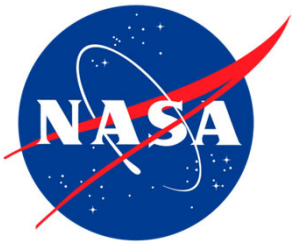


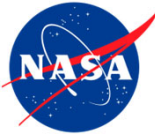
Ionic Liquids for a Regenerable Carbon Formation Reactor: Reactor Design Study and Ionic Liquid Parameterization

Kaitlin Oliver-Butler and Mitchell Woolever

July 18, 2023

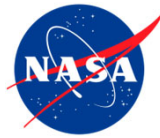


Agenda



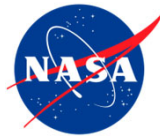
- CO₂ Reduction and the Bosch Process
- Prior Work
- IL-Based Reactor: Single-Volume Reactor Design
- IL Parameterization
- Electroplating Study Results
- Future Work

CO₂ Reduction



- Exploration goals of >75% O₂ recovery from CO₂
- Current state of the art: Sabatier process
 - $\text{CO}_2 + 4\text{H}_2 \leftrightarrow 2\text{H}_2\text{O} + \text{CH}_4$
 - Methane waste product → ~50% O₂ recovery rate
 - Ongoing work in processing the methane
- Bosch Process as a proposed alternative
 - Only solid carbon waste product → no O₂ or H₂ losses
 - Never flown due to complications that stem from carbon

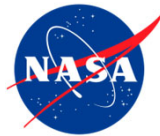
The Bosch Process



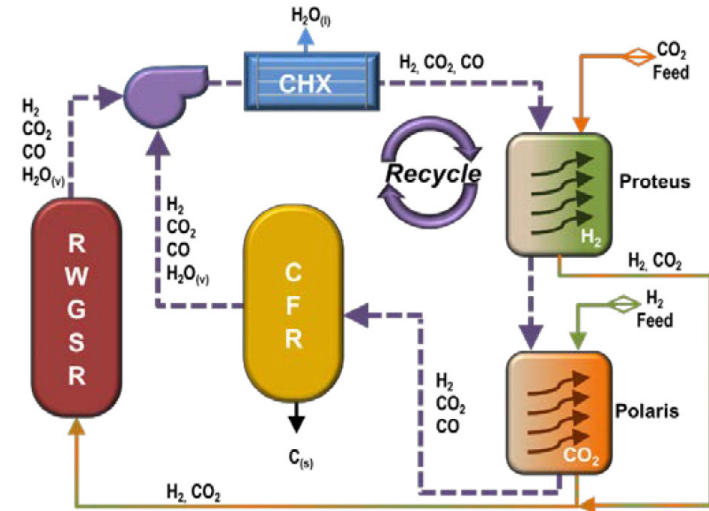
RWGS	$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{H}_2\text{O} + \text{CO}$	(1)
CO Hydrogenation	$\text{CO} + \text{H}_2 \leftrightarrow \text{H}_2\text{O} + \text{C(s)}$	(2)
Boudouard	$2\text{CO} \leftrightarrow \text{CO}_2 + \text{C(s)}$	(3)
Total Bosch Process	$\text{CO}_2 + 2\text{H}_2 \leftrightarrow 2\text{H}_2\text{O} + \text{C(s)}$	(4)

- Requires iron, nickel, cobalt catalyst
- Temperatures up to 550-700 °C
- Solid carbon product
 - Advantages: No trapped H₂ or O₂, ISRU applications
 - Drawbacks: Carbon degrades catalyst and causes clogs

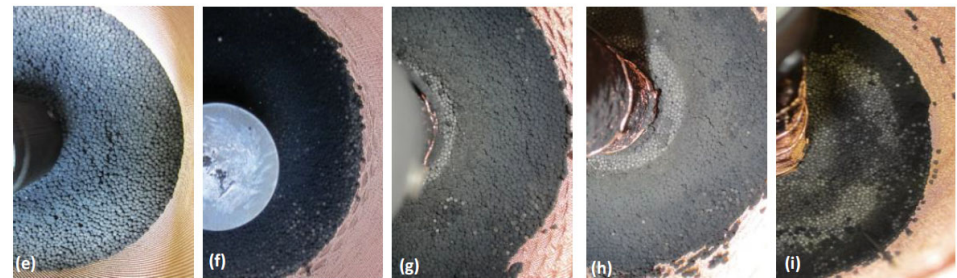
Prior Bosch Work



- Series Bosch (S-Bosch)
 - Split Bosch into sub-processes with independent reactors
 - Better process, catalyst optimization
 - Carbon containment in one subsystem
- Carbon Formation Reactors (CFRs)
 - Run only the CO Hydrogenation and Boudouard reactions
 - In-house design and testing
 - SBIR, industry collaborations
- Catalyst degradation by carbon buildup remains a primary challenge
 - Entraps catalyst material
 - Clogging, separation, contamination

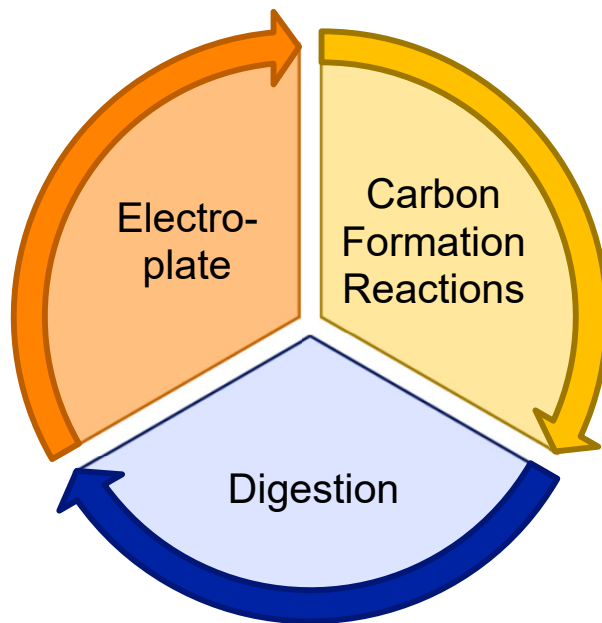
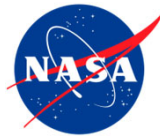


Credit: Stanley et al. (2018)



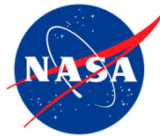
Credit: Stanley et al. (2017)

Ionic-Liquids-Based CFR

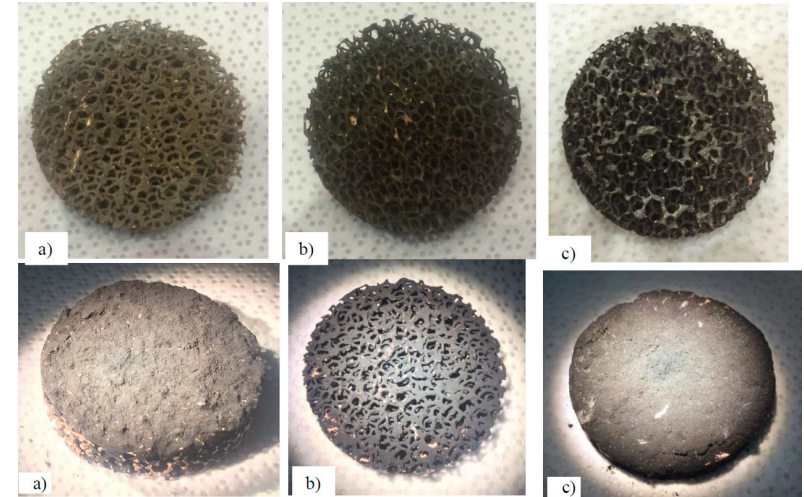


- Use an Ionic Liquid (IL) to reclaim catalyst from carbon product
 - ILs widely studied for ISRU scenarios
 - Harvest metals from regolith
- Renewal cycle for IL-based CFR
 1. Use IL-catalyst solution to electroplate catalyst onto substrate
 2. Use electroplated substrate in carbon formation reactions
 3. Digest catalyst into IL out from carbon buildup; filter out carbon
- Aims to greatly expand catalyst lifespan and reduce upmass/resupply needs

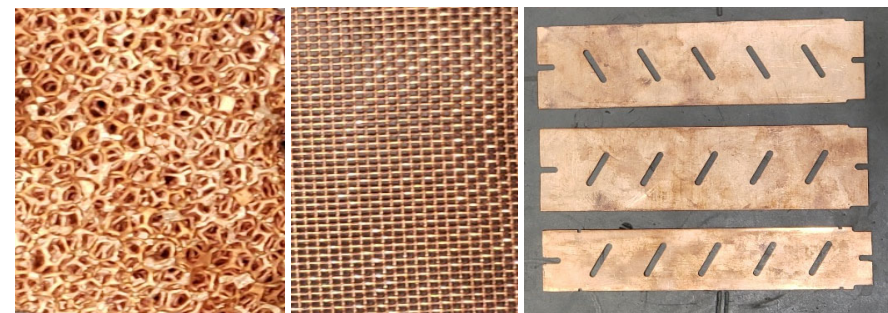
Prior Work in IL-Based CFR



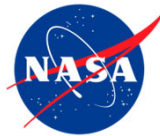
- Proof of concept work
 - Selected 1-M aqueous [Emim][HSO₄] as IL of choice
 - Electroplated iron onto copper substrates using the IL
 - Demonstrated catalytic activity of iron-electroplated pucks
 - Demonstrated feasibility of digestion
- Specialized setups
 - Each step independently tested in separate reactors
- High surface area substrates
 - Textured surfaces → great surface area to volume ratio but very difficult to clean



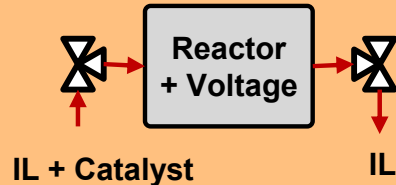
Credit: Abney et al. (2016)



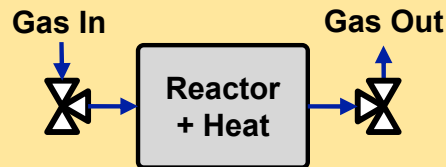
Single-Volume IL-Based Reactor



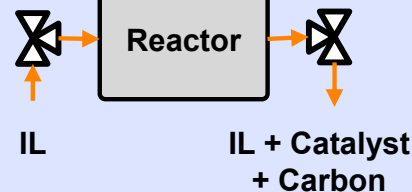
**Catalyst
Electroplating**



**Carbon Formation
Reactions**

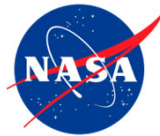


Catalyst Digestion



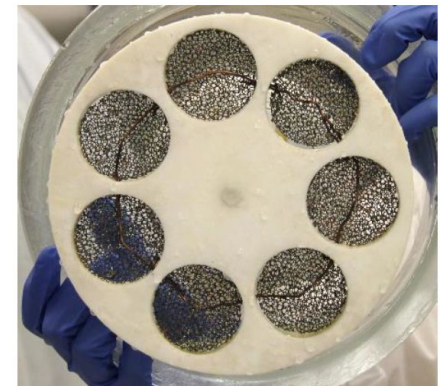
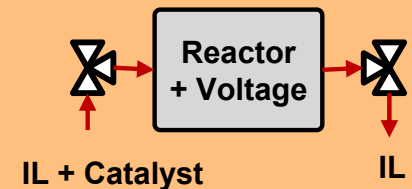
- Contain all three steps within single reactor
 - Alternate between IL inputs and gas inputs
- Each stage in renewal cycle has unique design criteria
 - Tolerate IL acidity and reaction temperatures
 - Focus on substrate cleanability and valid electroplating setup

Electroplating Requirements



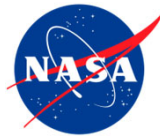
- Material compatibility with H_2 and IL
- Geometry constraints
 - H_2 delivery to anode surface
 - Anode surface area $\gg$ Cathode Surface area
 - Uniform current density $\rightarrow$ minimize holes and sharp edges
- Electrical continuity/conductivity
 - Minimize conductive surfaces to avoid unintended ground loops
 - Isolated, sealed passthroughs for wires
- Mitigate undesirable reactions and outcomes

Catalyst Electroplating



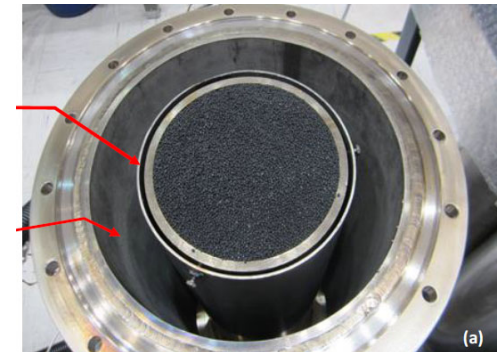
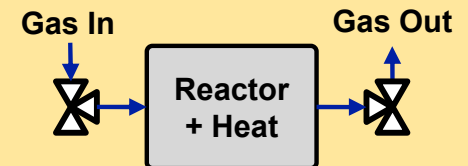
Credit: Brown et al. (2018)

Reactions Requirements



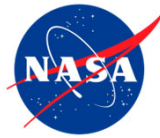
- Carbon Formation Reactions
 - Iron, nickel, cobalt catalyst
 - High catalyst surface area
 - Components that withstand 550-700 °C
 - Structural components hydrogen compatible at 550-700 °C (embrittlement risks)
- General gas-flow reactor considerations
 - Airtight seal
 - Distribute flow evenly/no dead space
 - Adequate pressure protections
- Mitigate carbon clogging/blockages

Carbon Formation Reactions



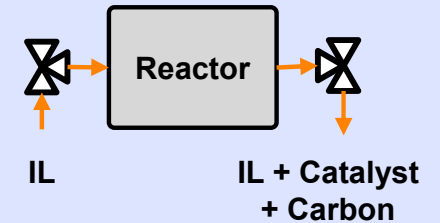
Credit: Stanley et al. (2017)

Digestion, Filtration Requirements

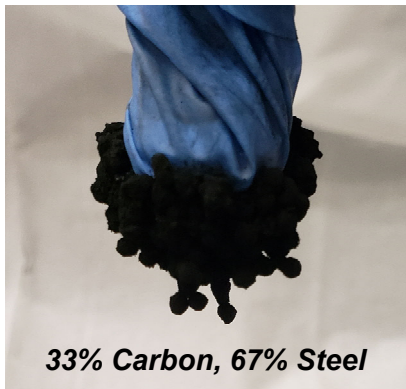
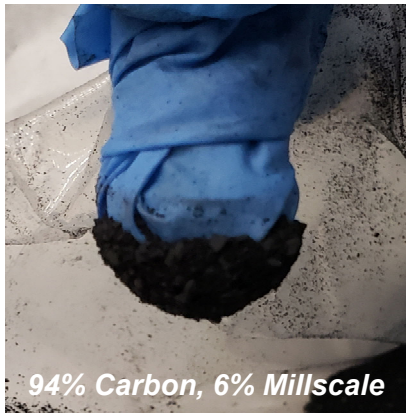
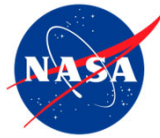


- No additional materials constraints
- Geometry Constraints
 - Cleanability of substrate
 - Robust to clogging issues
 - Breaks up large carbon chunks
- Vents H_2 from headspace
- Filtration
 - External to reactor
 - Carbon particulate can be <10 microns
 - Regenerable designs are highly desirable

Catalyst Digestion

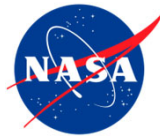


Design Problem Summary



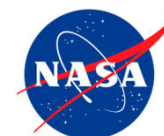
- Challenging materials compatibility problem
 - Temperature primary driver
 - H_2 and IL compatibility overlap is small
 - Minimizing conductive surfaces may require insulative coating for inner reactor surface
- Carbon handling and filtration
 - Liquid flushing will help with particulate travel
 - Reduce/minimize consumables in filtration
- Bosch carbon magnetism could be leveraged for regenerable filtration

IL Parameterization



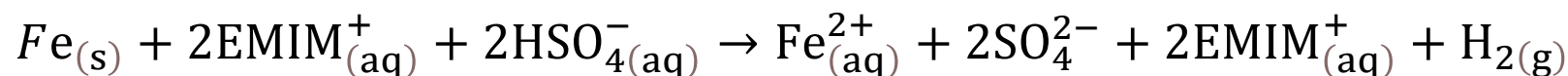
- 1-M aqueous [Emim][HSO₄] solution
 - Selected in prior work
 - Most well-characterized IL solution suitable to application
- Determine process parameters for renewal cycle
 - What are the baseline IL parameters?
 - What measurements indicate when digestion is complete?
 - What readings show electroplating progression?
 - What readings indicate issues? Where should we set our guardrails?

Baseline Parameters

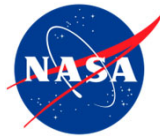


- Digestion and electroplating both change iron content in the solution
- Compare properties of stock IL and iron-rich solutions
 - Stock: Aqueous 0.9572 M [Emim][HSO₄]
 - Fe²⁺ Rich: 0.4920 moles Fe/IL
 - Conductivity and pH provide distinct, quantitative measurements
- Solution pH dependency on iron
 - Theory shows asymptotic pH behavior as solution nears maximum iron content
 - Agrees with measurements
 - Clear operational threshold

Physiochemical Property	Units	Stock Solution	Fe ²⁺ Rich Solution
Electrical Conductivity	mS/cm	106.3	59
pH	log[H ₃ O]	1.03	2.27
Dynamic Viscosity	mPa·s	1.3696	1.9297
Density	g/cm ³	1.0603	1.1076

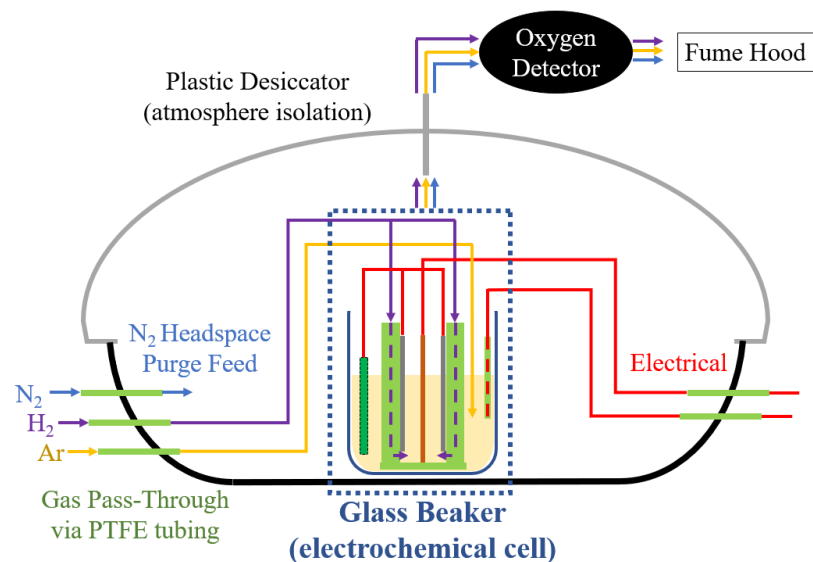
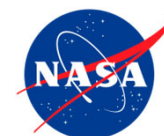


IL Electroplating



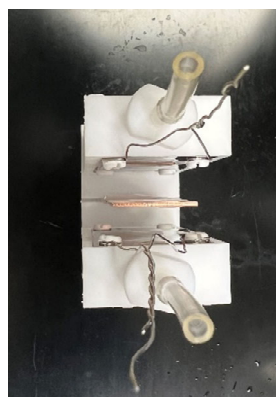
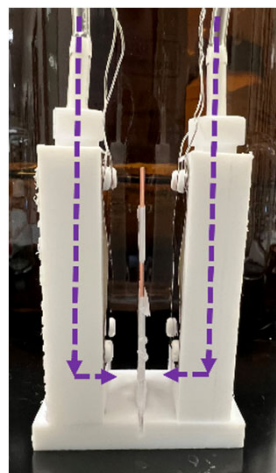
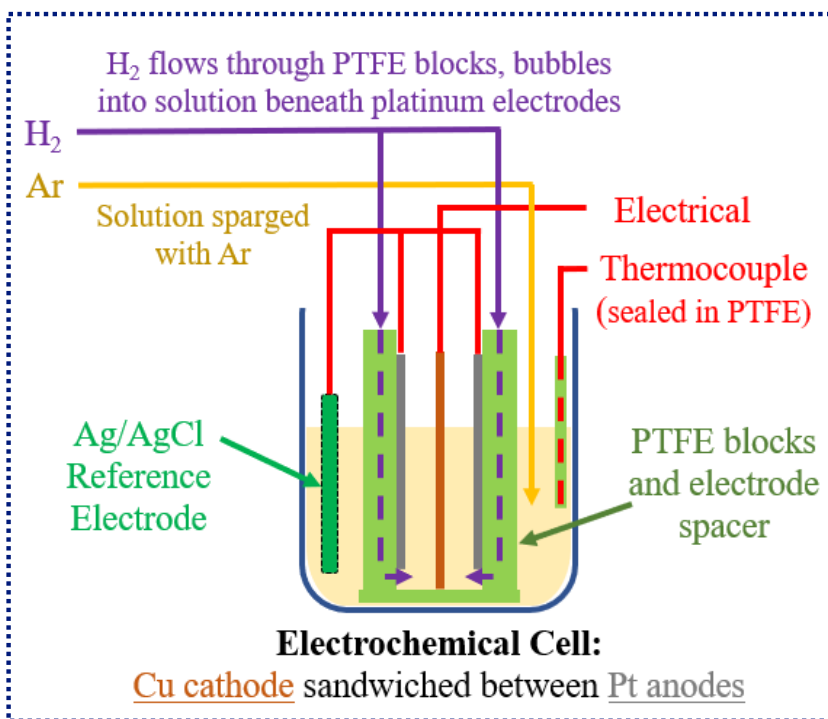
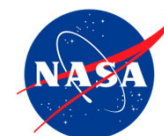
- Determine parameters for repeatable, reliable electroplating
- Several parameters to optimize in final design
 - Geometry
 - Voltage/cell potential
 - Process conditions
- Focused on cell potential in experiments
- Cyclic Voltammetry (CV)
 - Drive cell potential across a voltage sweep and back
 - Observe reactions as cell potential varies
 - Assists in determining safety, process limits

Electroplating Setup



- Electrochemical cell setup in glass beaker
- Desiccator enclosure for controlled environment
 - Headspace N₂ purge
 - Vent through fume hood
- Ar, H₂, and electrical supplied to electrochemical cell via sealed channels

Electrochemical Cell

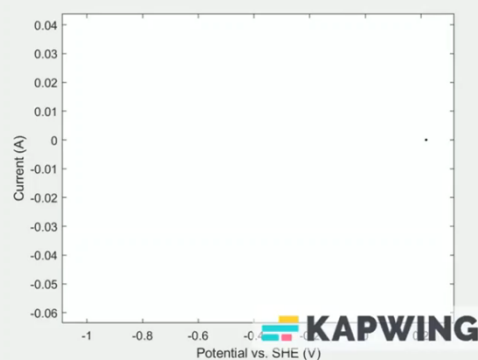
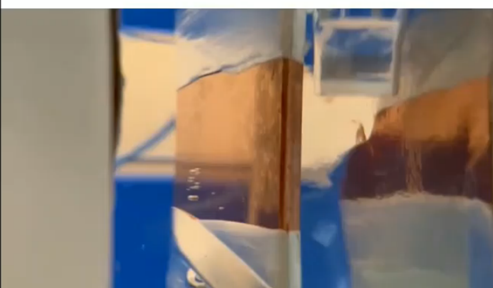


- Three-electrode potentiostat
 - Ag/AgCl reference electrode
- Ar sparging
- H₂ delivery to anode through structure
 - Issues with delivery mechanism during experiments
 - Experiments run with and without hydrogen bubbling
- Footage of cathode taken during experiments
 - Visual observation key
 - Aligned with CV readings in post-processing

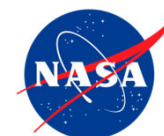
Cyclic Voltammetry Video



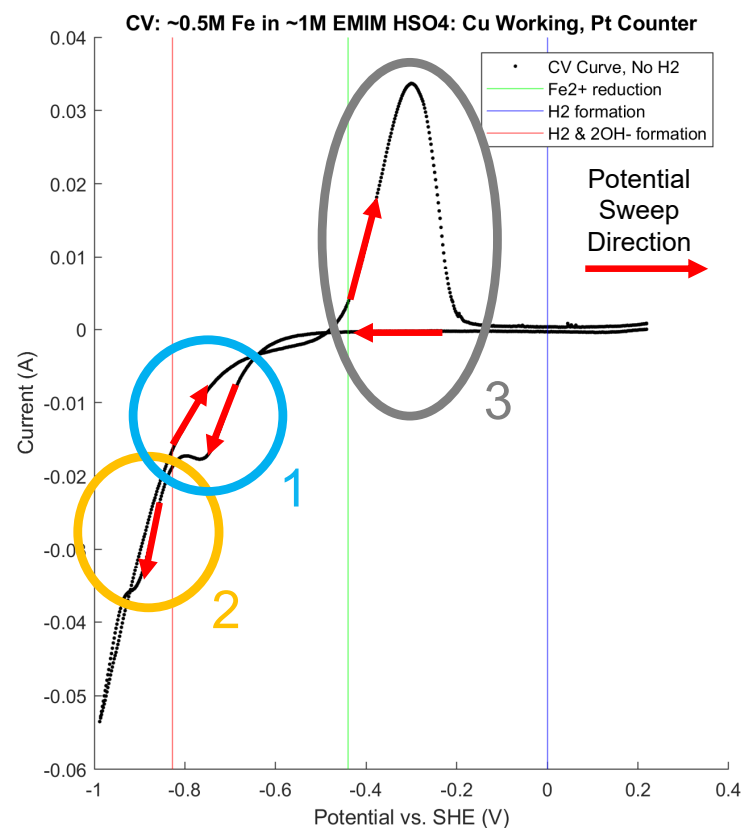
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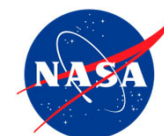
CV Results



- Representative CV curve with relevant standard redox potentials superimposed
- Three primary points of interest based on visual observations

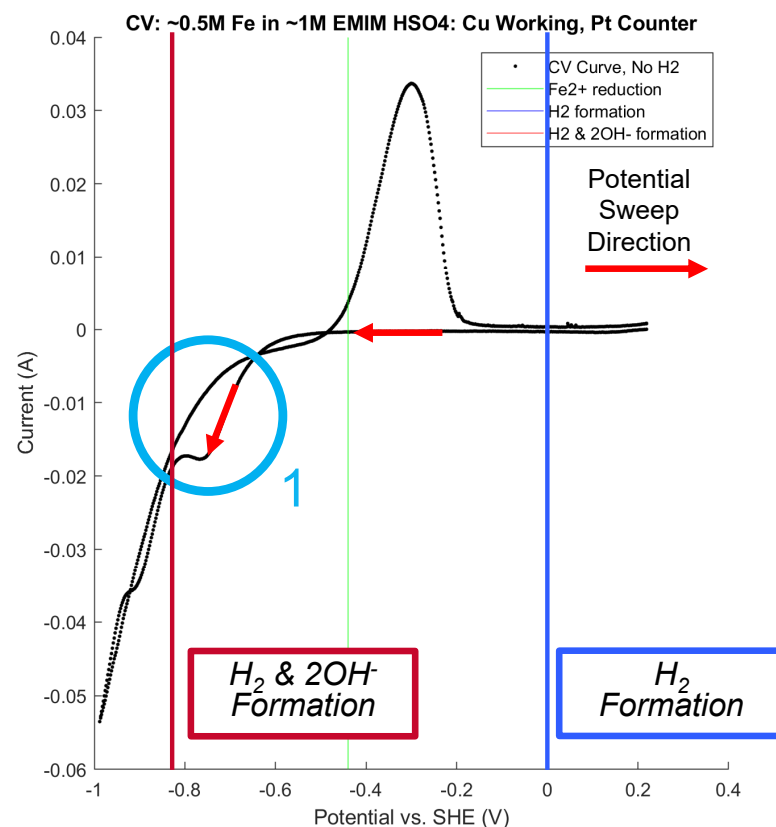


CV Results: Peak 1

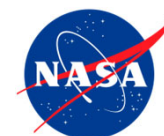


- CV curve with relevant standard redox potentials superimposed
- Highlights from Voltage Sweep:

1. Observed cathodic gas bubble formation
 - Suspiciously coincident with water electrolysis H_2 formation half-reaction, but no O_2 gas evolution observed on anode
 - Possibly hydrogen liberation, but observed bubble formation occurs at over double the potential shift (-0.15 V) than theory predicts (-0.07 V) for solution pH
 - pH actively changes during CV; monitoring during CV needed for further clarifications



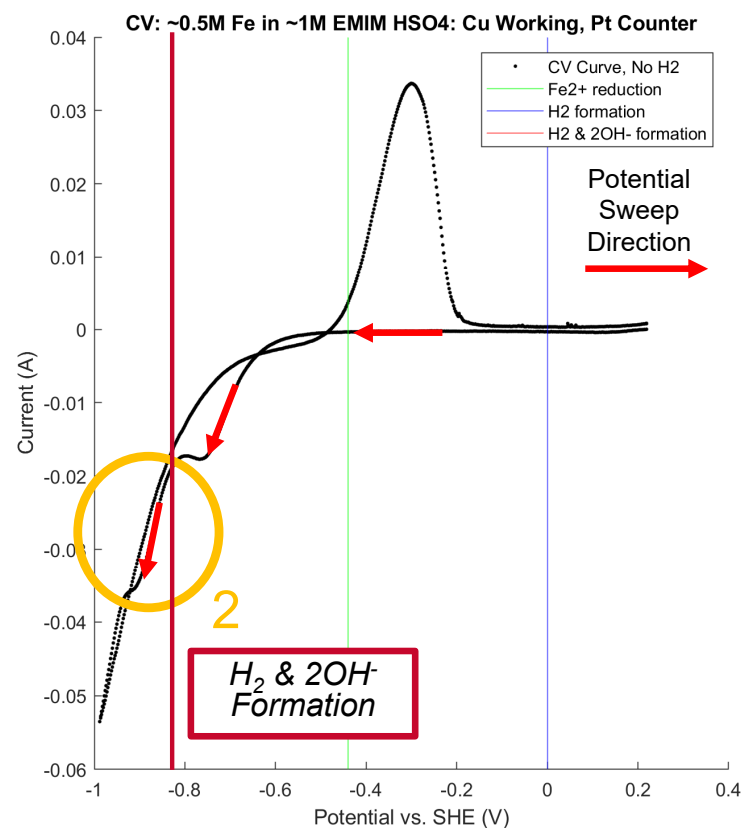
CV Results: Peak 2



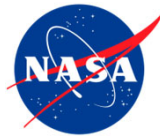
- CV curve with relevant standard redox potentials superimposed
- Highlights from Voltage Sweep:

2. Observed Fe plating

- Theoretically coincides with H_2 and 2OH^- formation at pH of 14
- Likely coincidental; not supported by measurements or observations



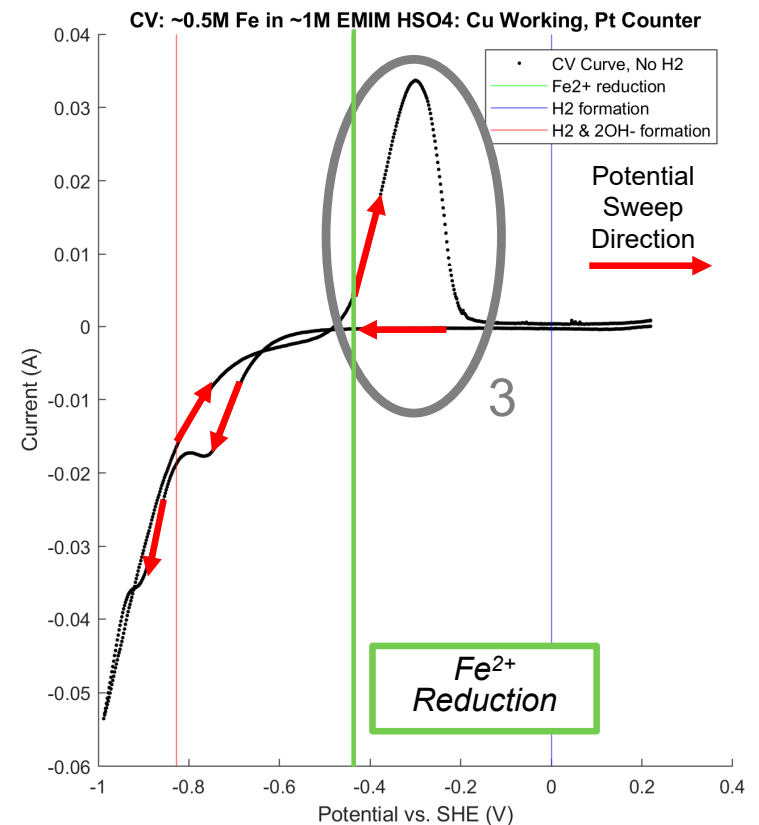
CV Results: Peak 3



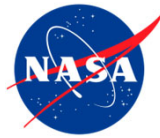
- CV curve with relevant standard redox potentials superimposed
- Highlights from Voltage Sweep:

3. Observed plated Fe reincorporation into IL

- At the expected redox potential of Fe^{2+}
- However, asymmetry with observed plating potential indicates more complex phenomena occurring
- Asymmetric curve suggests redox irreversibility $\rightarrow$ IL solution breakdown
- Bubble formation prior to plating also supports potential IL breakdown

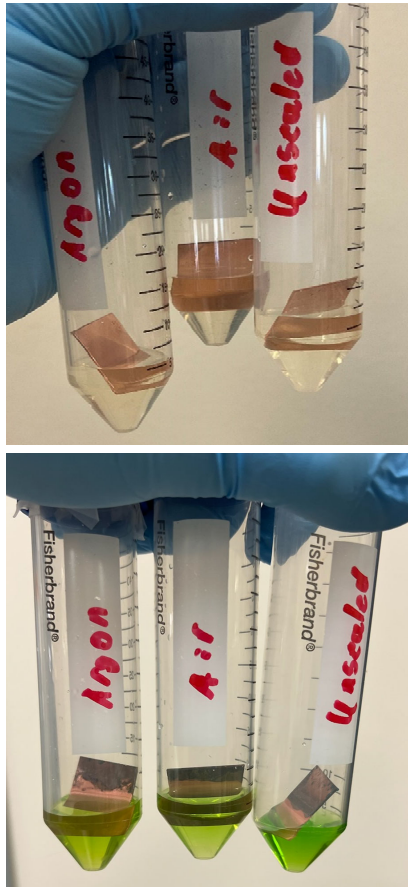


CV Discussion



- Bubble formation
 - Distinct change in bubble adherence and size
 - Possibly due to surface morphology changes as plating occurs
 - Possibly due to changing gas makeup as potential changes
- Three-electrode potentiostat
 - Designed to study working electrode half-reaction potentials w.r.t. reference electrode rather than complete cell potentials
 - Counter electrode potential can swing significantly w.r.t. reference electrode in order to deliver necessary current to complete half reaction at working electrode

Impacts on Reactor Design



- Possible water electrolysis requires further safety mitigations
 - Oxygen presence adds risk
 - Explore other catalysts
- Emphasizes need for careful hydrogen delivery design
- Copper incompatibility
 - Digestion clear after 12-day exposure
 - Might be acceptable digestion rate

Future work



- Materials assessment
 - Test wide range of materials and coatings
- Investigate alternative anodes (blackened Pt)
 - Temperature constraints must be accommodated
- Recreate cyclic voltammetry with improved setup
 - Add gas detection and pH measurement capabilities
 - Determine bubble composition
 - Vary cathode and anode geometry and materials
- Design, build, and test single-volume reactor

Questions?

Thank you for your time!

