The role of Fe incorporation in the oxygen evolution reaction electrocatalysts

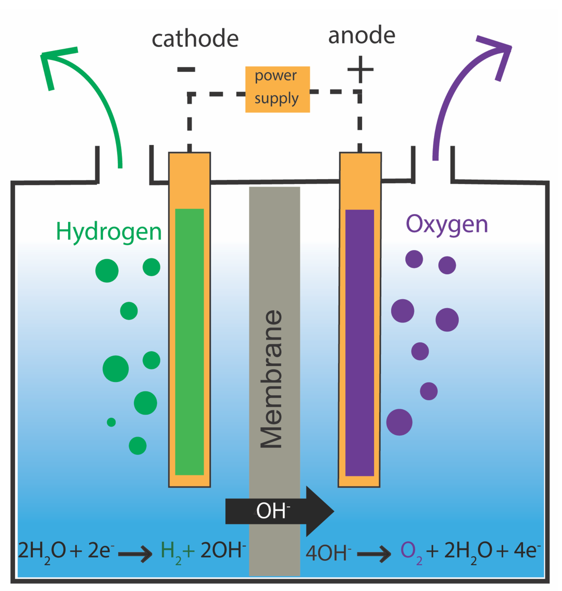
Renee D. Weissberger, Amanda J. Ritz, Isabella A. Bertini, Geoffrey F. Strouse, Robert A. Lazenby

Florida State University, Department of Chemistry & Biochemistry

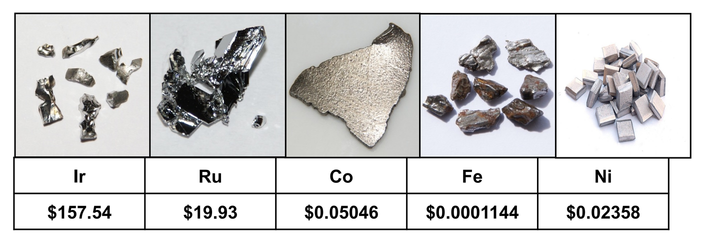
Introduction

Electrochemical water splitting, also known as electrolysis of water is an alternative method for the viable production of clean hydrogen, consisting of the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER).

- Alkaline water electrolyzer used for the production of oxygen and hydrogen gas.

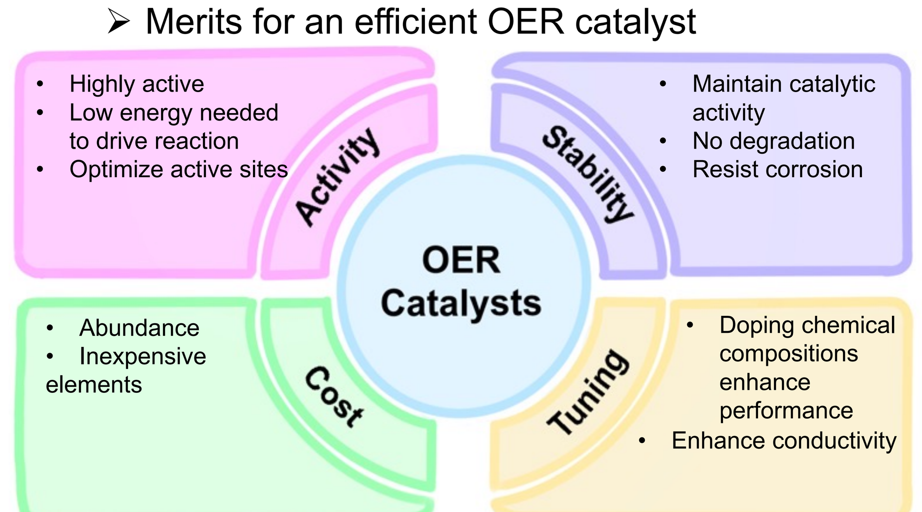


- Types of OER catalysts



- Layered double hydroxides (LDH)
- Oxides
- Non-oxides

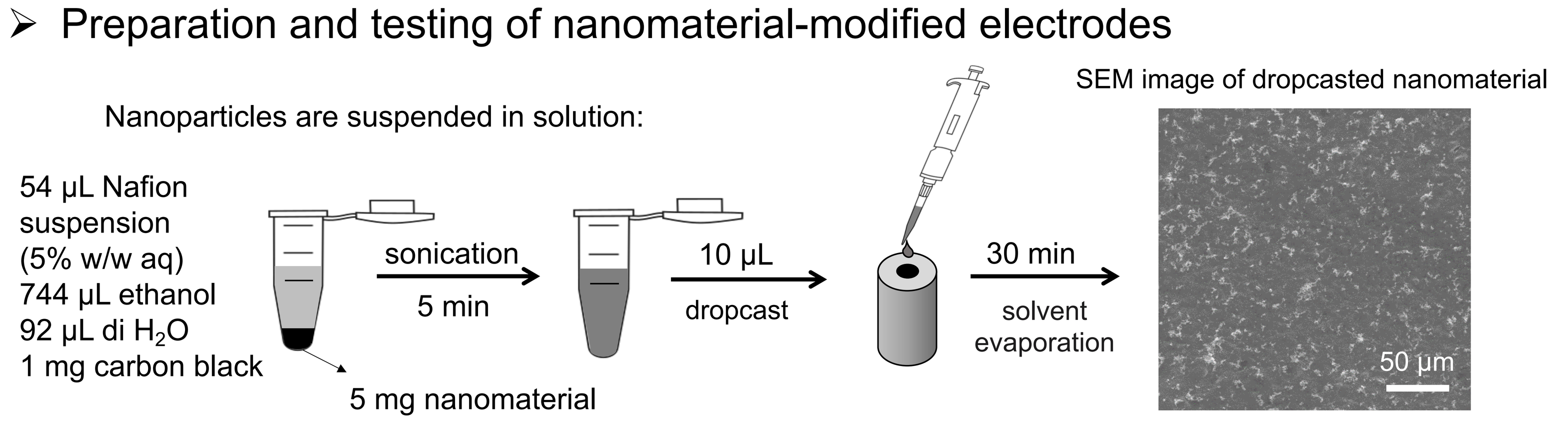
- Merits for an efficient OER catalyst



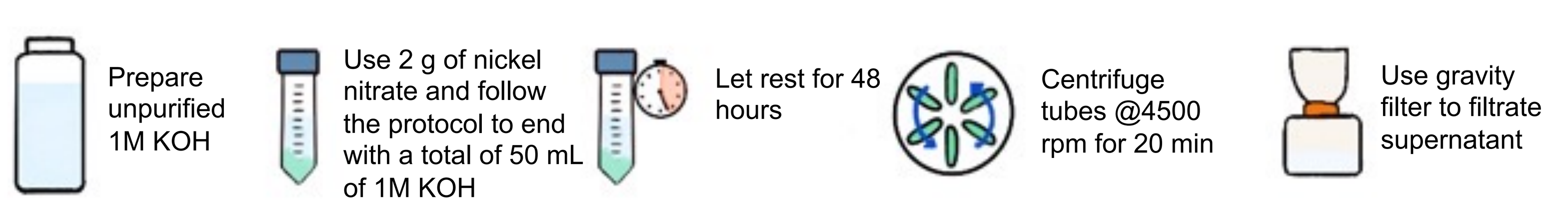
- Project Aims
  - Analyze long-term electrochemical stability of mono- and multi-metallic carbides to understand the complex effects of Fe in non-oxide-based catalysts.
  - Demonstrated the impact Fe has on initial OER activity enhancement and long-term electrochemical stability.

Electrochemical testing of nanocarbides

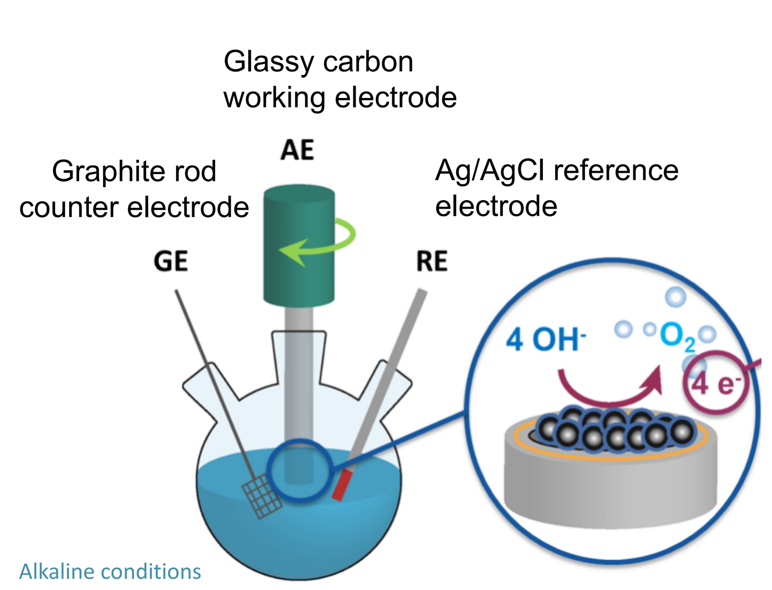
- Preparation and testing of nanomaterial-modified electrodes



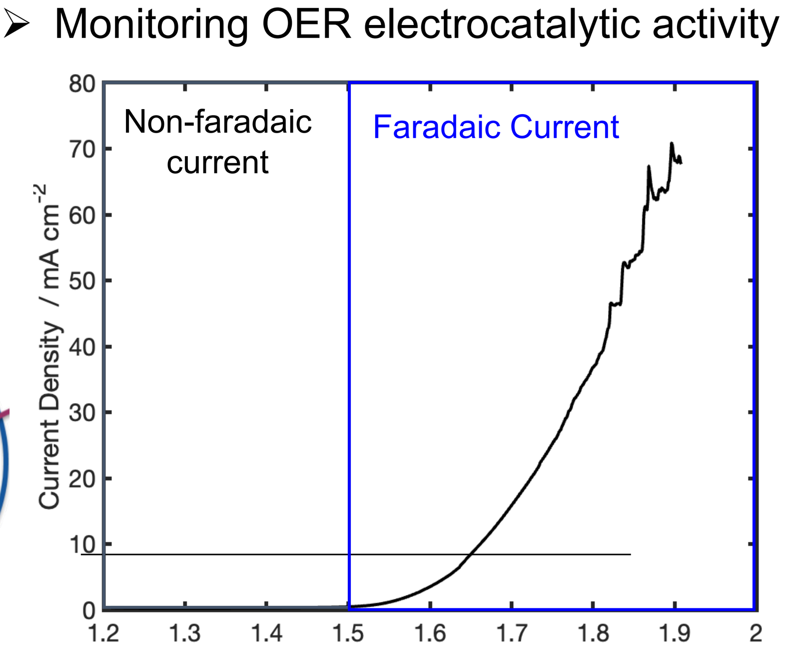
- Preparation of Fe-purified electrolyte[1]



- Electrode Setup



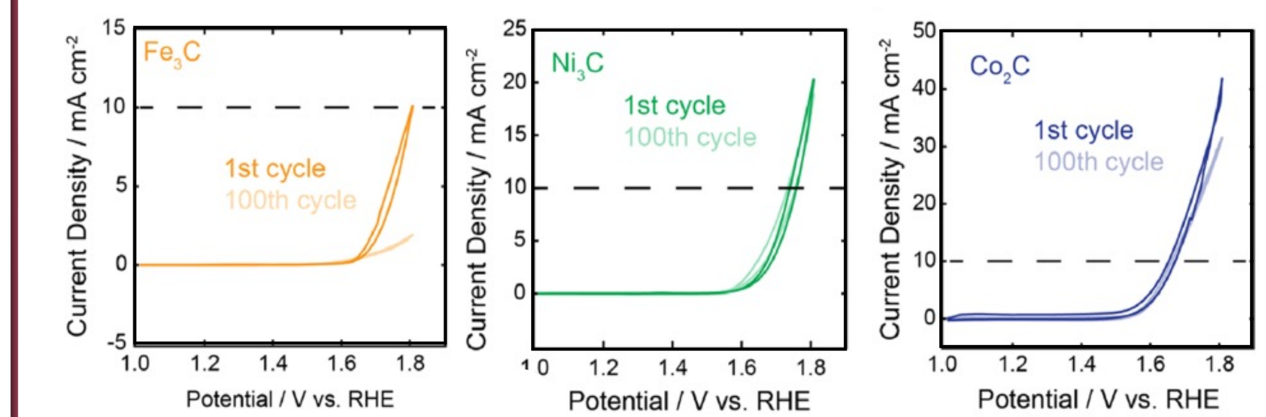
- Monitoring OER electrocatalytic activity



Electrochemical performance of OER catalysts

Monometallic (Fe, Ni, Co) carbides: OER electrocatalytic performance

- The electrochemical stability of Fe_3C, Co_2C, and Ni_3C was evaluated through repetitive cyclic voltammetry measurements conducted over 100 cycles.[2] The first and final CV cycles were compared to assess any changes over time.

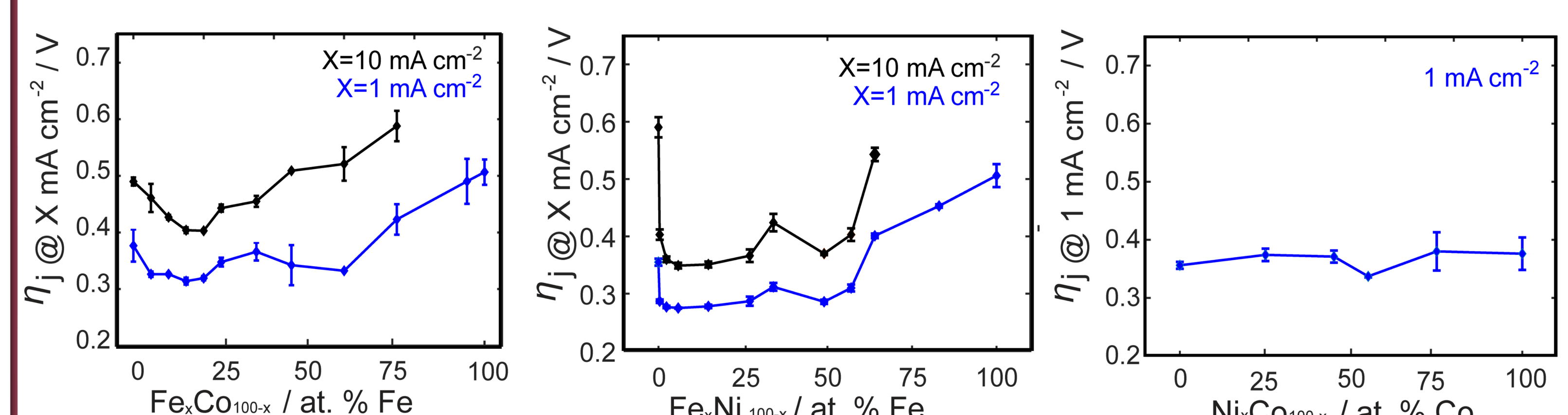


- The electrocatalytic activity of monometallic carbides followed the order Fe < Ni < Co

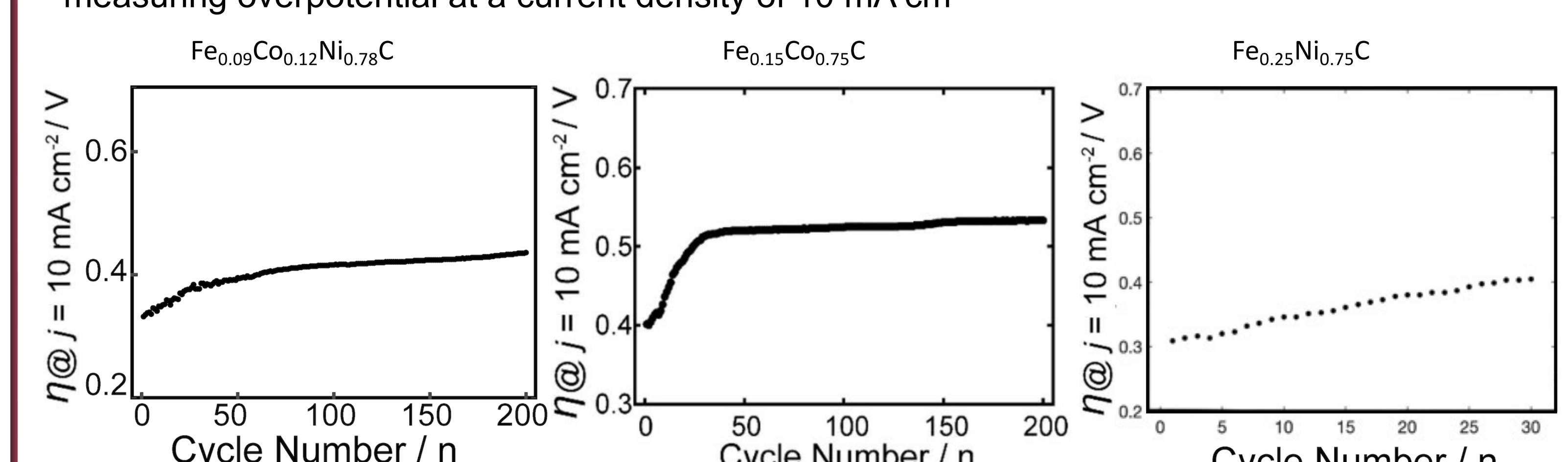
Bimetallic nanocarbides: OER electrocatalytic performance

Transition-metal (TM) doped bimetallic catalysts can be utilized for tuning changes in its catalytic behavior.[3]

- Optimal Fe-content in bimetallic nanocarbides tunes electrocatalytic activity for OER



- Electrochemical stability measurements of selected Fe incorporated nanomaterials measuring overpotential at a current density of 10 mA cm-2

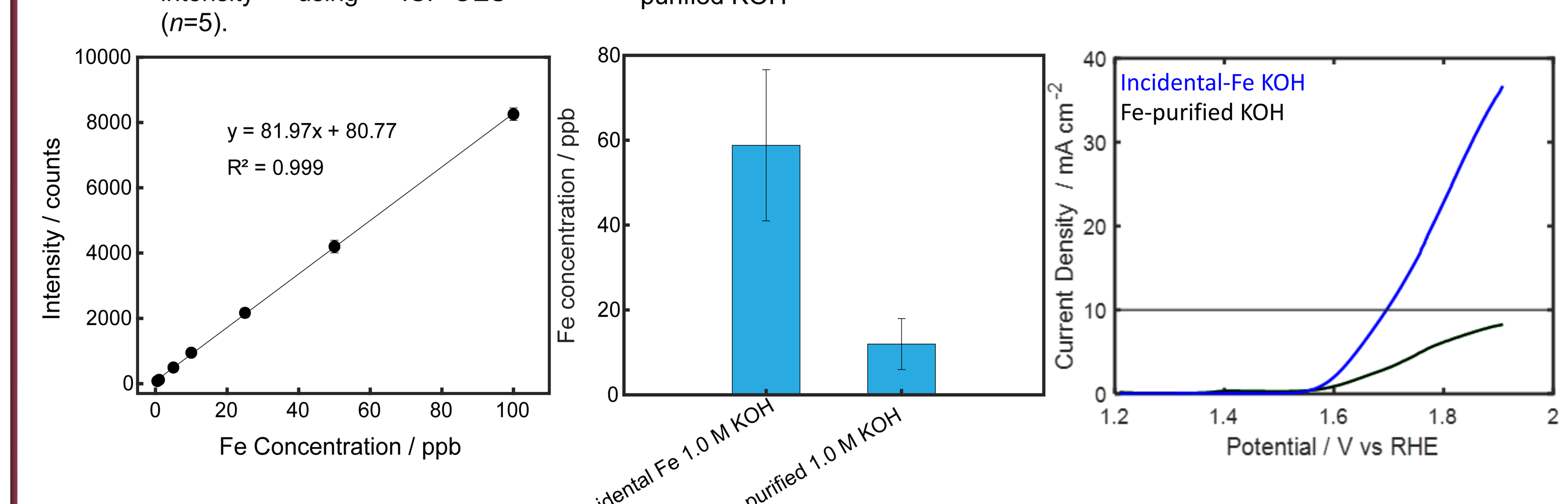


Effects of incidental Fe incorporation

- To understand the complex effects of Fe in non-oxide-based catalysts, Fe-purified KOH and KOH containing trace amounts of Fe (incidental Fe KOH) were used to compare the electrochemical performance of carbides.

Using inductively coupled plasma-optical emission spectrometry (ICP-OES) to analyze the concentration of iron (Fe) in incidental Fe KOH and Fe-purified KOH.

- A calibration curve of Fe concentration (ppb) and signal intensity using ICP-OES (n=5).
- Incidental Fe KOH has a much higher Fe concentration than Fe-purified KOH
- CV cycles of NiC in incidental-Fe KOH and Fe-purified KOH

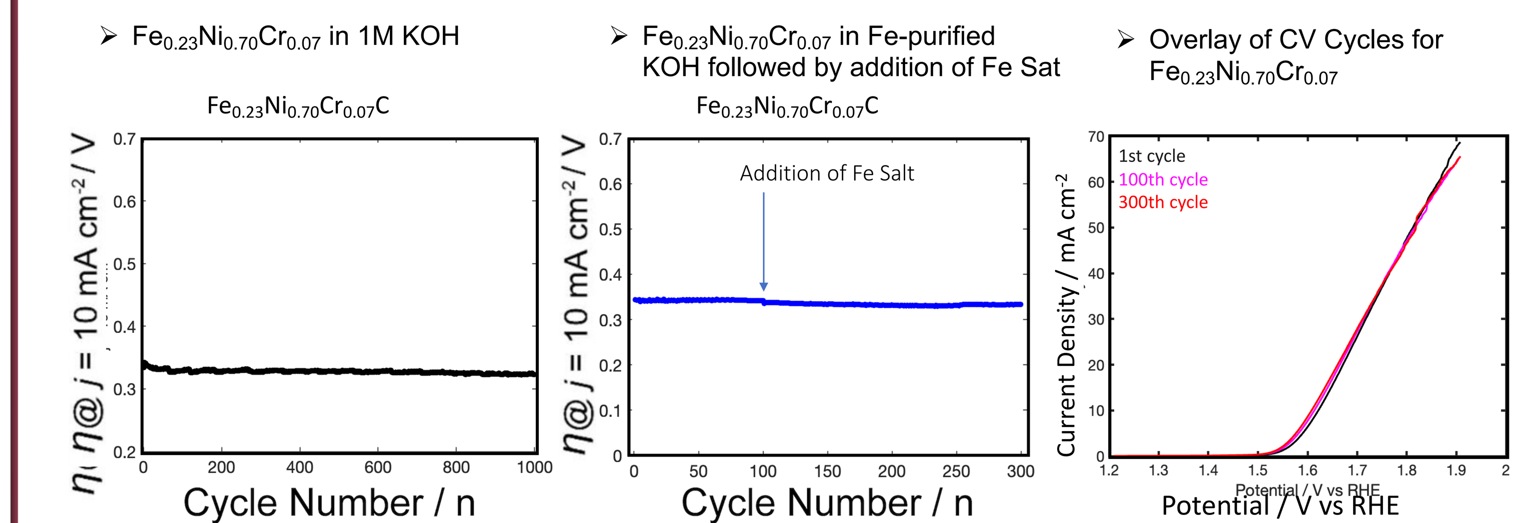


Effects of intentional Fe salt addition

Intentional addition of Fe salt into Fe-purified KOH

Electrochemical tests were conducted by introducing Fe salt into Fe-purified KOH as a method of understanding the role of intentional and incidental Fe incorporation on catalytic behavior.

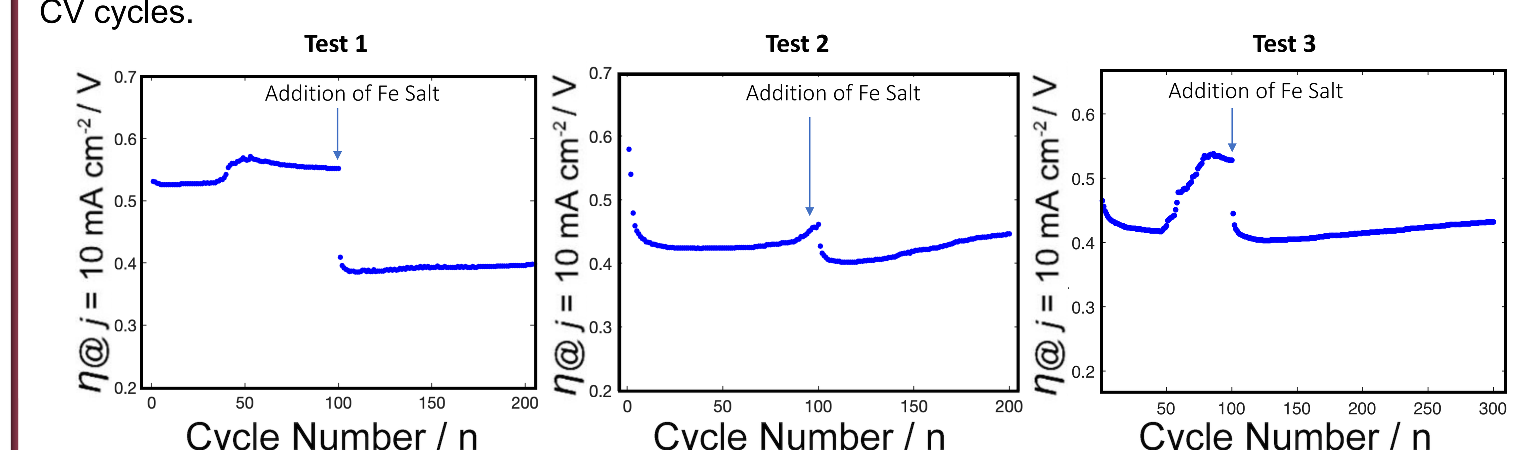
- $Fe_{0.23}Ni_{0.70}Cr_{0.07}C$: tailoring surface composition for longer-term electrochemical stability



This catalyst forms a protective Cr_2O_3 layer, which effectively prevents further degradation when exposed to Fe.

- NiC: addition of Fe impacts electrocatalytic stability

Long-term stability measurement of NiC in Fe-purified electrolyte followed by the addition of Fe Salt at 100 CV cycles.



Challenges:

- NiC nanomaterial does not remain on surface throughout the stability measurement.
- Inconsistent initial overpotentials.

Conclusions and future outlook

Conclusions:

- It was previously shown that Fe_3C exhibits poor catalytic activity and lacks long-term stability in comparison to Ni_3C and Co_2C.
- The intentional incorporation of Fe during synthesis aims to optimize catalytic activity for the OER; however, it leads to gradual catalytic degradation over time.
- Introducing Fe salt to the electrolyte during electrolysis enhances initial catalytic activity yet results in catalytic degradation.
- $Fe_{0.23}Ni_{0.70}Cr_{0.07}$ carbide remains robust in the absence and presence of Fe addition. It is likely that a protective Cr_2O_3 layer forms preventing long-term degradation of the catalyst.

Future Work:

- Utilizing ICP-OES to comprehend the dissolution of iron during OER.

References and Information

1. Marquez, R.; et. al, *ACS Energy Lett.* **2023**, 8, 1141−1146.
2. Nguyen, E.; Bertini, I.; Ritz, A.; et al., *Inorg. Chem.* **2022**, 61, *35*, 13836–13845.
3. Ritz, A.; Bertini, I.; Nguyen, E.; et al., *RSC Adv.* **2023**, *13*, 33413.

Group Website: https://www.chem.fsu.edu/~lazenby/

Follow us: @lazenbylab

Email: rdw21@fsu.edu