

Effect of the S/Se exchange on the HER and CO₂RR activity of Fe/Ni-Pentlandites

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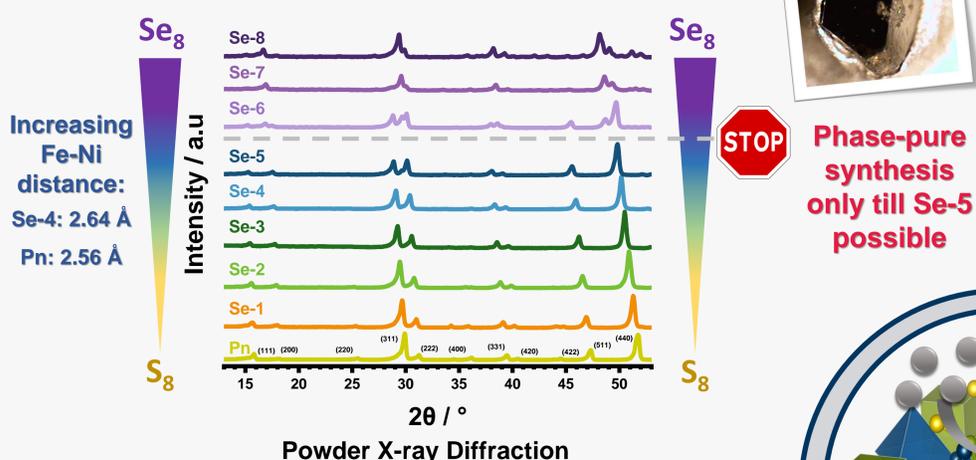
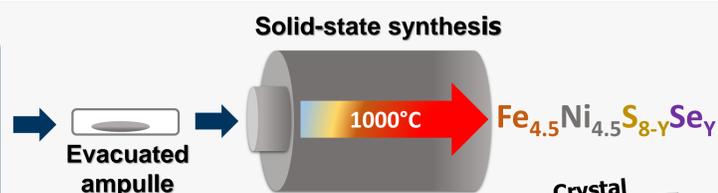
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INTRODUCTION

The electrochemical water splitting and electrocatalytic reduction of excess CO₂ are attractive strategies towards the mitigation of pollution by anthropogenic CO₂ emissions as well as production of bulk chemicals and fuels by renewables. Currently, bulk electrocatalysts are either financially unfavorable or suffer from low stability and selectivity, thus decelerating the large-scale application of these technologies.^[1] The bimetallic sulfide Fe_{4.5}Ni_{4.5}S₈ (pentlandite, Pn) was recently reported as a cheap and robust electrocatalyst for the electrochemical water splitting as well as for the CO₂ reduction with a solvent-dependent product selectivity.^{[2],[3]} Recent reports on MoS₂ and CoS₂ showed that monometallic sulfoselenides and selenides show higher catalytic activity for the hydrogen evolution reaction (HER) and the CO₂ reduction reaction (CO₂RR) than their sulfide counterparts.^[4] We thus investigated the effect of successive sulfur substitution with selenium on the pentlandite crystal lattice and subsequently on the electrocatalytic activity of the material towards the two reduction reactions. Herein, the successful synthesis and characterization of the seleno-pentlandites Fe_{4.5}Ni_{4.5}S_{8-y}Se_y (Y=1-5) as potential HER and CO₂ reducing catalysts is reported.

EXPANDING THE PENTLANDITE LATTICE

Pure elemental mixture:
4.5 eq. Fe
4.5 eq. Ni
8-Y eq. S
Y eq. Se

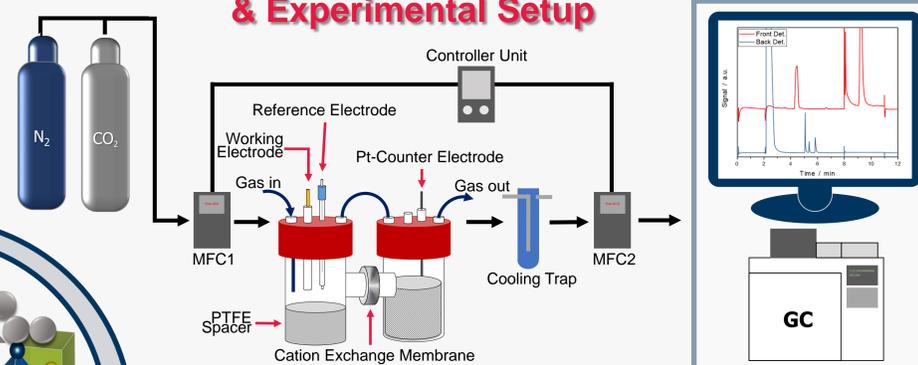


ELECTRODE PREPARATION & EXPERIMENTAL CONDITIONS



Straightforward Preparation

& Experimental Setup

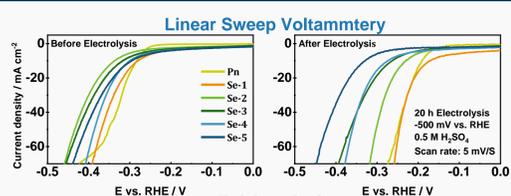


Conditions for the Electrochemical Reduction Experiments

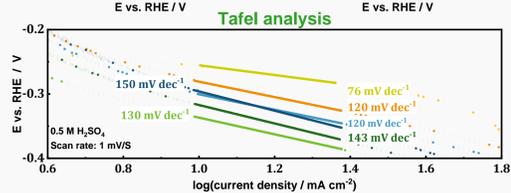
Temperature	22 °C
Pressure	1 bar
Volume	60 mL
Electrolyte (HER)	0.5 M H ₂ SO ₄
Electrolyte (CO ₂ RR)	0.1 M TBAPF ₆ in MeCN 24 – 30.000 ppm H ₂ O
Working electrode	Fe _{4.5} Ni _{4.5} S _{8-y} Se _Y
Reference electrode	Ag/AgCl
Counter electrode	Pt-mesh

HYDROGEN EVOLUTION REACTION

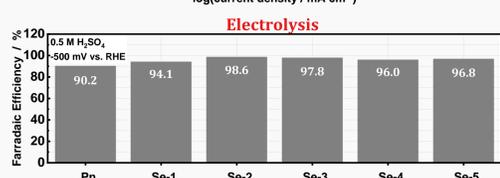
Se-1 shows the highest HER activity



Gradual decrease in proton-adsorption affinity



High faradaic efficiency in acidic media



Bifunctional catalysts

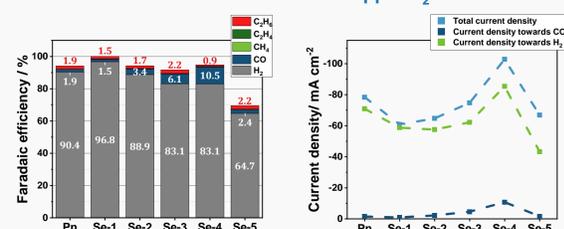
S/Se ratio controls selectivity for CO & H₂ generation

H⁺ concentration determines product composition

CO₂ REDUCTION REACTION

Electrolysis at -1.8 V vs. NHE in:

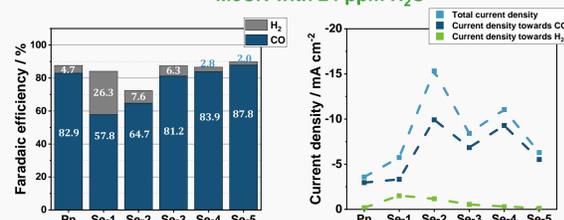
MeCN with 30.000 ppm H₂O



CO production increases with Se content

Se-4 shows the highest CO₂RR activity

MeCN with 24 ppm H₂O



Water content determines the product composition

CONCLUSION

We herein present seleno-analogues of the Fe/Ni-pentlandite as bifunctional catalysts for the HER and CO₂RR. Under acidic HER conditions, the sulfoselenide Fe_{4.5}Ni_{4.5}S₇Se₁ outperforms the reference material, whereas higher selenium-equivalents (Y=2-5) gradually lower the HER activity of the materials. In contrast to the decreased HER activity, the incorporation of higher selenium equivalents, gradually favors CO₂RR in organic solvents, with Fe_{4.5}Ni_{4.5}S₄Se₄ showing the highest activity for CO formation. The increased activity is attributed to the increase of interatomic distances in the enlarged crystal lattice and to a synergistic effect between the two chalcogens in the catalytic active center. This work offers an insight on the tunability of the pentlandite system based electrocatalysts, for the HER and CO₂RR via S/Se substitution.

References [1] J. Qiao, Y. Liu, F. Hong, J. Zhang, *Chemical Society Reviews* **2014**, 43, 631–675.

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[4] M. Smialkowski, D. Siegmund, K. Pellumbi, L. Hensgen, H. Antoni, M. Muhler, U.-P. Apfel, *Chemical Science* **2019**, 10, 8792 – 8795.

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