UNIVERSITY of HOUSTON

Self-Driving Laboratories for Autonomous Discovery of New Materials

Master Thesis Defense

by

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Chair of Committee: Dr. Xiaonan Shan

Committee Member: Dr. Jiefu Chen

Committee Member: Dr. Jiming Bao

Outline

1/ **Background Introduction**

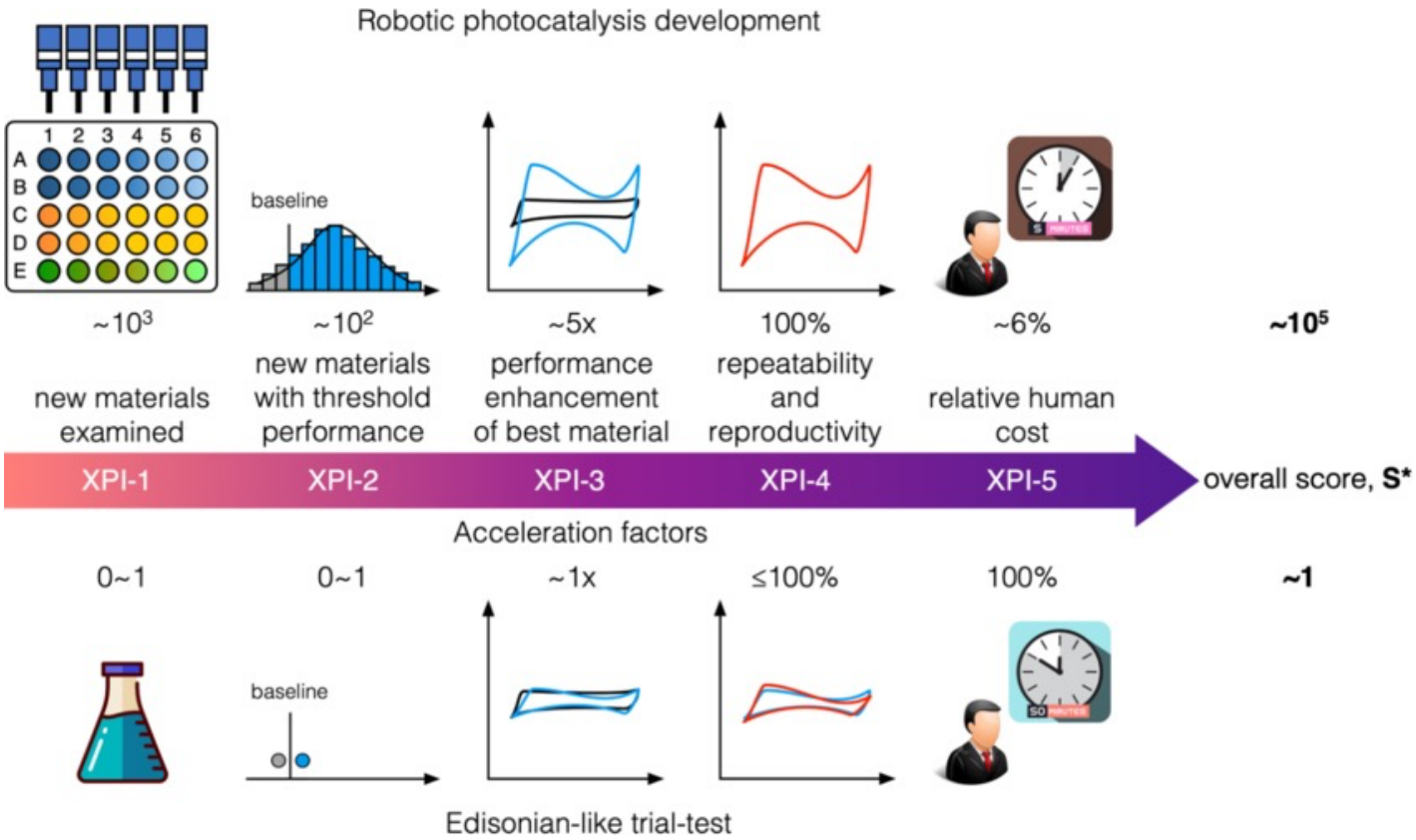
2/ Automatic electrochemical catalysts screening system design

3/ System optimization

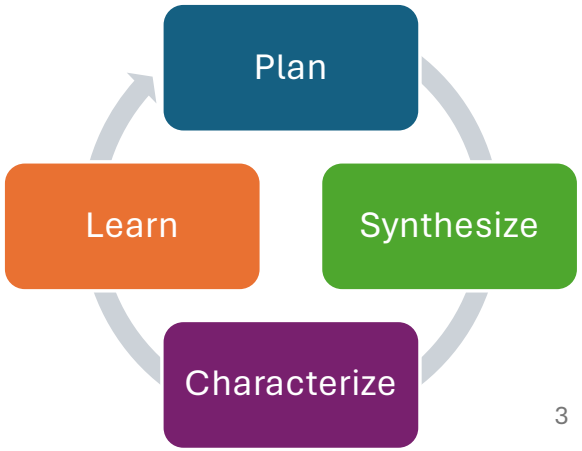
4/ Catalysts screening for the oxygen evolution reaction

5/ Future plan

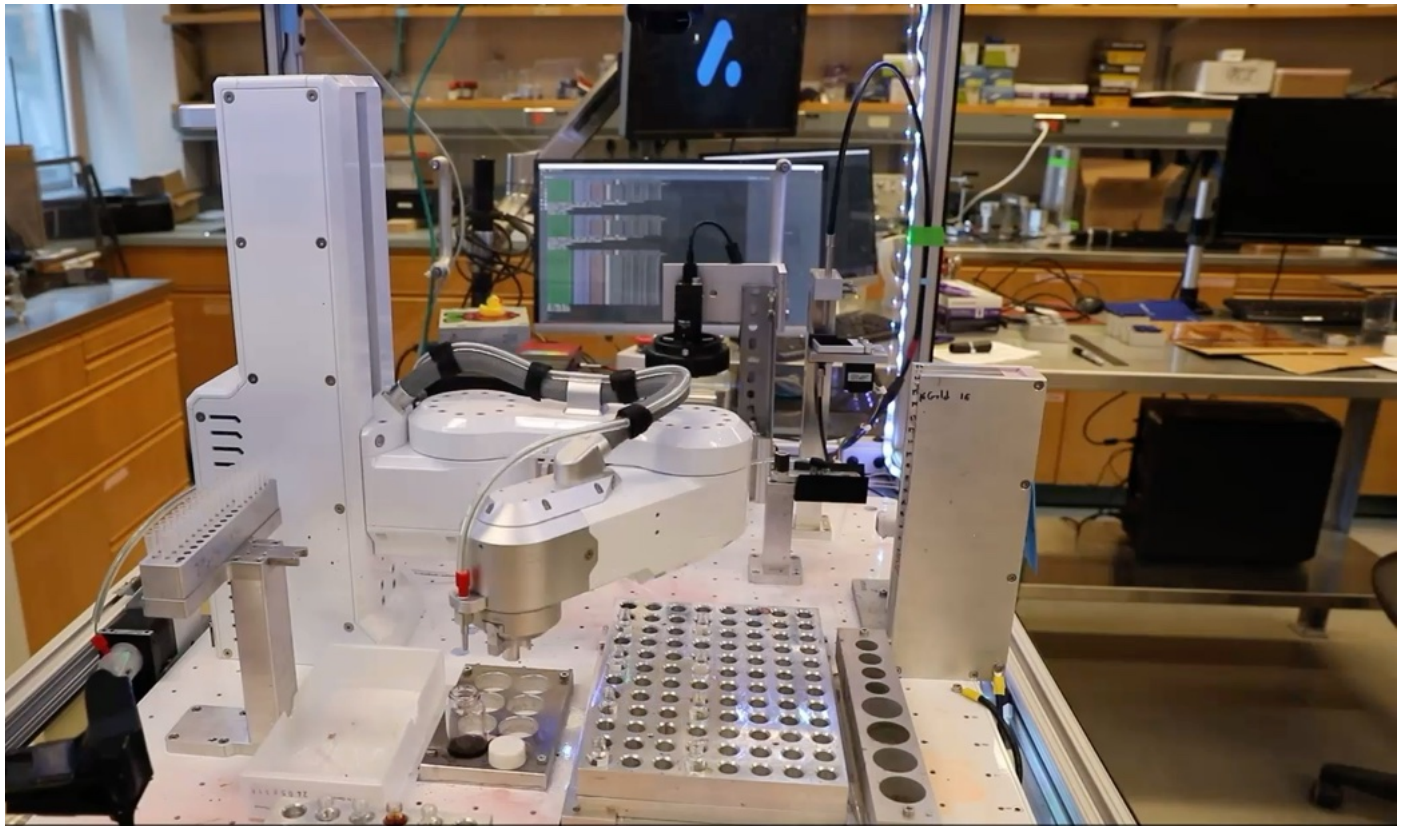
Need for Self-Driving Labs (SDLs)



- Traditional materials discovery relies on slow, resource-intensive Edisonian trial-and-error, testing one composition at a time.

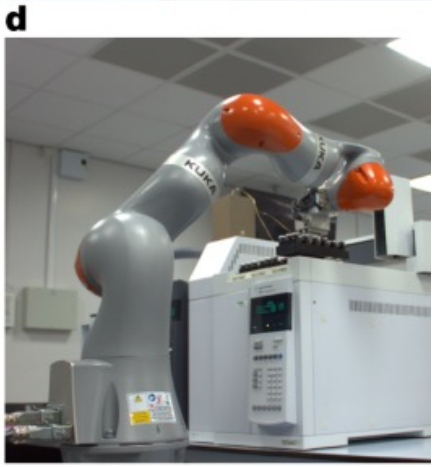


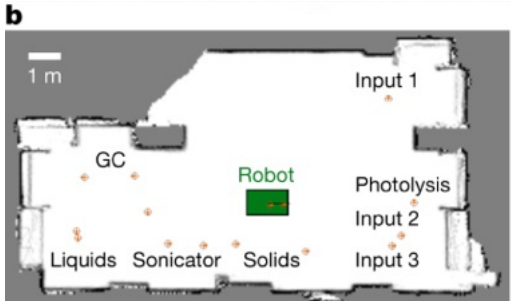
State of the art SDLs



Introduction

State of the art SDLs





Pros:

- Multi modal sample handling
- Autonomous chemical space search
- 24/7 operation

Cons:

- Bulky and high cost mobile platform
- Limited across electrochemical discovery

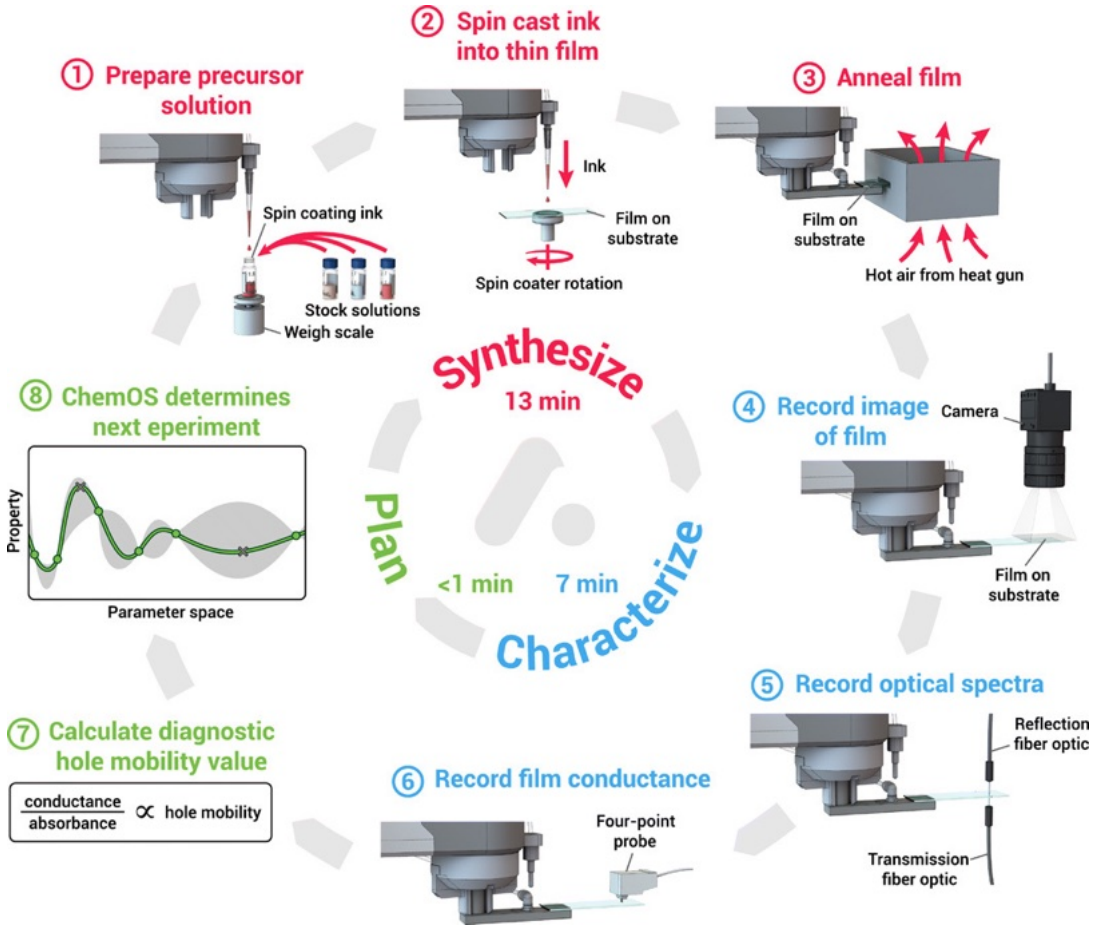
State of the art SDLs

Pros:

- Multimodal characterization
- Disposable pipettes
- Bayesian batch design

Cons:

- Thin film coating only
- Single fixed robot arm with small workspace.



Project Goal

- Near term goal:
  - Design and establish an automatic system to screen electrochemical catalysts with high throughput;
  - Catalysts synthesis: electrochemically deposition of metal alloys and metal phosphors;
  - Reactions: oxygen evolution reaction, and hydrogen evolution reaction;
  - Automatically synthesize, evaluate, and analyze the catalysts continuously;
  - We screen the entire library without any selectivity, human will make judgement from the results;
- Long term goal:
  - Autonomously and quickly converge to the best combination without the need to screen the entire search space (with minimized number of tests/iteration).
  - Machine learning guided catalysts and material design: AI model predict, and our system will synthesize automatically, and feedback the results to the model.

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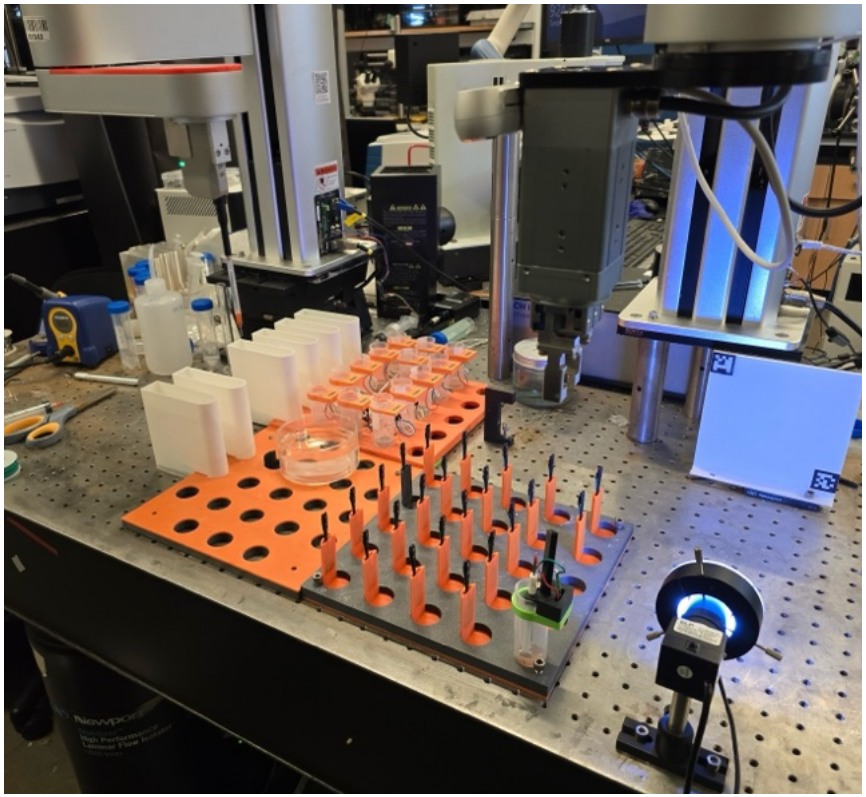
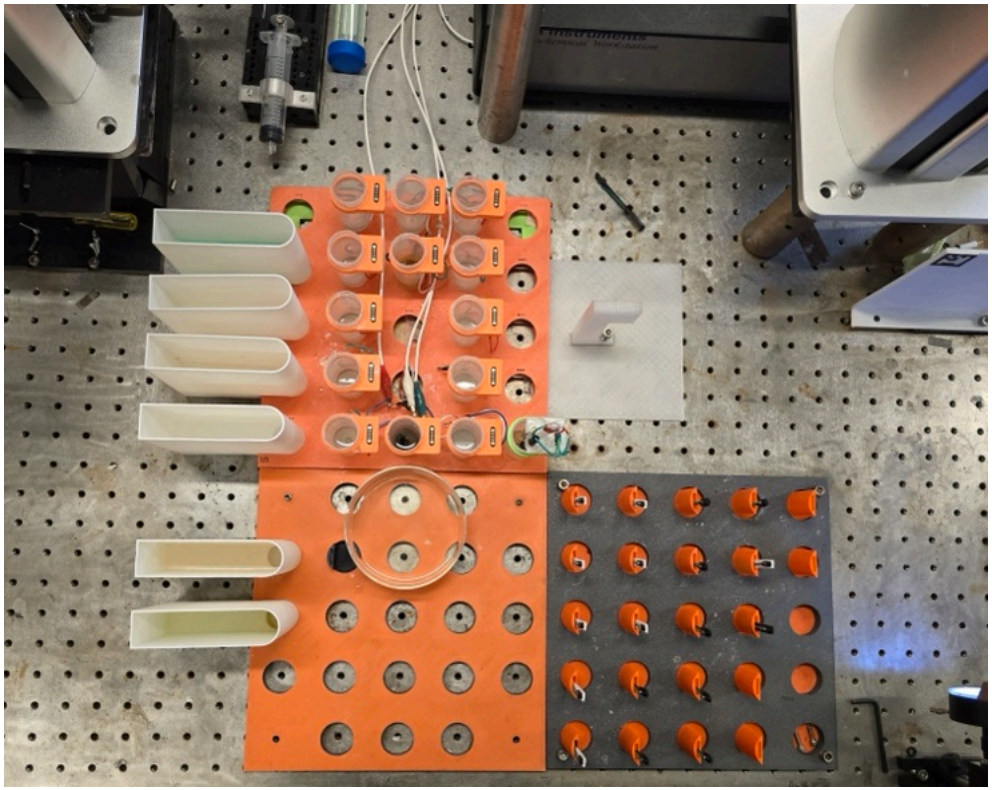
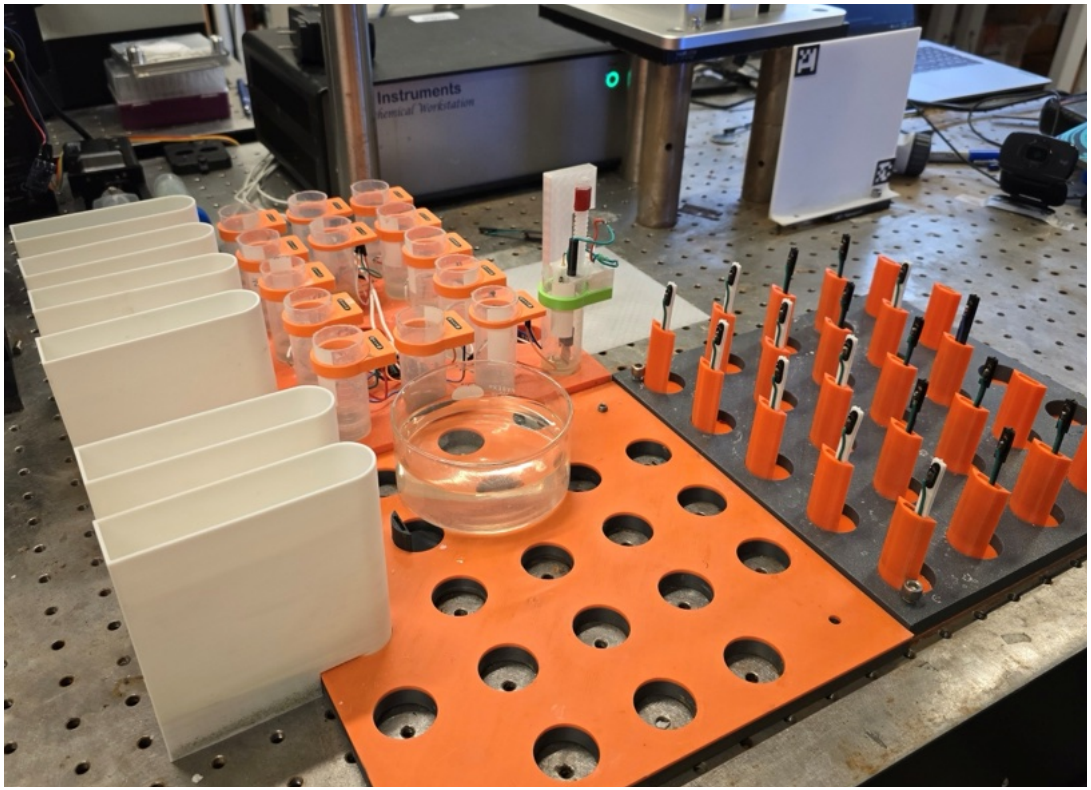
System Establishment



System Establishment

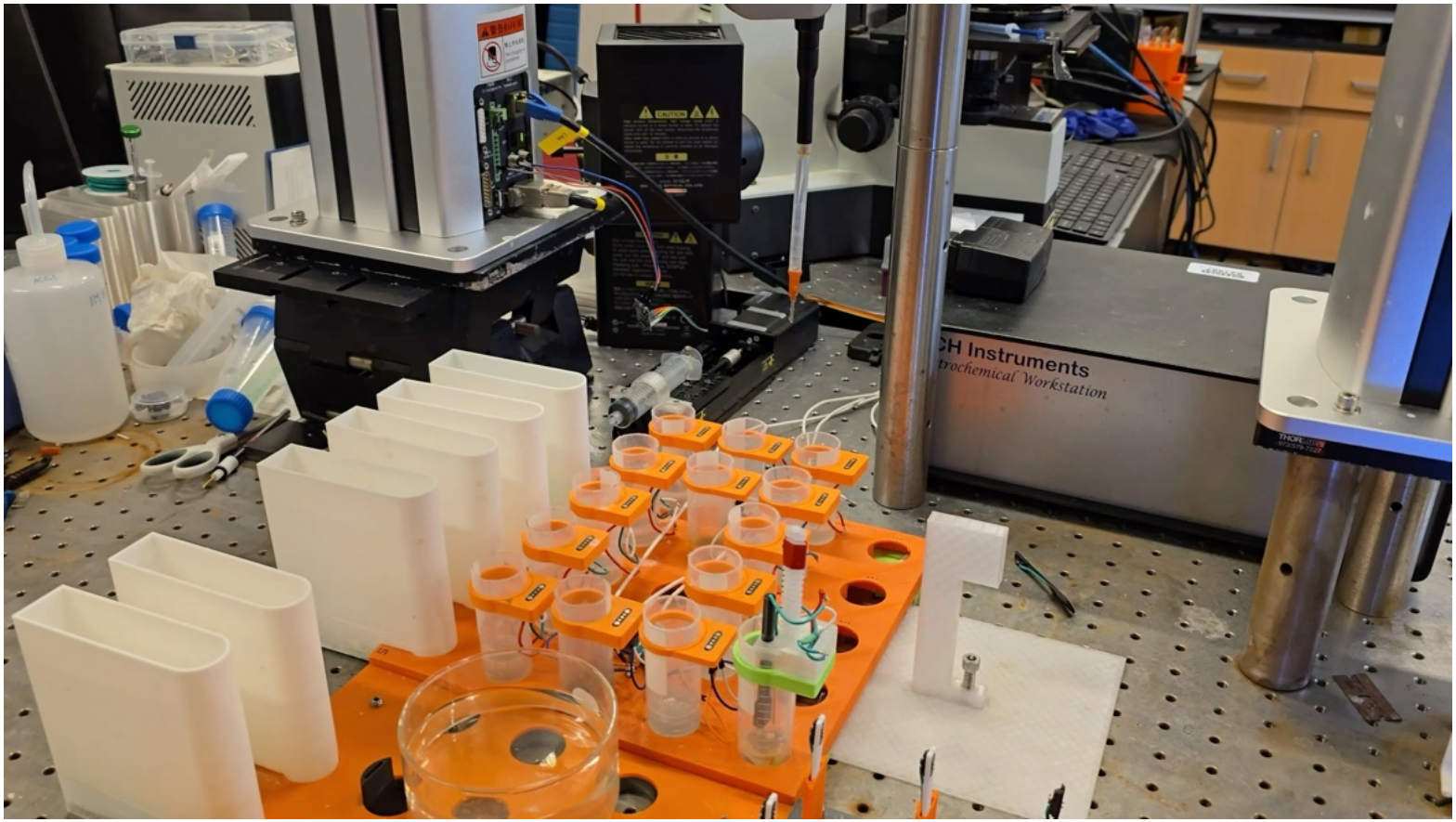




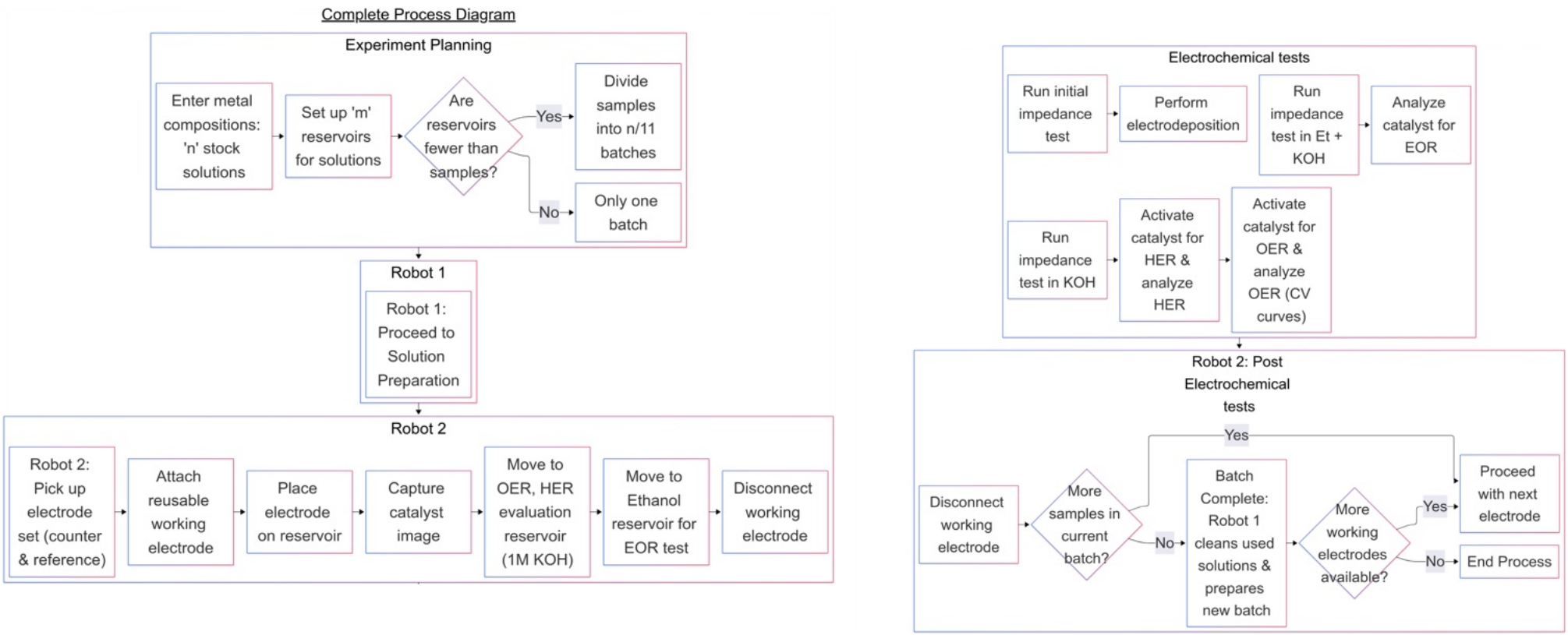
2.1 Components

- Components used in the setup
- 2 SCARA robot arm
- Digital Pipette
- Electric Gripper
- Linear Stage
- 2 Cameras, one for monitoring robot workflow. Other to take picture of samples.
- Potentiostat

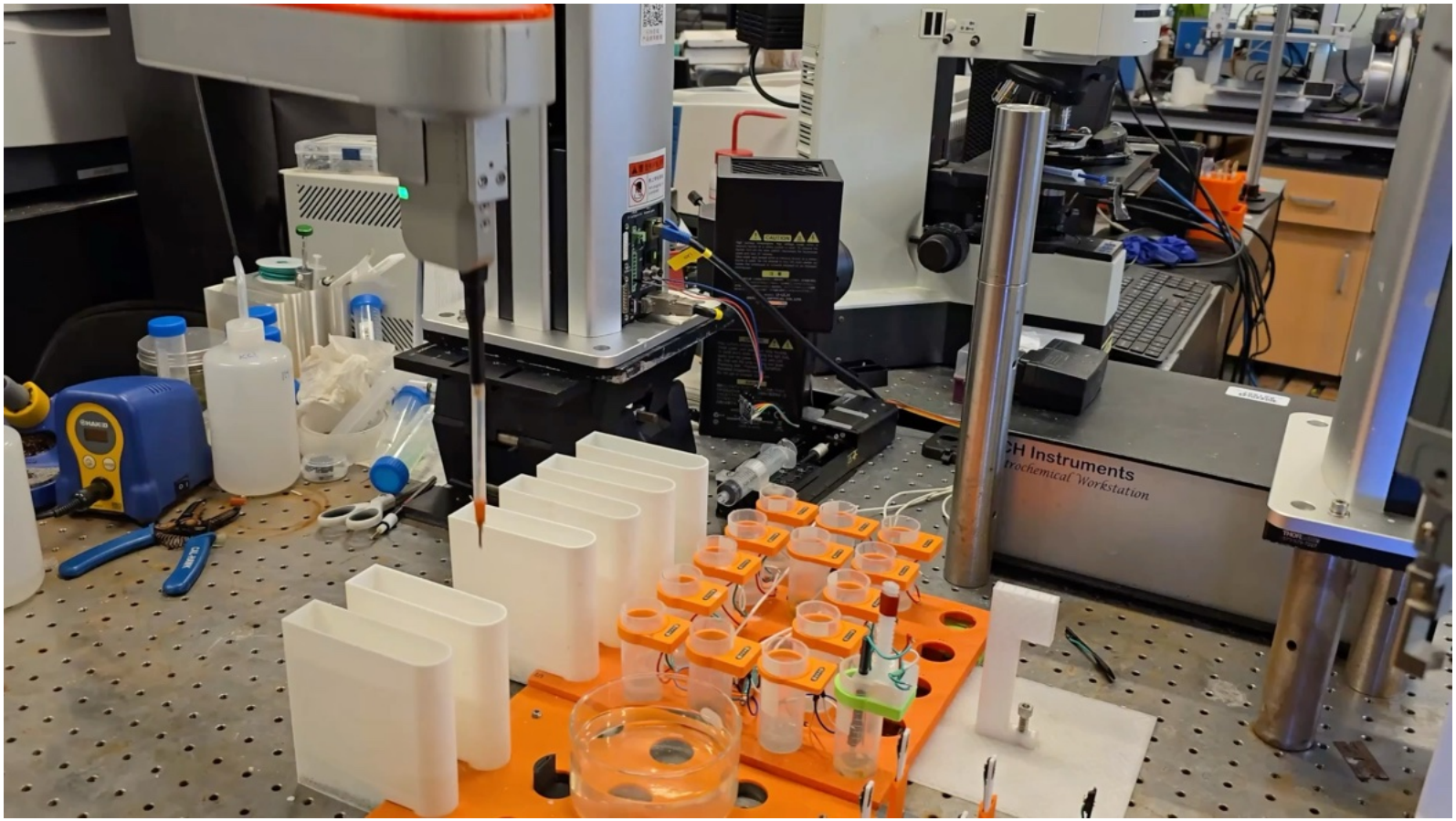
System Demonstration (Current Version)



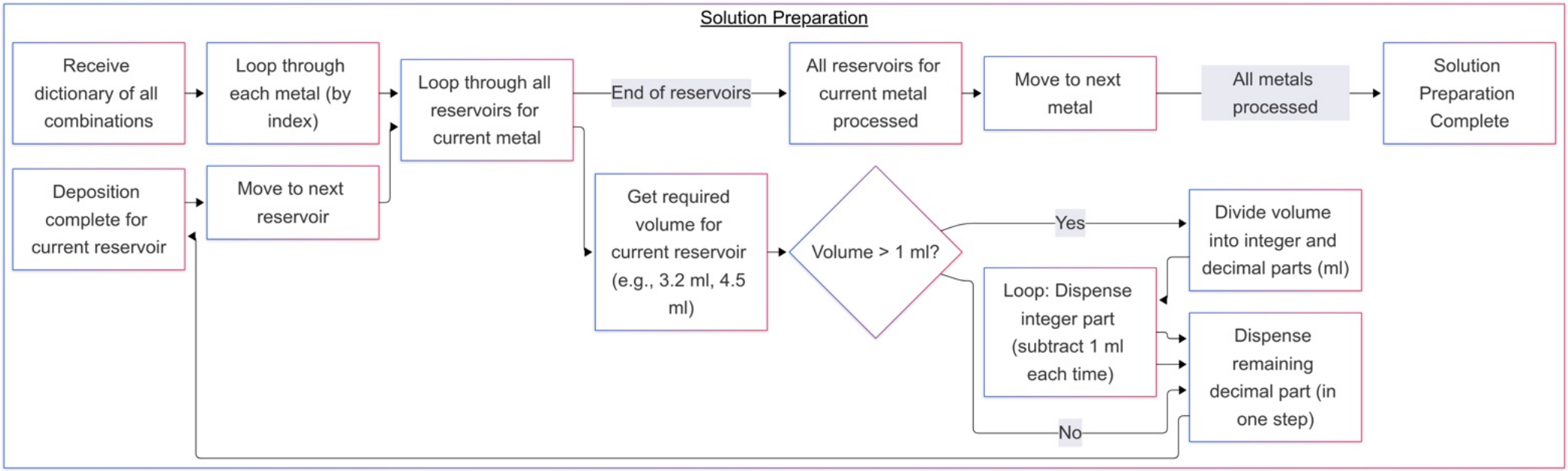
Control diagram for entire system



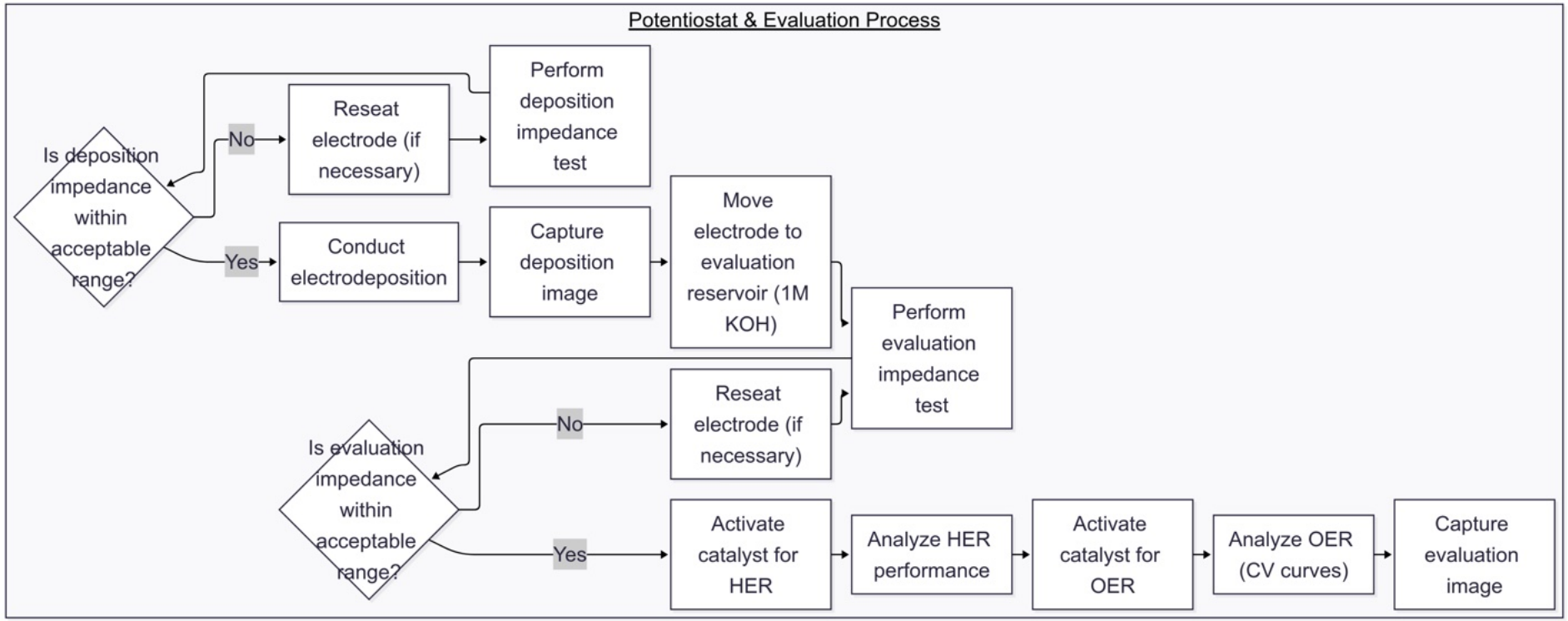
Solution Mixing Process



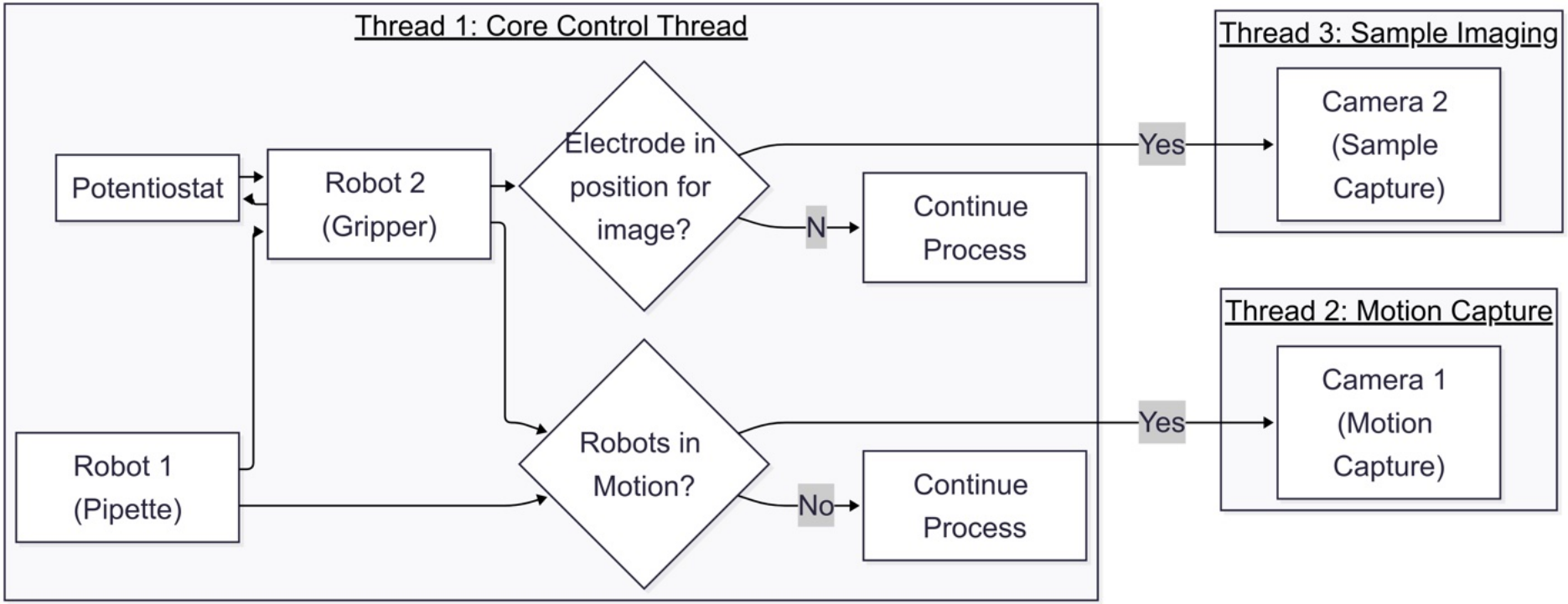
Control Diagram for Solution Mixing



Control Diagram for Catalysts Deposition and Evaluation



Thread control diagram



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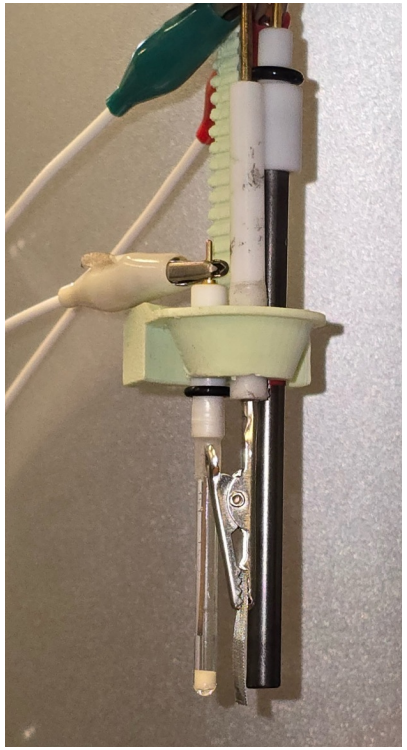
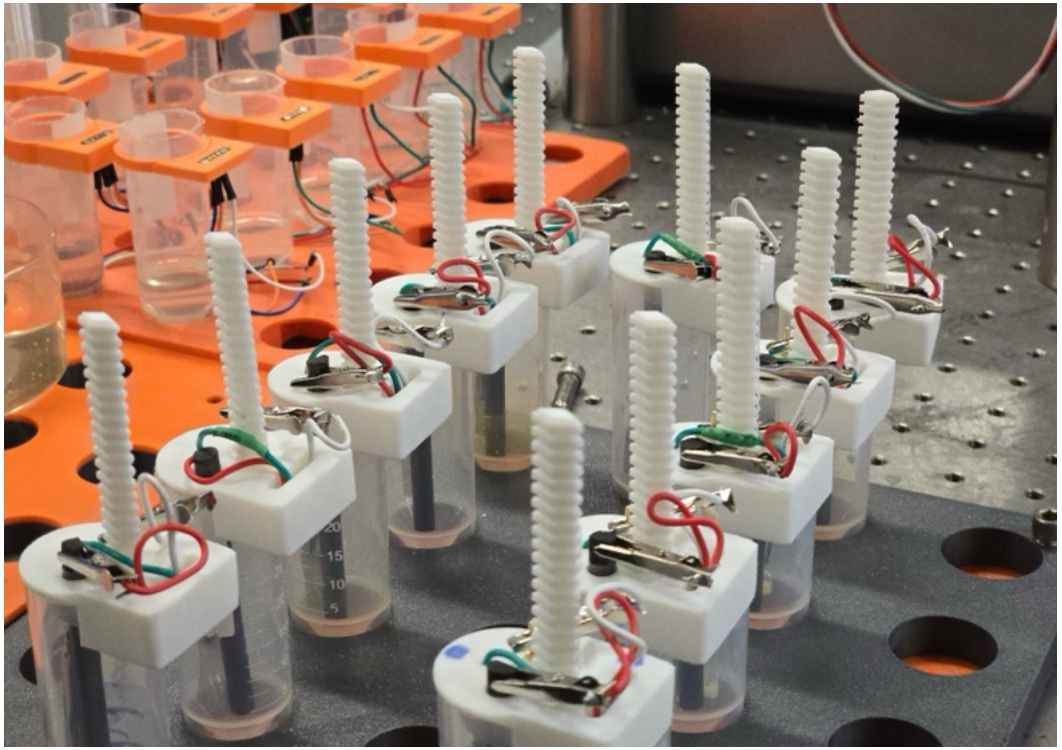
System Optimization

Early version of electrode holder

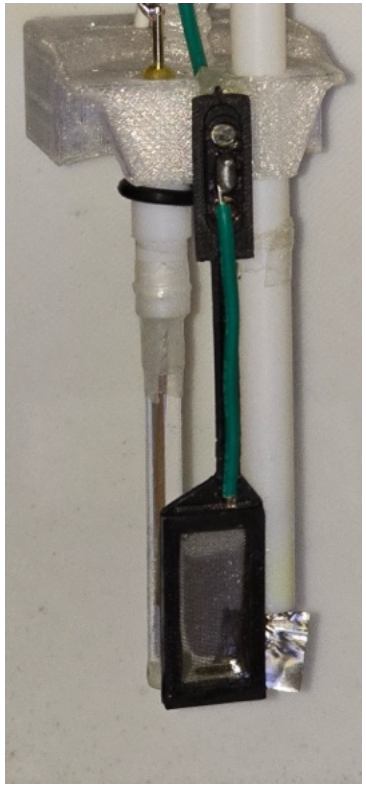




- **Counter Electrode:** Carbon rod
- **Working Electrode:** Stainless steel alligator clip
- **Reference Electrode:** Ag/AgCl
- No. of samples tested = No. of Working Electrode holders

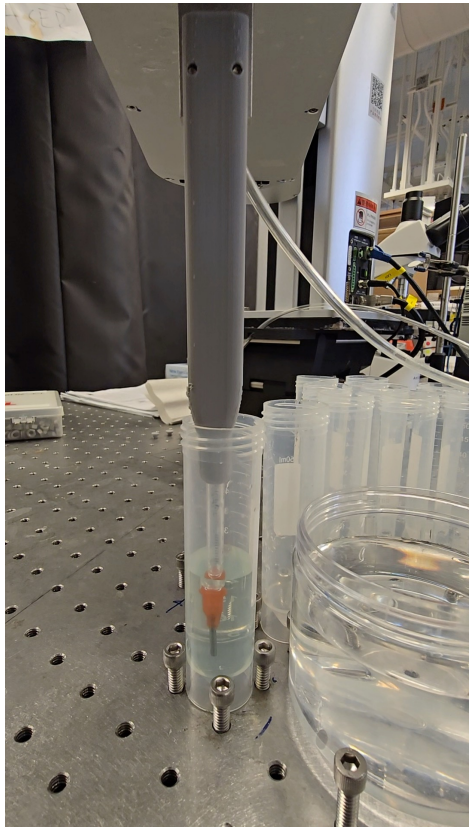
System Optimization

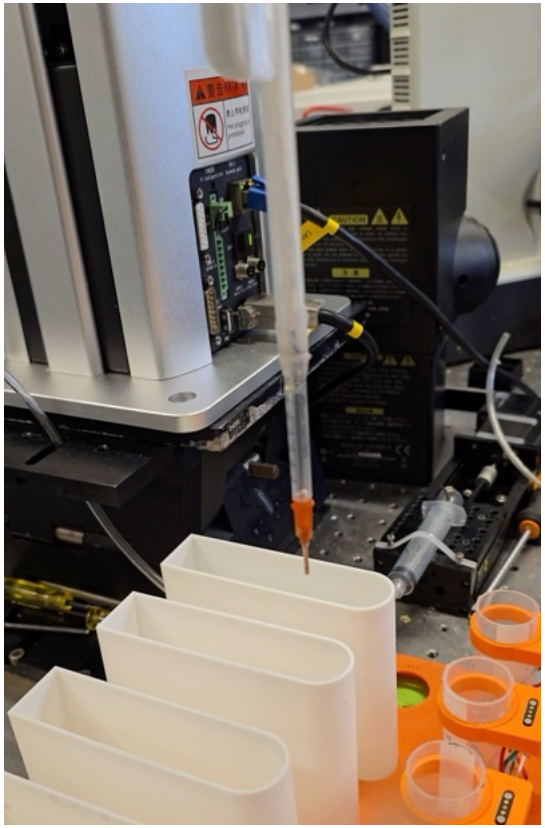
Detachable Working Electrode Design

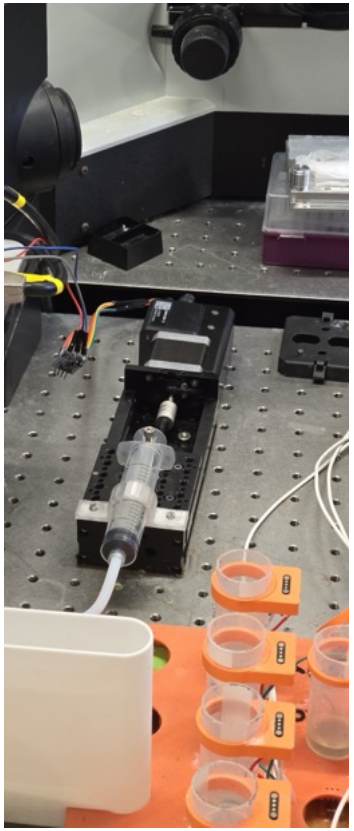


- **Counter Electrode:** Platinum sheet (10mm x 10mm)
- **Working Electrode:** Custom reusable magnetic clip design with stainless steel mesh
- **Reference Electrode:** Ag/AgCl
- No. of samples tested = No. of Working Electrode clips

Previous Design for Solution Dispensing







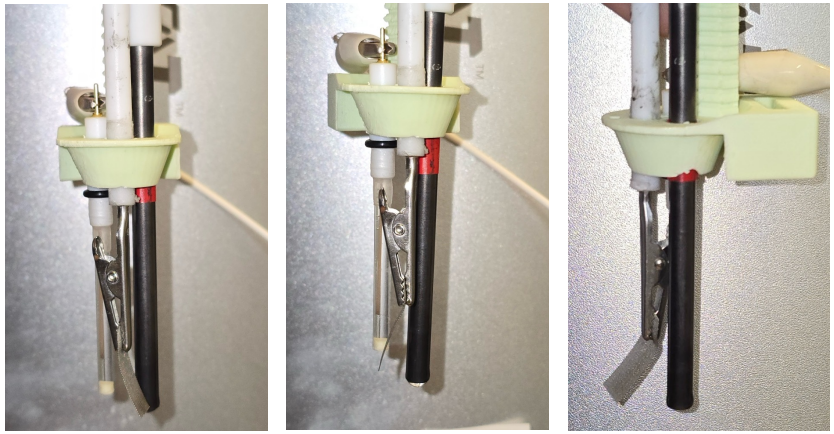
Pros:

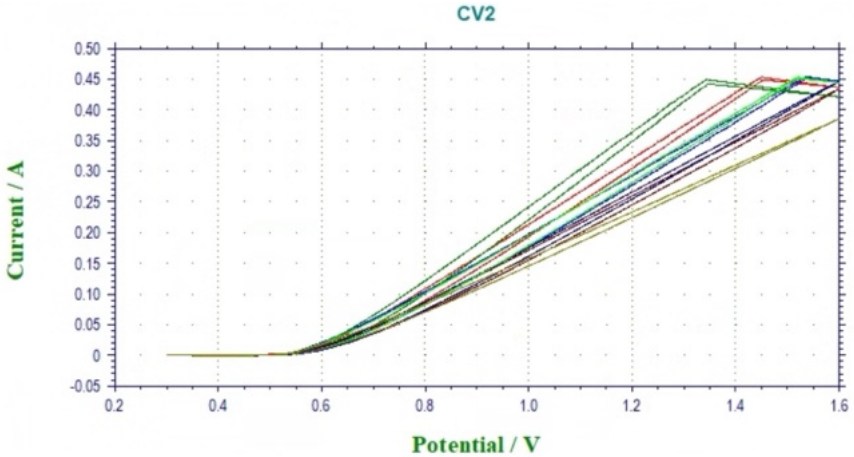
- Syringe can be changed to accommodate for larger volume.
- Faster dispensing and aspiration speeds.

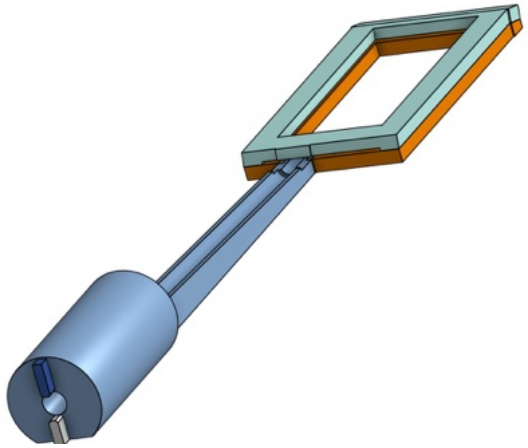
Cons:

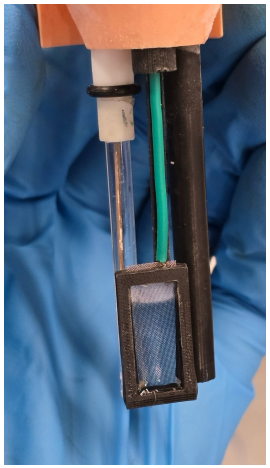
- Initial implementation involved a linear stage for solution dispensing.
- Accuracy decreased with increasing speed.
- Dispensing error of ~ 0.5-1ml

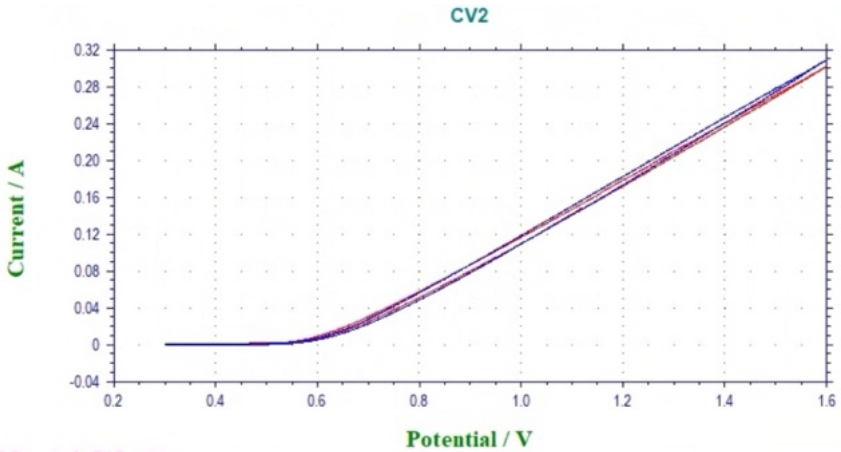
Working Electrode Clip Design Improvement



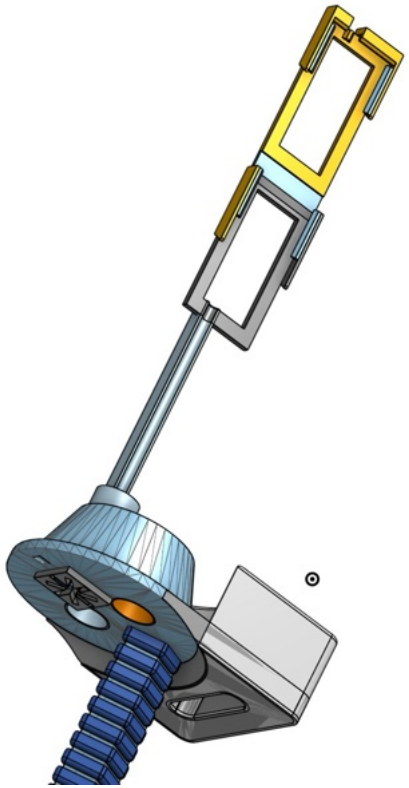






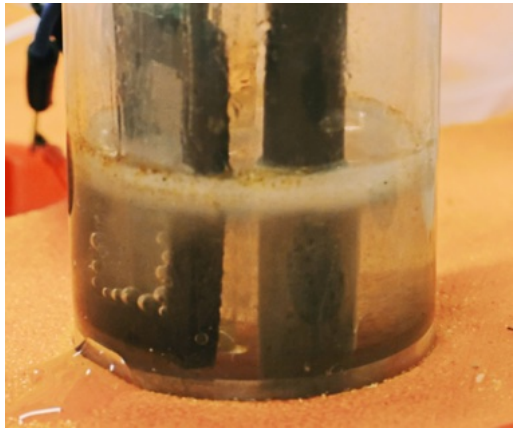


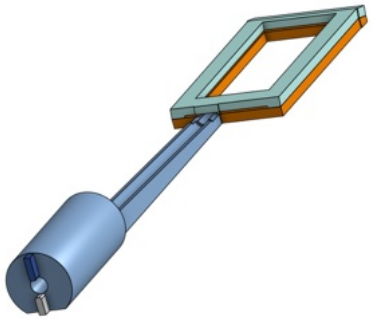
Working Electrode Clip Design Improvement

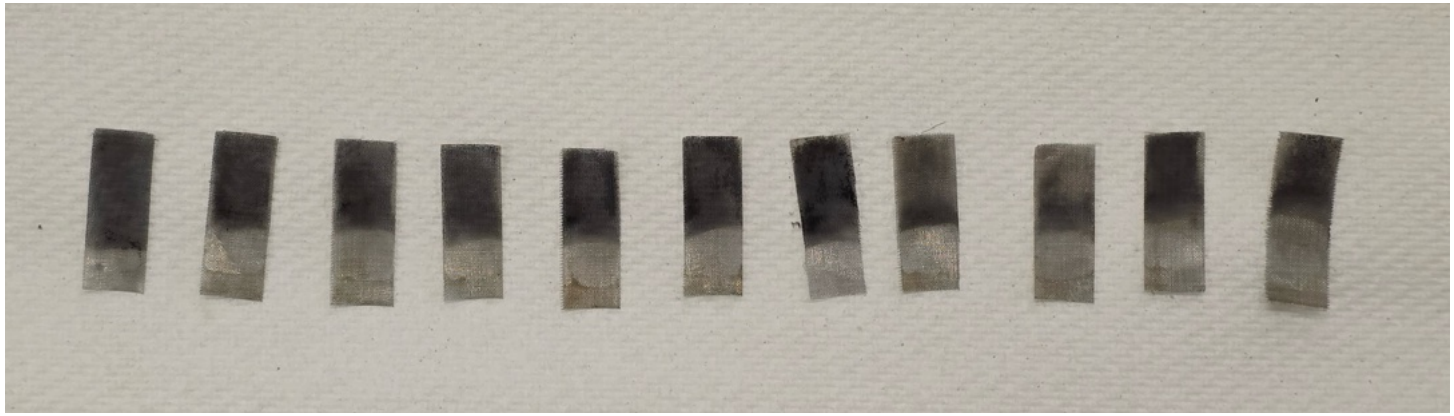


- Clip design for easier stainless steel mesh switching between different runs,
- Tried multiple materials sizes and designs to make tight connection with the wire while preserving interchangeability.
  PLA – breaks after few changes
- PETG – too rigid, layer lines aren't as strong
- TPU – too soft, leads to bad connection
- PP – best results, good connection due to slightly more rigidity than TPU while being malleable enough to allow stainless steel mesh change

Working Electrode Clip Design Improvement

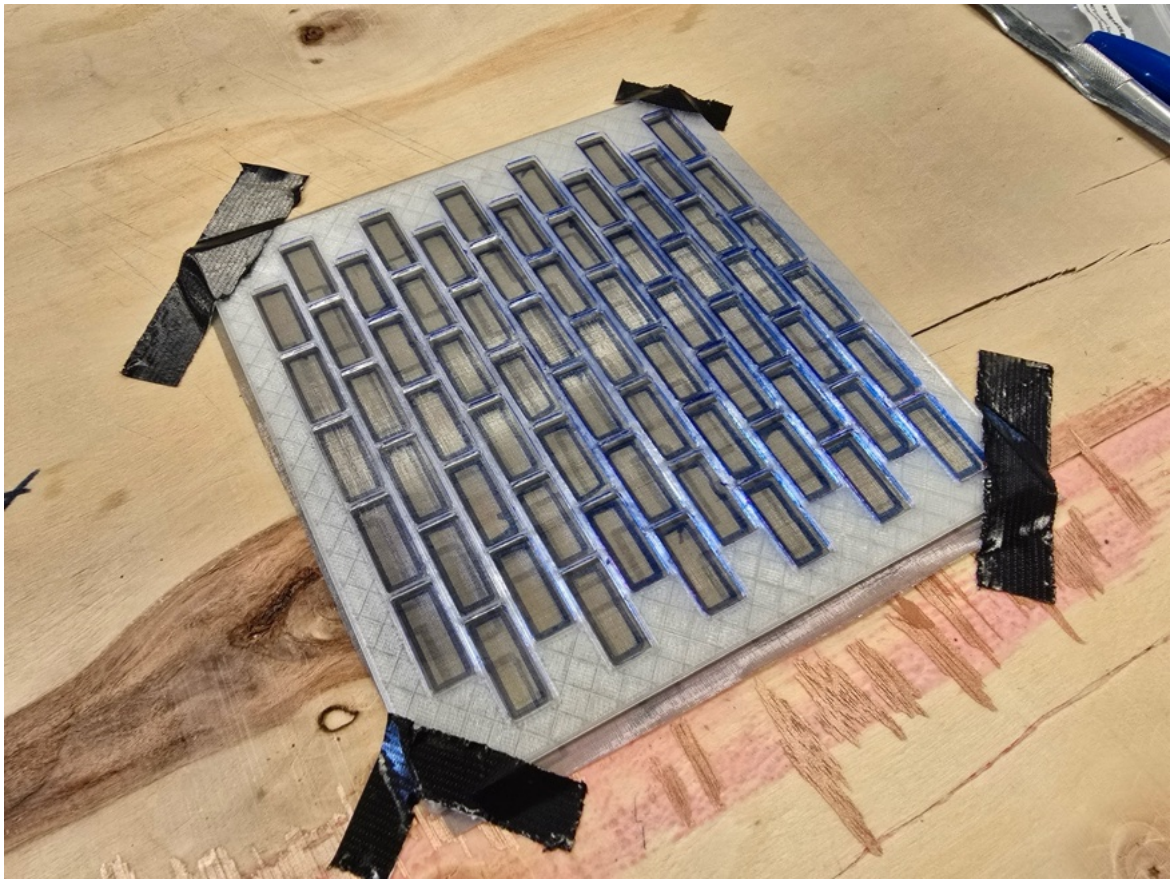






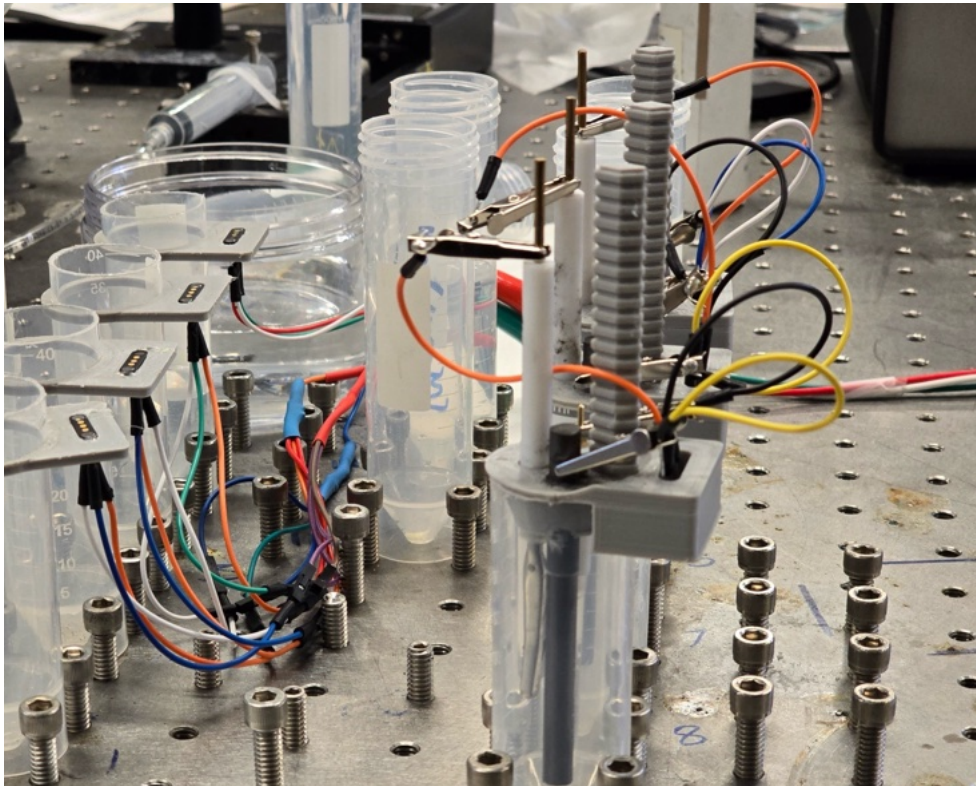
System Optimization

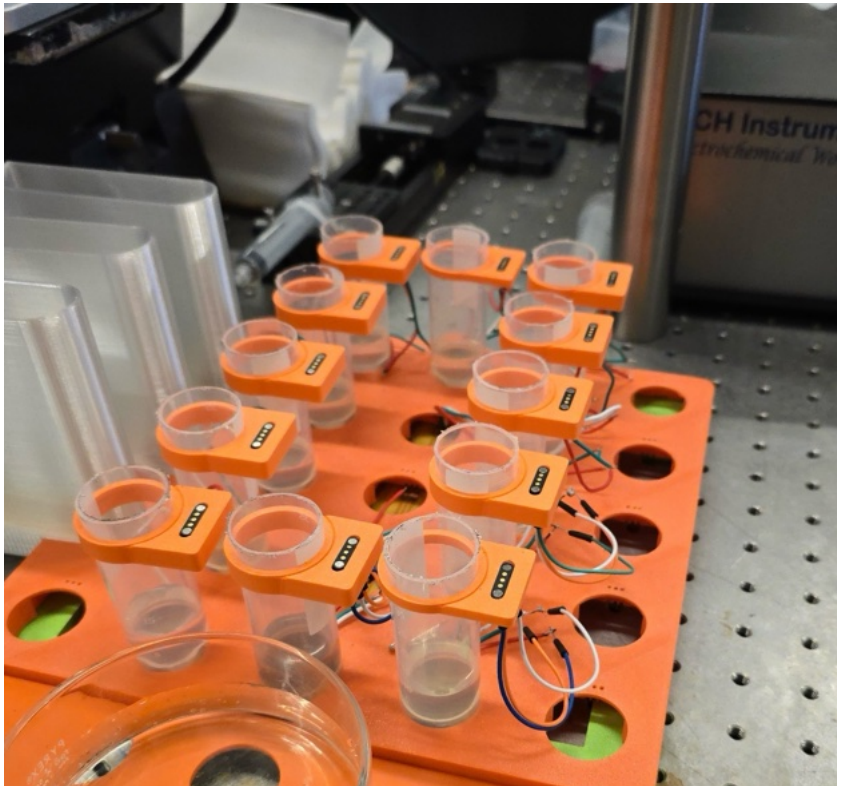
Stencil to standardize stainless steel size for better repeatability



System Optimization

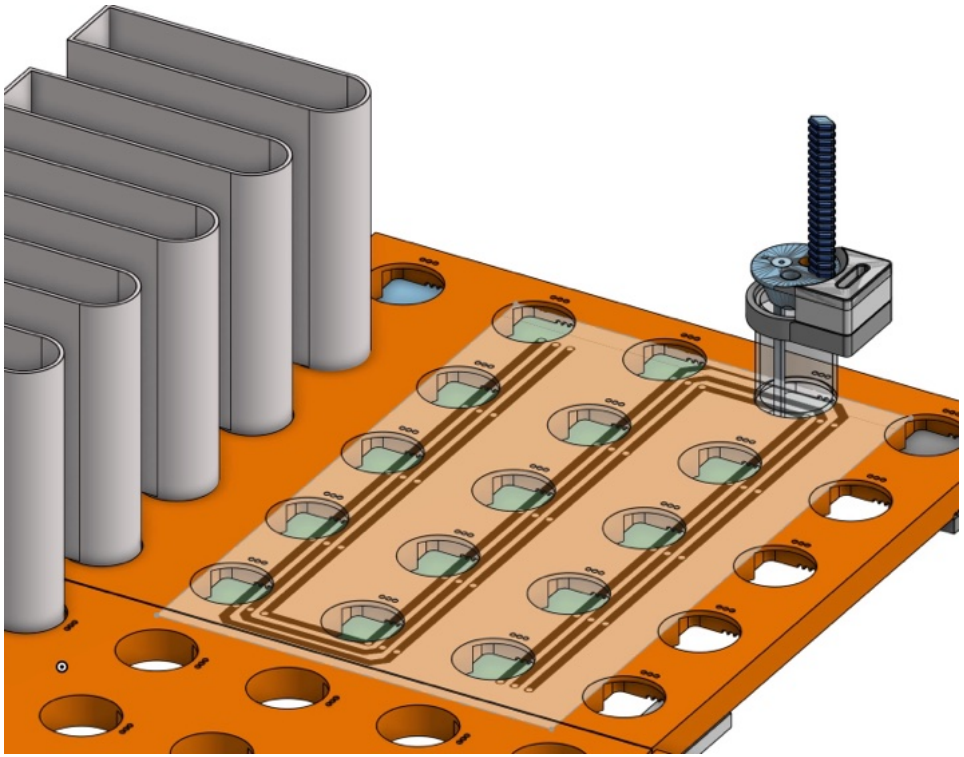
Tube Stand Design (before vs after PCB)

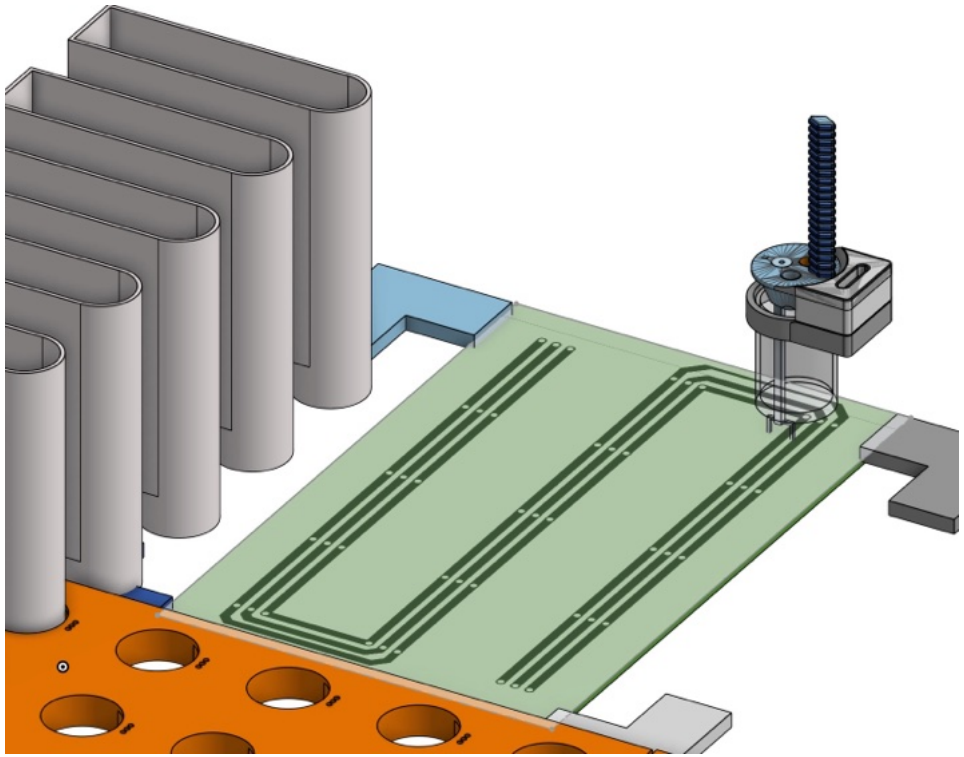




System Optimization

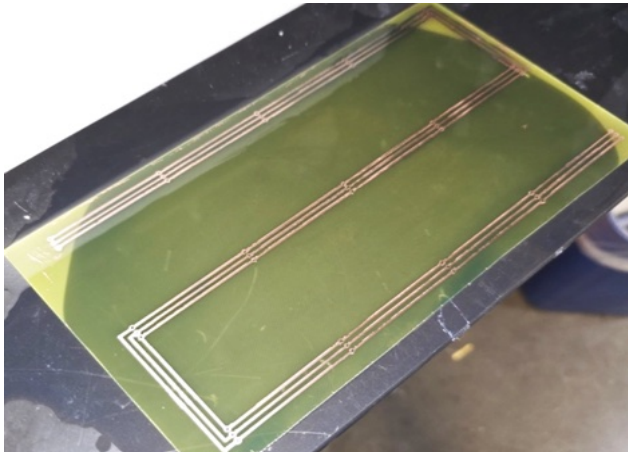
PCB Design

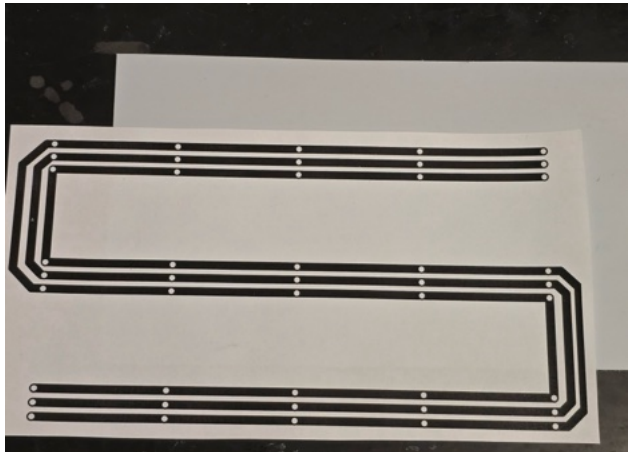


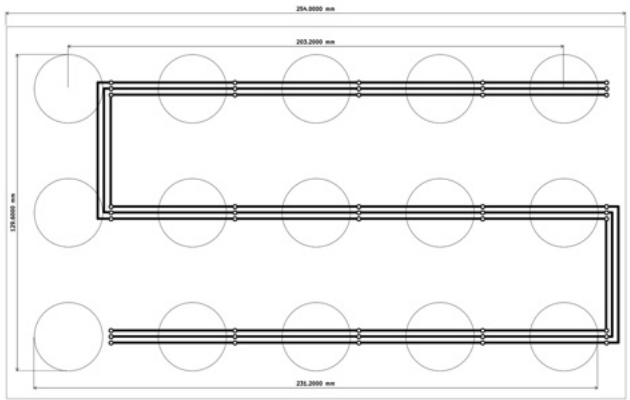


System Optimization

PCB Design



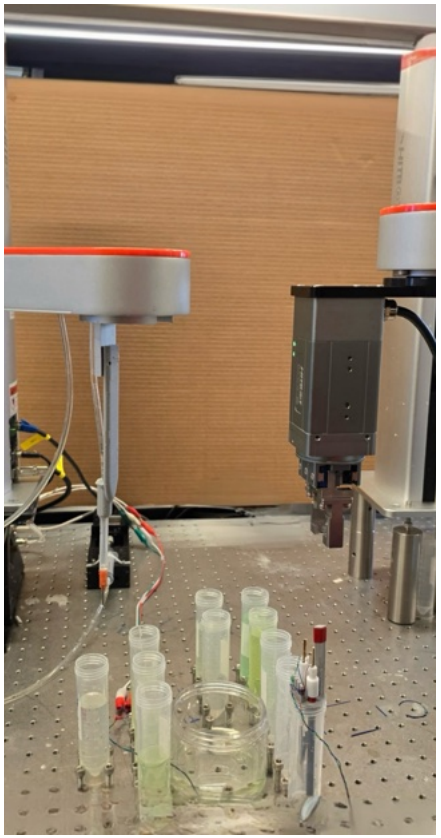


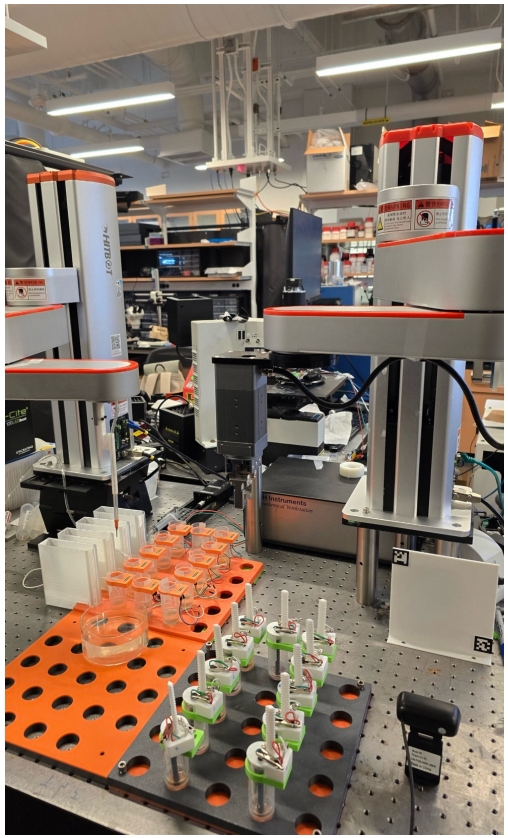


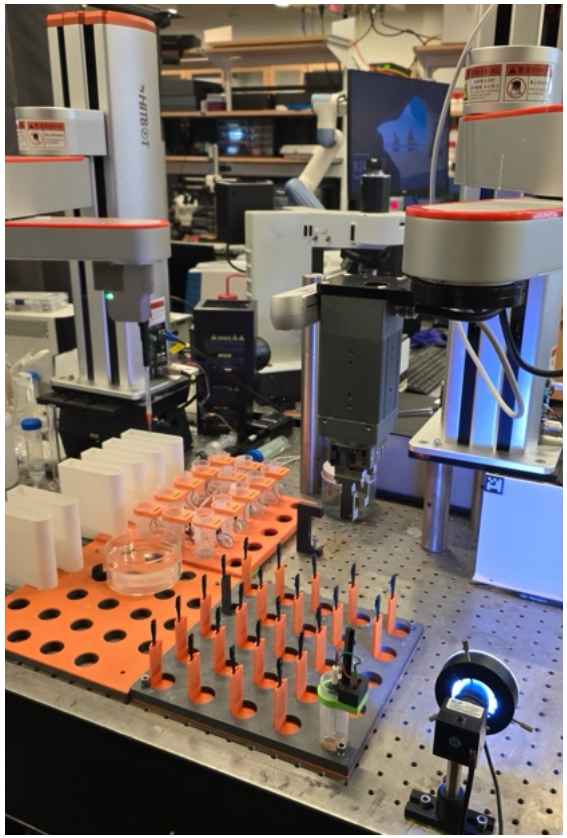
- Custom footprint to align with the 3D printed tube stand.
- Fabricated using Presensitized PCB board exposed to UV light under laser printer toner.
- Copper etched using FeCl3 solution.

System Optimization

Layout Design (First prototype to most recent setup)







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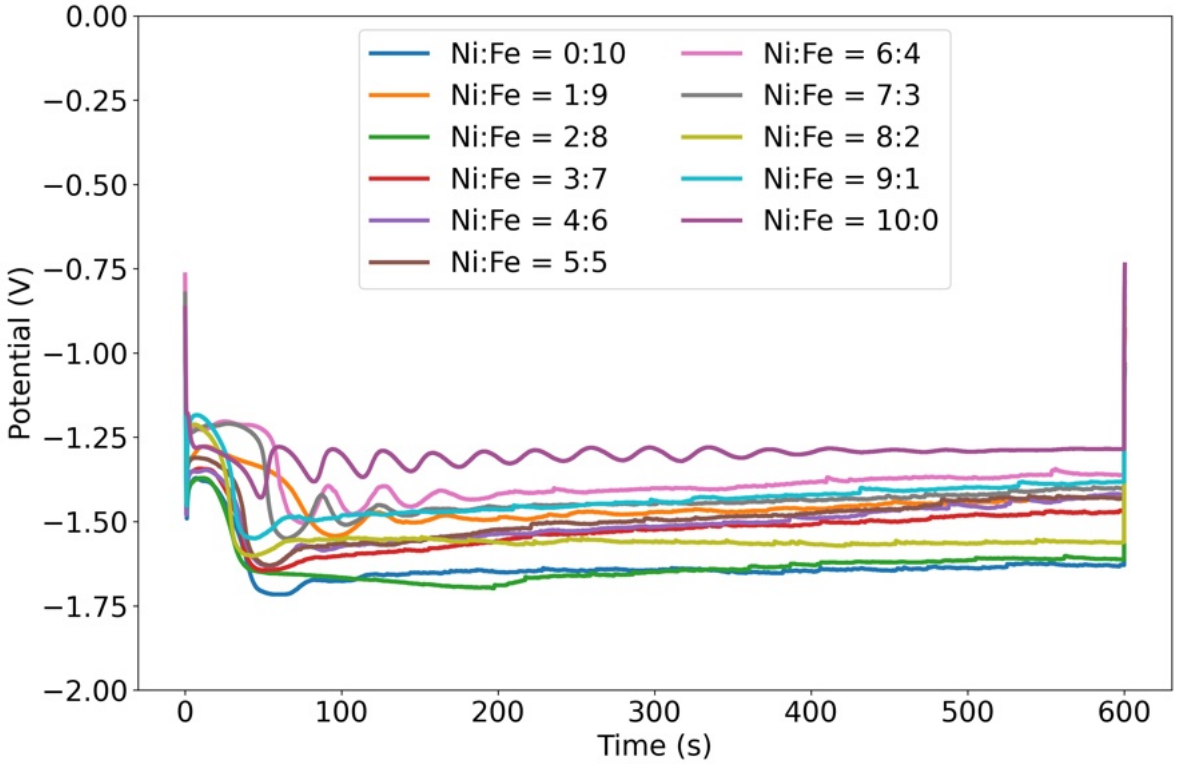
Results

1. Bimetals
    1. NiFe
    2. NiCu
2. Ternary metals
    1. NiMoP
    2. NiFeCo

1. NiFe

Deposition Curve at 5.5 mA constant current

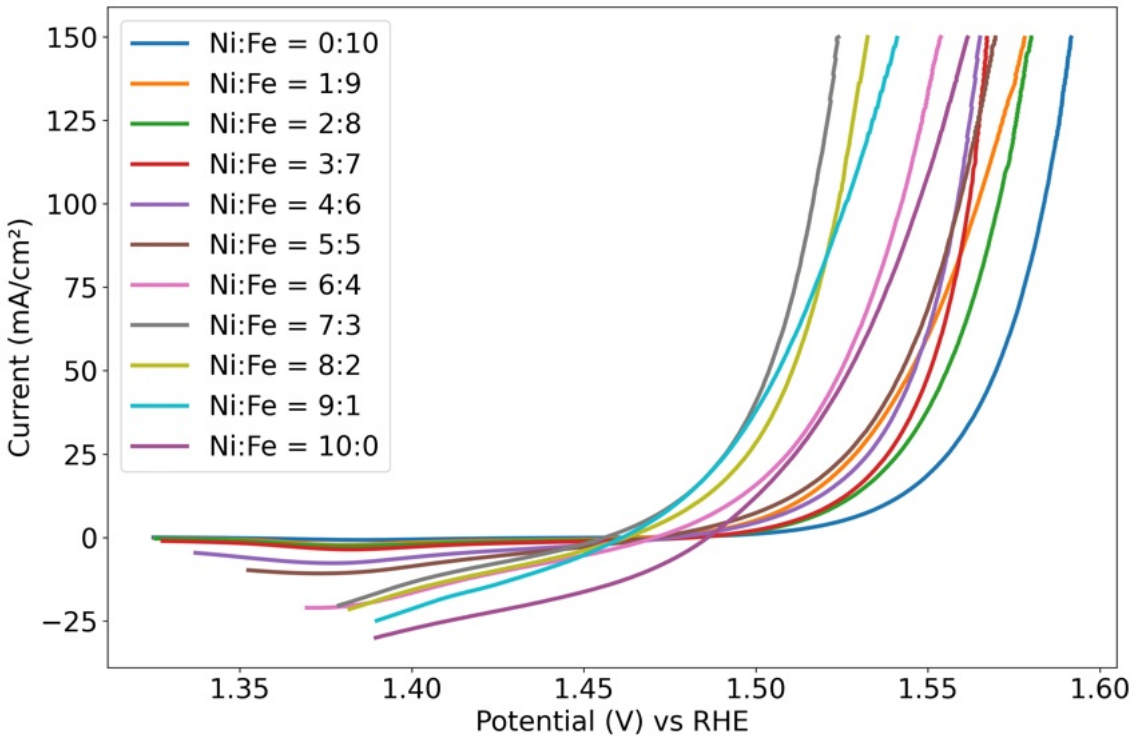


Experimental parameters:

- **Chronopotentiometry Technique:**
  - Cathodic Current: 5.5mA
  - Time cathodic: 600s
  - Scan Rate: 100mVs^{-1}
  - Sensitivity: 10^{-2}
  - No. of sweeps: 1

1. NiFe

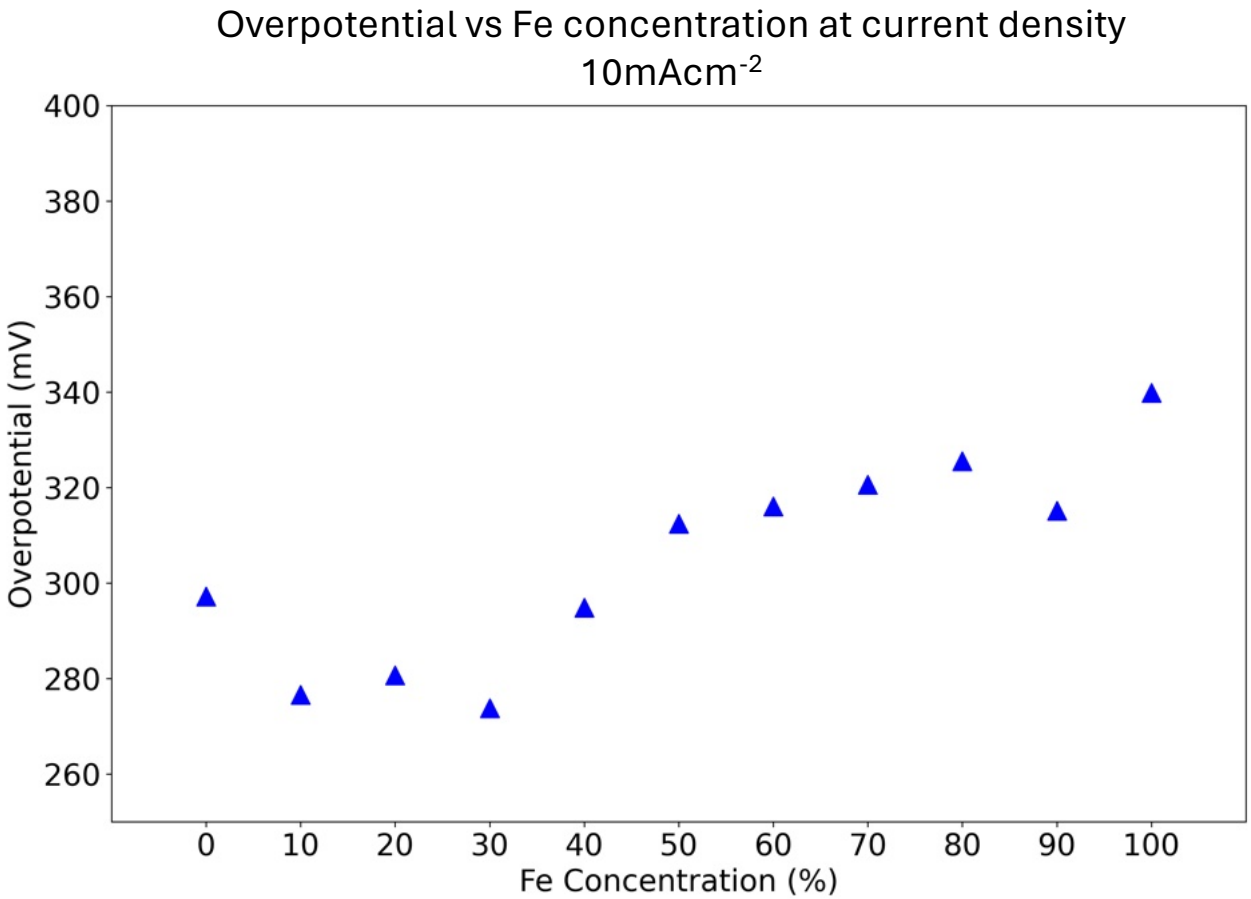
CV scan for OER evaluation



Experimental parameters:

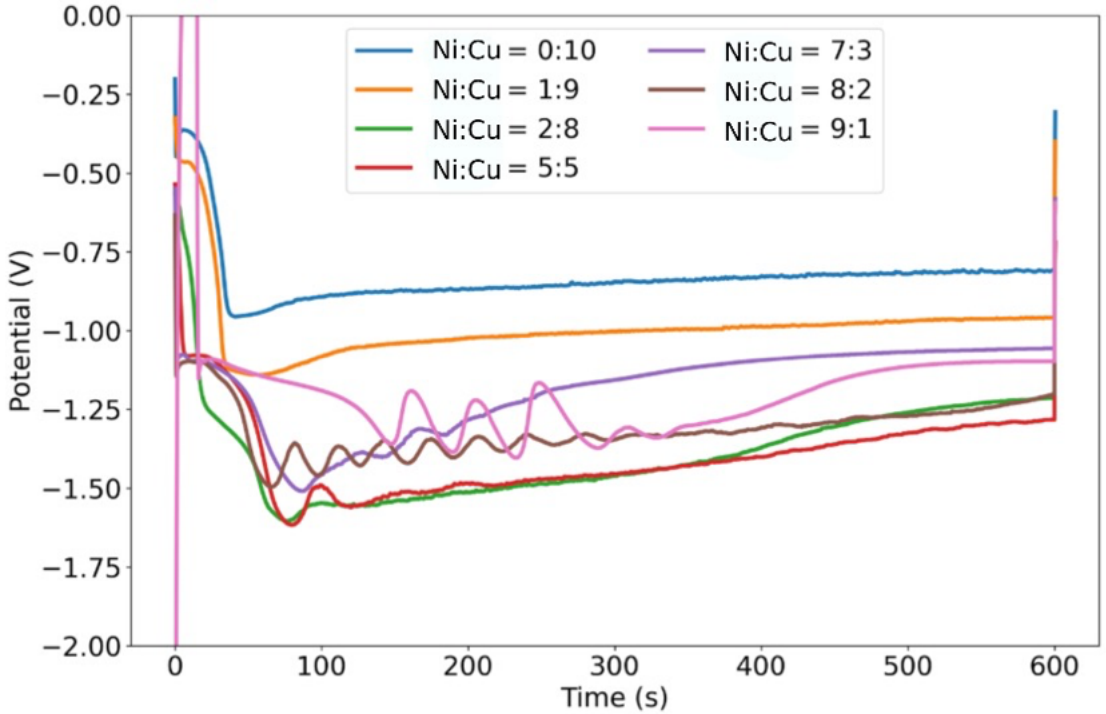
- **Cyclic Voltametry (activation):**
  - Initial potential: 0.3V
  - Final potential: 1.6V
  - Scan rate: 100mVs^{-1}
  - No. of cycles: 10
- **Cyclic Voltametry (evaluation):**
  - Initial potential: 0.3V
  - Final potential: 1.6V
  - Scan rate: 100mVs^{-1}
  - No. of cycles: 1
- **Electrochemical Impedance Spectroscopy:**
  - Frequency range: 1000Hz – 50000Hz
  - Amplitude: 0.01V
  - Sensitivity: 10^{-4}

1. NiFe


Overpotential vs Fe concentration at current density 10mAcm-2
Overpotential (mV)
400
380
360
340
320
300
280
260
0
10
20
30
40
50
60
70
80
90
100
Fe Concentration (%)

2. NiCu

Deposition curve at 5.5mA constant current



Experimental parameters:

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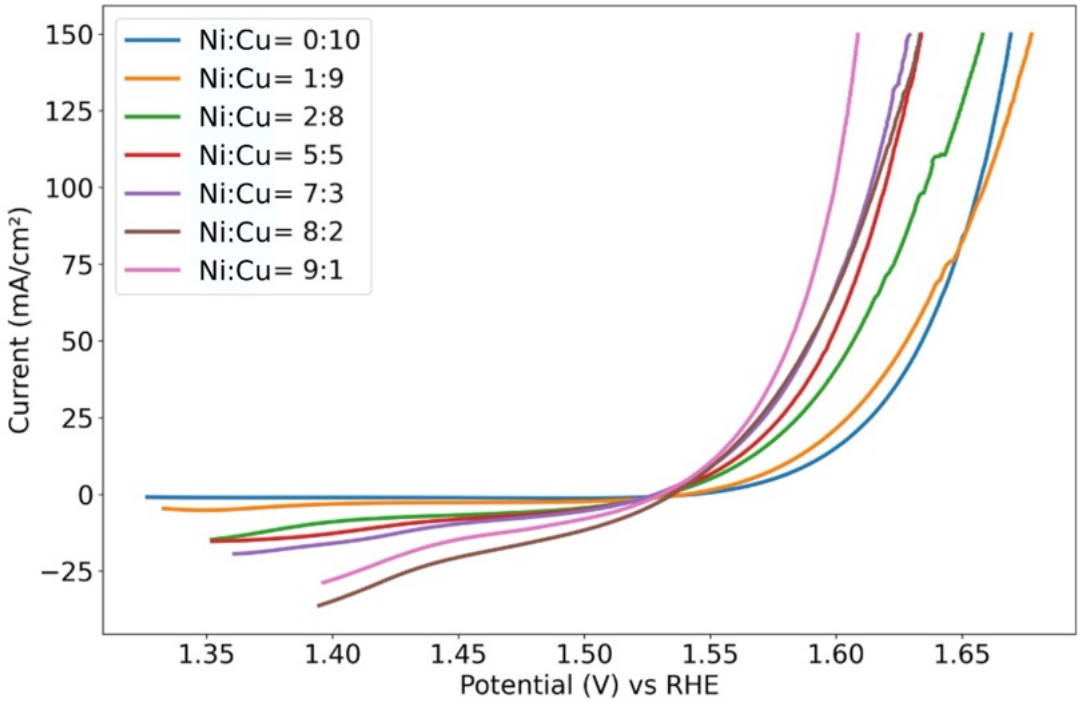
  - Cathodic Current: 5.5mA
  - Time cathodic: 600s
  - Scan Rate: 100mVs-1
  - Sensitivity: 10^{-2}
  - No. of sweeps: 1

2. NiCu

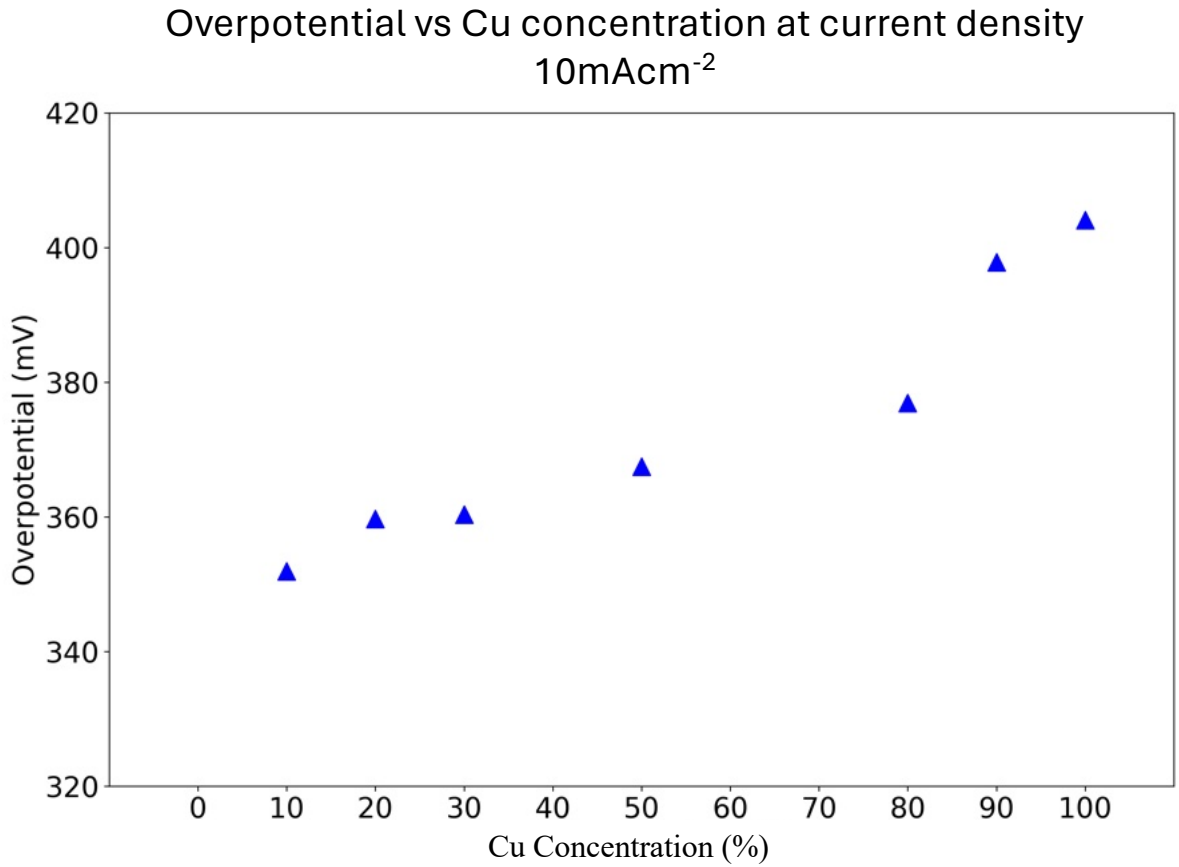
CV scan for OER evaluation



Experimental parameters:

- **Cyclic Voltametry (activation):**
  - Initial potential: 0.3V
  - Final potential: 1.6V
  - Scan rate: 100mVs-1
  - No. of cycles: 10
- **Cyclic Voltametry (evaluation):**
  - Initial potential: 0.3V
  - Final potential: 1.6V
  - Scan rate: 100mVs-1
  - No. of cycles: 1
- **Electrochemical Impedance Spectroscopy:**
  - Frequency range: 1000Hz – 50000Hz
  - Amplitude: 0.01V
  - Sensitivity: 10^{-4}

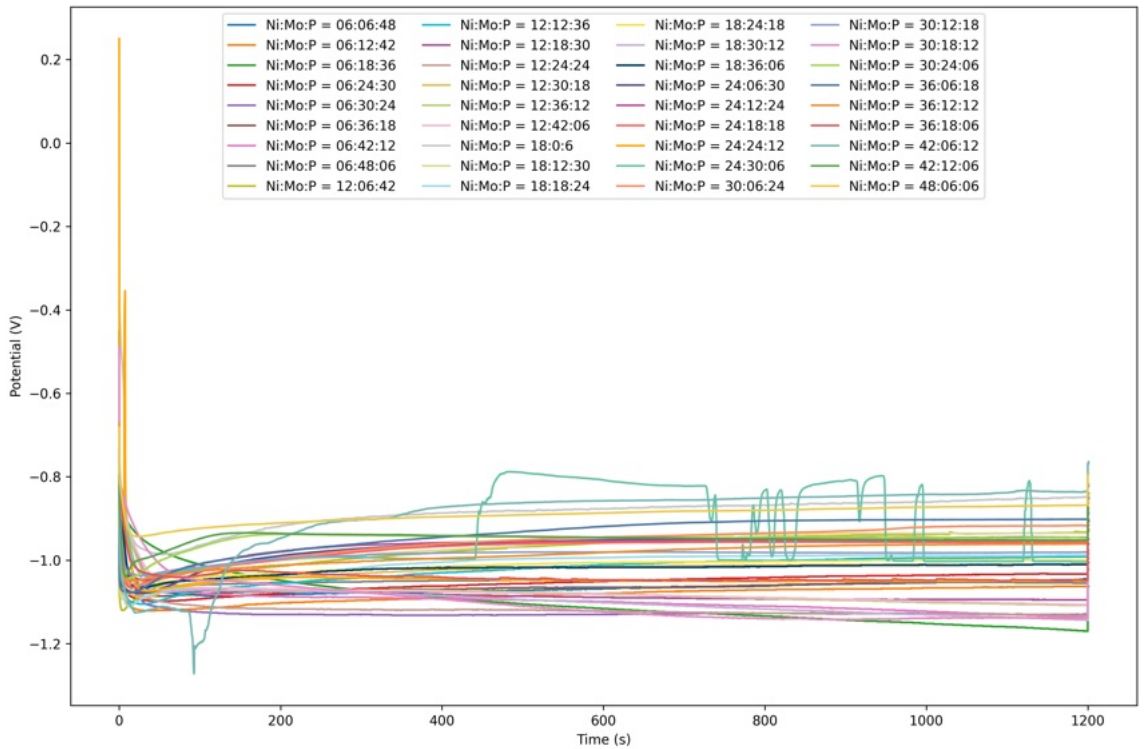
2. CuFe


Overpotential vs Cu concentration at current density 10mAcm-2
Overpotential (mV)
420
400
380
360
340
320
0
10
20
30
40
50
60
70
80
90
100
Cu Concentration (%)

Ternary metals

1. NiMoP

Deposition curves at 4mA constant current



NMP_final_sr_0.1

Experimental parameters:

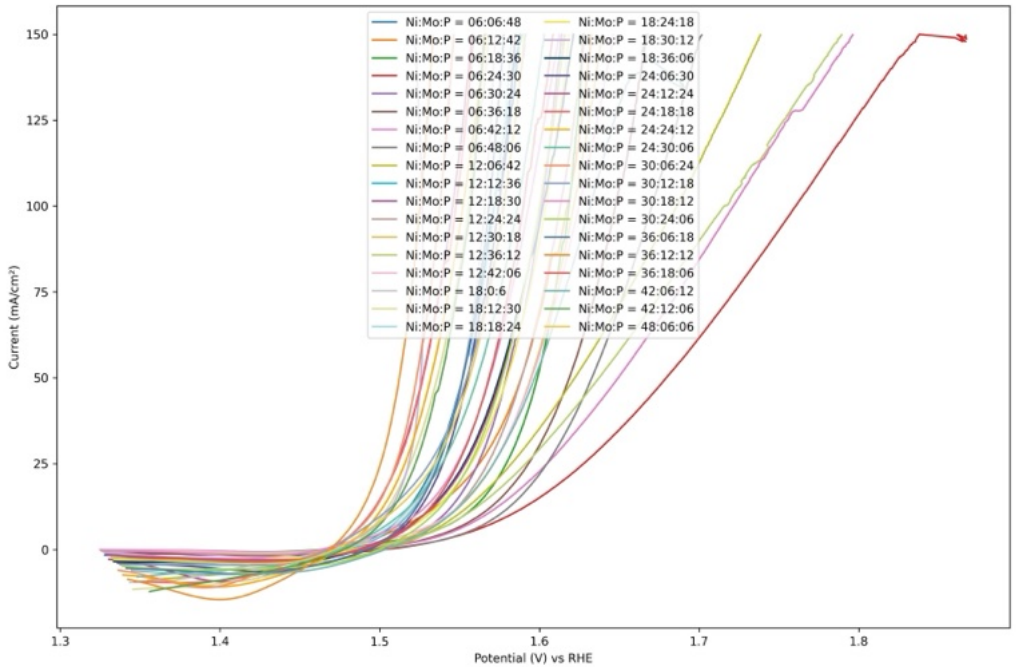
- **Chronopotentiometry Technique:**
  - Cathodic Current: 4mA
  - Time cathodic: 1200s
  - Scan Rate: 100mVs^{-1}
  - Sensitivity: 10^{-2}
  - No. of sweeps: 1

- **Electrochemical Impedance Spectroscopy:**
  - Frequency range: 1000Hz – 50000Hz
  - Amplitude: 0.01V
  - Sensitivity: 10^{-4}

Ternary metals

1. NiMoP

CV scan for OER evaluation



Experimental parameters:

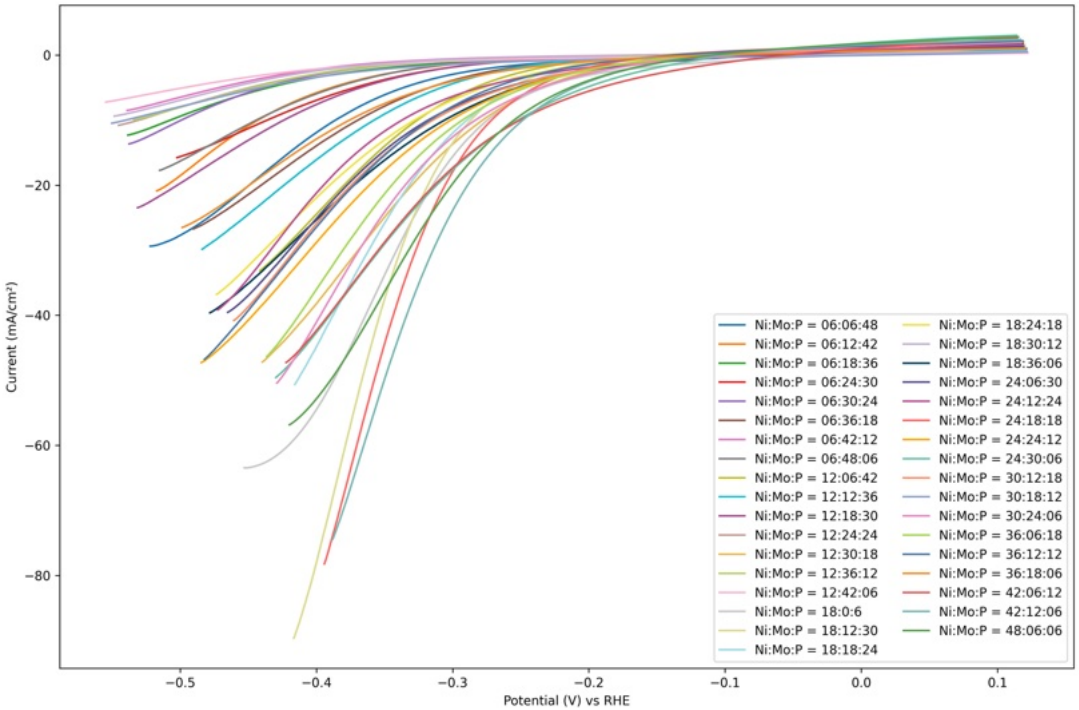
- **Cyclic Voltametry (activation):**
  - Initial potential: 0.3V
  - Final potential: 1.6V
  - Scan rate: 100mVs^{-1}
  - No. of cycles: 10
- **Cyclic Voltametry (evaluation):**
  - Initial potential: 0.3V
  - Final potential: 1.6V
  - Scan rate: 100mVs^{-1}
  - No. of cycles: 1

NMP_final_sr_0.1

Ternary metals

1. NiMoP

CV scan for HER evaluation



NMP_final_sr_0.1

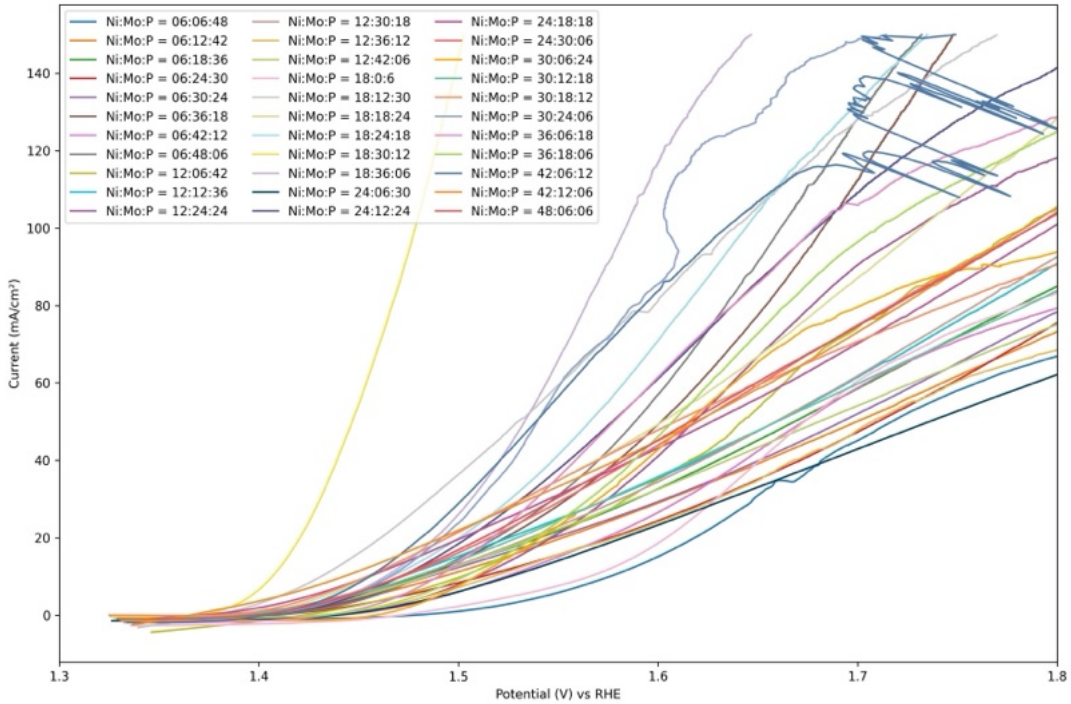
Experimental parameters:

- **Cyclic Voltametry (activation):**
  - Initial potential: - 0.9V
  - Final potential: - 1.4V
  - Scan rate: 100mVs^{-1}
  - No. of cycles: 10
- **Cyclic Voltametry (evaluation):**
  - Initial potential: - 0.9
  - Final potential: - 1.6V
  - Scan rate: 100mVs^{-1}
  - No. of cycles: 1

Ternary metals

1. NiMoP

CV scan for EOR evaluation



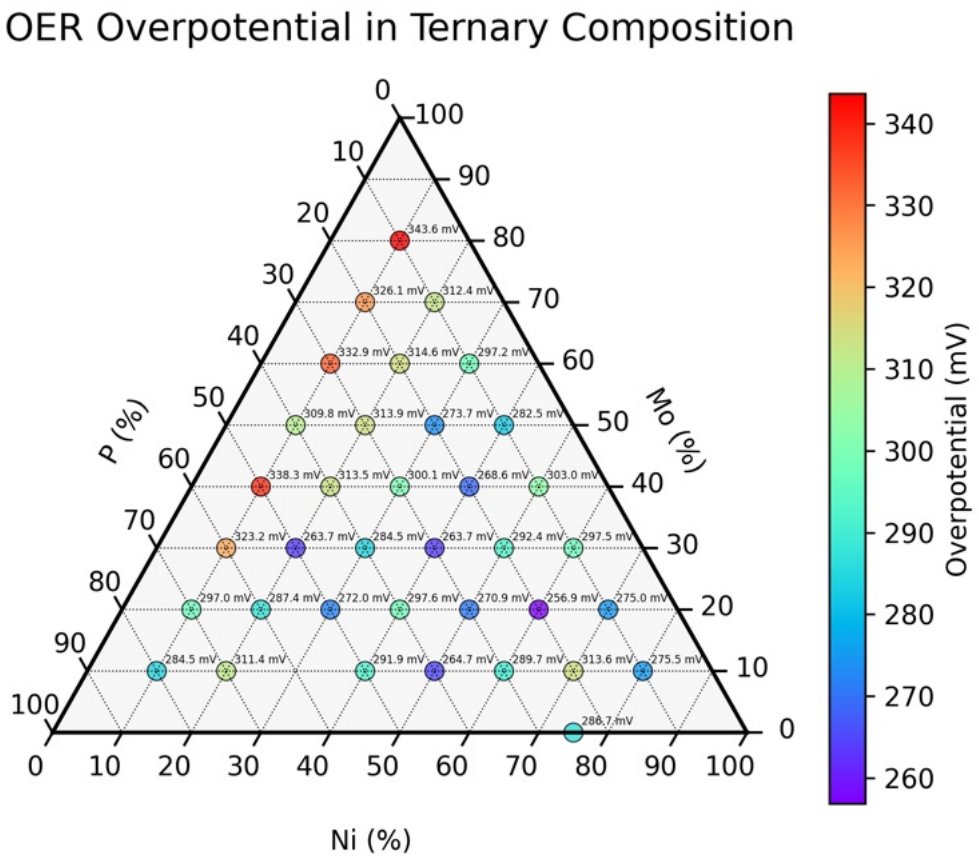
NMP_final_sr_0.1

Experimental parameters:

- **Cyclic Voltametry (evaluation):**
  - Initial potential: 0.3V
  - Final potential: 1.6V
  - Scan rate: 100mVs-1
  - No. of cycles: 1

Ternary metals

1. NiMoP



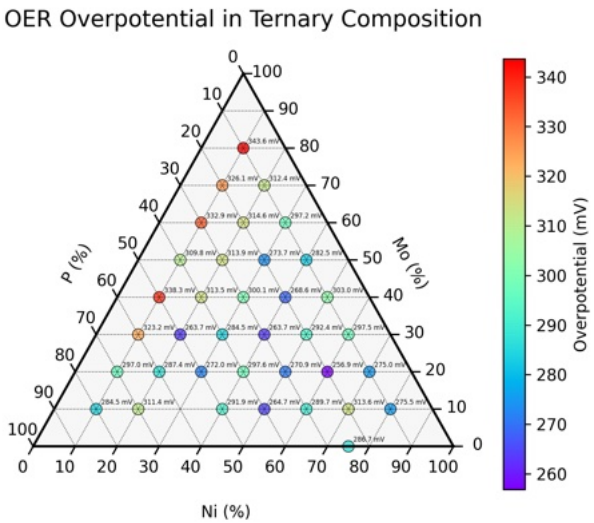
NMP_final_sr_0.1

- OER overpotential plots at 10mAcm^{-2} current density
- Each metal is represented on one side of the triangle.
- The overpotentials are distribuited over a normalized colormap.

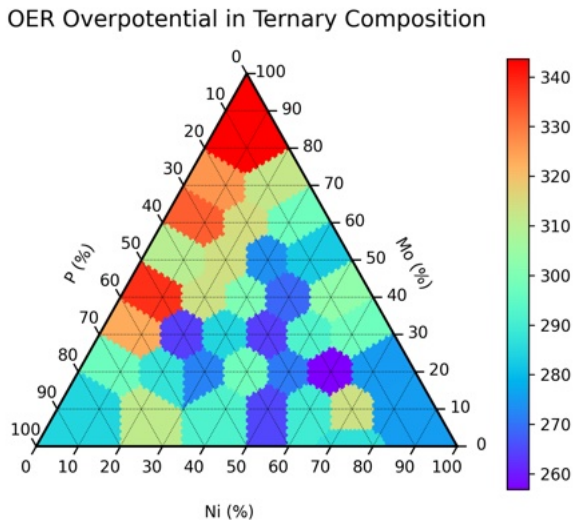
Ternary metals

1. NiMoP

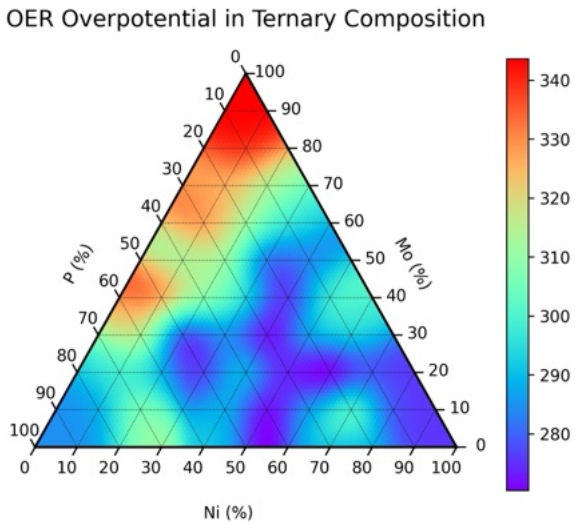
OER overpotential plots at 10mAcm^{-2} current density



Scatter Plot



Nearest Neighbor Interpolation



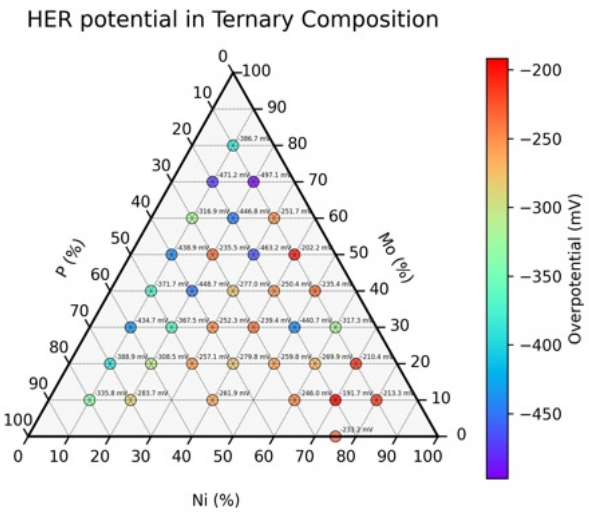
Radial Basis Function Interpolation

NMP_final_sr_0.1

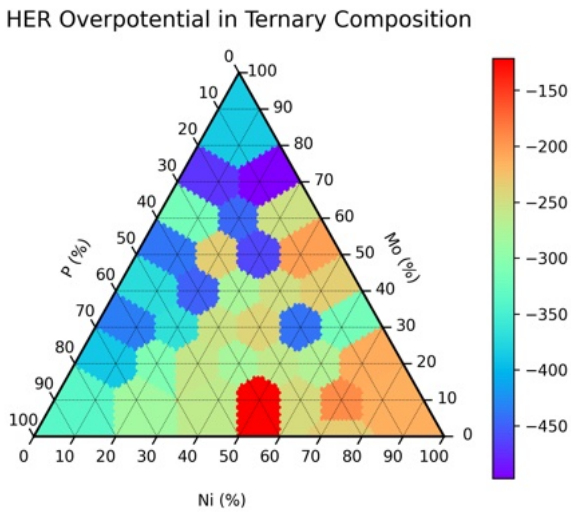
Ternary metals

1. NiMoP

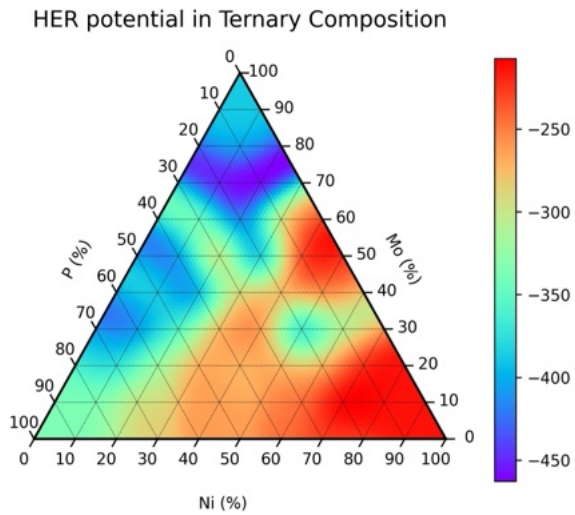
HER overpotential plots at 10mAcm^{-2} current density



Scatter Plot



Nearest Neighbor Interpolation



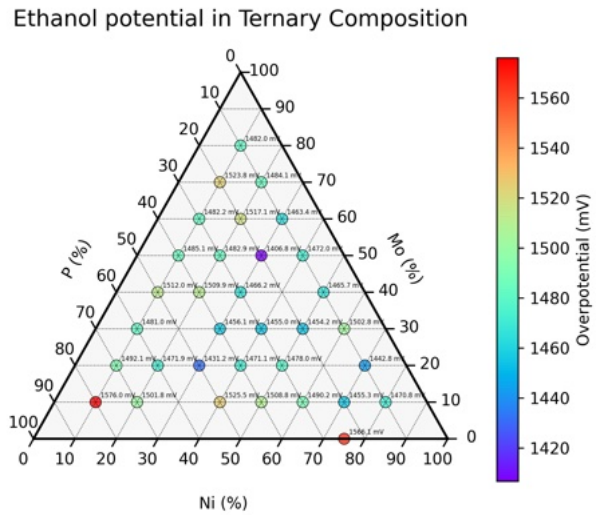
Radial Basis Function Interpolation

NMP_final_sr_0.1

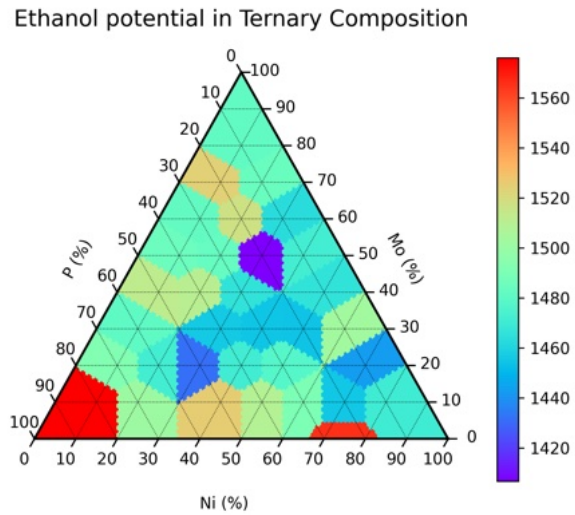
Ternary metals

1. NiMoP

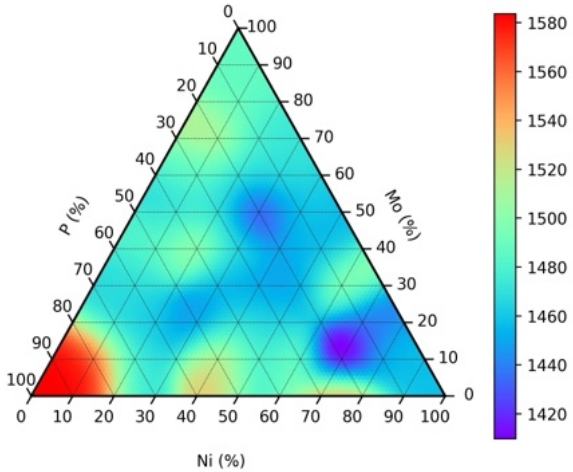
EOR overpotential plots at 10mAcm^{-2} current density



Scatter Plot



Nearest Neighbor Interpolation



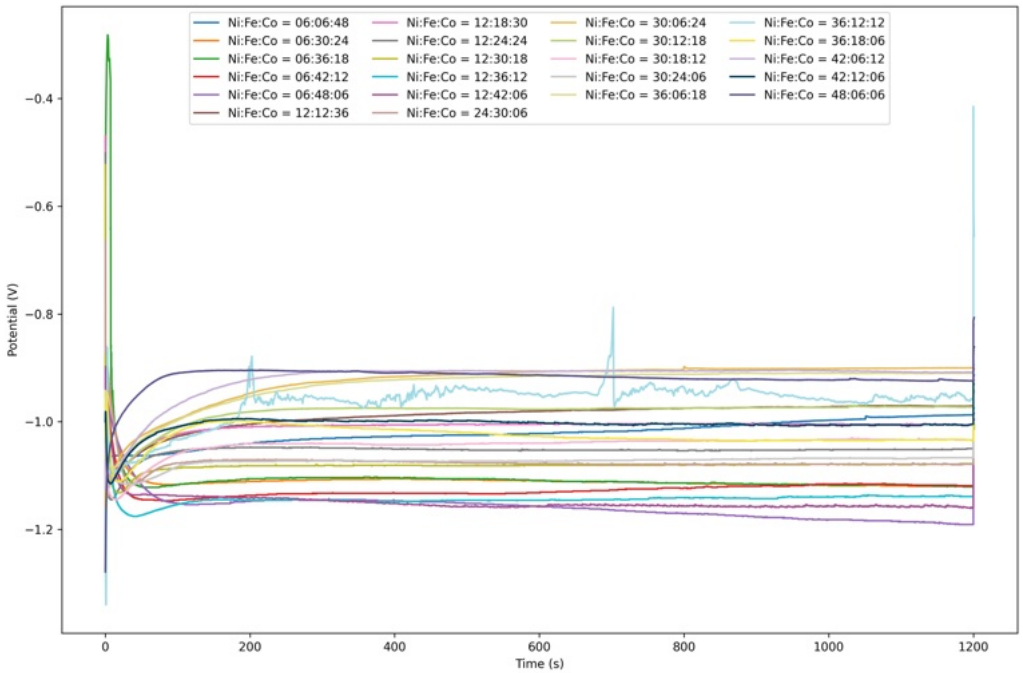
Radial Basis Function Interpolation

NMP_final_sr_0.1

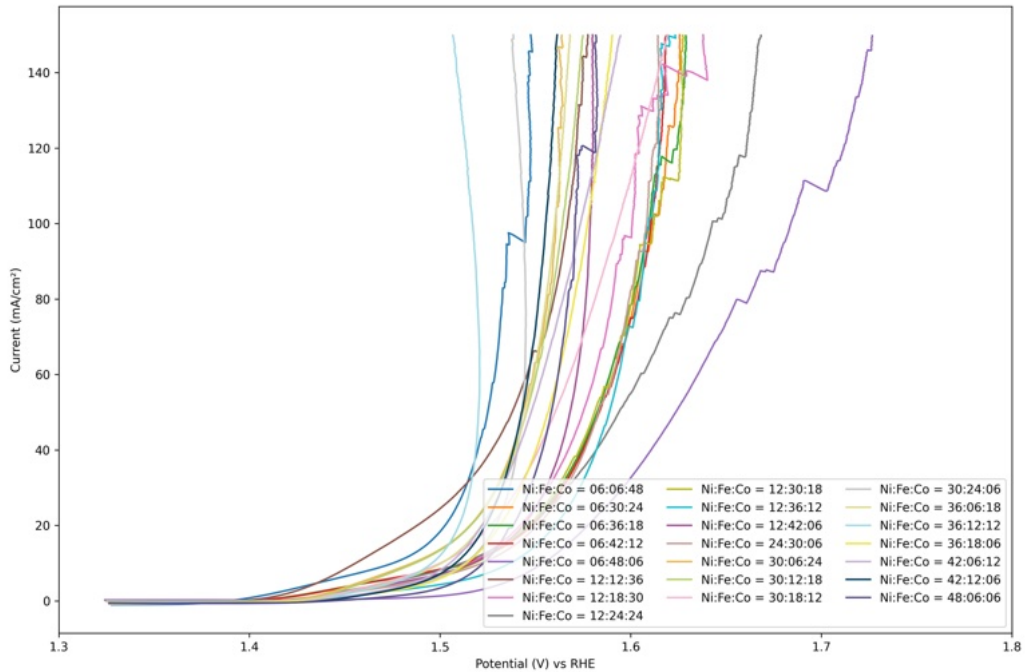
Ternary metals

1. NiMoP

Deposition curves at 4mA constant current



CV scan for OER evaluation

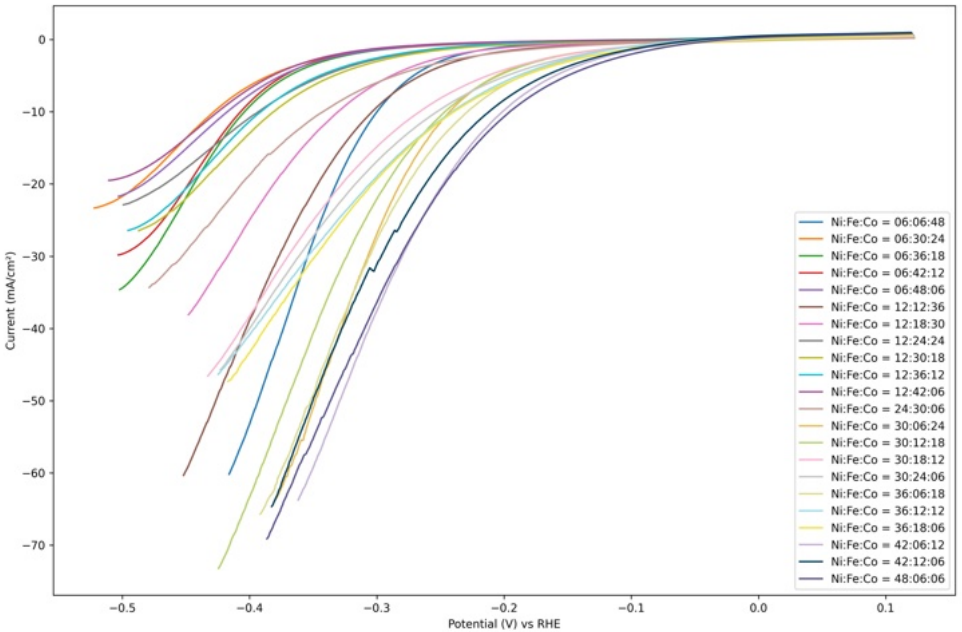


NMP combined 04_06

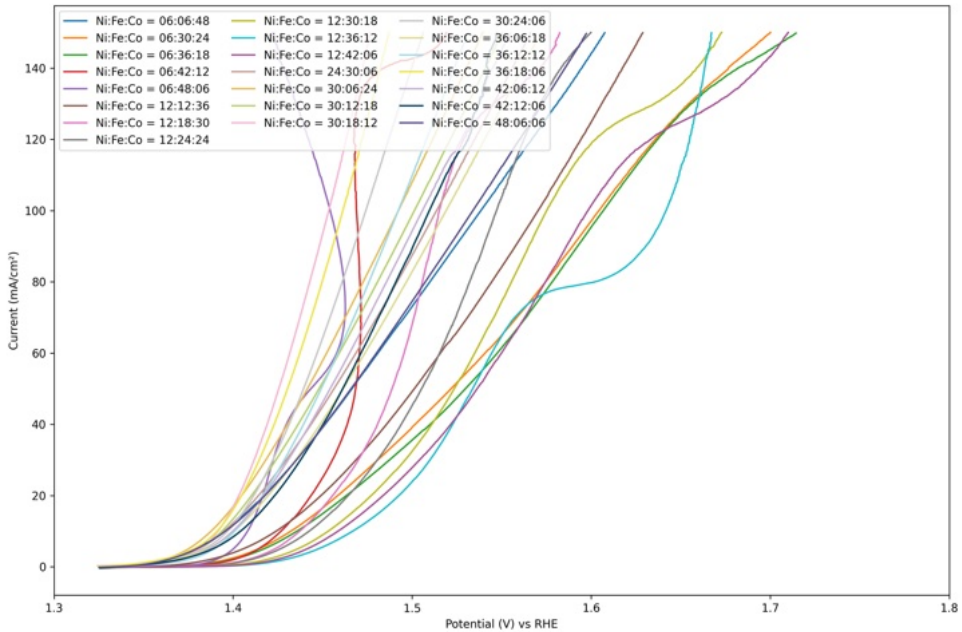
Ternary metals

1. NiMoP

CV scan for HER evaluation



CV scan for EOR evaluation

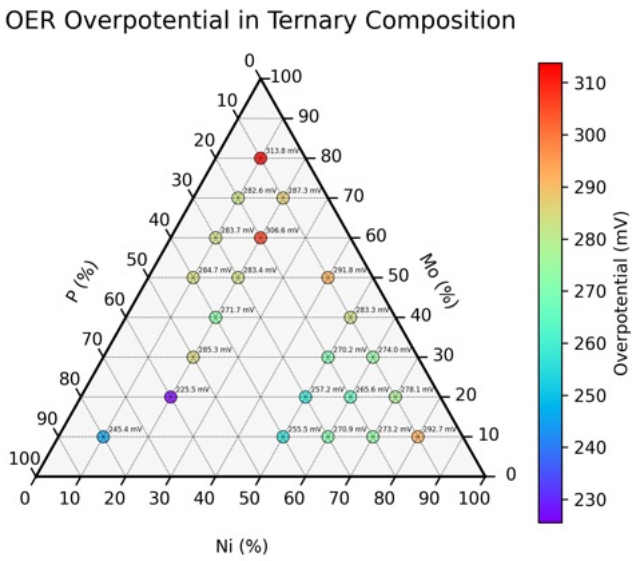


NMP combined 04_06

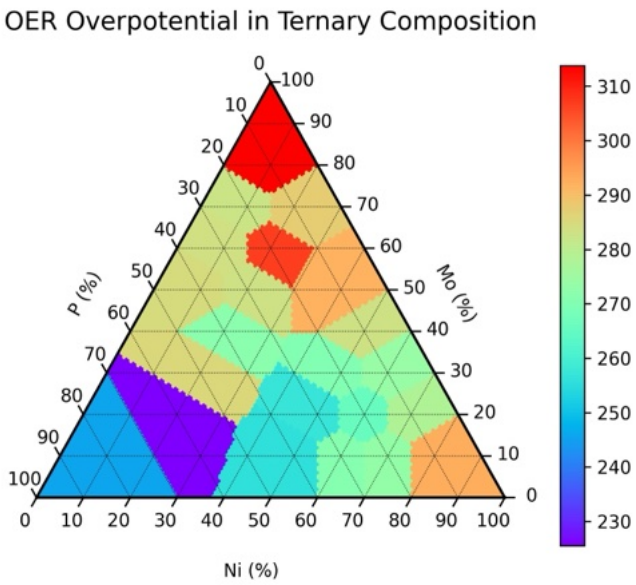
Ternary metals

1. NiMoP

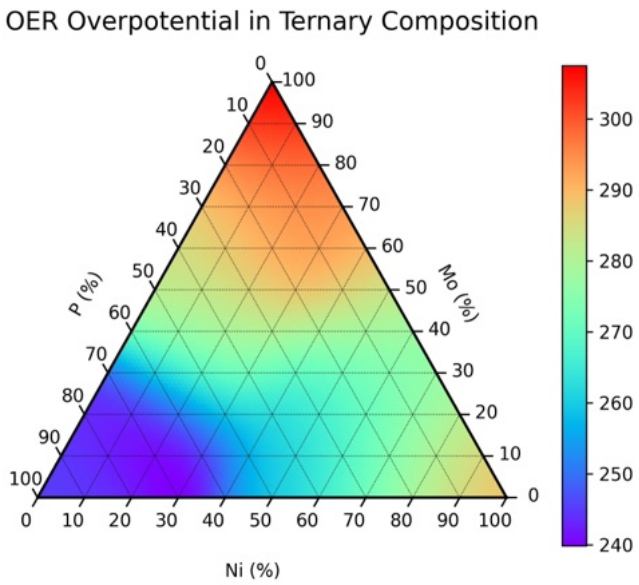
OER overpotential plots at 10mAcm^{-2} current density



Scatter Plot



Nearest Neighbor Interpolation

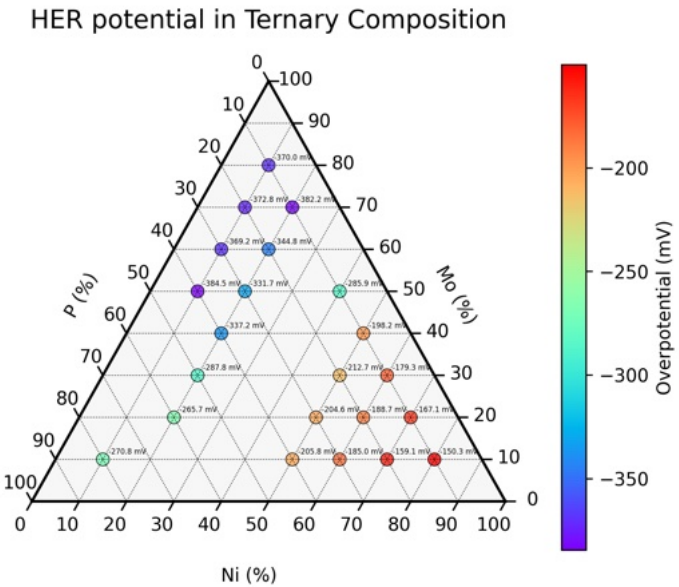


Radial Basis Function Interpolation

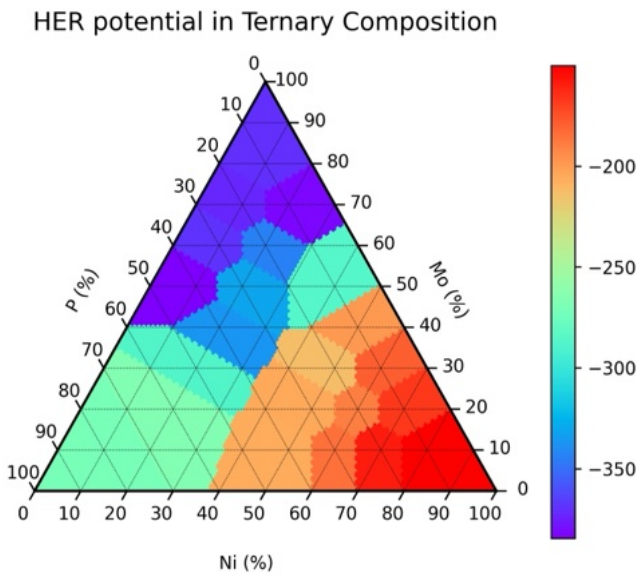
Ternary metals

1. NiMoP

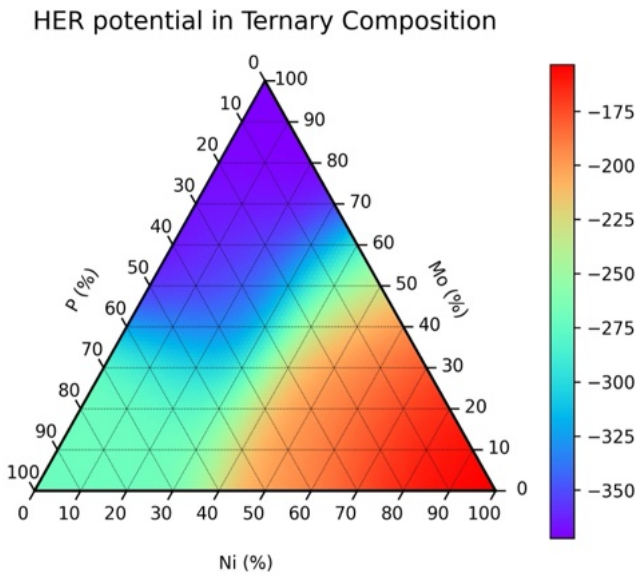
HER overpotential plots at 10mAcm^{-2} current density



Scatter Plot



Nearest Neighbor Interpolation



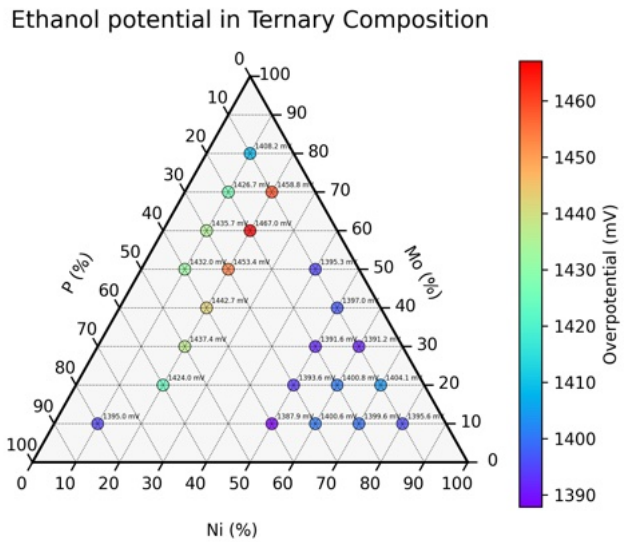
Radial Basis Function Interpolation

NMP combined 04_06

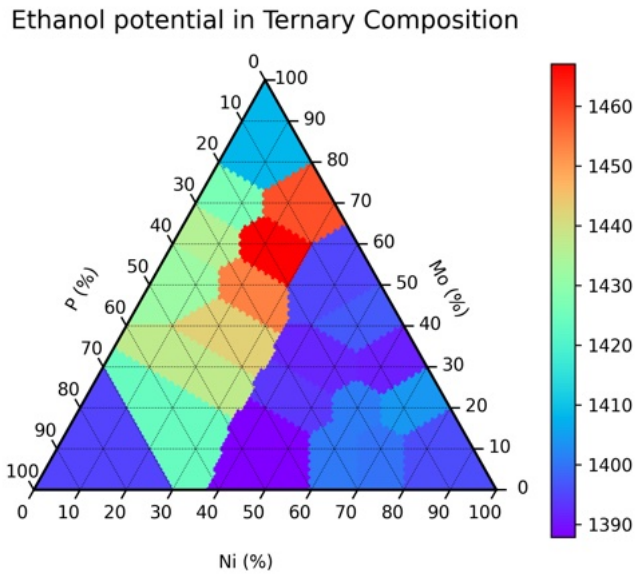
Ternary metals

1. NiMoP

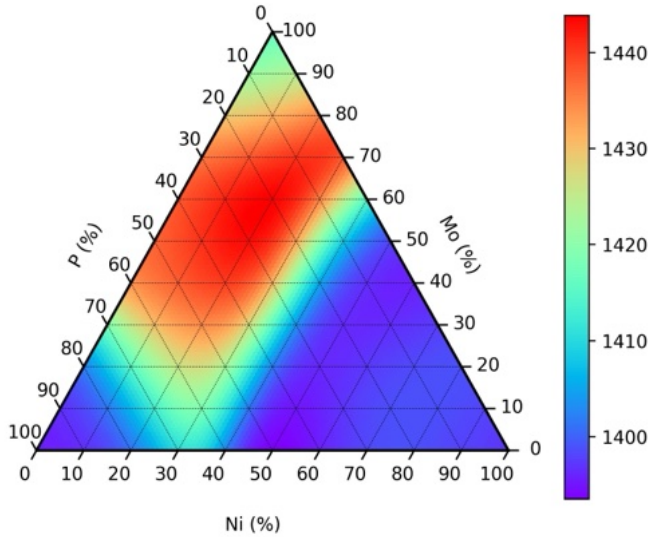
EOR overpotential plots at 10mAcm^{-2} current density



Scatter Plot



Nearest Neighbor Interpolation

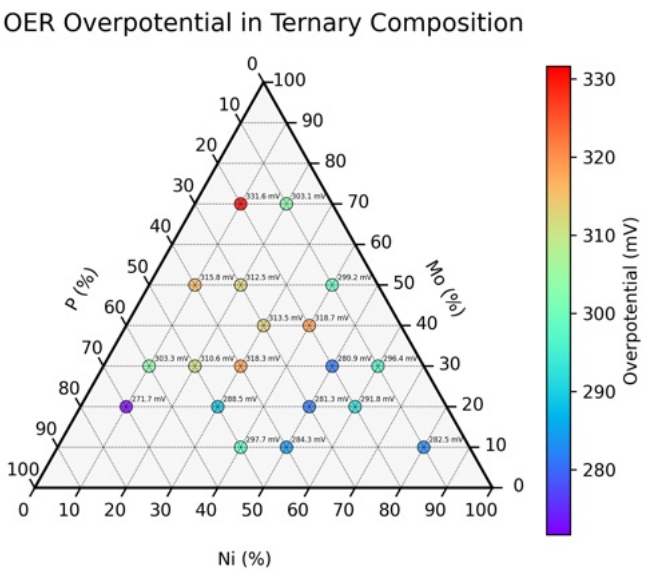


Radial Basis Function Interpolation

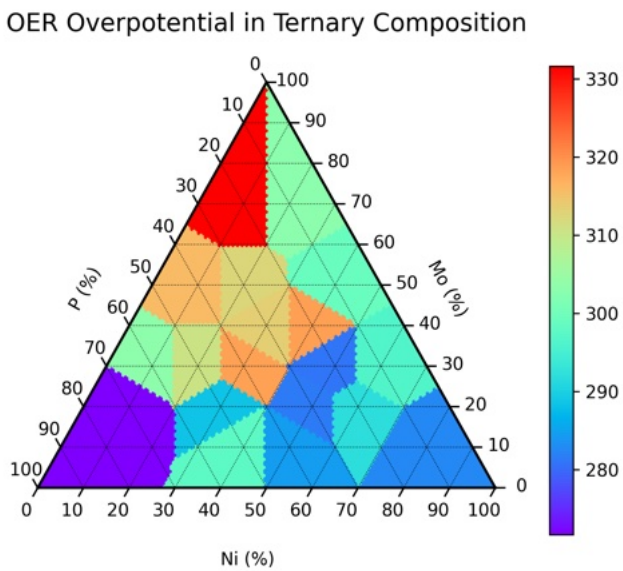
Ternary metals

1. NiMoP

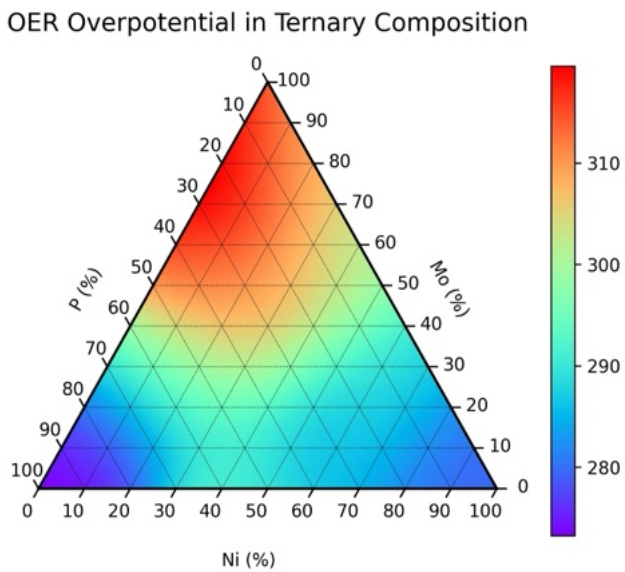
OER overpotential plots at 10mAcm^{-2} current density



Scatter Plot



Nearest Neighbor Interpolation



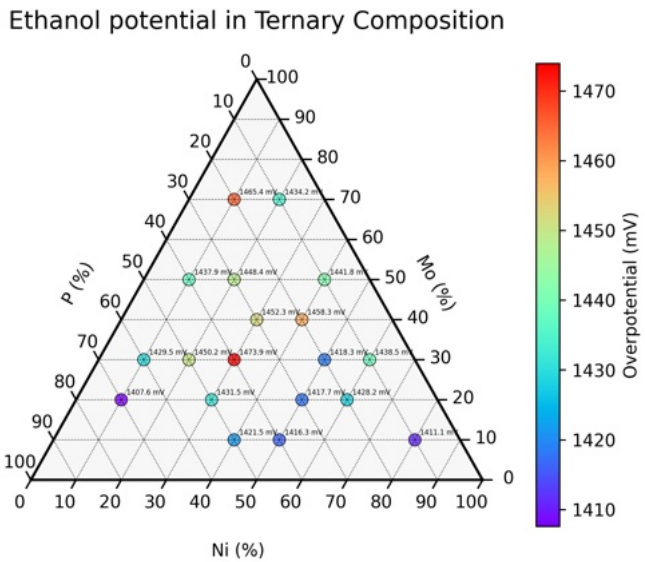
Radial Basis Function Interpolation

NMP_4_OER_only_sr_0.1

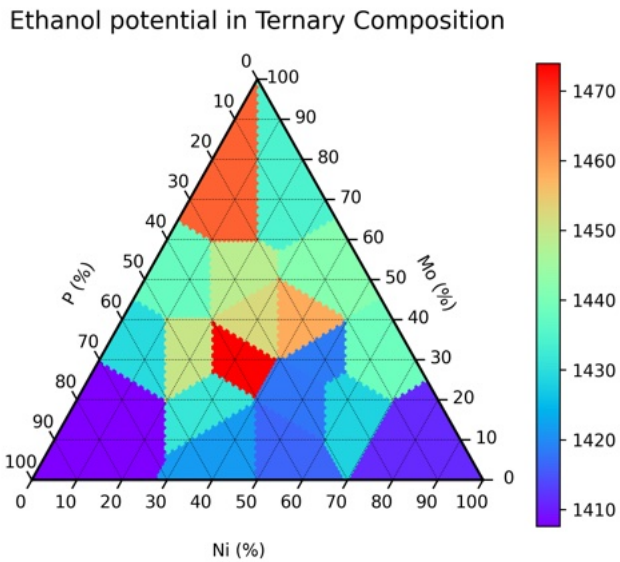
Ternary metals

1. NiMoP

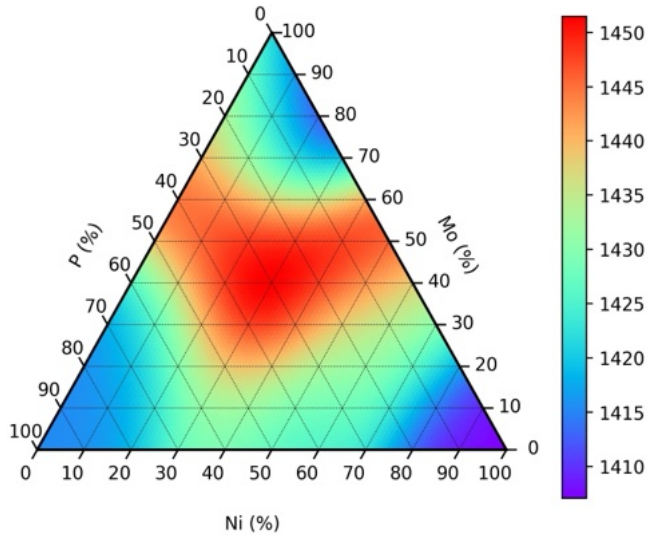
EOR overpotential plots at 10mAcm^{-2} current density



Scatter Plot



Nearest Neighbor Interpolation



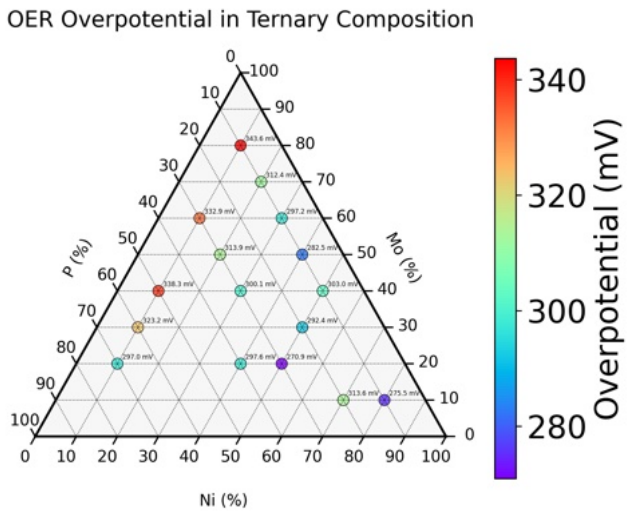
Radial Basis Function Interpolation

NMP_4_OER_only_sr_0.1

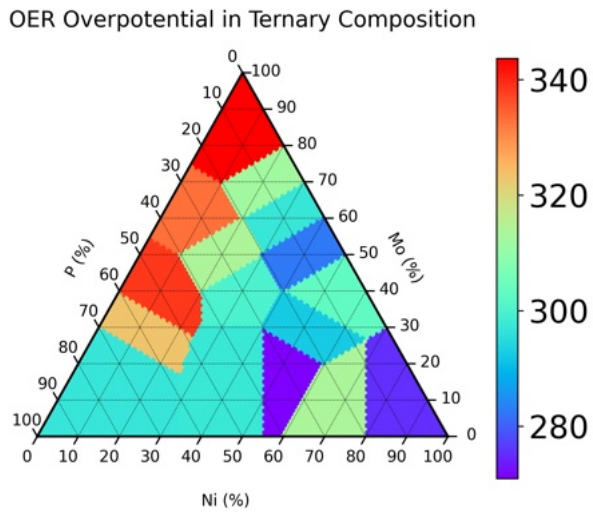
Ternary metals

1. NiMoP

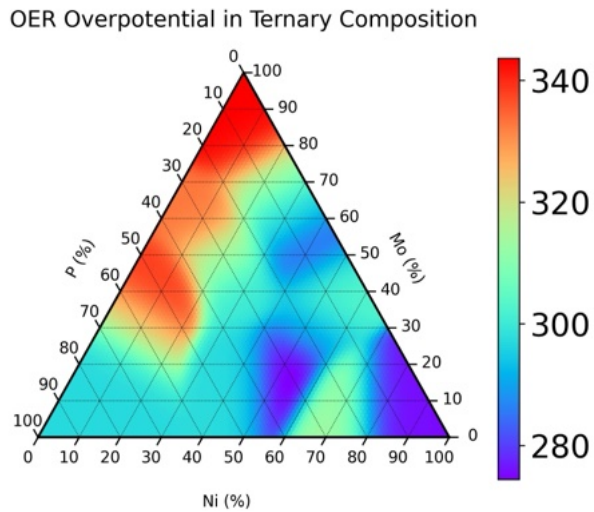
OER overpotential plots at 10mAcm^{-2} current density



Scatter Plot



Nearest Neighbor Interpolation



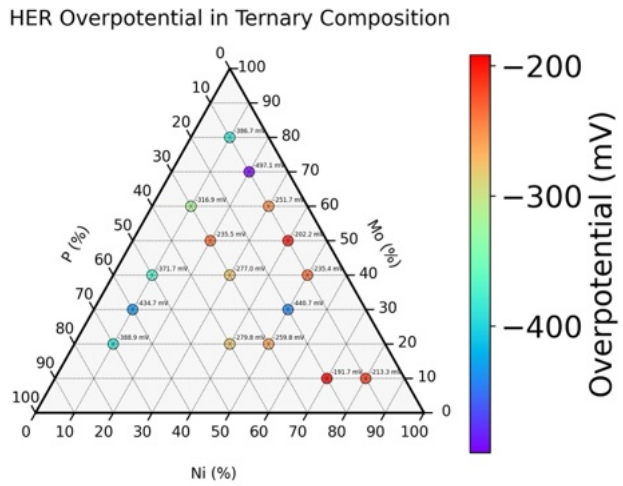
Radial Basis Function Interpolation

Folder- NMP(42)

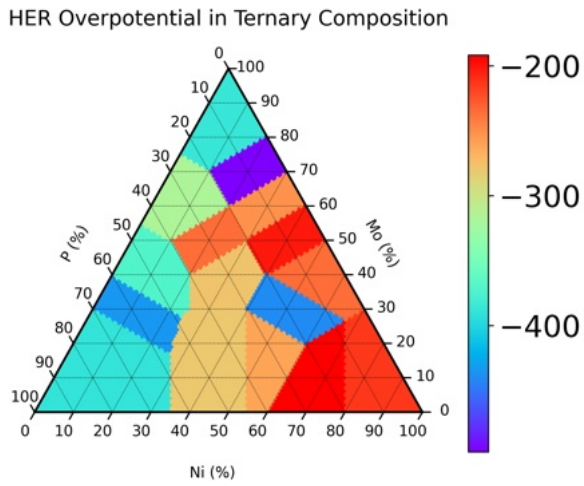
Ternary metals

1. NiMoP

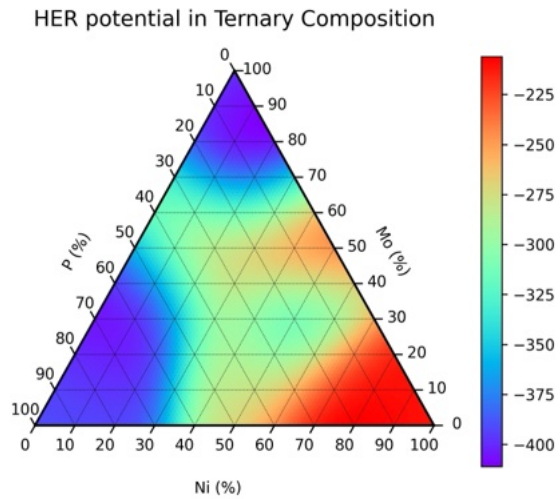
HER overpotential plots at 10mAcm^{-2} current density



Scatter Plot



Nearest Neighbor Interpolation



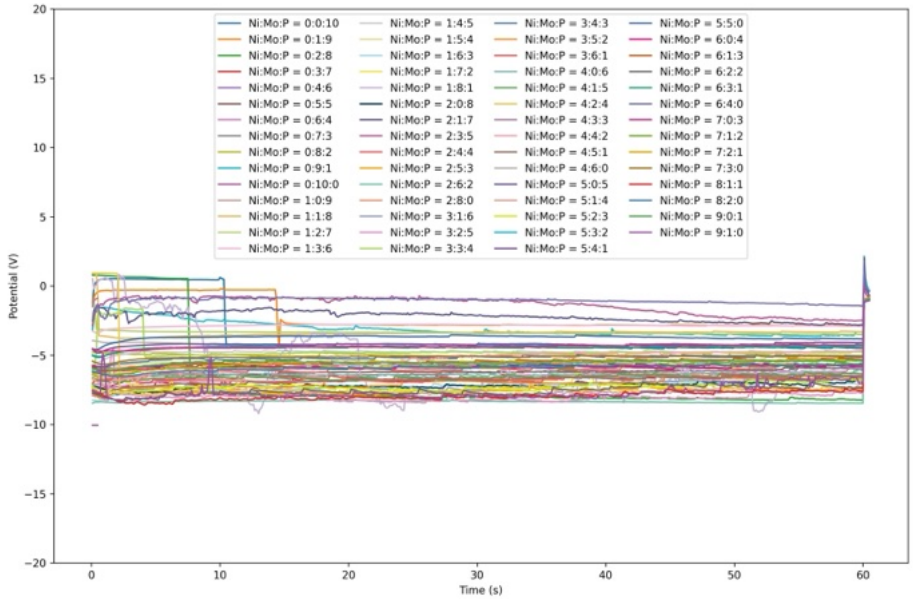
Radial Basis Function Interpolation

Folder- NMP(42)

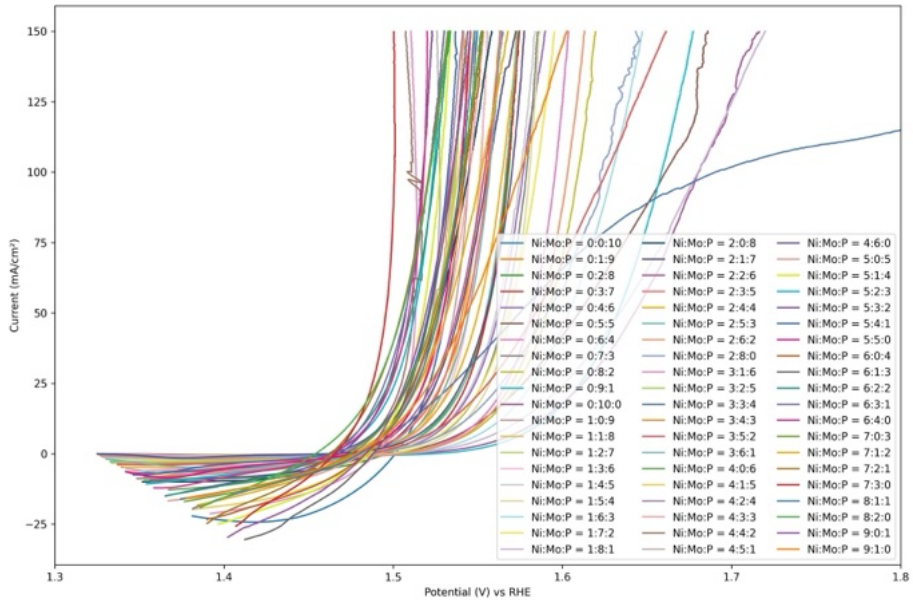
Ternary metals

2. NiFeCo

Deposition curves at 100mA constant current

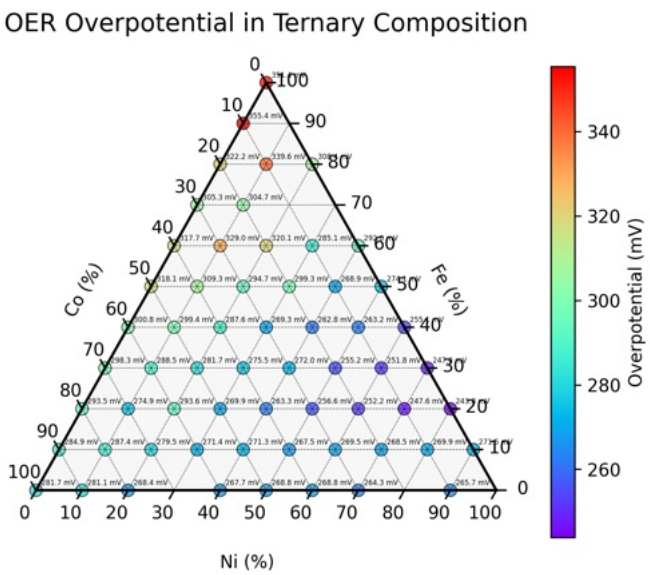


CV scan for OER evaluation

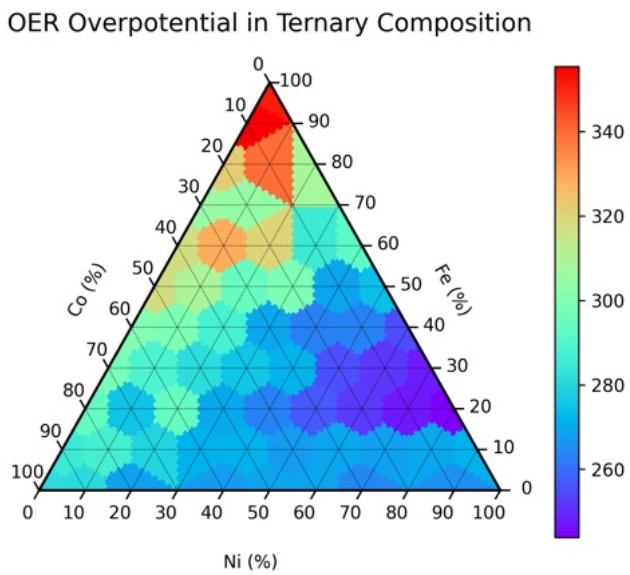


Ternary metals

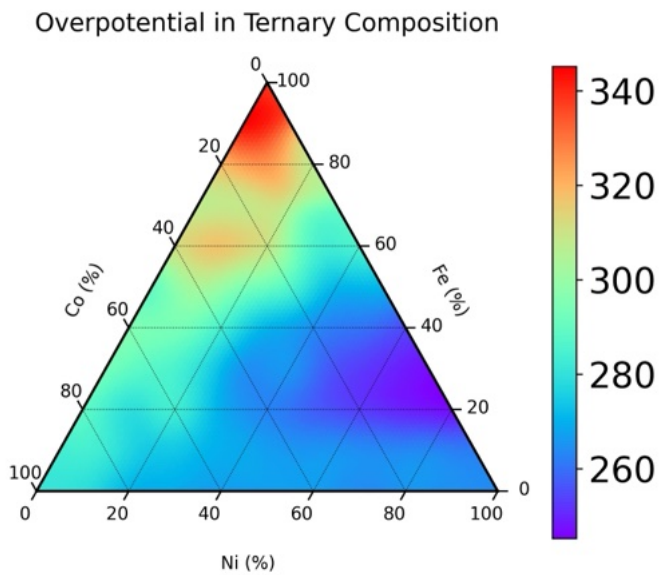
2. NiFeCo



Scatter Plot



Nearest Neighbor Interpolation

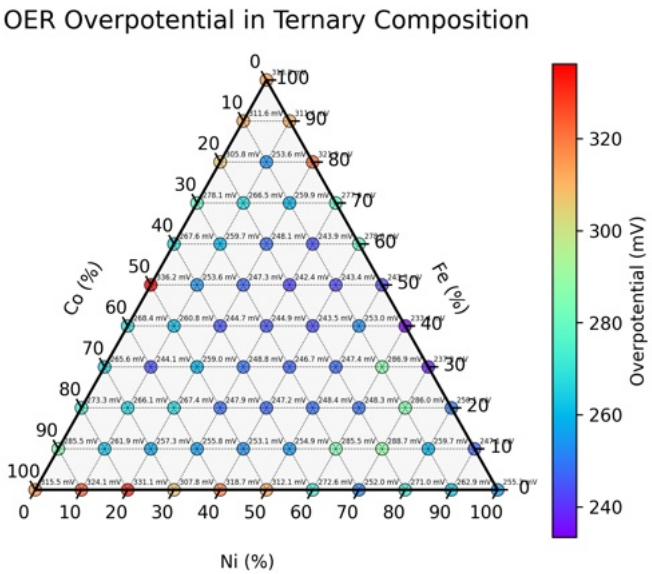


Radial Basis Function Interpolation

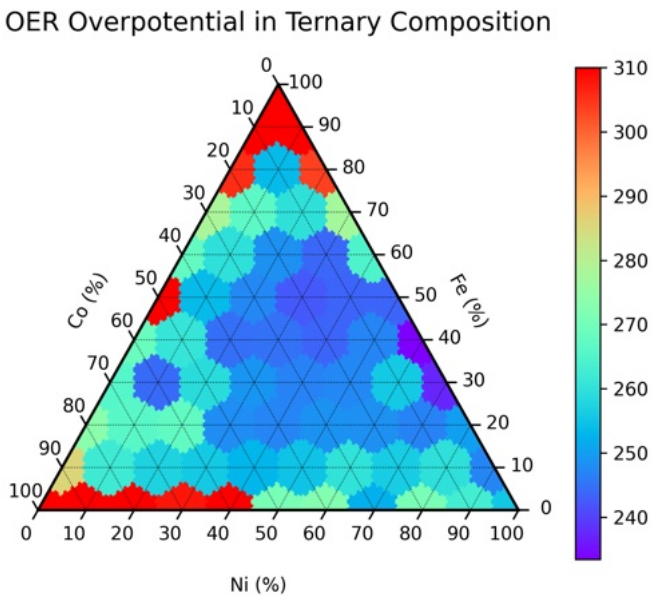
NFC_full

Ternary metals

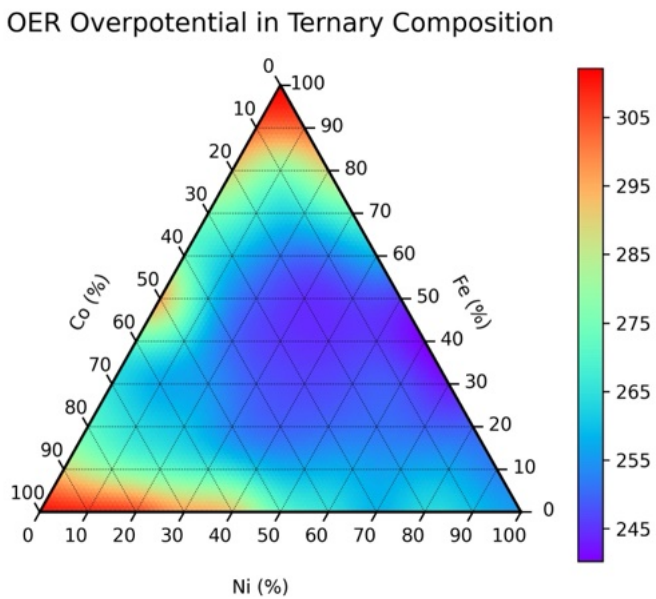
2. NiFeCo



Scatter Plot



Nearest Neighbor Interpolation

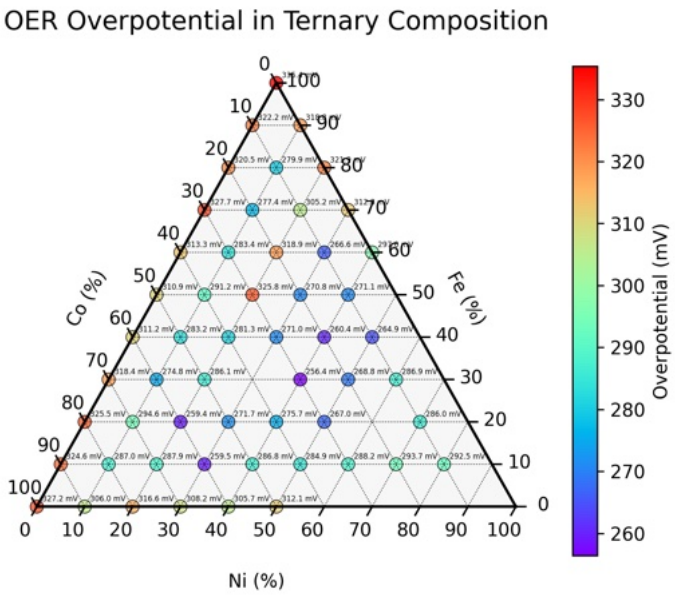


Radial Basis Function Interpolation

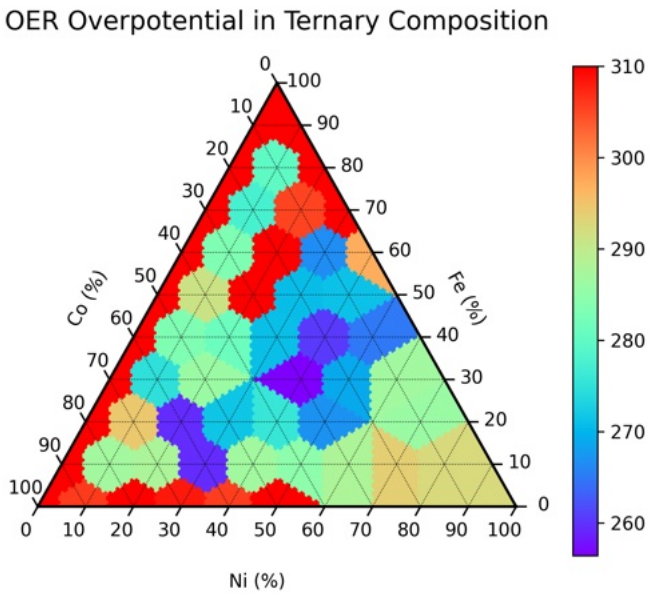
NFC_full

Ternary metals

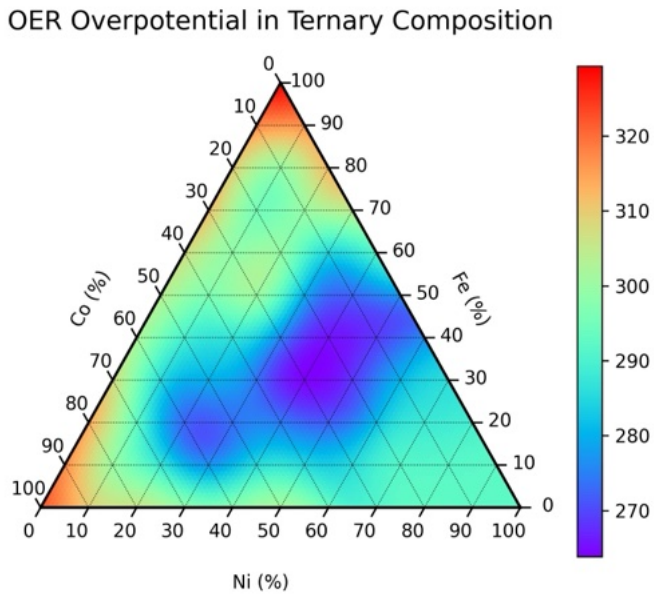
2. NiFeCo



Scatter Plot



Nearest Neighbor Interpolation



Radial Basis Function Interpolation

NFC_full

Outline

1/ Background Introduction

2/ Automatic electrochemical catalysts screening system design

3/ System optimization

4/ Catalysts screening for the oxygen and hydrogen evolution reaction

5/ Future plan

Future Plan

- Run experiments for quarternary metals like NiMoFeCo and NiMoFeP.
- Integrate machine learning models like bayesian optimization to quickly converge to the best ratios in complex spaces like quarternary metals.
- Use computer vision to automatically calibrate the robot to its workspace with the help of cleverly placed position stickers like apriltags.

Automation Procedure

- Step #1: Solution mixing:
  - The system can programmatically mix any number of metal ion solutions (2, 3, 4 components) at any desired ratio.
  - A robotic arm picks up solutions from large stock reservoirs and distributes them into deposition tubes. Currently, we support up to 11 tubes per batch.
  - The pipette tip is automatically cleaned between each solution transfer to avoid cross-contamination.

- Step #2: Catalyst deposition:
  - Electrode setup:
    - We use stainless steel mesh as the working electrode (WE), which is cleaned with acid before each experiment.
    - The electrode holder integrates a working electrode (WE), a fixed reference electrode (RE, Ag/AgCl), and a counter electrode (CE, Pt wire).
    - During experiments, only the working electrode (WE) is replaced between tests

Automation Procedure

- Catalyst deposition procedure:
  - WE will be pick up first, rinse, move to 1 of 11 deposition solution tube, perform deposition (10~20 mins), rinse again, and take picture, and go to evaluation, after evaluation, the WE will be dumped, and start a new WE;
  - Deposition data (current and voltage) will be recorded and saved;
  - We use CHI for the deposition;
- Step #3: Catalyst evaluation procedure;
  - After deposition, the electrode will be immersed in 1 M KOH for OER evaluation:
  - We use python to control the CHI (a potentiostat) for EC measurements;
  - Activation process: activate the catalysts by slow CV scans for 10 cycles in KOH;
  - Measure the impedance for iR correction;
  - Perform the OER test and data (CV scan) will be saved automatically;
  - iR correction will be automatically processed;
  - Overpotential will be extracted and plotted;