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

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PROJECT PROFILE

Topic: Zinc and Lead Batteries | Vertical: Material and System Innovation | Strategic Pathway : Grow, optimize
Project start and finish: FY25-FY26

PROBLEM

Metal sulfoselenides (MSSe) and high-entropy alloys (HEAs) exhibit promising bifunctional activity for the Oxygen Evolution Reaction (OER) and Oxygen Reduction Reaction (ORR) in rechargeable metal–air batteries.

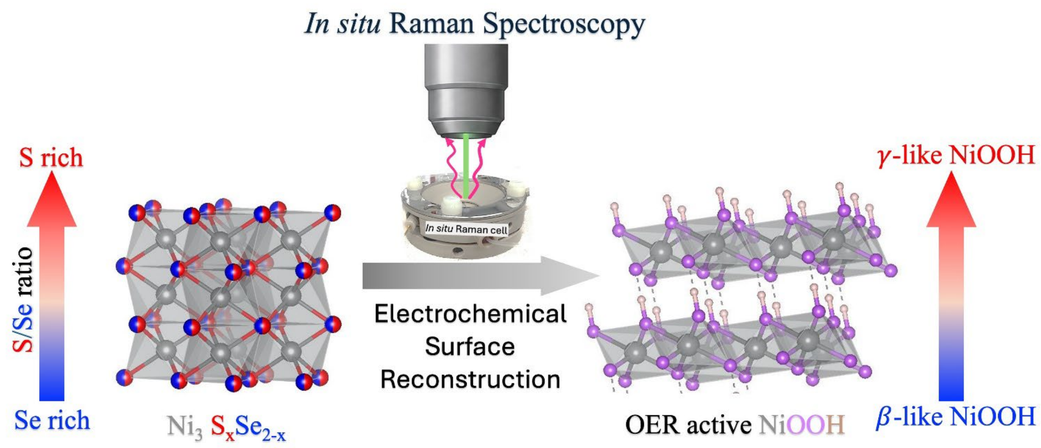
However, under electrochemical conditions, catalyst surfaces undergo dynamic surface change and phase transformation, affecting electrochemical reactivity and stability.[1]

The relationship between these transformations—including the formation of distinct active phases and their reversibility—and electrocatalytic performance remains poorly understood.

Key Goals:
- Understand how pre-catalyst composition and active phase formation through surface reconstruction affect the observed catalytic activity
- Reveal composition-dependent evolution of oxyhydroxide phases during electrochemical oxidation
- Investigating the reversibility and stability of reconstructed phases under applied potentials
- Correlating dynamic structural evolution with electrocatalytic performance to guide catalyst design

APPROACH

We are conducting a systematic *in situ* Raman spectroscopic investigation of compositionally tuned $Ni_3S_xSe_{2-x}$ (x = 0–2) and HEA catalysts during OER to understand how pre-catalyst composition influences surface reconstruction, phase evolution, reversibility, and electrocatalytic performance. Electrochemical measurements were integrated with in situ and ex situ spectroscopic techniques to monitor catalyst evolution under reaction conditions:



✓ $Ni_3S_xSe_{2-x}$ exhibits dynamic formation and reduction of NiOOH during potential cycling
✓ S/Se Ratio governs both the phase evolution of NiOOH and the corresponding OER activity

RESULTS – *In situ* Raman study on NiSSe

Key findings:
- *In situ* Raman spectra reveal the emergence of two bands (~480 and ~560 cm^{-1}) upon applying oxidation potentials, indicating the surface change from NiSSe to NiOOH during OER with no detectable formation of $Ni(OH)_2$ as an intermediate phase.
- *Detailed* peak fitting analysis demonstrates that the S/Se ratio in the precatalysts governs NiOOH phase and subsequent phase evolution. S-rich compositions favor more γ-like structures, whereas Se-rich compositions promote β-like phases, highlighting composition-dependent structural transformation.
- S-rich compositions result in higher OER activity and enhanced phase stability than Se-rich compositions. The addition of Se to S-rich compositions (S70 and S90) yields optimal OER performance by balancing the higher conductivity of β-like phases with the greater intrinsic activity of γ-like phases.
- Upon reversing the potential toward OCP, NiOOH features diminish while Ni–S and Ni–Se vibrations reappear, demonstrating reversible structural evolution and dynamic transformation of oxyhydroxide phases.

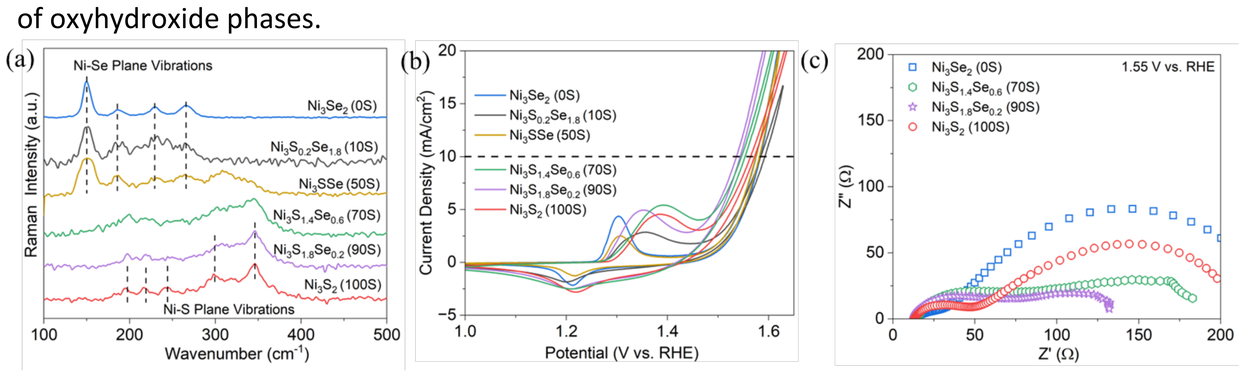


Figure 1. (a) Ex situ Raman spectra confirm Se and S incorporation in NiSSe. (b) CVs for the OER in 1 M KOH and (c) EIS results in 1M KOH indicating the oxidation process and OER activity are strongly affected by S/Se ratio.

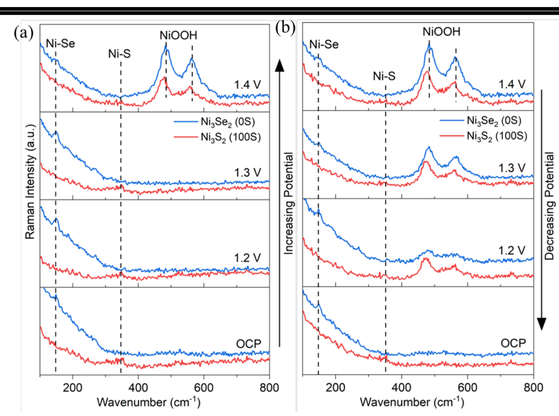


Figure 2. *In situ* potential-dependent Raman spectra showing (a) structural evolution and (b) structural recovery of NiOOH from Ni_3S_2 and Ni_3Se_2 pre-catalyst.

- In situ Raman spectra of Ni_3Se_2 and Ni_3S_2 at 1.4 V vs. RHE show the peaks ~ 480 and 560 cm^{-1}, indicating NiOOH formation.
- NiOOH Raman peak shifts at 1.4 V vs. RHE, from 476 and 557 cm^{-1} for Ni_3S_2 to 485 and 564 cm^{-1} for Ni_3Se_2, indicating the formation of distinct γ-like and β-like NiOOH phases.
- Upon applying a reductive potential, the NiOOH bands progressively diminish, while the Ni-S and Ni-Se peaks re-emerge, indicating dynamic behavior.

Mixed S/Se composition may enhance OER performance by balancing higher conductivity β-like phases with greater intrinsic activity of γ-like phases.
- S-rich NiSSe pre-catalysts → disordered, expanded highly OER active γ-like NiOOH phase
- Se-rich NiSSe pre-catalysts → more ordered, highly conductive β-like NiOOH phase

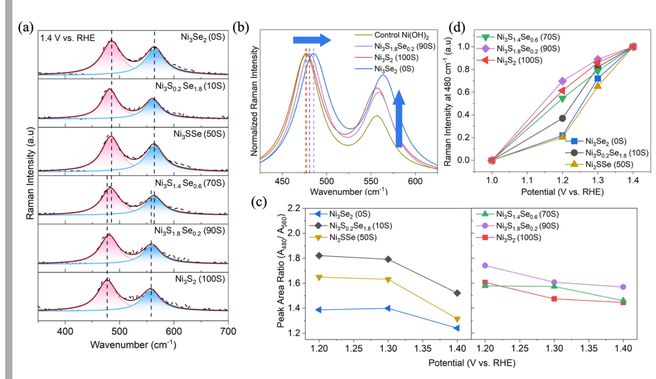


Figure 3. (a) *In situ* Raman spectra at 1.4 V with varying S/Se ratio (b) Normalized Raman spectra at 1.4 V compared with $Ni(OH)_2$-derived NiOOH (c) peak area ratio (A_{480}/A_{560}) with applied potential, (d) reversibility of NiSSe reconstruction.

Lorentzian fitted Raman spectral analysis of *in-situ* formed NiOOH reveal that spectral positions and peak area ratios (A_{480}/A_{560}) are sensitive to S/Se ratio:

S-rich NiSSe pre-catalysts → γ-like NiOOH due to:
- Low-wavenumber NiOOH peaks,
- High peak area (A_{480}/A_{560}) ratios at 1.4 V vs. RHE,
- The change in potential-dependent peak area ratio (A_{480}/A_{560}) shows smaller variations with phase stability

Se-rich NiSSe pre-catalysts → β-like NiOOH due to:
- High-wavenumber NiOOH peaks,
- Low peak area (A_{480}/A_{560}) ratios at 1.4 V vs. RHE,
- The change in potential-dependent peak area ratio (A_{480}/A_{560}) shows greater structural rearrangement

$Ni(OH)_2$ control converts to primarily γ-NiOOH but shows poor OER performance(not shown here) due to high electrical resistance,
- Highlights importance of balancing high activity (γ-phase) and electrical conductivity (β-phase).

RESULTS - HIGH ENTROPY ALLOY NANOPARTICLES

New FeNiMnCrCo HEA catalysts supported on carbon nanotubes (CNTs) were synthesized using a similar approach to that described in the previous article.[2] The multicomponent composition enables tunable electronic structures and synergistic interactions among constituent elements.[3] This hybrid HEA/CNT catalyst exhibits promising bifunctional electrocatalytic activity toward both OER and ORR. HEAs, indicated by weak bands in the 450–650 cm^{-1} region. During OER, the emergence of peaks at ~470 and ~550 cm^{-1} suggests the formation of oxyhydroxide phases which diminish at the potential is lowered back to OCP.

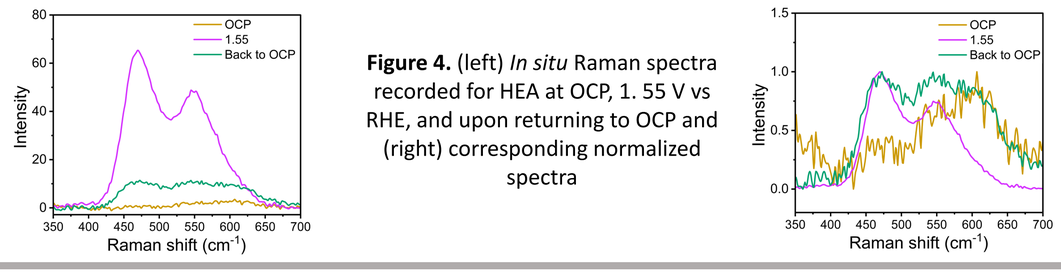


Figure 4. (left) *In situ* Raman spectra recorded for HEA at OCP, 1. 55 V vs RHE, and upon returning to OCP and (right) corresponding normalized spectra

CONCLUSIONS & IMPACT

In situ Raman spectroscopic studies of NiSSe determined composition-dependent surface change, dynamic phase evolution, reversibility, and their influence on electrocatalytic performance during OER. ***This information will aid in the battery construction and help ensure compositions are phase stable and active will be used***.

Impact:

1. Paper: Sharma, P.; Chandrasiri, N.; Espano, J. B.; Thapa, A.; Lambert, T.; Percival, S. J.; Wygant, B. R.; Kim, D. Y.; "In situ Raman Spectroscopic Studies of Composition-tuned Nickel Sulfoselenides for the Oxygen Evolution Reaction". *Under Review, ACS Catalysis*.

FUTURE DIRECTIONS

Future work will focus on operando spectroscopic investigations of other compositions of NiSSe and HEA catalysts during bifunctional OER/ORR processes to elucidate surface evolution, phase transformation, reversibility, and structure–activity relationships governing electrocatalytic performance.
- *FeSSe composition effects on activity.*
- *HEA NPs ORR reactive sites (MnOx, Cobalt sites, etc.)*
- *Effect of continued ORR/OER switching on catalyst structure.*

ACKNOWLEDGEMENT

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(1) *ACS Catalysis* **2023,** *13* (13), 9245-9253;
(2) *Small* **2024**, *20*, 2308756;
(3) *Langmuir* **2022,** 38(5), 1923–1928