Design of Iron-Nickel Nanocatalysts for Low-Temperature Electrochemical Ammonia Generation

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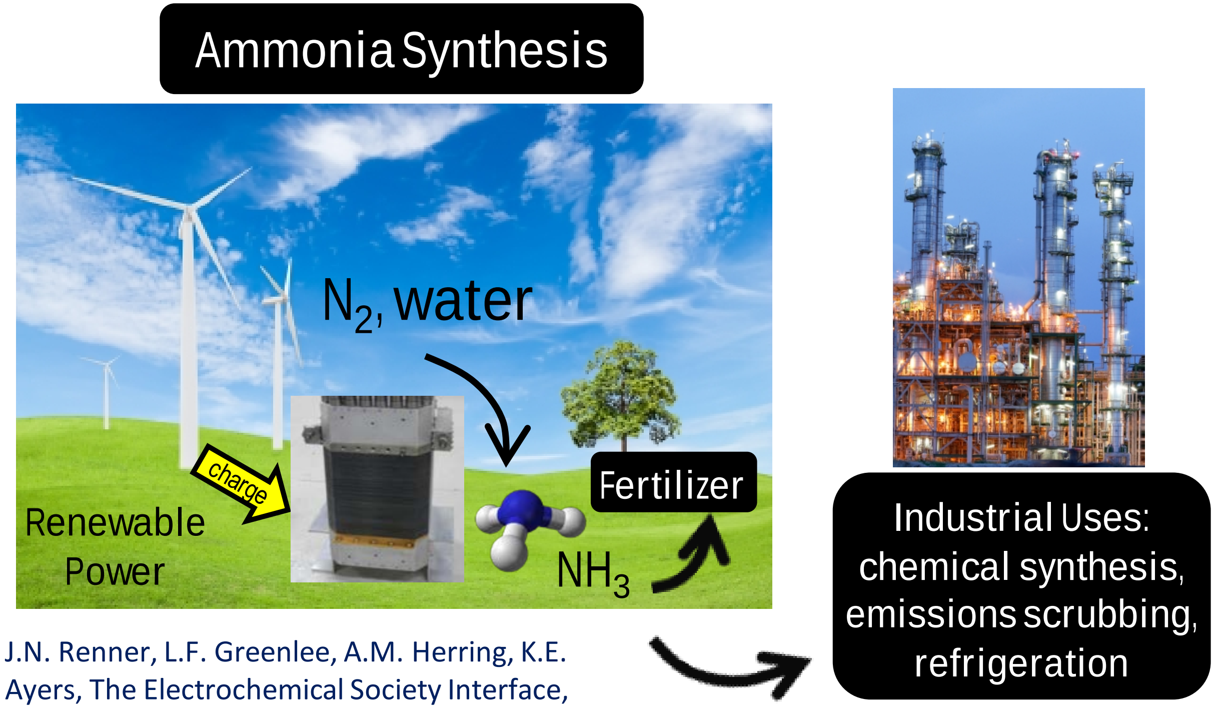
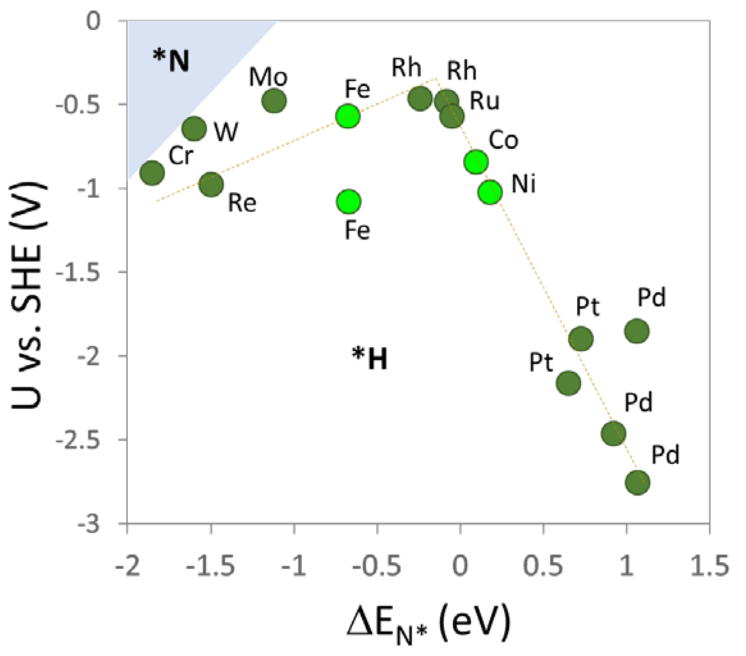
Vision for Electrochemical Ammonia Production



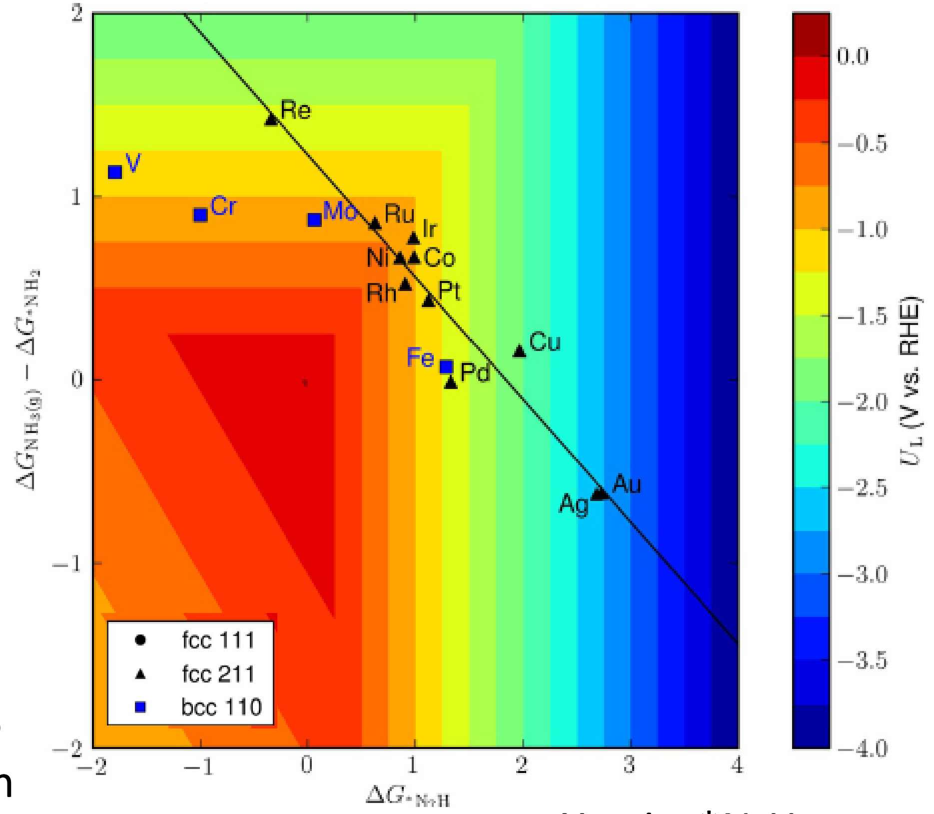
J.N. Renner, L.F. Greenlee, A.M. Herring, K.E. Ayers, The Electrochemical Society Interface, Summer 2015.

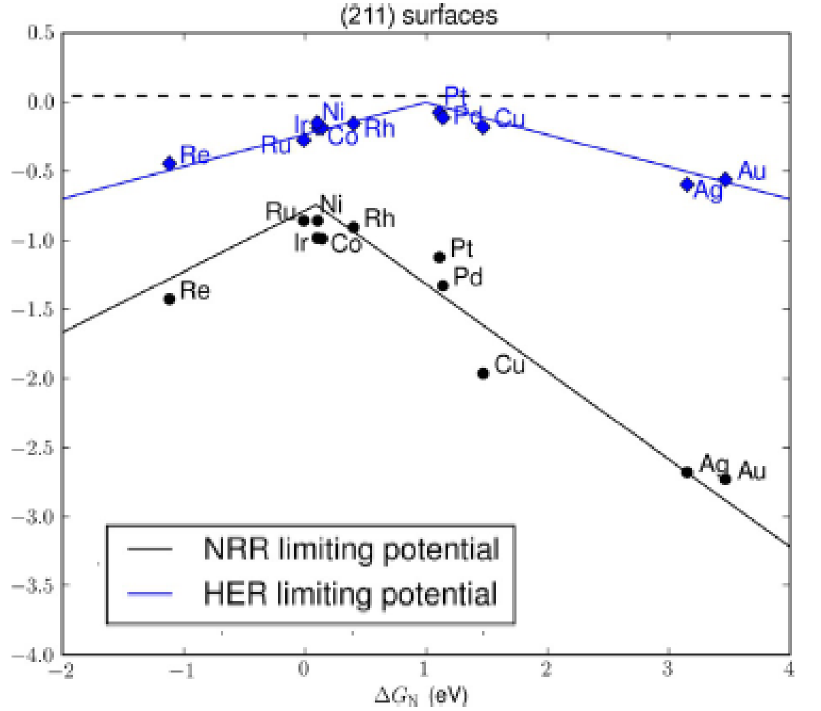
- Electrically driven process for low temp/pressure/emissions
- Compatible with intermittent operation
- High regional demand for fertilizer co-located with renewables

Linear Scaling Relationships Suggest Dominance of HER



Right leg: N_2 ads/1st protonation step
Left leg: Final protonation/desorption





X-axis: $*N_2H$
Y-axis: reductive desorption

Conclusions from theory on novel catalyst design:

- Energetics must scale differently
- Depart from linear scaling relationships completely

E. Skúlason, et al. *Physical Chemistry Chemical Physics*, 14 (2012).
Montoya, et al. *ChemSusChem* 2015, 8, 2180 – 2186.

A Team Approach

2014: USDA SBIR Phase I

2015-2017: USDA SBIR Phase II

2016-2017: DOE SBIR Phase I

2016-2019: DOE BES NH_3

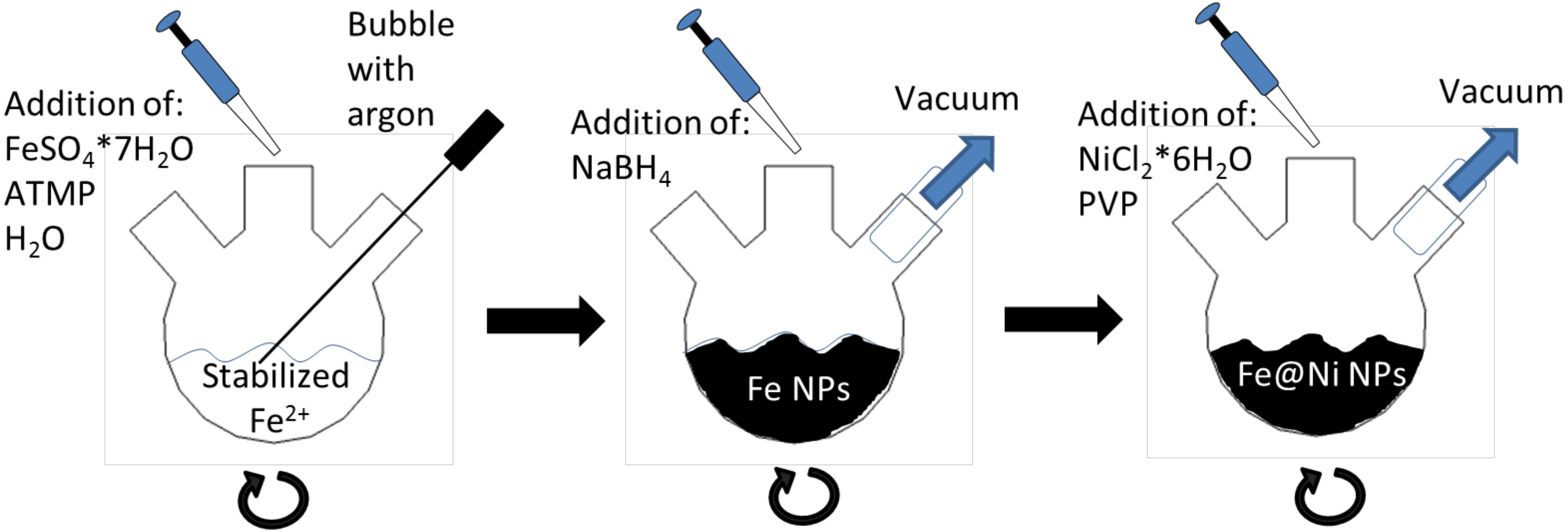
- Can we make ammonia with alkaline, low-temp electrochemistry?
- Can we make ammonia with FeNi catalysts?
- How do catalyst composition and morphology affect NH_3 production?
- Ammonia contamination: Controls and experimental design?
- What can we learn about the catalyst surface?
- Can we control the surface environment of the catalyst?

Phase I: Initial Results

Can we make ammonia at low temperature?

- ➢ Alkaline electrolyte & FeNi catalysts

Synthesis Method & Parameter Variation to Control NP Performance

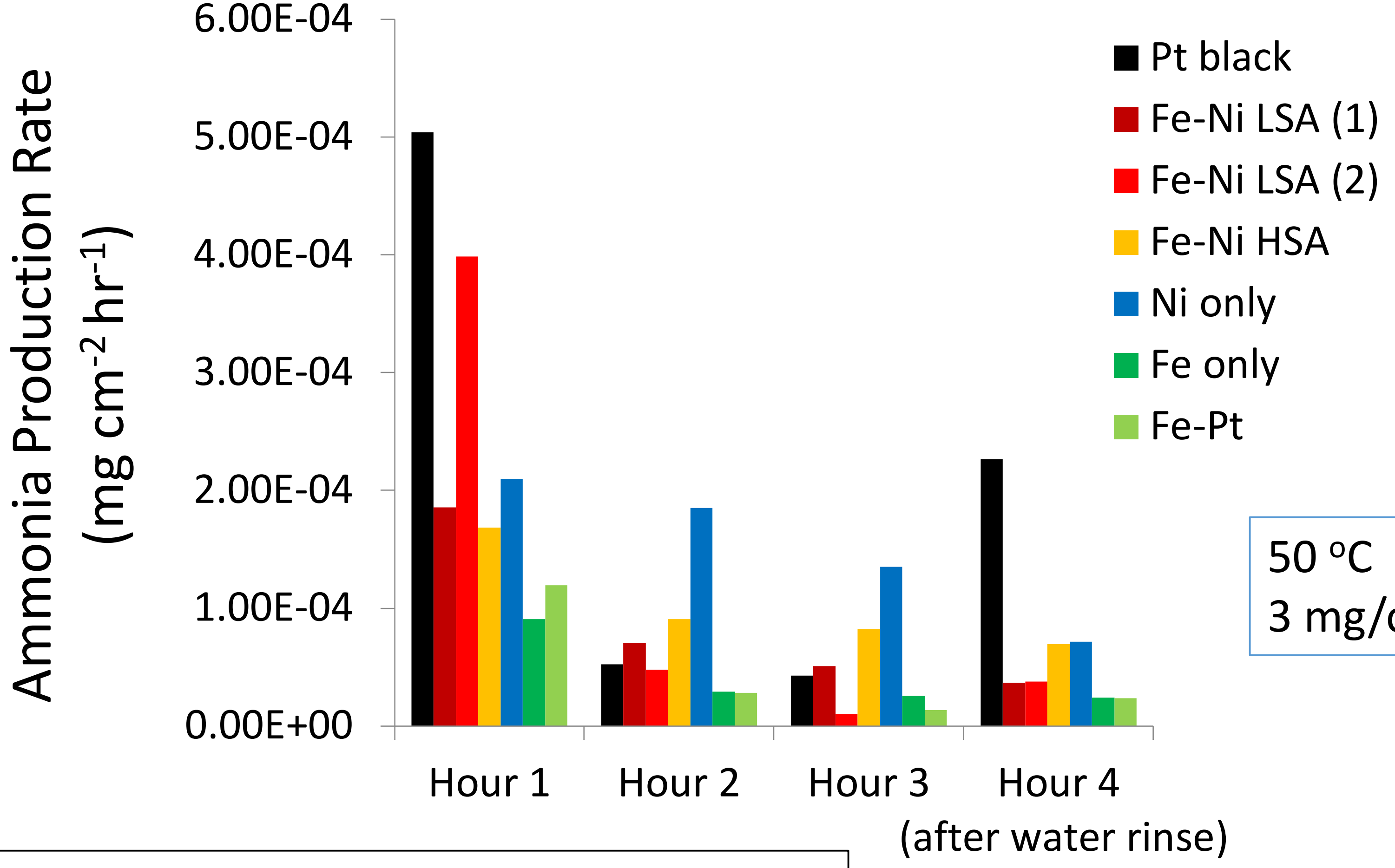


- Molar ratio of stabilizer:Fe
- Fe concentration
- Fe salt / oxidation state
- Type of stabilizer
- 1-step vs 2-step synthesis

- Molar ratio of BH_4:Fe
- Rate of $NaBH_4$ addition
- Age of $NaBH_4$

- Molar ratio of stabilizer:Ni
- Molar ratio of Ni:Fe
- Type of stabilizer
- Rate of Ni/stabilizer addition
- Time between BH_4 addition and Ni/stabilizer addition

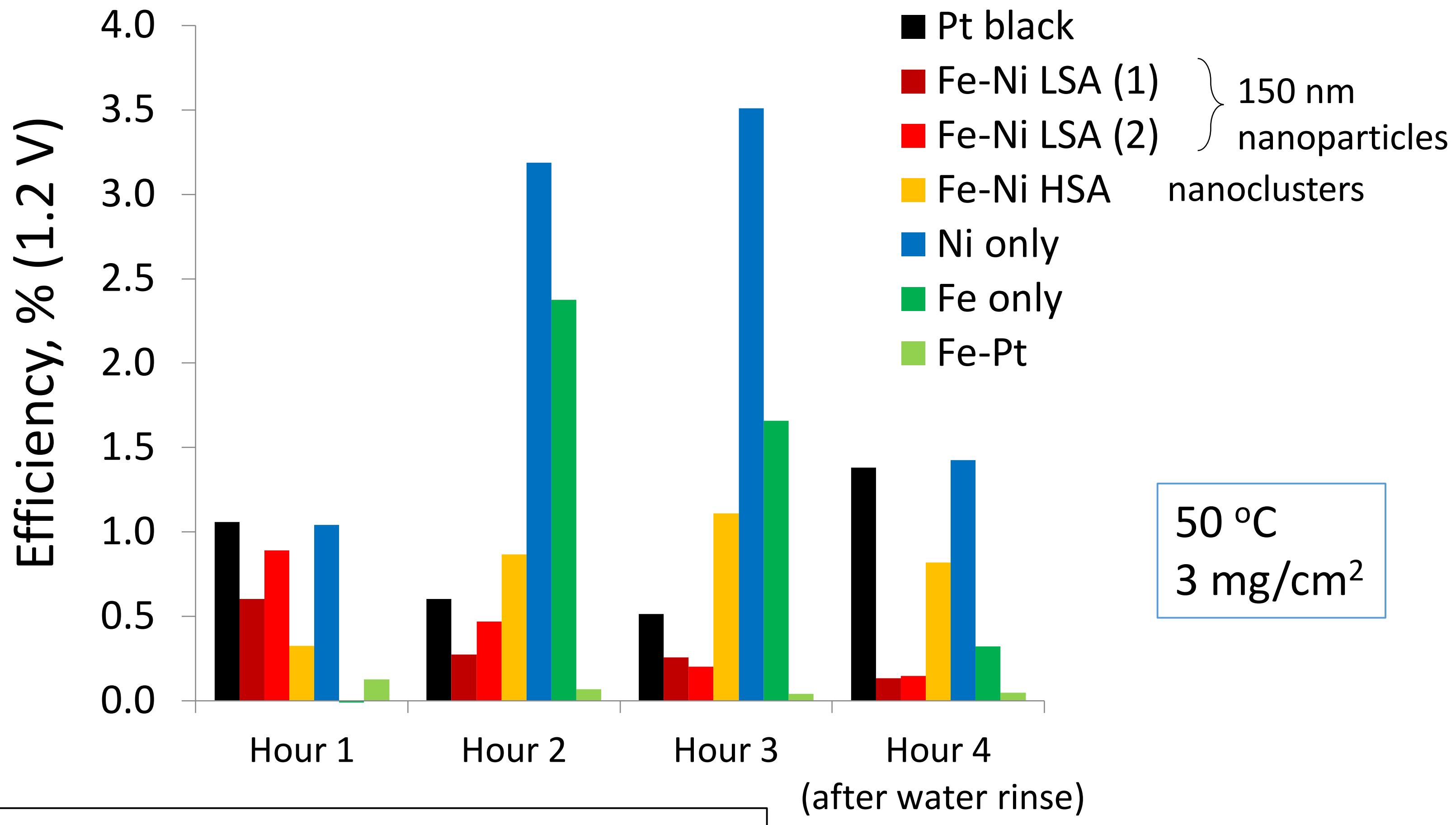
Ammonia Production Rate at 1.2 V



50 ^{o}C
3 mg/cm^2

Li and Licht (2014): 200 ^{o}C, molten NaOH electrolyte
@ 1.2 V, 2 mA/cm^2: 0.147 $mg/cm^2/hr$, 37% efficiency
@ 1.4 V, 25 mA/cm^2: 0.41 $mg/cm^2/hr$, 7% efficiency

Coulombic Efficiency



50 °C
3 mg/cm²

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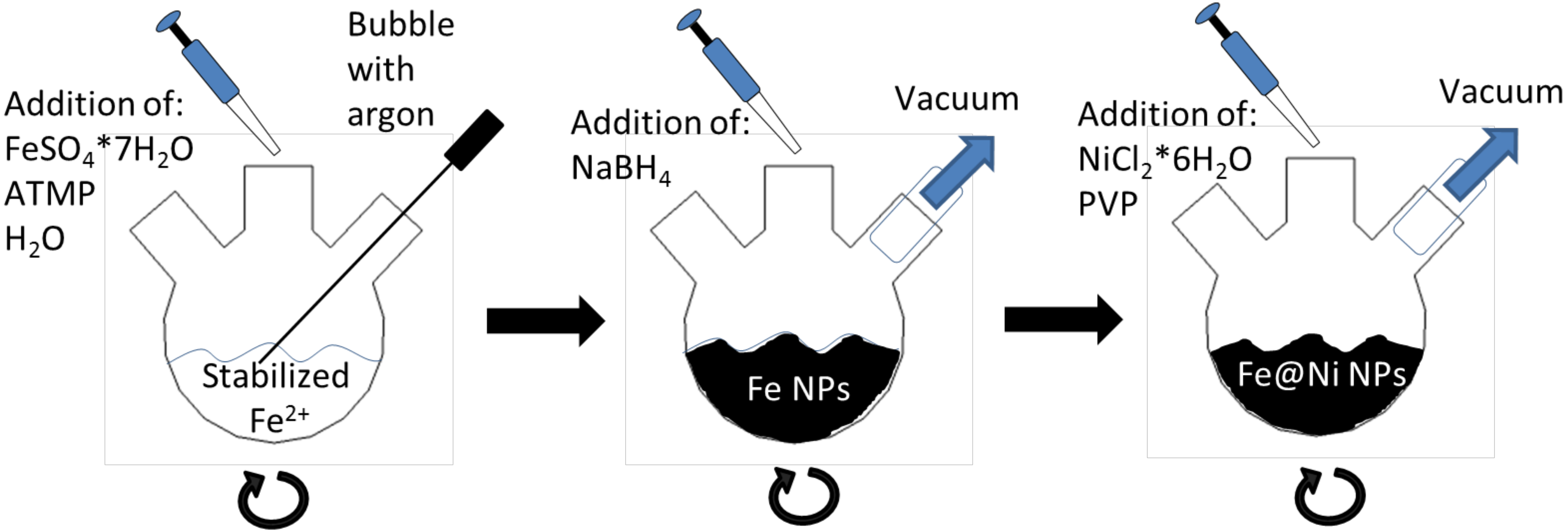
Phase II: Catalyst Composition & Morphology

Synthesis Method & Parameter Variation to Control NP Performance



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- Molar ratio of Ni:Fe
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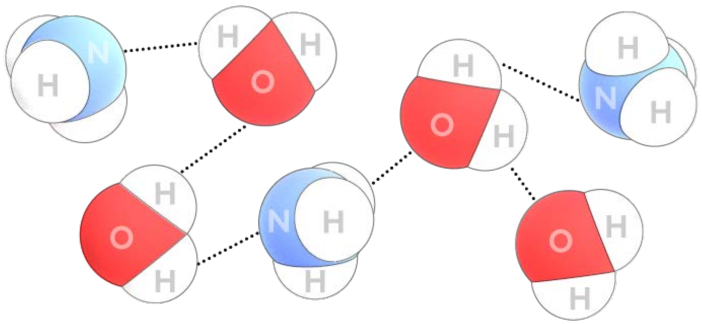
Ammonia Contamination

Experimental Design Considerations

- Ammonia adsorption – materials of setup
- Gas tight setup
- Gas flow rate
- Electrode positioning/contamination
- Liquid electrolyte vs. gas phase cell
- Acid trap sampling position
- Catalyst/electrode preparation
- Ionomer degradation
- Electrode surface area / size



$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

	Absorbance	Concentration (µM)
Top	0.122	63.7
Top	0.126	67.2
Middle	0.105	48.7
Middle	0.125	66.3
Bottom	0.115	57.5
Bottom	0.127	68.1
Average	0.12	61.9
STDev		7.5

Polymer	N_s
PVDF	1.0
PELD	4.4
PTFE	7.5
FEP	8.6
PFA	13.9

$N_s = 10^{12}$ molec. NH_3/cm^2

Conclusions - Questions

Can we make ammonia at low temp with alkaline electrochemistry?

- Yes, but efficiencies remain low
- Much we do not understand about catalysts and engineering

Do we have the appropriate controls in place?

- Acid trap background, Ar flow, Ar e-chem, N_2 flow

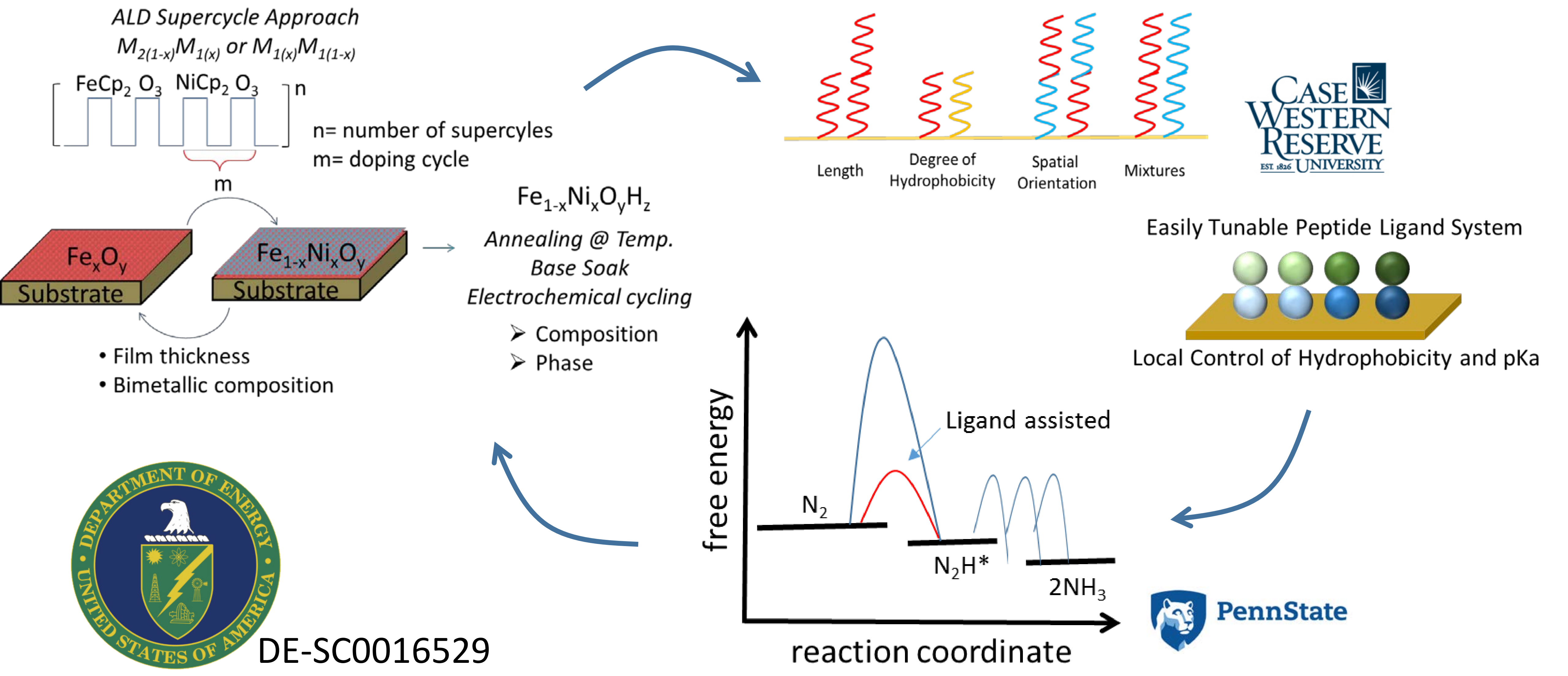
Do we have a robust experimental design and testing setup?

- Gas tight, flow meters, materials with low NH_3 adsorption
- Next: Gas-phase cell / larger electrode SA / electrode engineering

Can we control the surface environment of the catalyst?

- Future work: Inspirations from nitrogenase enzyme
- Catalyst morphology & composition

Coordinated Catalyst-Surface Chemistry-Theory Approach



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