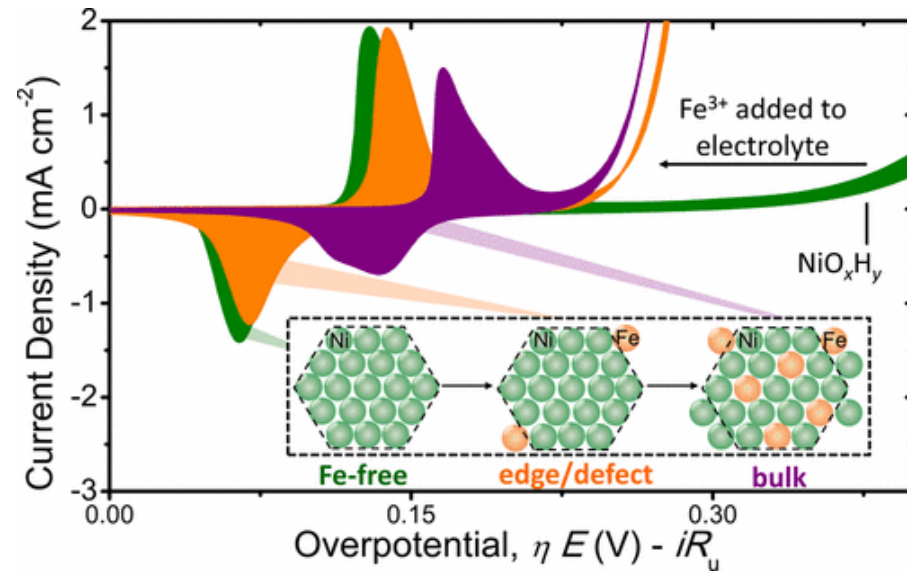
Where does catalysis really happen?

Trapping an Iron(VI) Water-Splitting Intermediate in Nonaqueous Media

Reactive Fe-Sites in Ni/Fe (Oxy)hydroxide Are Responsible for Exceptional Oxygen Electrocatalysis Activity

Michaela Burke Stevens, Christina D. M. Trang, Lisa J. Enman, Jiang Deng, and Shannon W. Boettcher*

Department of Chemistry and Biochemistry, University of Oregon, Eugene, Oregon 97403, United States



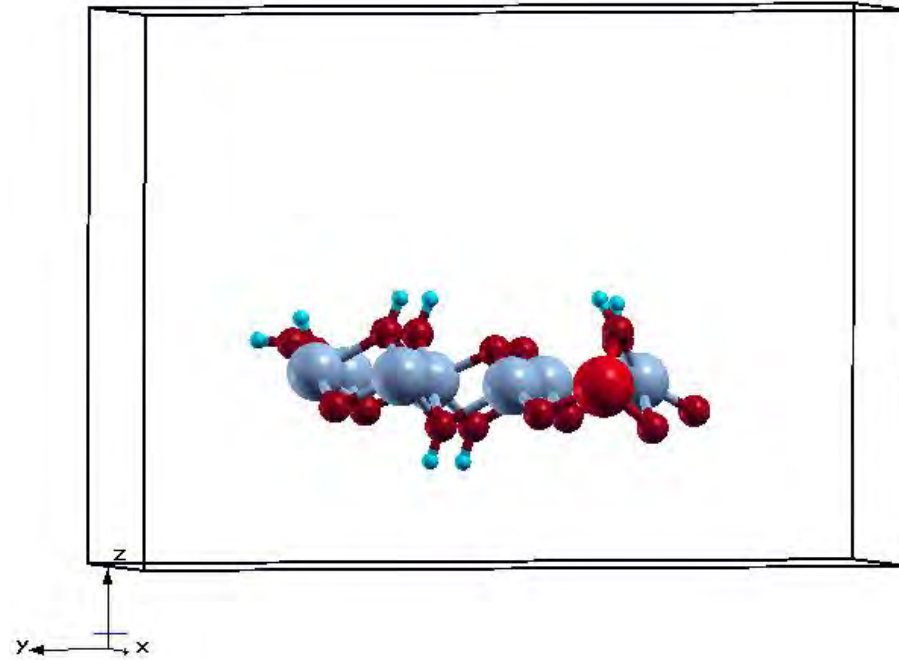
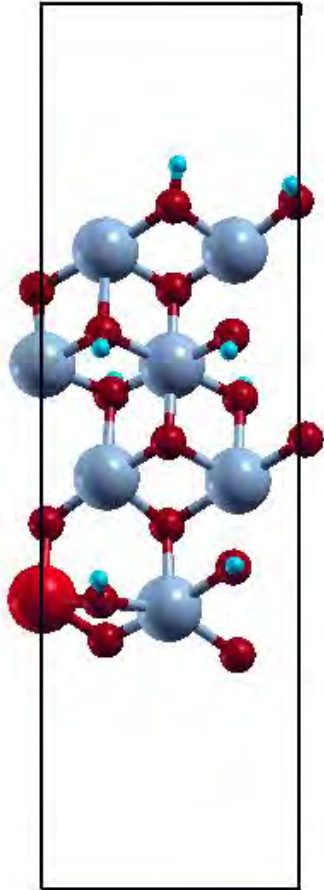
Bryan M. Hunter, Niklas B. Thompson, Astrid M. Müller, George R. Rossman, Michael G. Hill, Jay R. Winkler, Harry B. Gray

JACS 2017, 139, 11361

Joule 2018, 2, 747–763

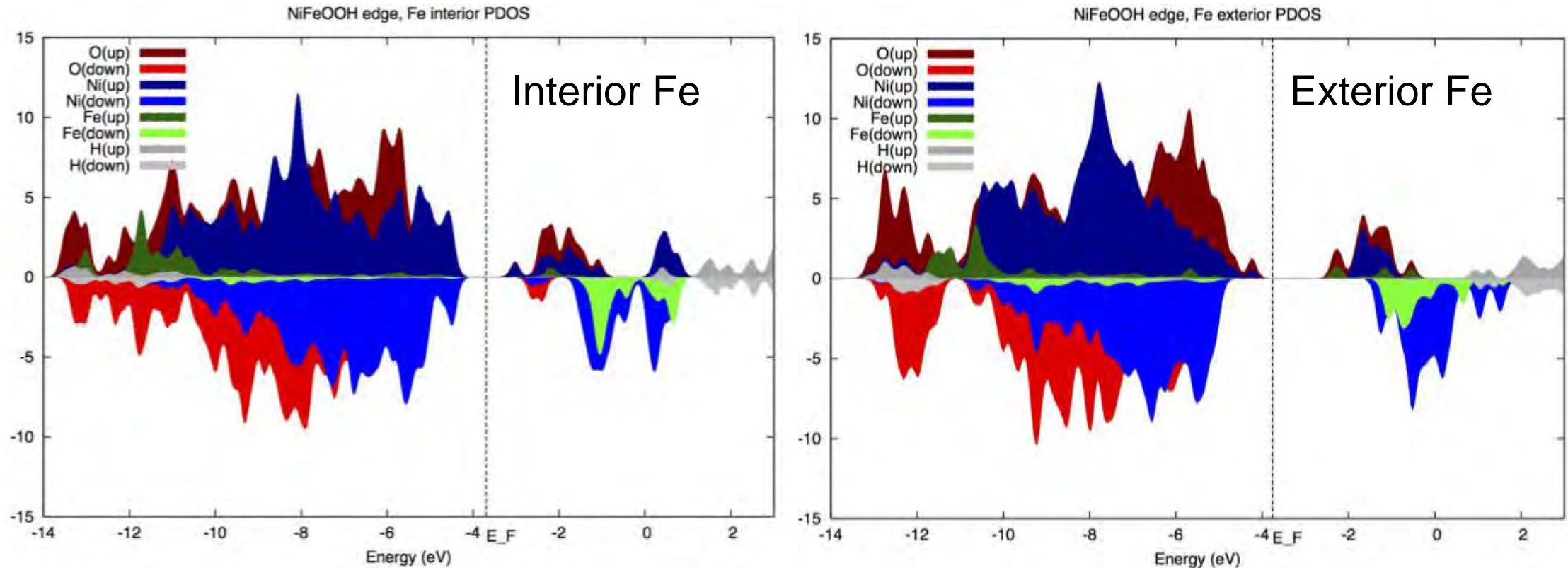
- Most of the OER chemistry happens at edge/defect Fe sites!
- Can we model these sites' electronic structure, oxidation states, etc.?
- What are the conditions for high oxidation state Fe edges?

NiFe oxyhydroxide nanowires



- Insert vacuum in one of the in-slab dimensions to represent terminations to the oxyhydroxide films
 - Terminations yield under-coordinated Ni and Fe sites
 - Both interior and exterior characteristic metal sites
-
- Calculations of large, broken periodicity systems with hybrid functionals made possible by highly parallel computing on Blue Waters

Electronic structure of edge Fe sites



- **Big energetic preference for exterior Fe: ca. 2 eV**
- Fe oxide motifs only comprise the CBM when Fe is at the edge

Ongoing studies:

- What are the Fe edge oxidation states, particularly in response to proton-coupled oxidation?

Acknowledgements

Yale/University of Illinois

- Prof. Sharon Hammes-Schiffer
- Aparna Harshan



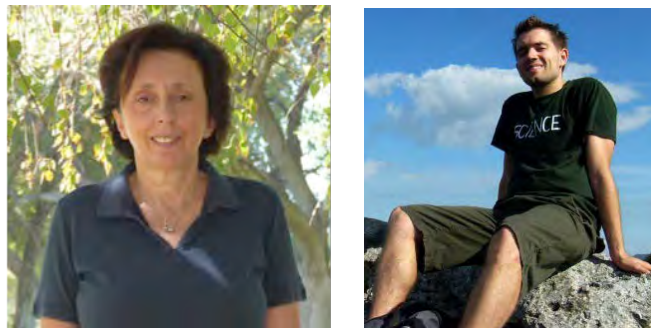
University of Wisconsin-Madison

- Prof. Shannon Stahl
- Dr. James Gerken



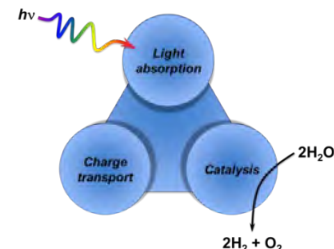
University of Chicago

- Prof. Giulia Galli
- Dr. Márton Vörös



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- Graduate Fellowship Program
- Victor Anisimov (POC)



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