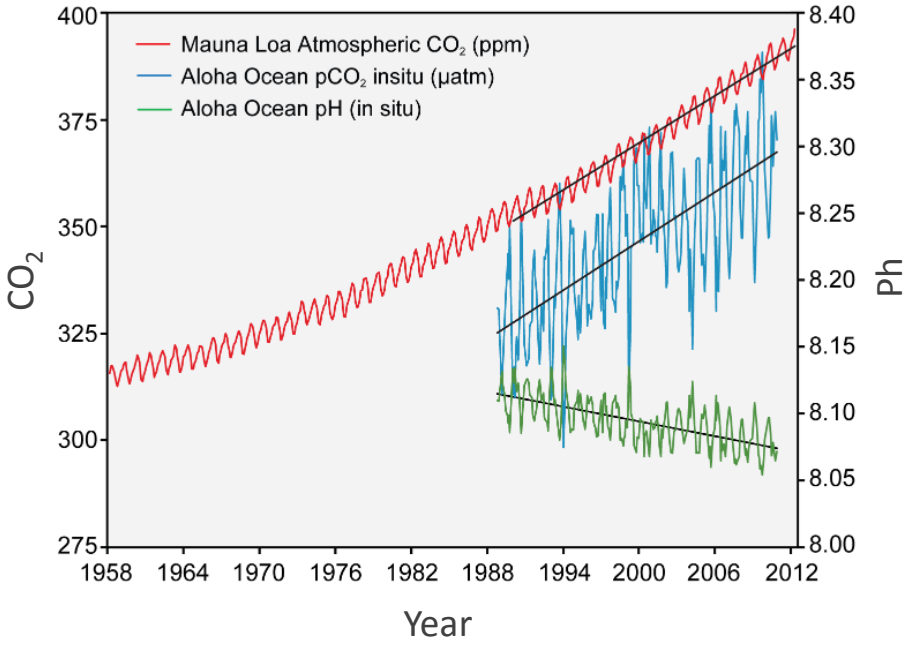
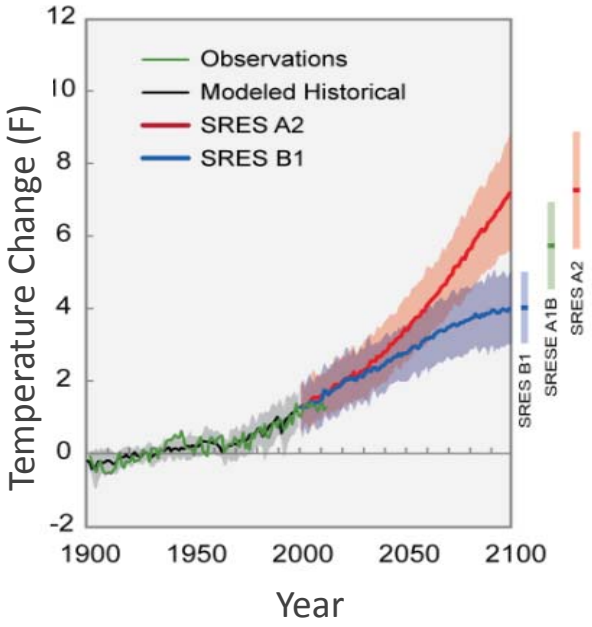
Characterizing the physical and electrochemical properties of four novel proton reduction catalysts

ORION COHEN

McCormick Lab

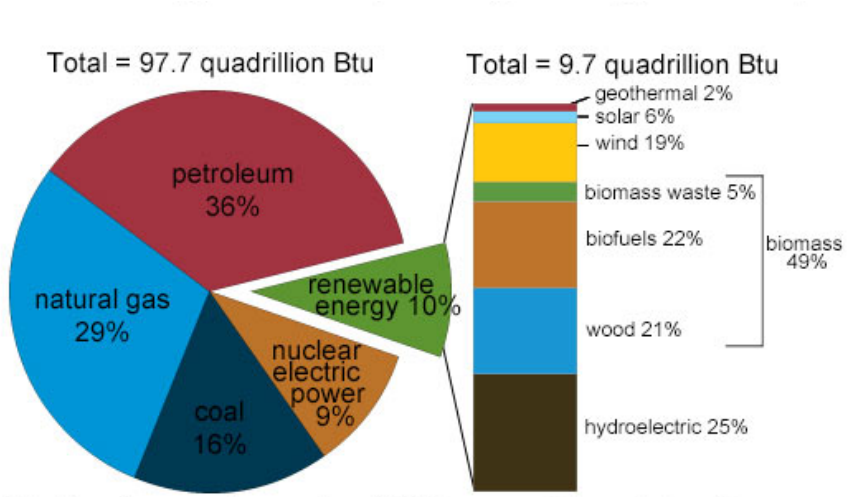
Climate change is a demonstrated threat

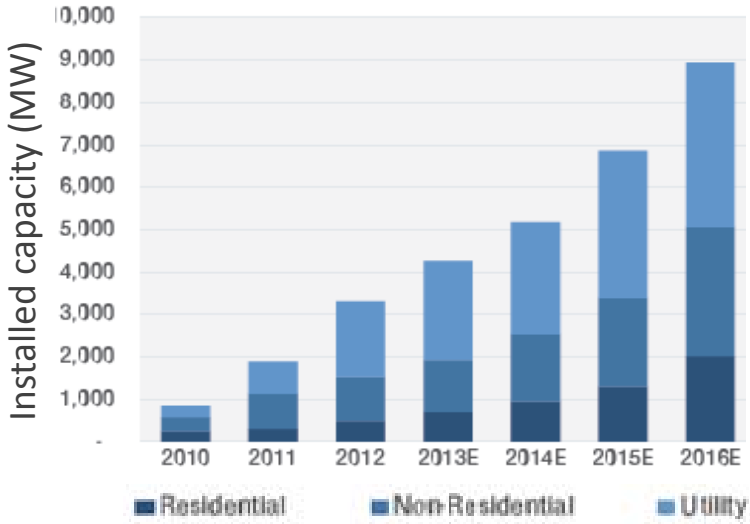




"No challenge poses a greater threat to future generations than climate change."
- Barack Obama

Current renewable energy technology cannot fully replace fossil fuels





"All of the studies of a clean energy system I've ever seen identify the same two technology gaps. Massive grid-scale energy storage to compensate for the intermittency of wind and solar power, and an energy-dense, carbon-neutral liquid transportation fuel."
- Nate Lewis, Director of Joint Center for Artificial Photosynthesis

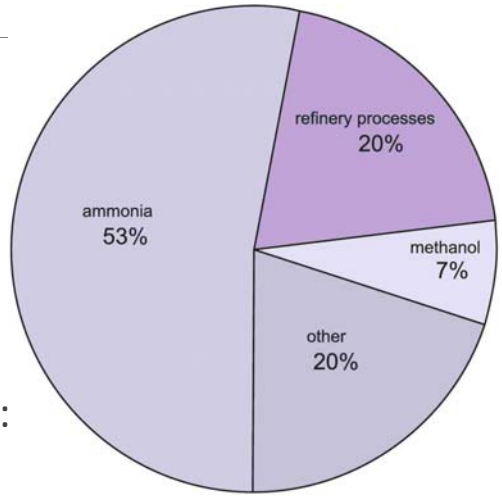
SC1
SC2

Renewable hydrogen production has immediate and long term benefits

Current Hydrogen Usage:

- Steam reforming
  - Uses energy equivalent of 180 billion kg oil annually
- Used for fertilizer production and gas processing

Energy Density	(Mj/kg)	(Mj/L)
Gasoline	46.4	34.2
Diesel	48	35.2
Hydrogen gas (1 atm)	141.9	0.01
Hydrogen gas (690 atm)	141.9	4.5
Liquid Hydrogen	141.9	8.5
Lithium Battery	~0.5	~1.5



Future Usage:

- Vehicles
- Long term energy storage
- Energy dense solar fuel

Slide 4

SC1 Stuart Cohen, 8/3/2016

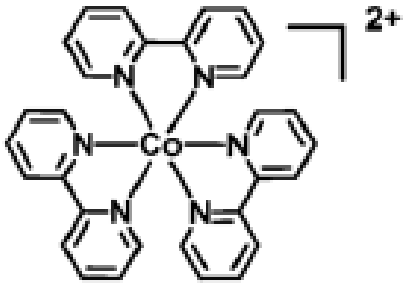
SC2 roughly equivalent to annual vehicle fuel usage
Stuart Cohen, 8/3/2016

Dedicated research has produced compounds capable of photocatalytic proton reduction

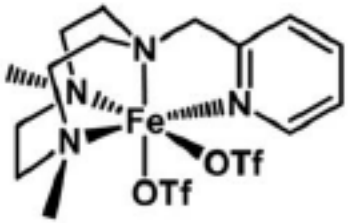
- First successful attempts involved rare or toxic catalysts

- Recent research focused on using earth abundant elements

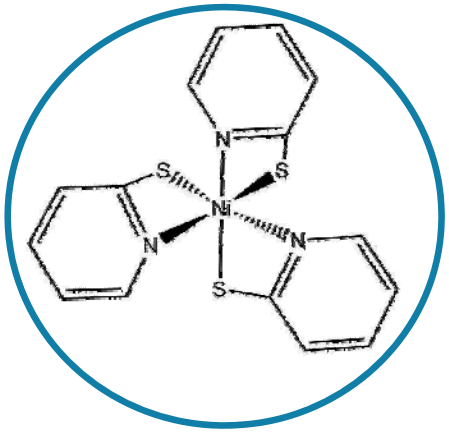
Cobalt



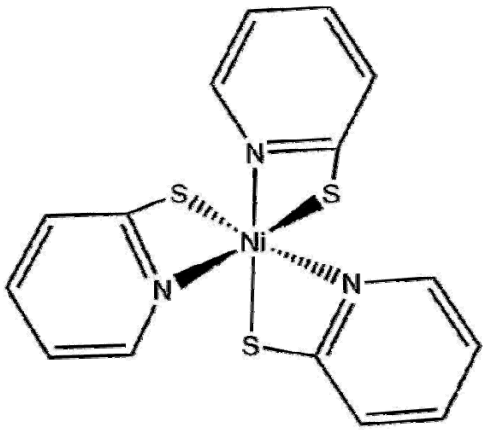
Iron



Nickel



Nickel pyridine-thiolate catalysts are a promising family of compounds



Nickel pyridine-thiolate

$Ni(PyS)_3^-$

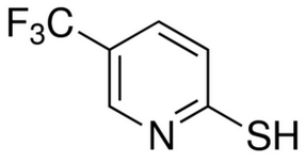
Terms:

pKa: acid disassociation constant

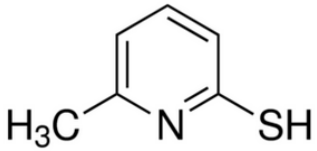
Reduction Potential: tendency of a compound to acquire electrons

Turnover number (TON): hydrogen gas produces

Ligand: molecule coordinated to a metal atom



Ligand A



Ligand B

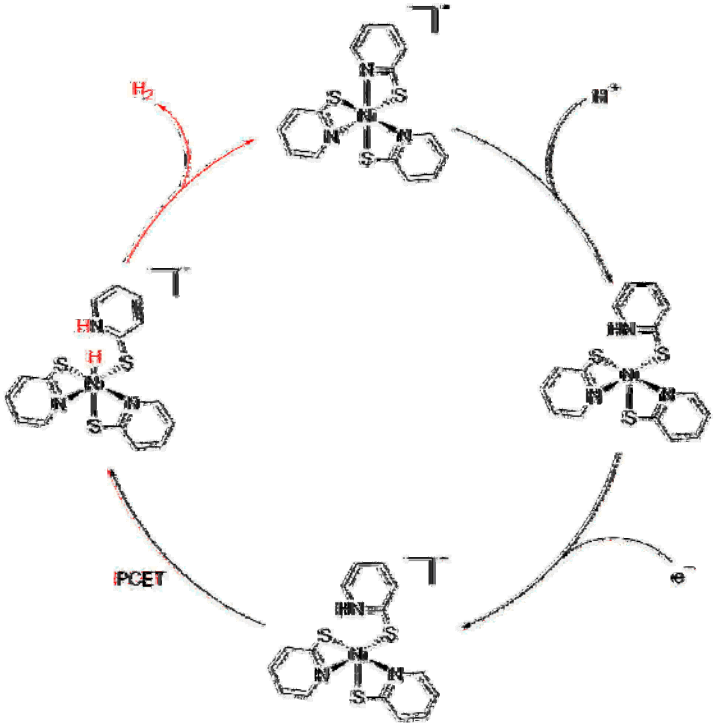
NiA_3

NiA_2B

$NIAB_2$

NiB_3

Nickel pyridine thiolate catalytic cycle



Protonation

Reduction

Proton coupled electron transfer (PCET)

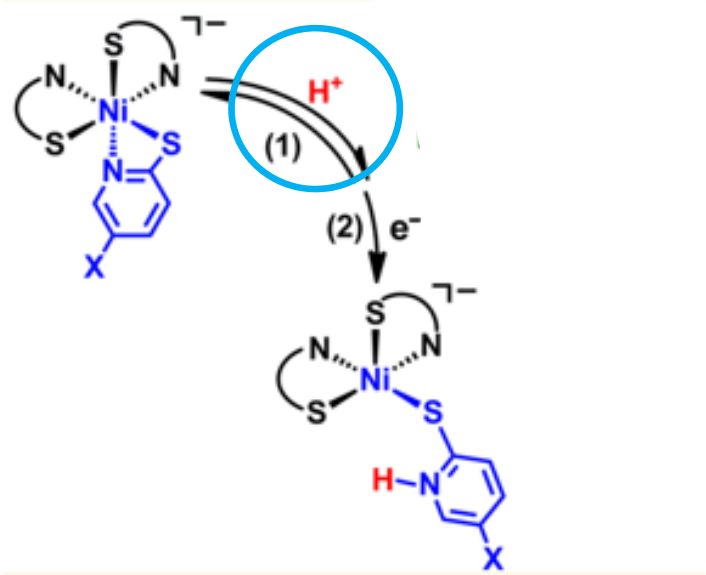
Hydrogen gas production

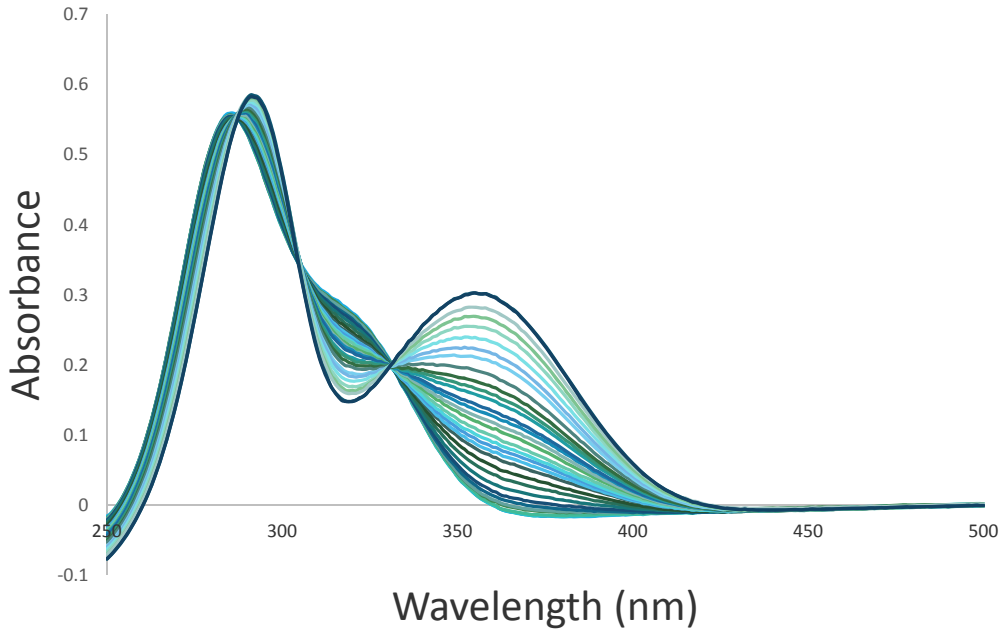
$$2H^+ + 2e^- \longrightarrow H_2$$

$$H_2O \longrightarrow 2H^+ + 2e^- + \tfrac{1}{2}O_2$$

$$H_2O \longrightarrow H_2 + \tfrac{1}{2}O_2$$

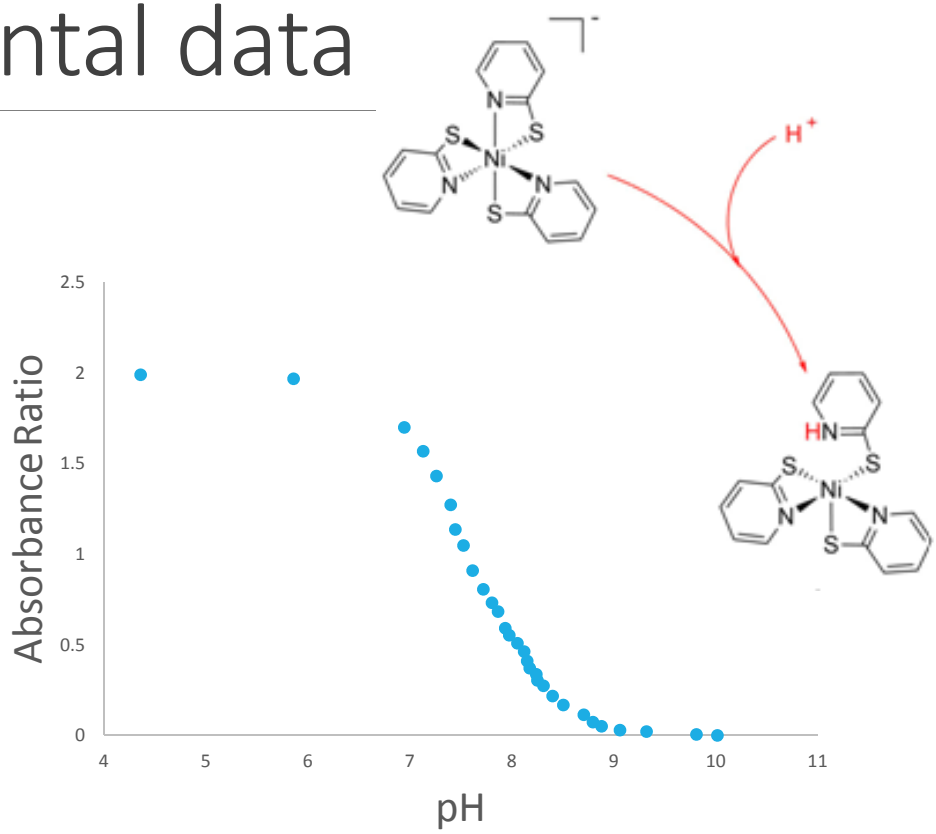
Step 1:
Measuring protonation with UV Spectroscopy



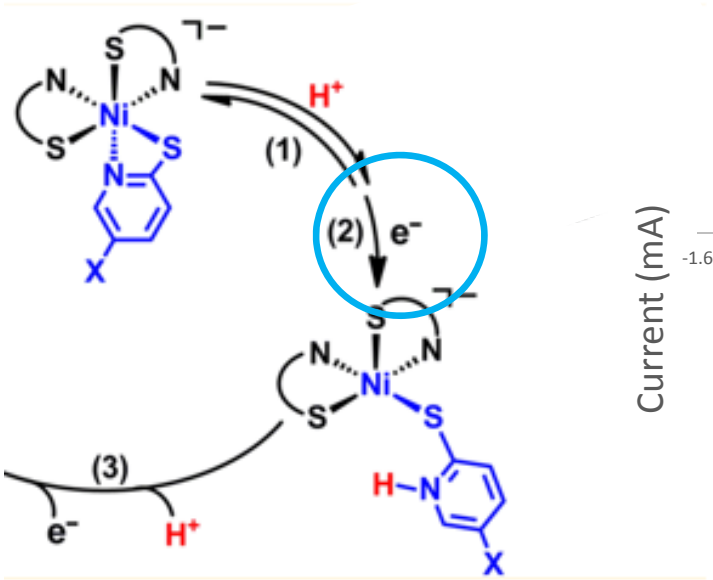


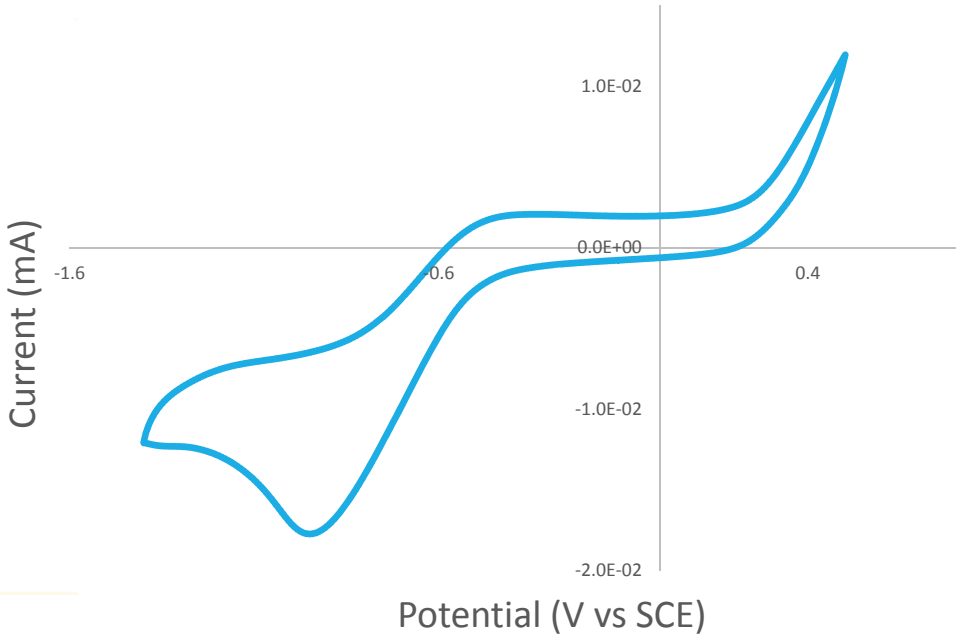
Calculated predictions due not closely resemble experimental data

Catalyst	Calculated pKa	Experimental pKa
NiA_3	9.5	7.37
NiA_2B	12.1	7.53
$NiAB_2$	19.2	9.63
NiB_3	17.6	10.71



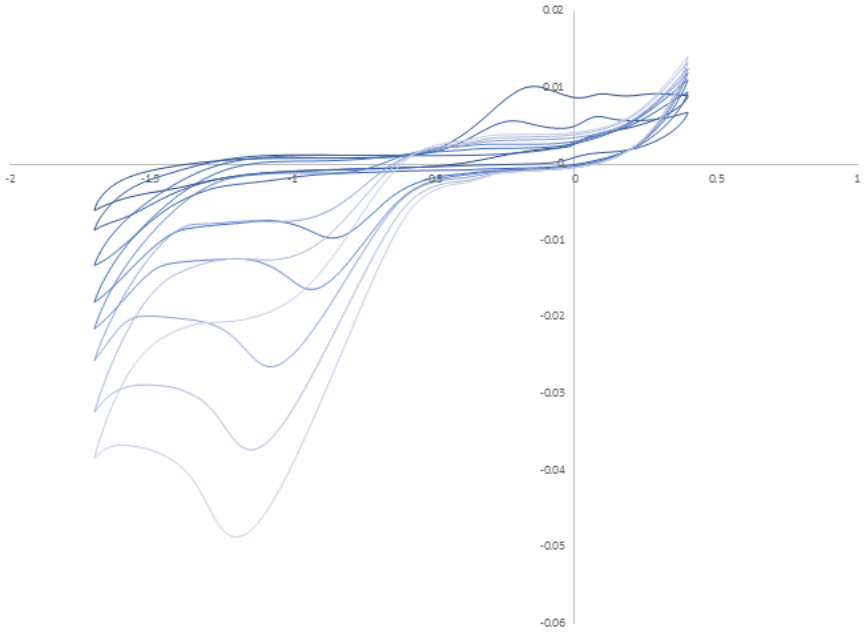
Step 2:
Measuring reduction with cyclic voltammetry





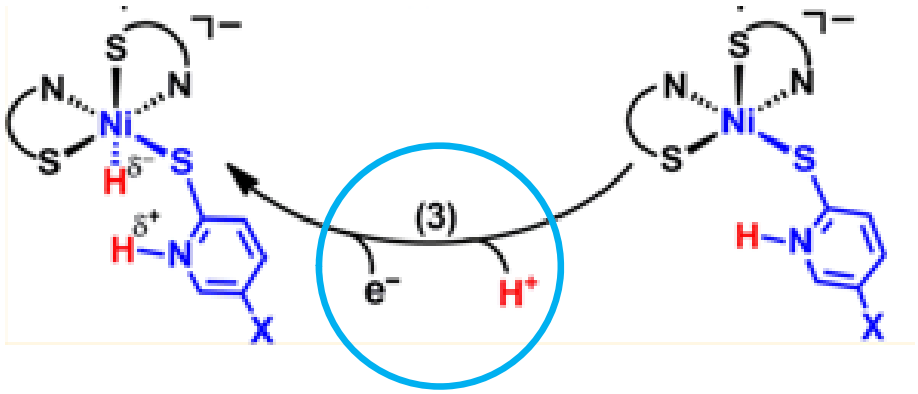
Experimental data corresponds to calculated

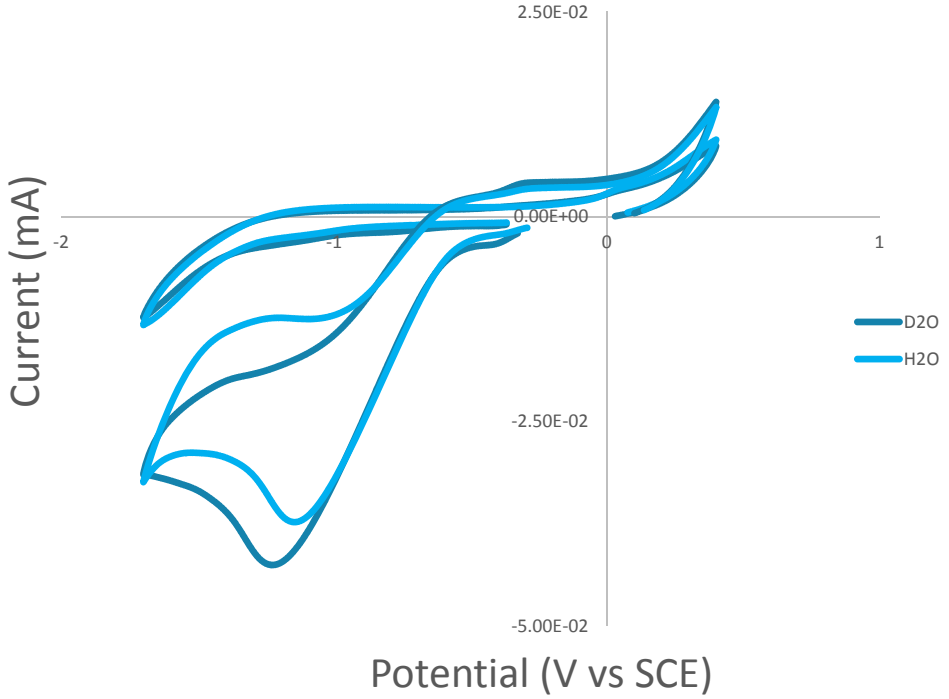
Catalyst	Calculated Reduction Potential	Experimental Reduction Potential
NiA_3	-1.0 V	-0.80 V
NiA_2B	-0.94 V	-0.98 V
$NiAB_2$	-1.27 V	-0.93 V
NiB_3	-1.18 V	-1.1 V



Step 3:
Identifying proton coupled electron transfer

- Characterized by shifting reduction potential
- Identified by using D_2O instead of H_2O





Future Research

- Complete hydrogen production testing
- Identify better catalysts for hydrogen production
- Develop commercially available solar hydrogen production methods

Acknowledgements

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Portland State UNIVERSITY

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Questions?

Density Functional Theory yay