Investigating Ni(II) Centered Heteroleptic H2 Production

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Alternative Fuel Production

How do we do that?

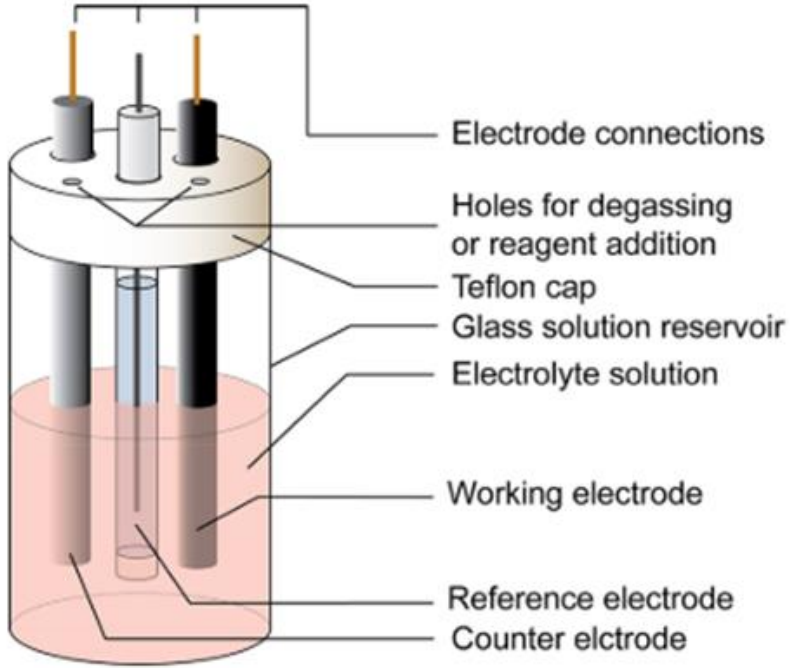
- Hydrogen gas can provide 2-3x the efficiency of internal combustion motors
- Current storage and fueling methods require high pressure or low temperature
- Necessary development of production and storage methods for hydrogen gas

Cyclic Voltammetry

What the heck is that?

- Technique to measure electrochemical cycles in a manufactured cell
- Our cell contains a nickel centered molecule with two 3-(trifluoromethyl)pyridine-2-thiol and one 2-pyridinethiol ligand
- Heteroleptic ligands target the necessary reactions more efficiently

The Cell



Working electrode: glassy carbon

Reference electrode: AgCl

Counter electrode: Ag wire

The Solution

In three parts

1. Solvent: 8:1:1 mixture of DCM/EtOH/H_2O
2. Supporting Electrolyte: 0.1M TBATFB
3. Acid: 2.0M acetic acid in 8:1:1 with DCM/EtOH/H_2O and 0.1M TBATFB

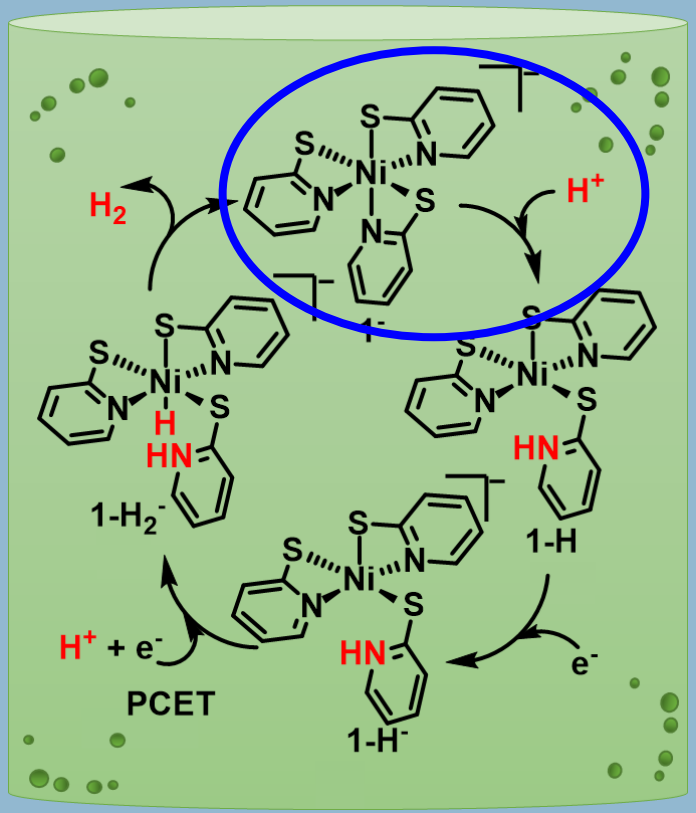
- Atmosphere is purged with nitrogen
- Final run with ferrocene

The Cycle

Also in three parts

First step - protonation of N

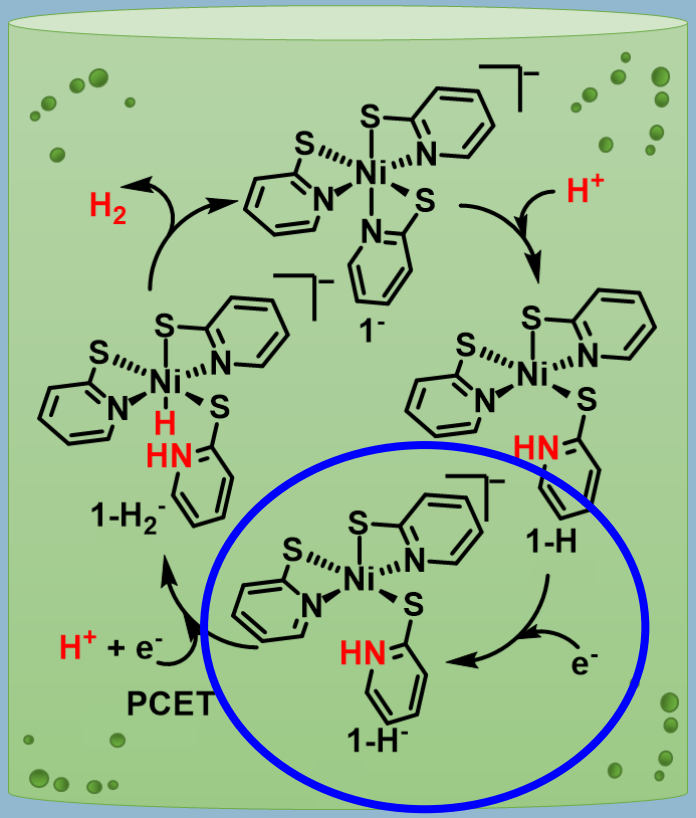
Ligands create a negative area, attracting protons from the acid



The Cycle, pt 2

Primary Reduction - nickel accepts electron

Electron withdrawing groups created by ligands ease electron acceptance.



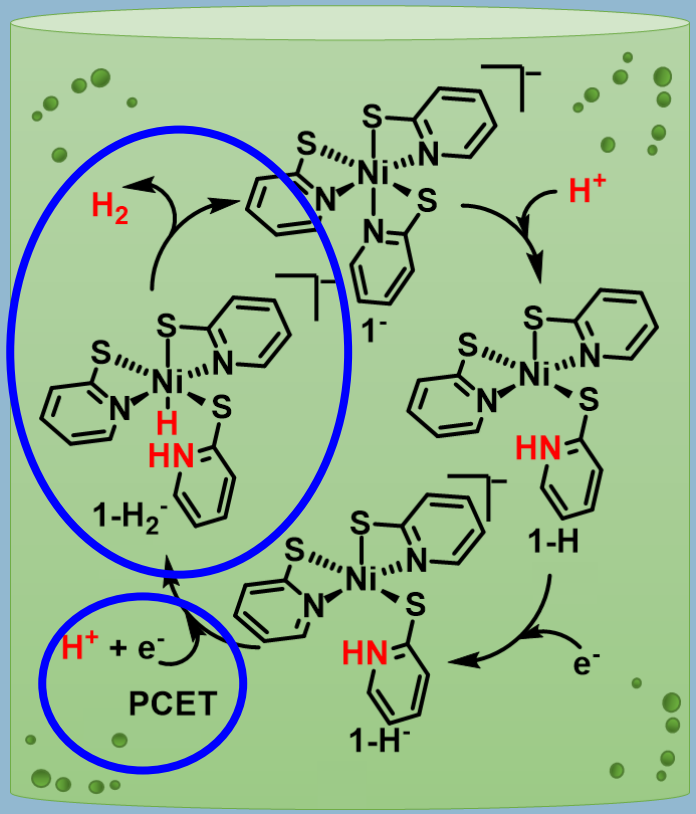
The Cycle, pt 3

The money step

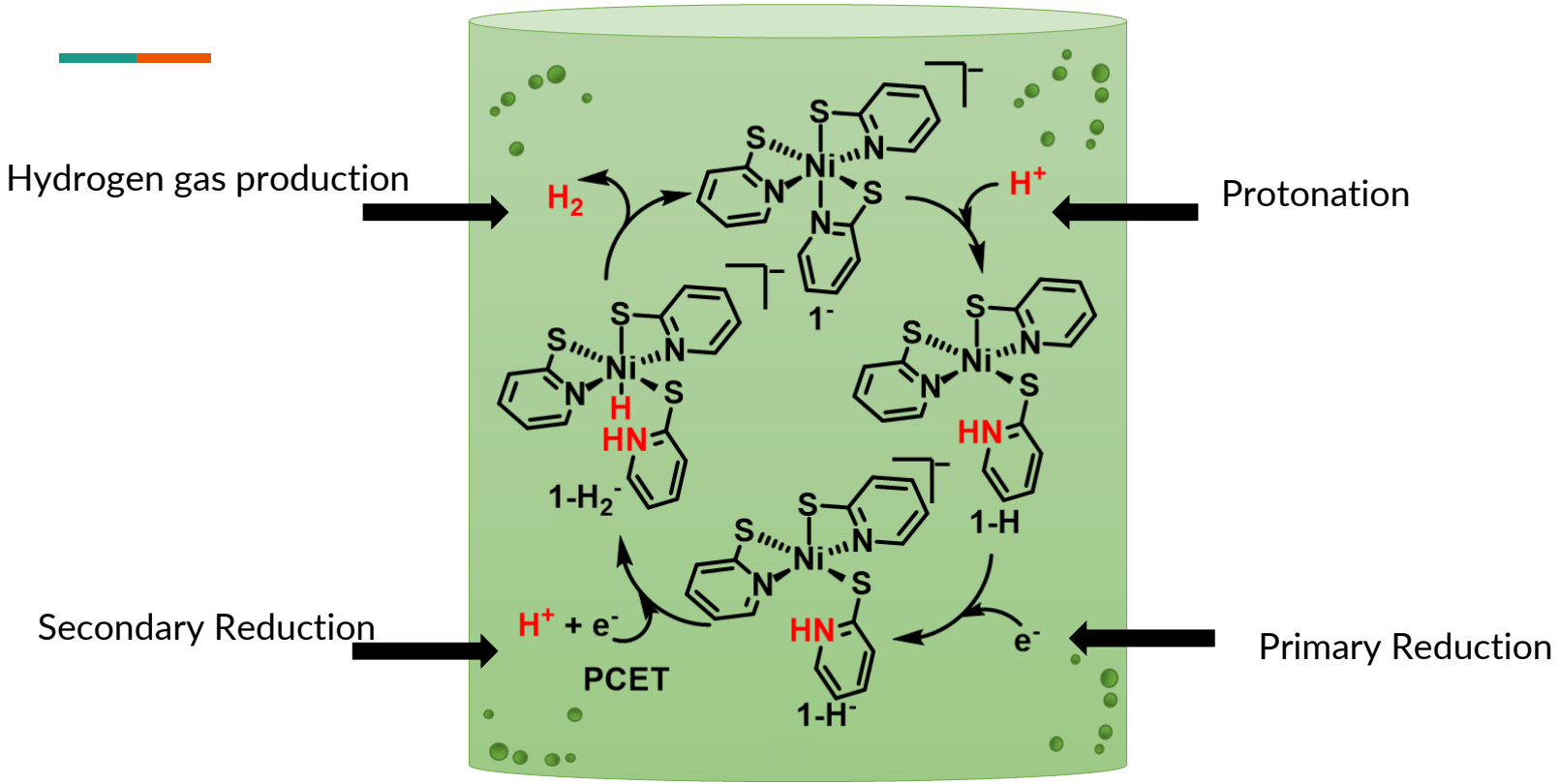
Secondary Reduction - nickel accepts electron and proton

PCET - proton coupled electron transport

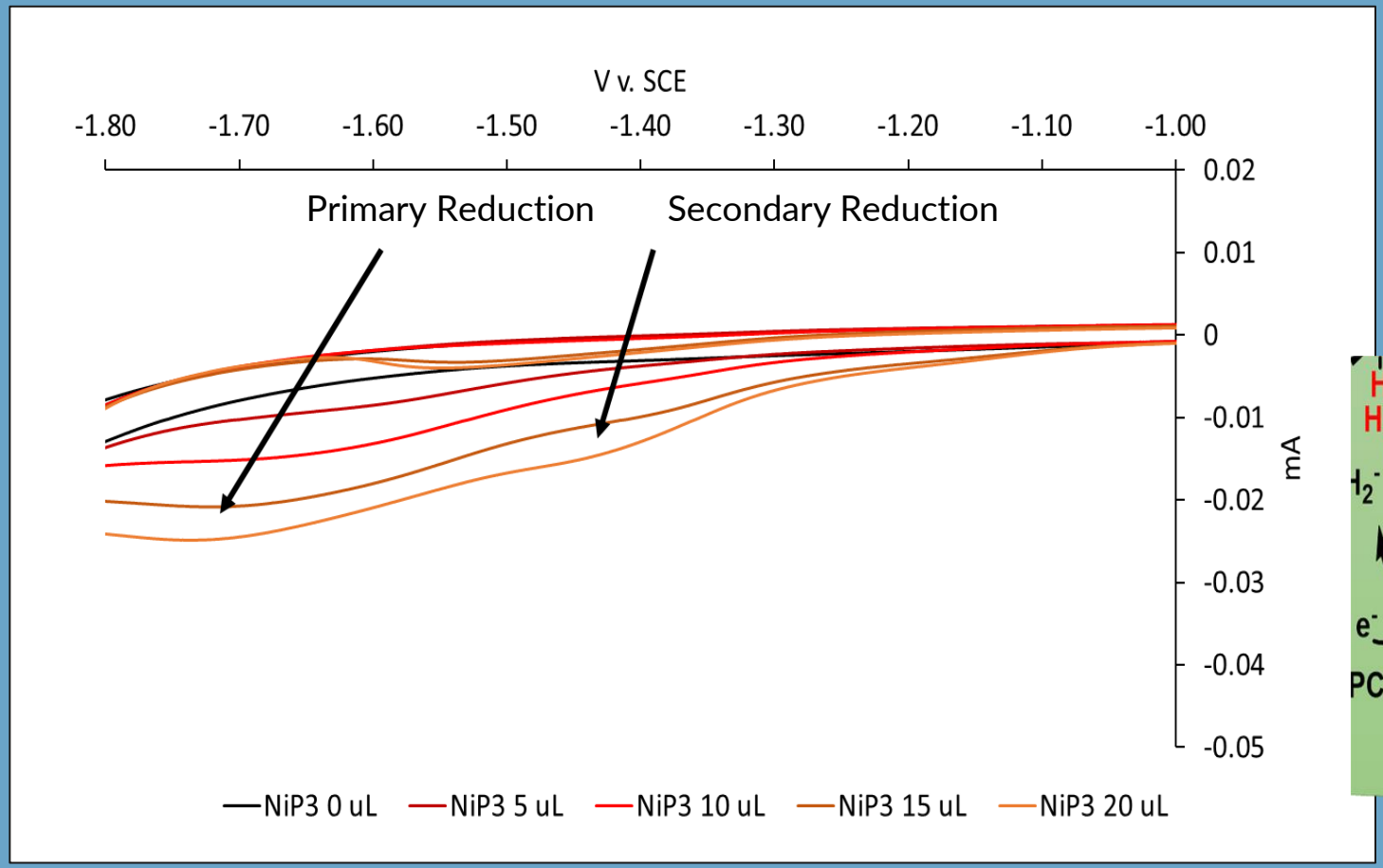
Requires two protons and two electrons to produce hydrogen gas.



The Electrocatalytic Cycle



4th Equivalence of Acid



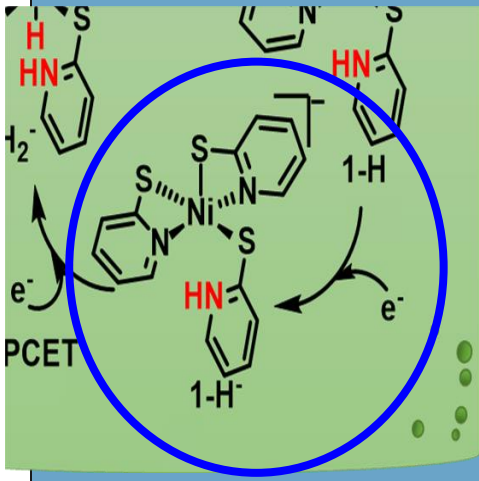
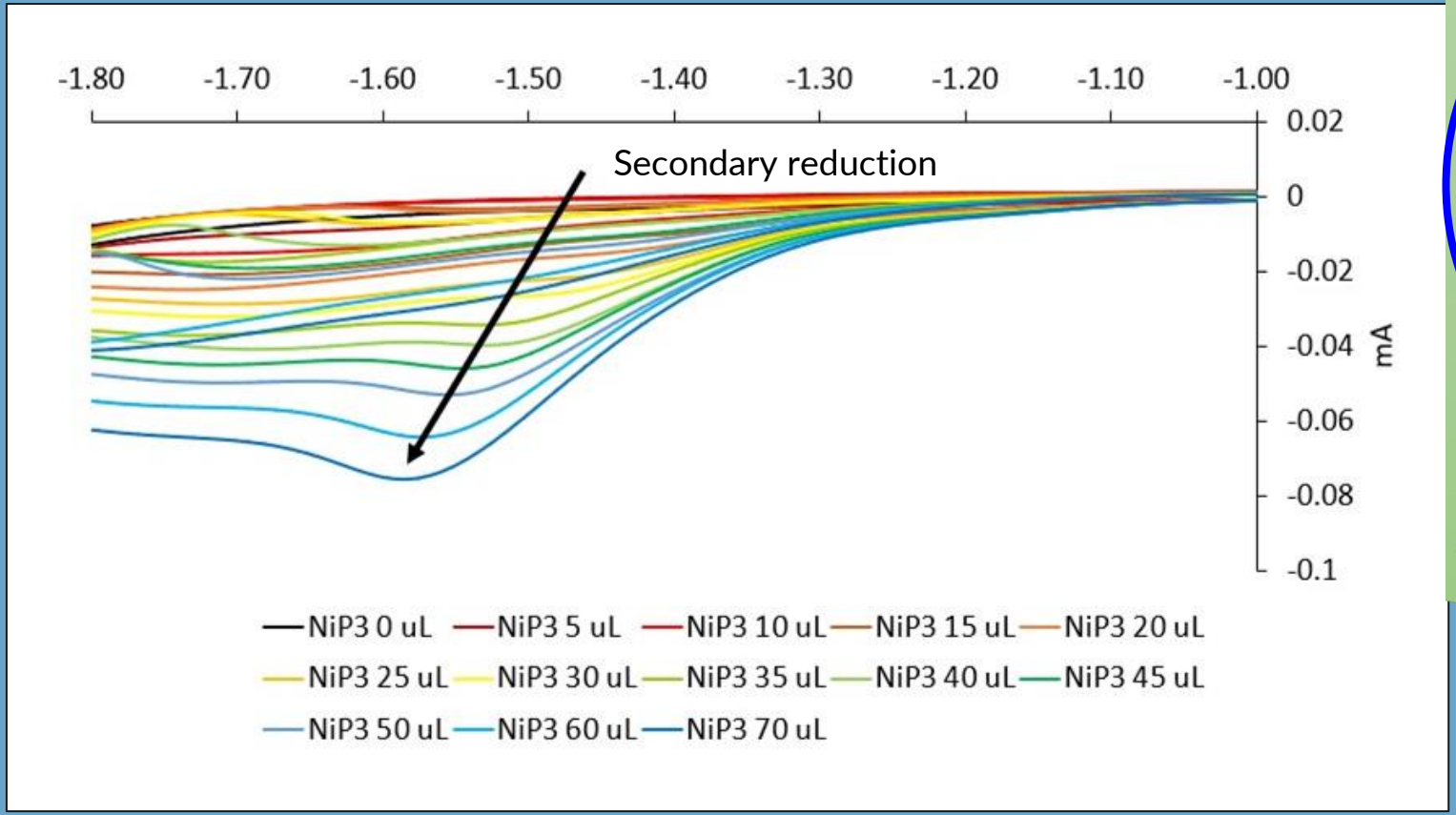


Image credit: Dayalis SV Brown

Additional Acid



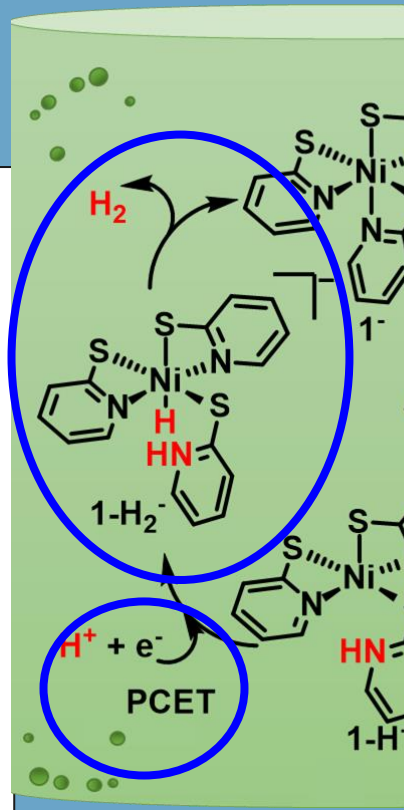
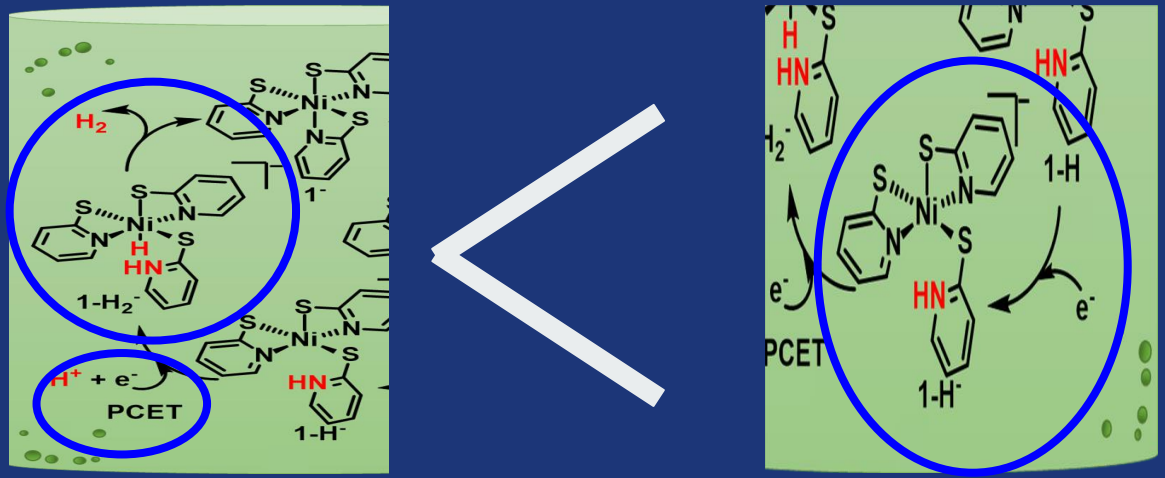


Image credit: Dayalis SV Brown

Secondary Reduction “consumes”

- ➔ This points to an increase of hydrogen production
- ➔ Excess acid allows for consumption of protons
- ➔ Ligands pull / push electron groups to allow N and Ni to reduce and protonate



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Any questions?

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