

# Electrochemical and In-situ Spectroscopic Investigation of Bifunctional Electrocatalysts for Rechargeable Metal-Air Batteries



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## PROJECT OVERVIEW

High entropy oxide (HEO) and metal sulfoselenide (MSSe) catalysts are promising electrocatalysts for oxygen evolution (OER) and oxygen reduction (ORR) reactions—crucial for metal-air batteries. This project focuses on understanding how catalyst surfaces evolve under electrochemical conditions and how these changes impact activity and stability. Key goals include:

- **Tracking surface reconstruction and phase changes** during electrolysis
- **Identifying active sites** under applied potentials
- **Revealing reaction mechanisms and intermediate species** in OER/ORR

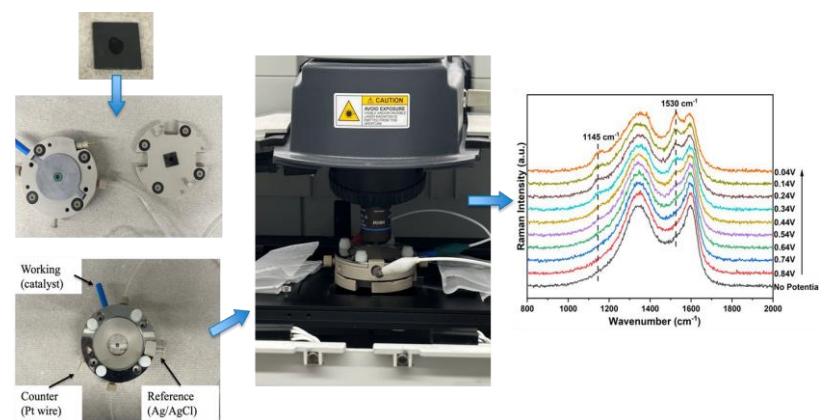
We combine electrochemical testing with advanced spectroscopic techniques:

- **Operando Raman spectroscopy** to monitor surface activation/evolution and intermediates in real time
- **In situ UV-vis spectroscopy** to probe electronic structure and band-gap changes
- **Ex situ XPS** to assess surface composition before and after reaction

### Long-term objectives:

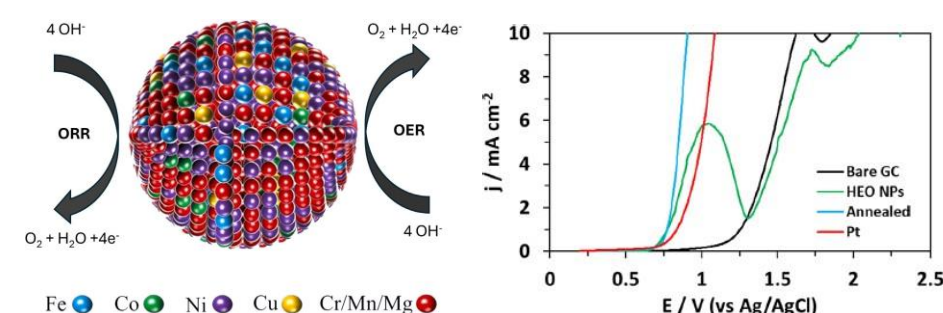
- Correlate applied potentials with dynamic surface chemistry and reconstruction
- Uncover reaction intermediates and rate-limiting steps
- Guide rational design of efficient and durable OER/ORR catalysts

## IN-SITU RAMAN STUDY



In-situ Raman spectroscopy will monitor phase transitions, defect formation, and surface chemical species in real time during electrochemical processes. Catalysts will be mounted on a commercial flow-type in-situ cell (see above). Raman spectra recorded during ORR are also shown above.

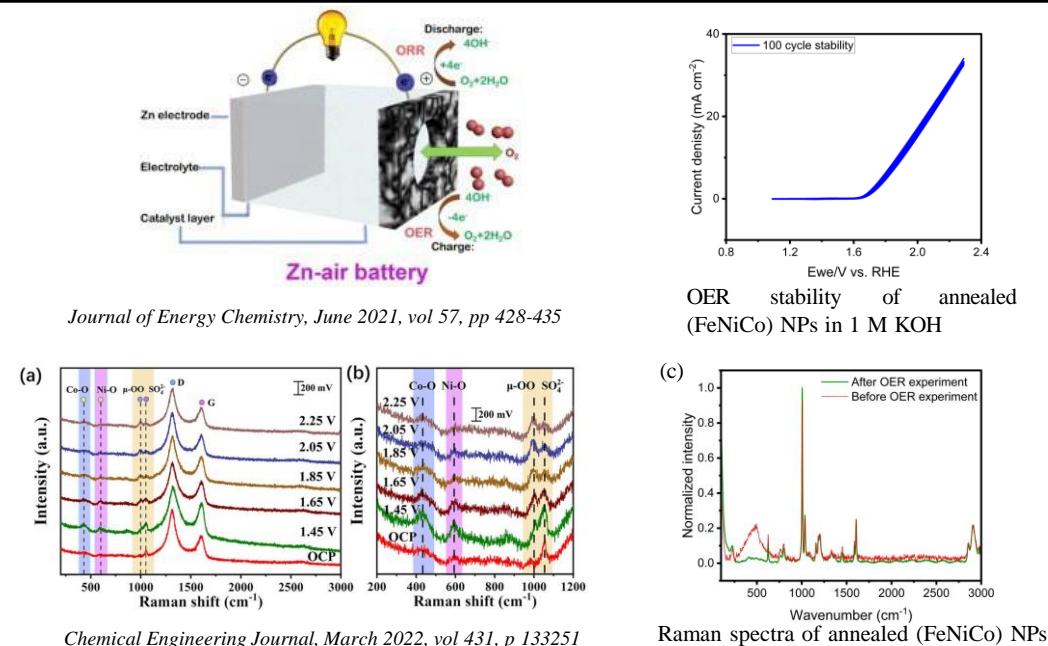
## HIGH ENTROPY ALLOY OXIDES



*Colloids and Surfaces A: Physicochemical and Engineering Aspects*, March 2025, vol 709, p 136106

FeNiMnCrCo high-entropy oxides function as effective bifunctional catalysts for both OER and ORR. First, a complex five element amorphous FeNiCoCrMn HEO was formed by electrodeposition from a nanodroplet emulsion, and this amorphous oxide phase is then thermally reduced at 570–600 °C to yield crystalline FeNiCo alloy nanoparticles with a separate CrMnOx cophase.<sup>1</sup> The FeNiCo nanoparticles demonstrate excellent electrocatalytic activity for OER and good stability in alkaline conditions.

Evaluation of the OER for the as made HEO NPs, the annealed (FeNiCo) NPs, bare GC, and Pt foil in 0.1 M KOH solution.

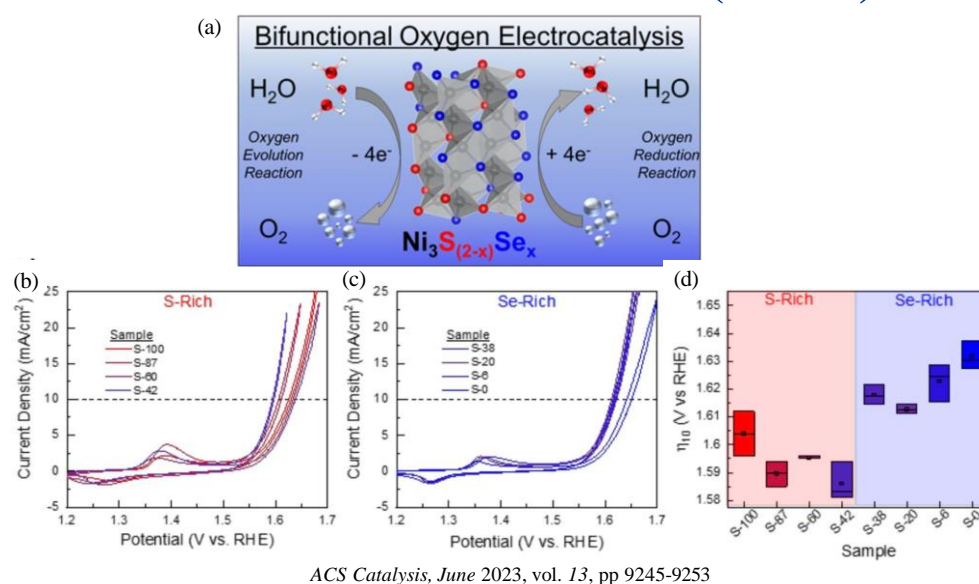


*Journal of Energy Chemistry*, June 2021, vol 57, pp 428-435

(a, b) In situ Raman spectro-electrochemical study of FeCoNiRu HEO NPs in 0.5 M H<sub>2</sub>SO<sub>4</sub> as the potential increases from 0 to 2.25 V (vs. RHE) (Zhu et al). (c) Preliminary Raman spectra of FeNiMnCrCo HEOs

In-situ Raman spectroscopy enables real-time monitoring of key OER intermediates (\*OH, \*O, and \*OOH) on HEOs, offering valuable insights into reaction pathways.<sup>2</sup> Preliminary Raman spectra reveal microstructural features and suggest the presence of organic species, likely originating from ligands in emulsion nanodroplets. This in-situ spectroscopy will aid in identifying active sites, rate-determining steps, and surface/structural changes, guiding the discovery of optimal HEO composition for enhanced activity.

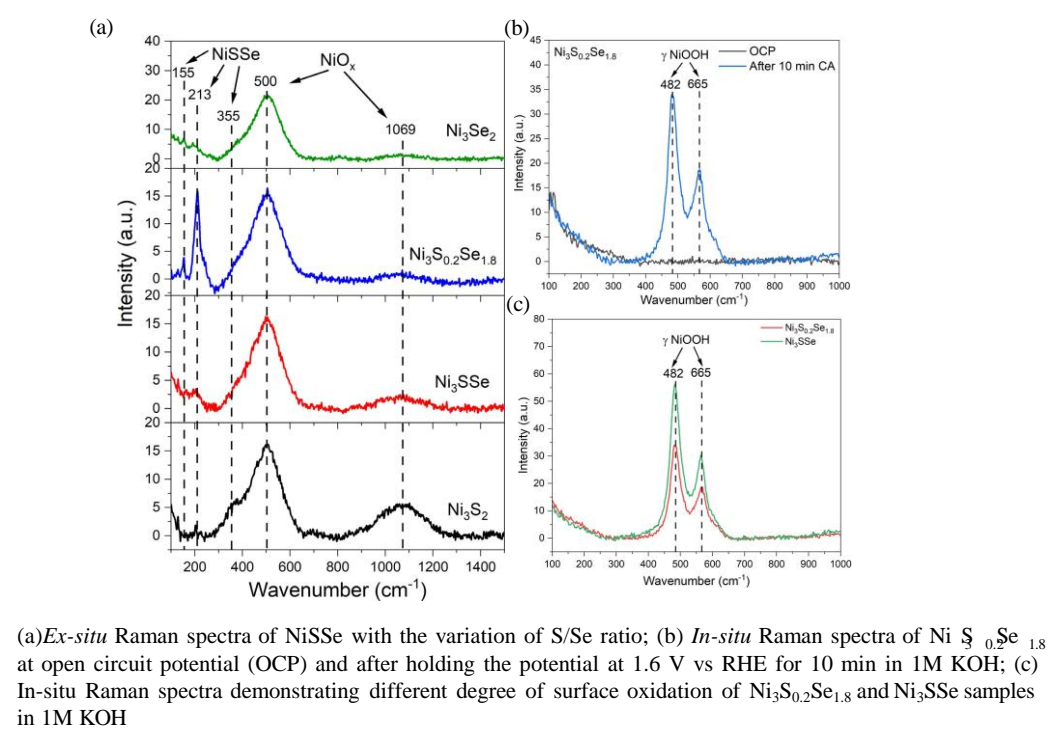
## NICKEL SULFO-SELENIDES (NiSSe)



*ACS Catalysis*, June 2023, vol. 13, pp 9245-9253

NiSSe with varying concentration of S/Se exhibiting (a) the role of bifunctional catalyst (OER/ORR); (b) OER activity of S rich and Se rich NiSSe in 1M KOH; (c) Average OER overpotential for NiSSe samples

Nickel sulfo-selenides (NiSSe) synthesized by SNL exhibit excellent activity for both OER and ORR.<sup>3</sup> Notably, Se-rich NiSSe demonstrates superior stability, outperforming Pt/C catalysts. The catalytic performance of NiSSe is highly sensitive to the S/Se ratio. Furthermore, research has demonstrated that S-rich nickel composites tend to oxidize to nickel (oxy)hydroxides under electrochemical conditions, which are highly active for OER. The optimal extent of oxidation is crucial for producing highly performing catalysts, that is presumably influenced by the S/Se ratio. This project will conduct real-time investigation of (1) phase and structural transformations/reconstructions and (2) surface chemical group formation during electrochemical processes.

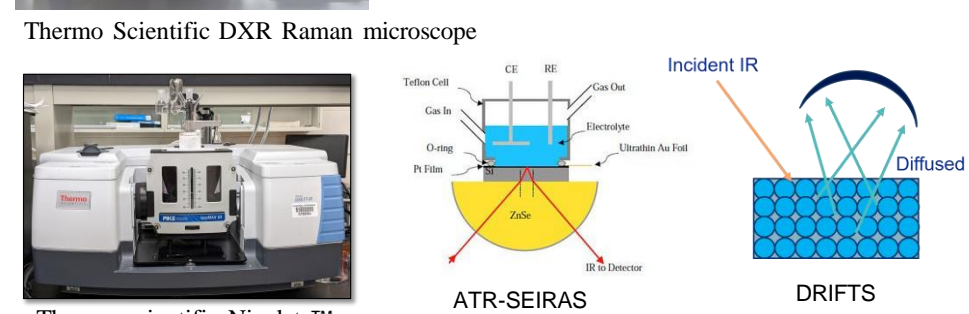


(a) Ex-situ Raman spectra of NiSSe with the variation of S/Se ratio; (b) In-situ Raman spectra of Ni<sub>3</sub>S<sub>2</sub>Se<sub>1.8</sub> at open circuit potential (OCP) and after holding the potential at 1.6 V vs RHE for 10 min in 1M KOH; (c) In-situ Raman spectra demonstrating different degree of surface oxidation of Ni<sub>3</sub>S<sub>2</sub>Se<sub>1.8</sub> and Ni<sub>3</sub>S<sub>2</sub>Se samples in 1M KOH

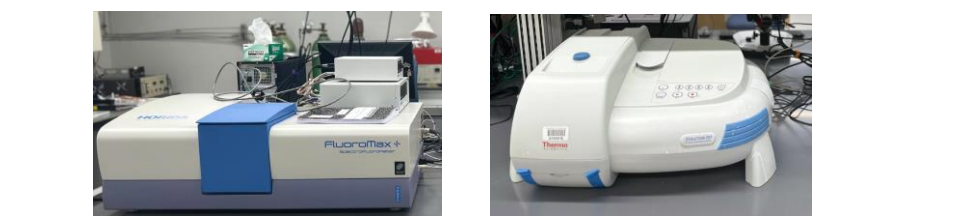
Raman spectra of NiSSe samples with varying S/Se ratios reveal the presence of nickel oxide (500 - 1069 cm<sup>-1</sup>),<sup>4</sup> along with sharp peaks in the range from 155 cm<sup>-1</sup> to 355 cm<sup>-1</sup> that are characteristic of NiSSe vibration.<sup>5,6</sup> Preliminary in-situ Raman spectra show pronounced peaks (482 and 565 cm<sup>-1</sup>), implying the structural transformation of NiSSe into nickel oxyhydroxides (NiOOH) while positive potential is applied.<sup>7</sup> This study also demonstrates that the degree of surface oxidation is significantly influenced by the S/Se ratio.

## LAB CAPABILITY

This Raman microscope is equipped with spectro-electrochemical cells for monitoring in-situ structural and surface changes.



Thermo scientific Nicolet™ ISSO FT-IR Spectrometer  
Journal of the American Chemical Society, May 2006, vol 128, pp 7408-7409  
Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) and surface enhanced infrared absorption spectroscopy (SEIRAS) will monitor the binding of adsorbate molecules on active sites.



Horiba Fluoromax 4C (left): steady-state and time-resolved photoluminescence (PL), Thermo UV-VIS absorption spectrometer (right): in-situ spectro-electrochemistry



Differential electrochemical mass spectrometry (DEMS) instrument (Hidden Analytical) can be used for mechanistic studies with isotope labeling.

## CONCLUSIONS AND FUTURE STEPS

We have successfully performed electrochemical and Raman spectroscopic characterizations of high entropy alloy oxides and nickel sulfo-selenides. Preliminary results reveal the structure and surface chemistry of the catalysts. More thorough spectroscopic analyses (Raman, SEIRAS, in-situ UV-VIS) will be conducted, and results will be correlated with electrochemical activity and stability of catalysts.

## ACKNOWLEDGEMENT



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## REFERENCES

(1) *Langmuir*, 38(5), 1923–1928; (2) *Chemical Engineering Journal* 2022, 431, 133251; (3) *ACS Catalysis* 2023 13 (13), 9245-9253; (4) *Green Chemistry Letters and Reviews*, 14(3), 444–454; (5) *The Journal of Physical Chemistry C* 2007 111 (49), 17997-18000; (6) *Journal of Alloys and Compounds*, 2021, 855; (7) *Angew. Chem. Int. Ed.* 2019, 58, 12999.