In situ metal incorporation vs. compounded doping of nickel (hydr)oxides

Effect on the oxygen evolution reaction

Konstantin Rücker, Dereje H. Taffa, Elliot Brim, Darius Hayes, Omeshwari Bisen, Marcel Risch, Corinna Harms, Ryan M. Richards, Michael Wark, Julian Lorenz

20th Aug. 2024, ISE 75th Annual Meeting Montreal

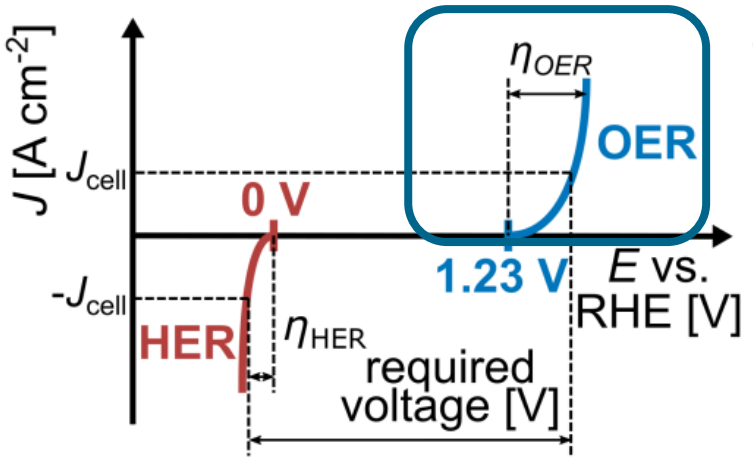
DLR

In situ metal incorporation vs. compounded doping

Effect on the oxygen evolution reaction

Overall Picture

Water electrolysis



- Oxygen evolution reaction (OER) in 0.1 M KOH alkaline media for AEMWE application

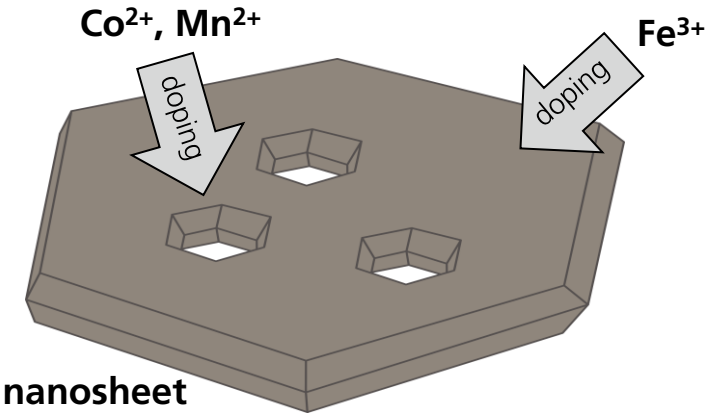
Outline

Compounded doping of Co and Mn into faceted NiO(111)

- Phase pure doping with microwave-assisted synthesis

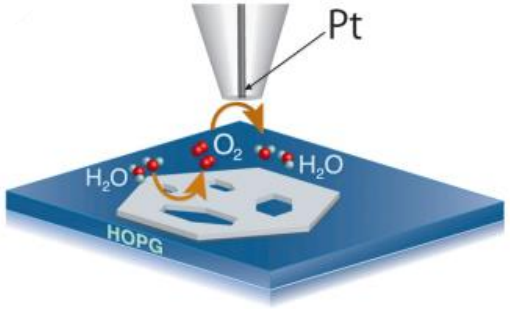
In situ Fe^{3+} incorporation vs. compounded Fe doping of NiO and $Ni(OH)_2$

- Optimized **compounded** Fe doping of NiO(111)
- **In situ** doping of Fe^{3+} into host structures of NiO(111), NiO(100) and α-$Ni(OH)_2$

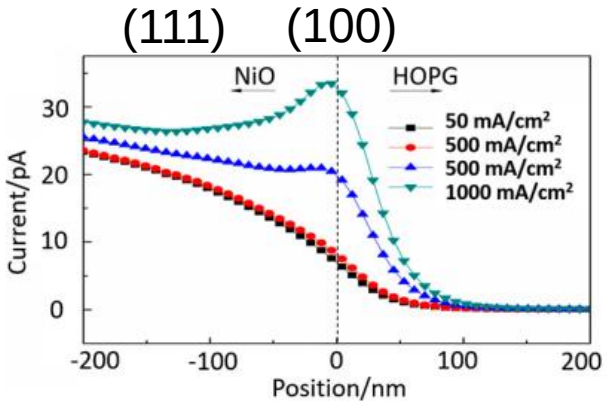


Motivation of faceted NiO nanosheets

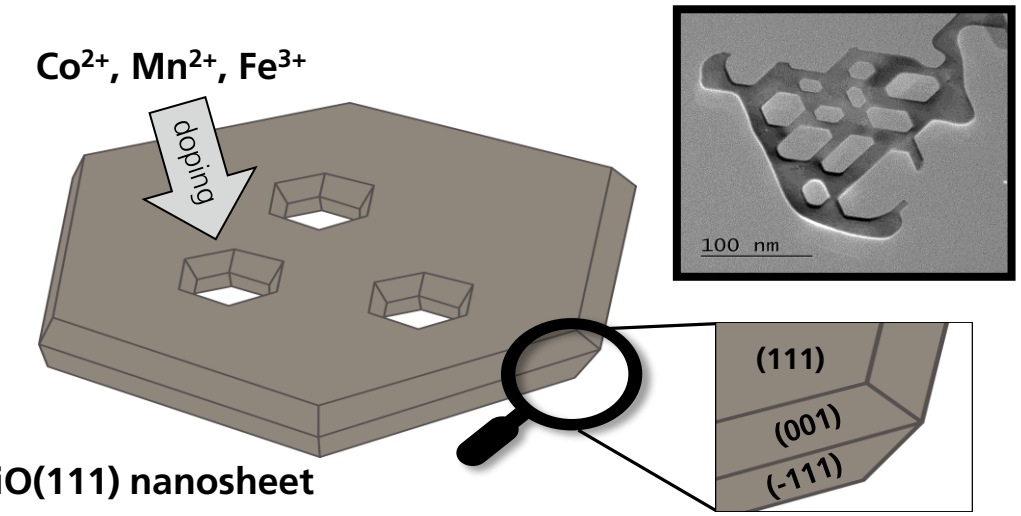
- Structure and property relationships in catalysis
  - ➢ Control of surface faceting of rock salt NiO



SECM study



Nanosheets with hexagonal hole structure (**Richards group**) Sun et al. PNAS 2019, 116, 11618.



NiO(111) nanosheet

- ➢ Use of synthesis routes to investigate the role of different facets and dopants

Compounded doping of Co and Mn into faceted NiO(111)

Konstantin Rücker, DLR Institute of Engineering Thermodynamics,
20th Aug. 2024

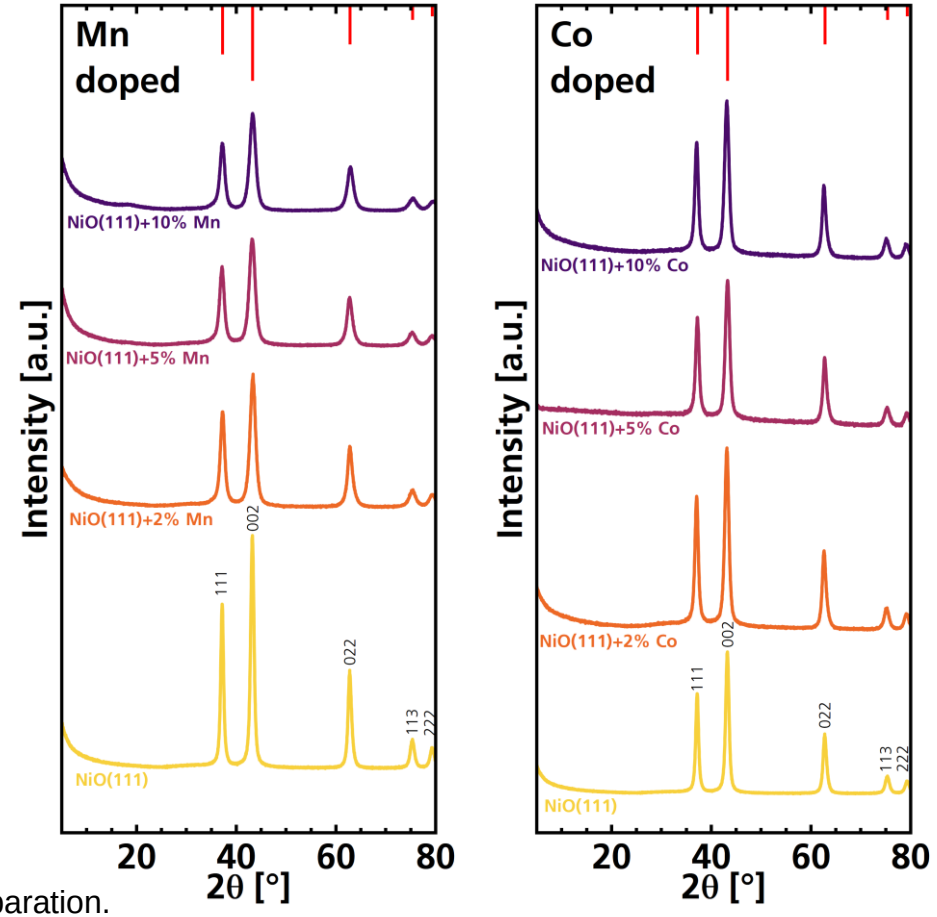
Compounded doping of Co and Mn into faceted NiO(111) - Synthesis

- Adaption of microwave-assisted synthesis (**Wark group**) for NiO(111) synthesis

Dereje H. Taffa *et al.*, in preparation.

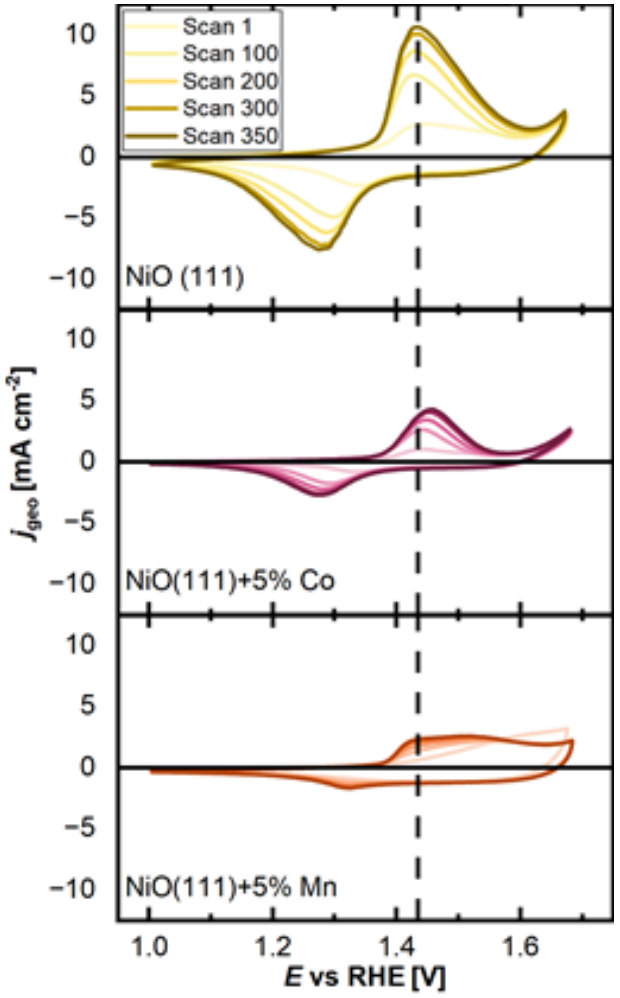
- Phase pure synthesis of **Fe** doped NiO **not successful** with standard procedure
  - ➢ Optimization needed

- XRD indicates structural integrity of the dopants (**Mn**, **Co**) into the rock salt lattice



K. K. Rücker *et al.*, in preparation.

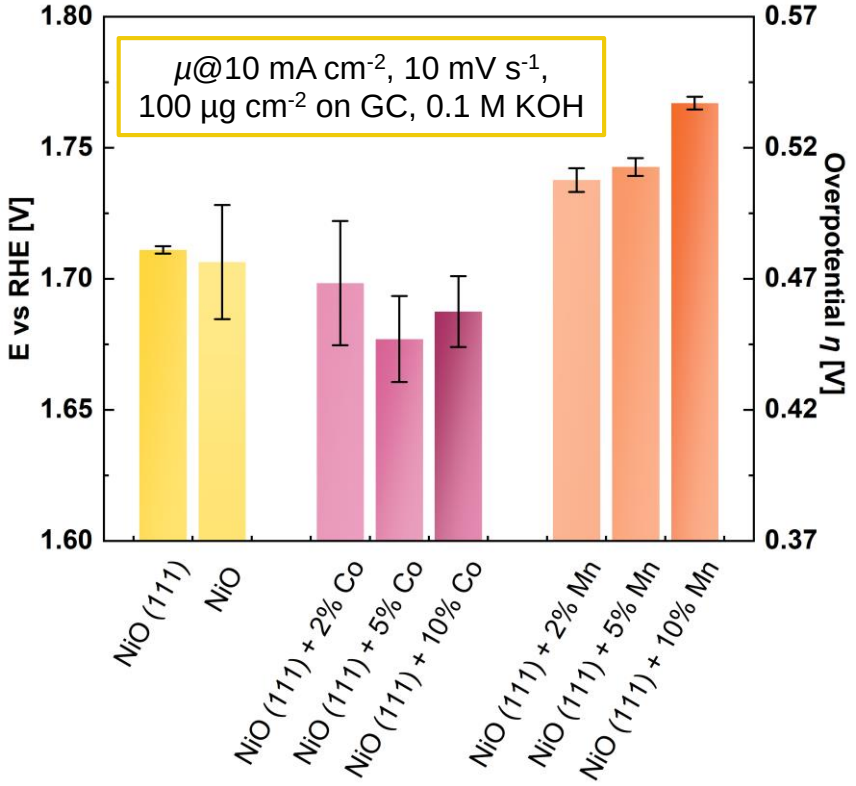
Compounded doping of Co and Mn into faceted NiO(111) - Electrochemical testing



100 mV s^{-1}, 100 µg cm^{-2} on GC, 0.1 M KOH

- Co doping: change of magnitude of Ni^{II}/Ni^{III} oxidation peak
  - ➢ Cobalt mixes into $Ni(OH)_2$ surface [1]
- Mn doping: change of magnitude of Ni^{II}/Ni^{III} oxidation and potential position
  - Oxidation peak broadened
  - Multiple oxidation peaks
  - Surface reconstruction into different phases[1]

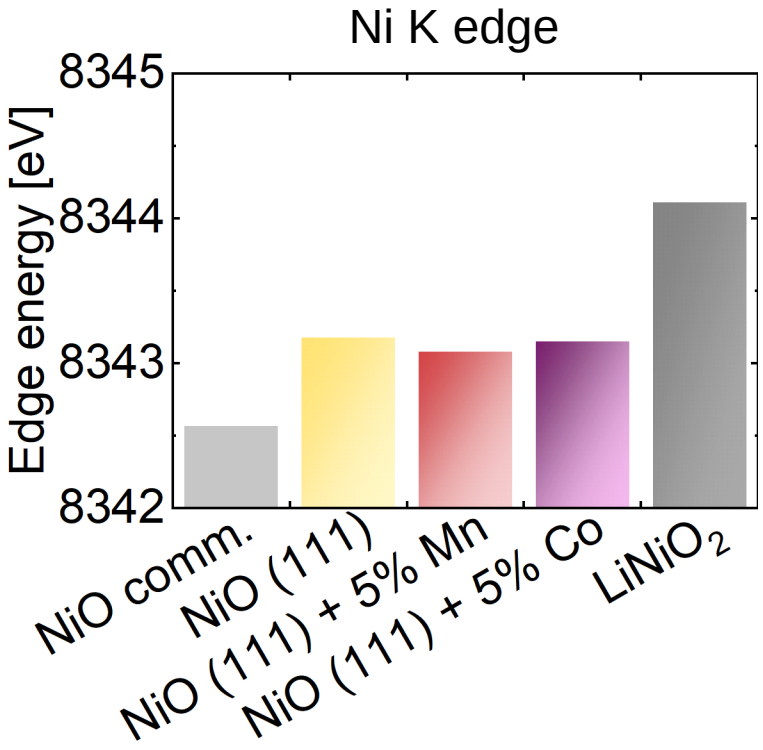
[1] Ou, Y., Twight, L.P., Samanta, B. et al. Nat Commun 14, 7688 (2023).

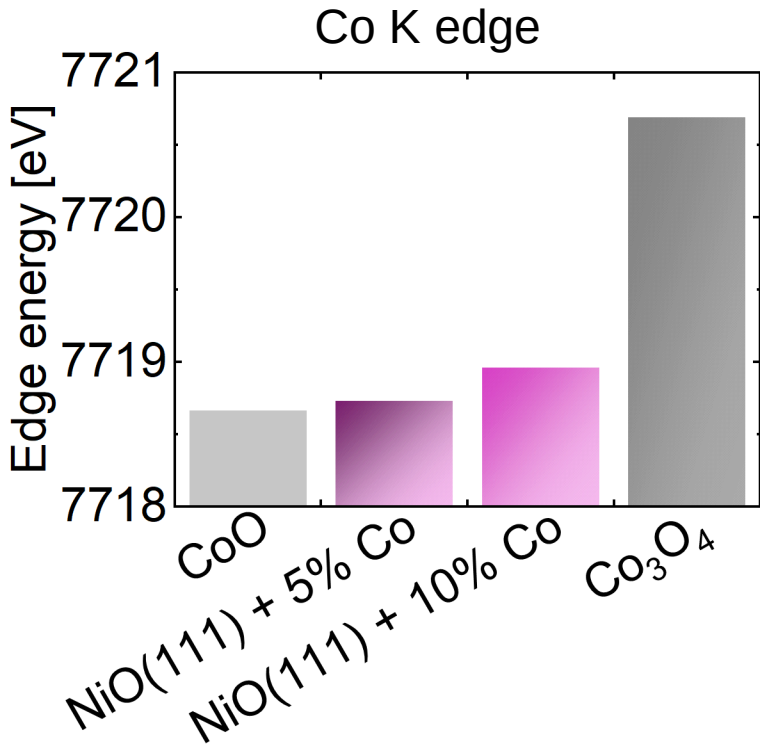


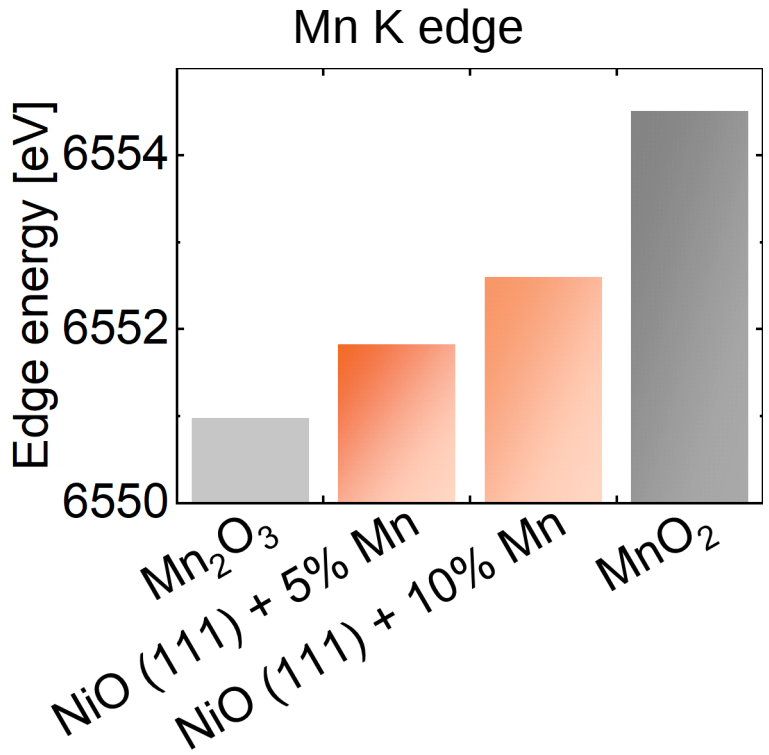
- Overpotential after 350 CV cycles: increased for Mn, decreased for Co

K. K. Rücker *et al.*, in preparation.

Compounded doping of Co and Mn into faceted NiO(111)-Structural analysis







- Rather no oxidation state change by doping

After Electrochemistry:

- Ni oxidation for Co-doped and Ni reduction Mn-doped samples

- Co oxidation state close to +2 (low OER activity)

After Electrochemistry:

- Co oxidation (5%) and reduction (10%)

- Mn oxidation state close to +3 (low OER activity)

After Electrochemistry:

- Rather no oxidation state changes in case of Mn samples

K. K. Rücker *et al.*, in preparation.

In situ Fe^{3+} incorporation vs. compounded Fe doping of NiO and $Ni(OH)_2$

Konstantin Rücker, DLR Institute of Engineering Thermodynamics,
20th Aug. 2024

Optimization of compounded Fe doping of NiO(111) and $Ni(OH)_2$

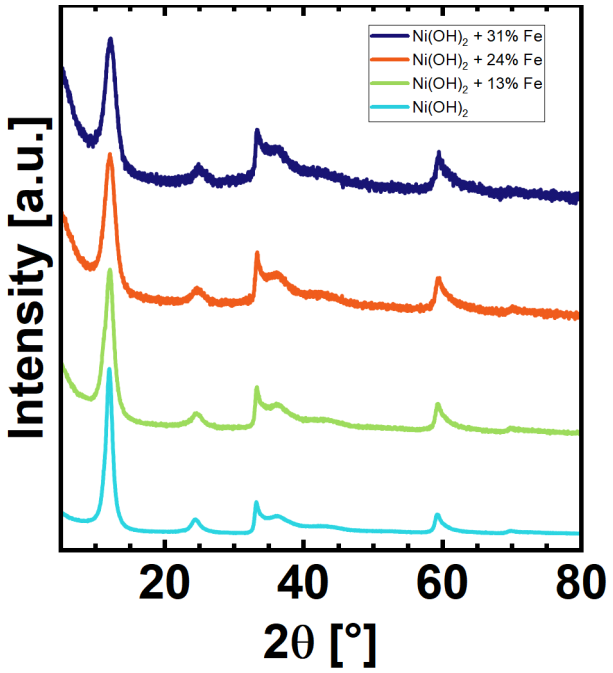
- Phase pure iron doping was achieved
  - pH control of precursor solution
  - Longer synthesis times to reach target metal ratio
- Comparison of hydroxide and oxide host structures

ICP-MS results

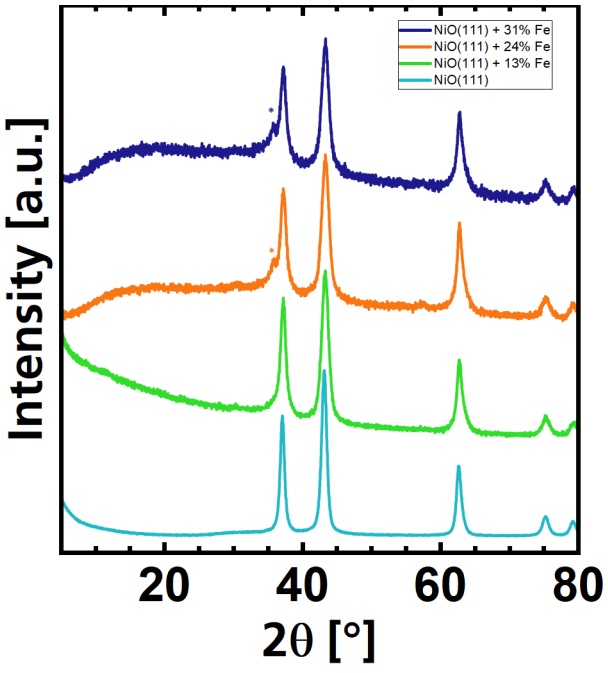
Sample	Intended	x_{Fe} [mol %]	x_{Ni} [mol %]
$Ni(OH)_2$ + 5% Fe	2% Fe	5.3	94.7
$Ni(OH)_2$ + 13% Fe	5% Fe	12.7	87.3
$Ni(OH)_2$ + 24% Fe	10% Fe	24.4	75.5
$Ni(OH)_2$ + 31% Fe	15% Fe	30.7	69.3

- Iron oxide phase impurities (*) of oxide occur with more than 24% Fe doping

α-Hydroxide

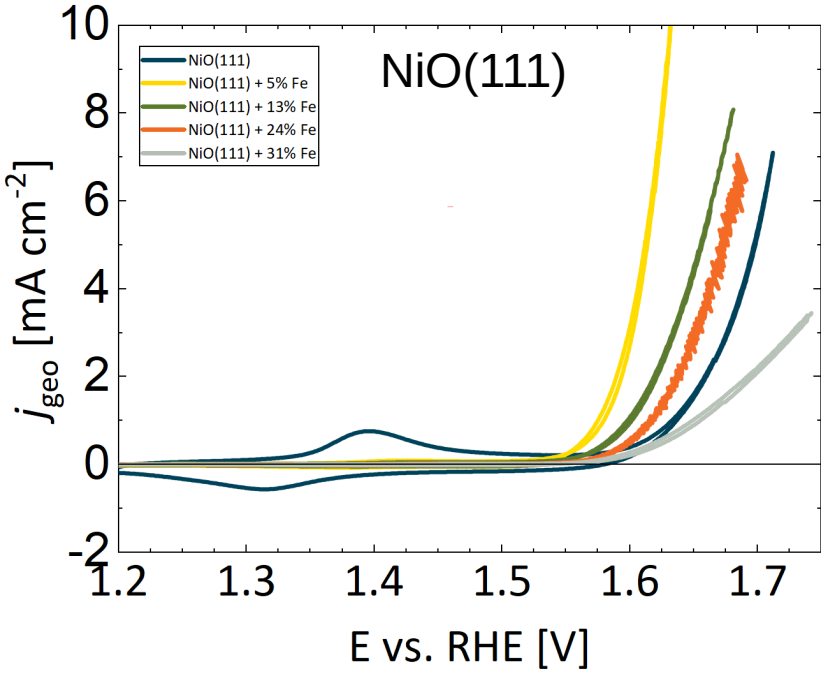


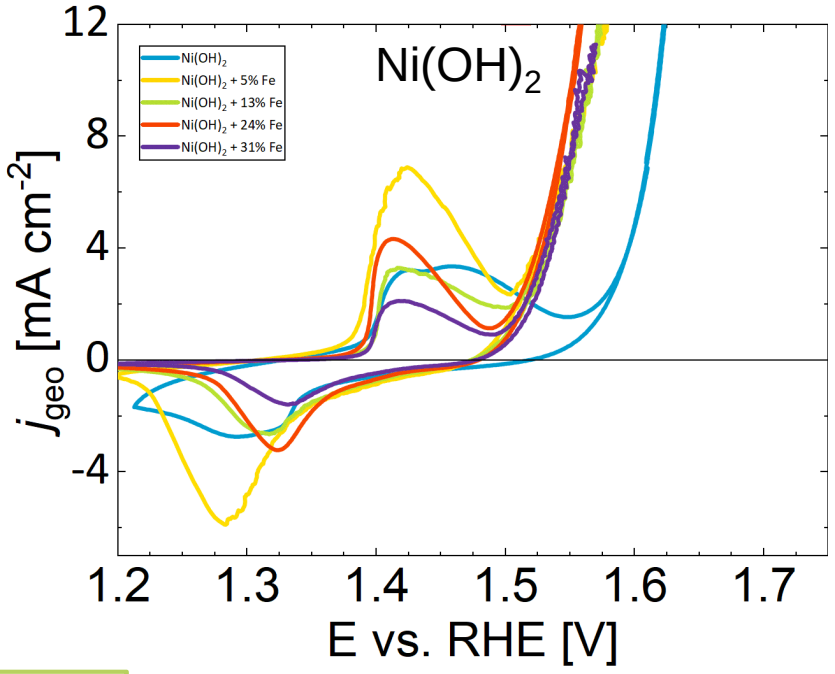
NiO(111) rock salt

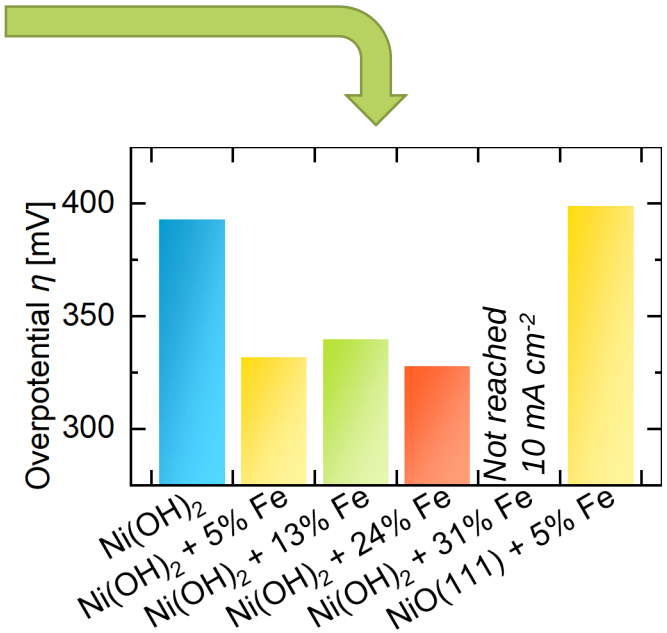


OER activity of compounded Fe doped samples

- Higher doping levels of Fe exhibited decrease in OER activity in case of oxide
  - Crystalline separate phases at 24% Fe and higher
- Hydroxide more active but equal activity of doped materials





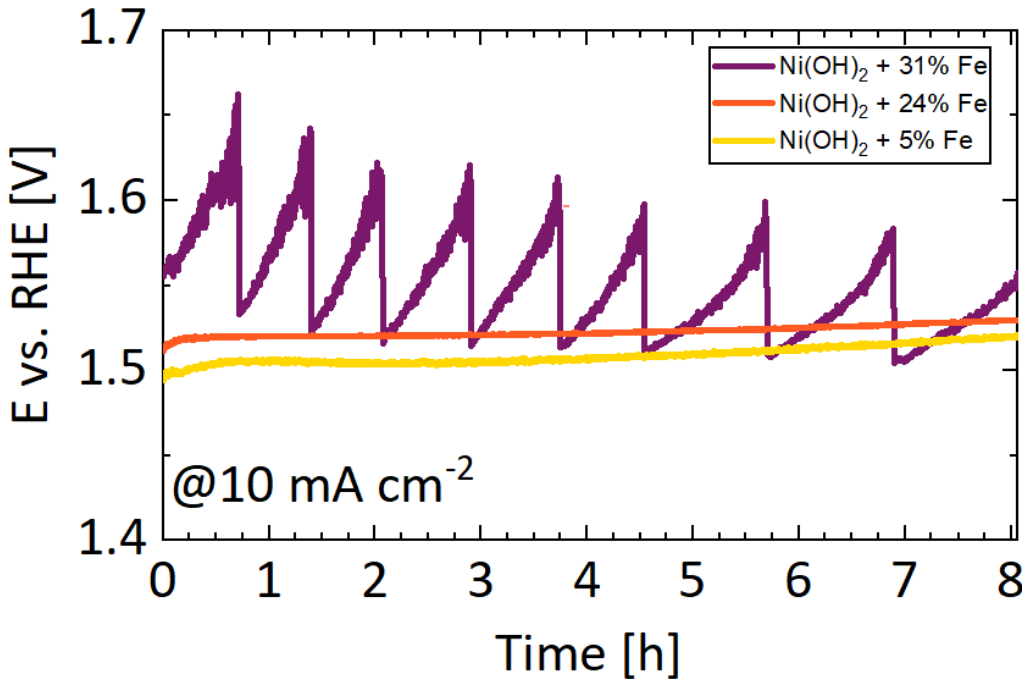


10 mV s^{-1}, 100 µg cm^{-2} on GC, 0.1 M KOH purified[1]

η @10 mA cm^{-2}, 10 mV s^{-1}, 100 µg cm^{-2} on GC, 0.1 M KOH purified

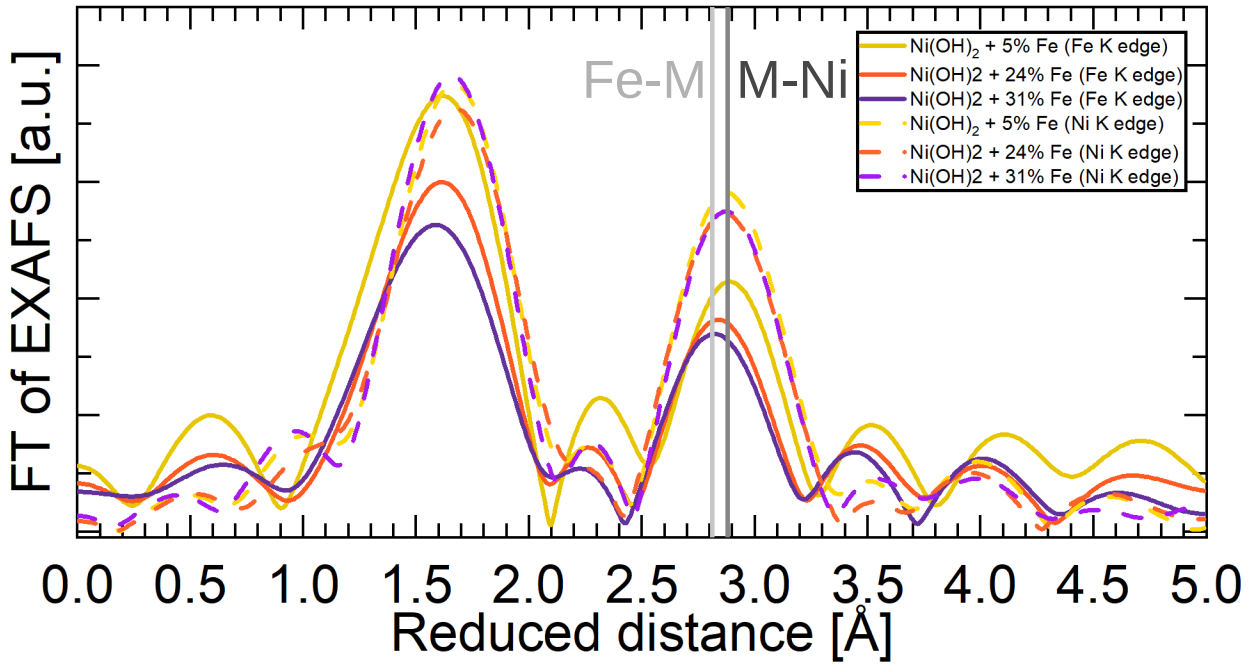
[1] Márquez, R. A. et al. ACS Energy Lett. 8, 1141 (2023)

OER activity of compounded Fe doped samples



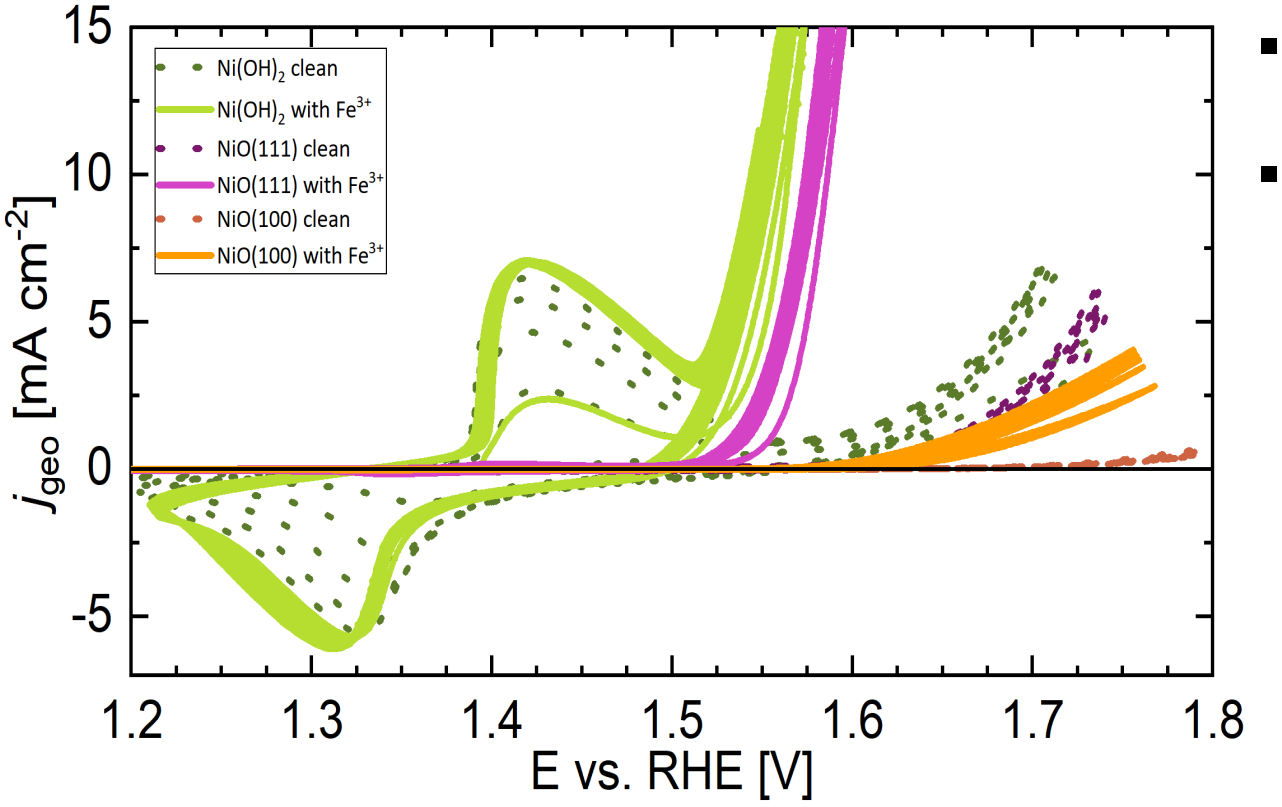
Hold @10 mA cm^{-2}, 100 µg cm^{-2} on GC, 0.1 M KOH purified

- Galvanostatic hold supports CVs
- 31% Fe with shows higher overpotential & bubble detachment issues



- XRD indicates one hydroxide phase
- EXAFS after EC
  - Changes in local coordination environment with increased doping
  - Only 5% Fe sample shows Fe-M ~ M-Ni (doping)

In situ Fe^{3+} incorporation into different host structures



0.1 ppm $Fe^{3+}(NO_3)_3$ added,10 mV s^{-1}, 100 µg cm^{-2} on GC, 0.1 M KOH purified

- Drastic improvements after in situ Fe^{3+} doping
- Fe-k edge after in situ doping close to compounded samples

Max current improvements:

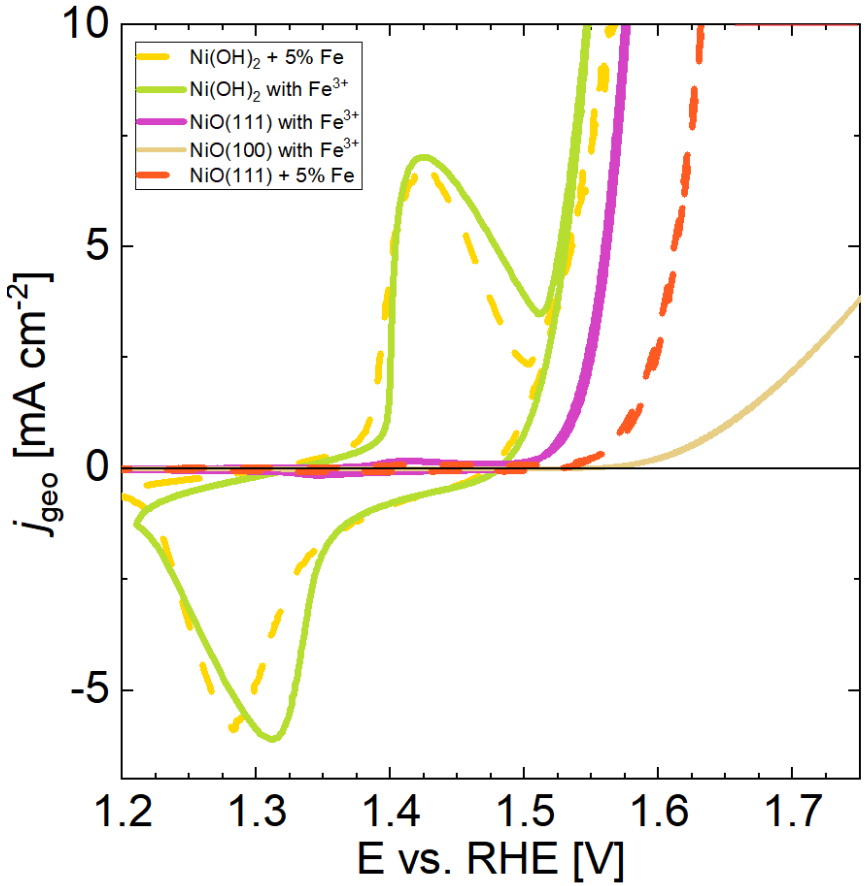
$Ni(OH)_2$ + Fe^{3+} 6.53 → 17.7 mA cm^{-2} **(270%)**

NiO(111) + Fe^{3+} 6.15 → 20.2 mA cm^{-2} **(330%)**

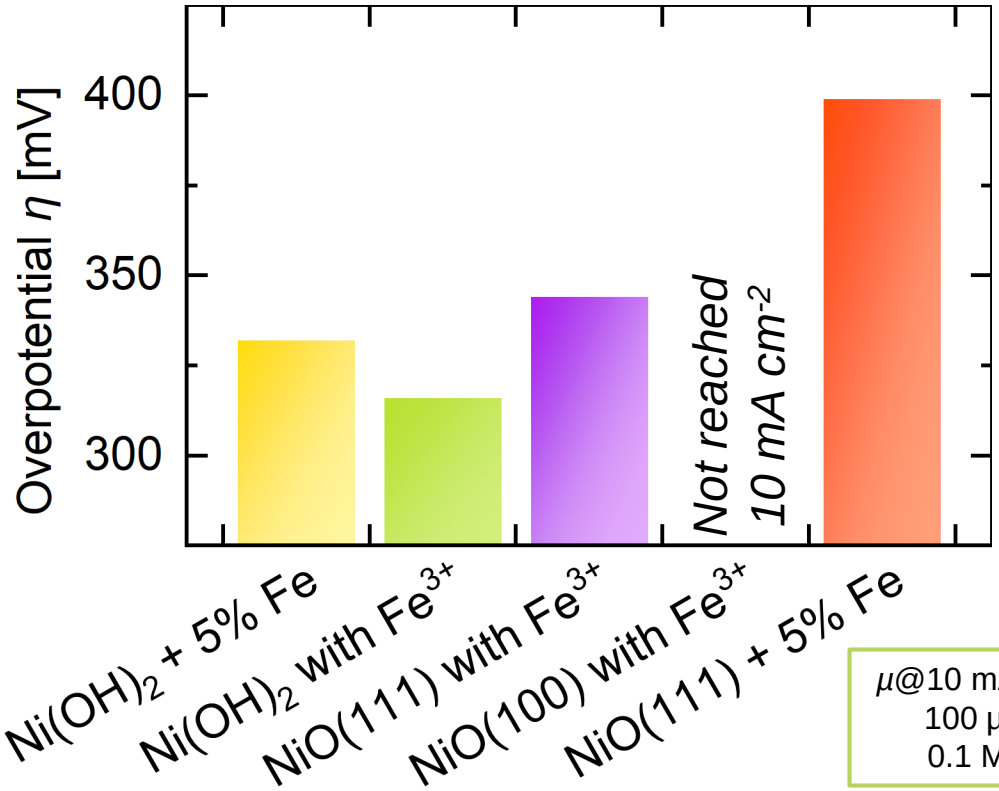
NiO(100) + Fe^{3+} 0.47 → 4.03 mA cm^{-2} **(860%)**

Sample	Fe K Edge energies
$Ni(OH)_2$ + 5% Fe	7.128 keV
$Ni(OH)_2$ + Fe^{3+}	7.127 keV
NiO(111) + Fe^{3+}	7.128 keV
NiO(100) + Fe^{3+}	7.126 keV

In situ Fe^{3+} incorporation vs. compounded Fe doping



10 mV s^{-1}, 100 µg cm^{-2} on GC, 0.1 M KOH purified



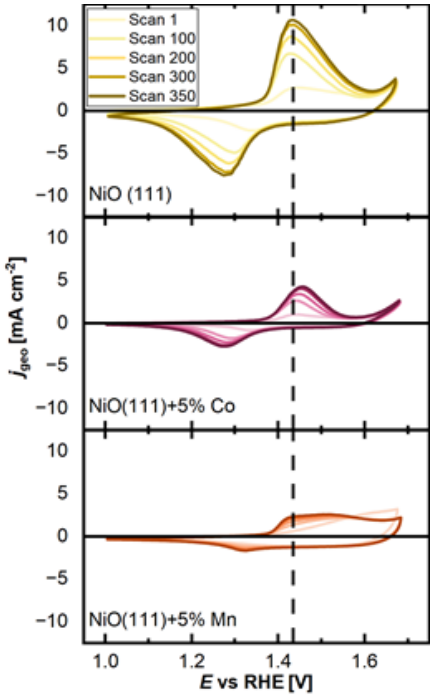
μ@10 mA cm^{-2}, 10 mV s^{-1}, 100 µg cm^{-2} on GC, 0.1 M KOH purified

- In situ doping with Fe exceeds activities of compounded doped samples
- Amount of incorporated Fe needs investigation

Conclusion

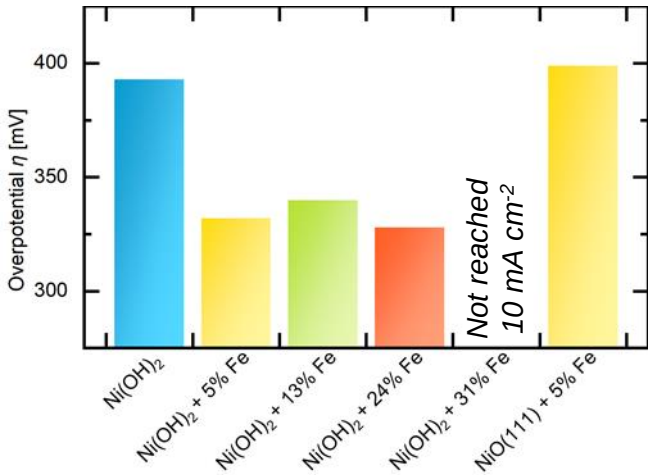
Doping of Co and Mn into faceted NiO(111)

- Co ions integrates into faceted nanosheets
- Mn shows with multiple redox signals

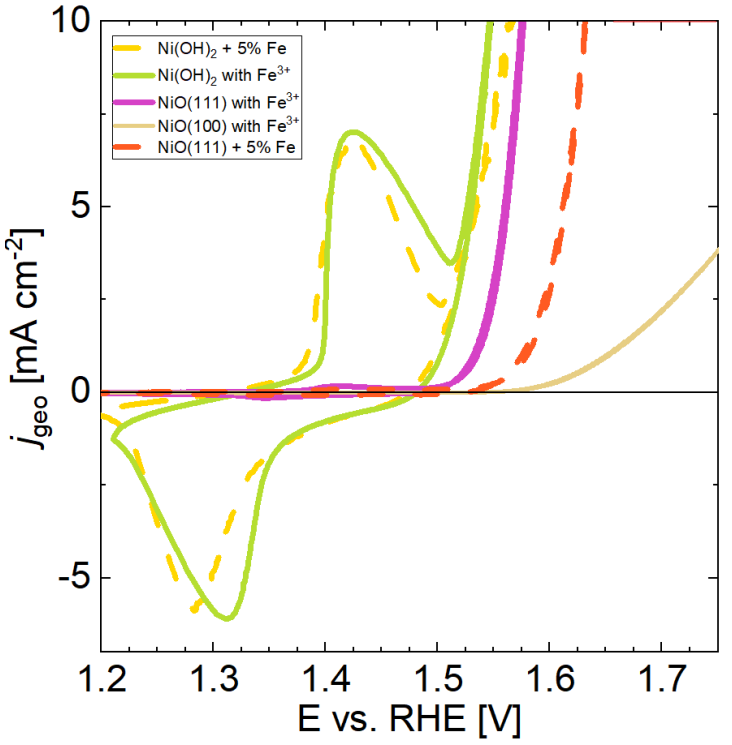


In situ Fe incorporation vs. compounded Fe doping of NiO(111) and $Ni(OH)_2$

- 5% Fe is the optimum of Fe doping NiO(111)
  - ➢ Further structural analysis necessary



- In situ Fe^{3+} doping by exceeds compounded doping
- Influence of host structure on OER activity after Fe^{3+} doping



Aknowledgement

Project consortium

Carl von Ossietzky Universität Oldenburg

School of Mines 1874 Colorado

HZB Helmholtz Zentrum Berlin

NREL Transforming ENERGY

Funding

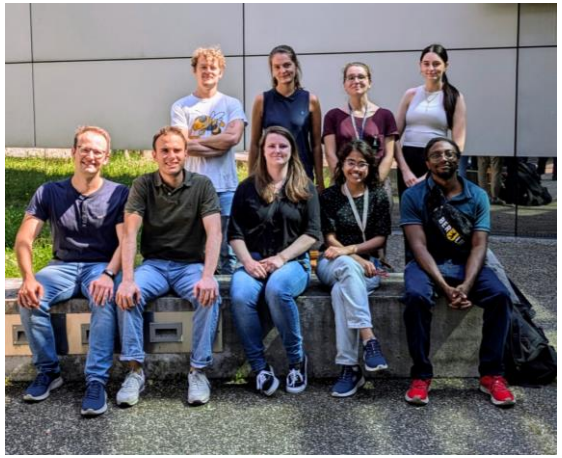
Funded by DFG Deutsche Forschungsgemeinschaft German Research Foundation

DFG-Project number 460244535

NSF

NSF project #2139971

Beamtime Team



My colleagues

- Jana Ewert (DLR)
- Heinrich Vocke (UOL)

Thank your for your attention!

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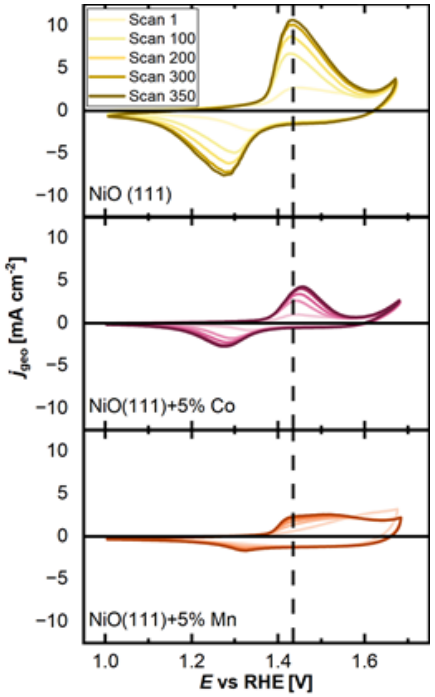
- Mn shows with multiple redox signals



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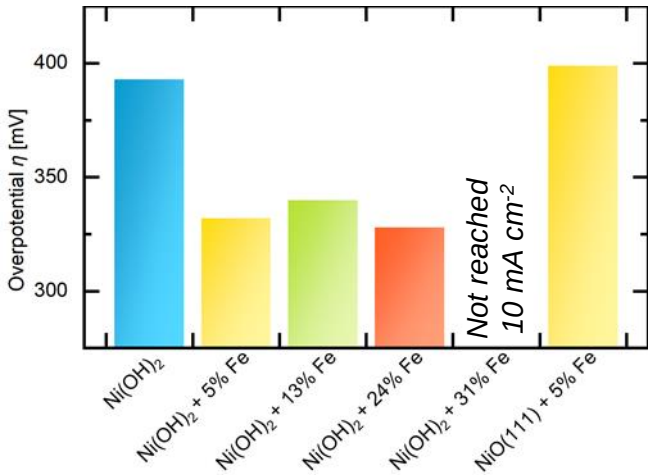
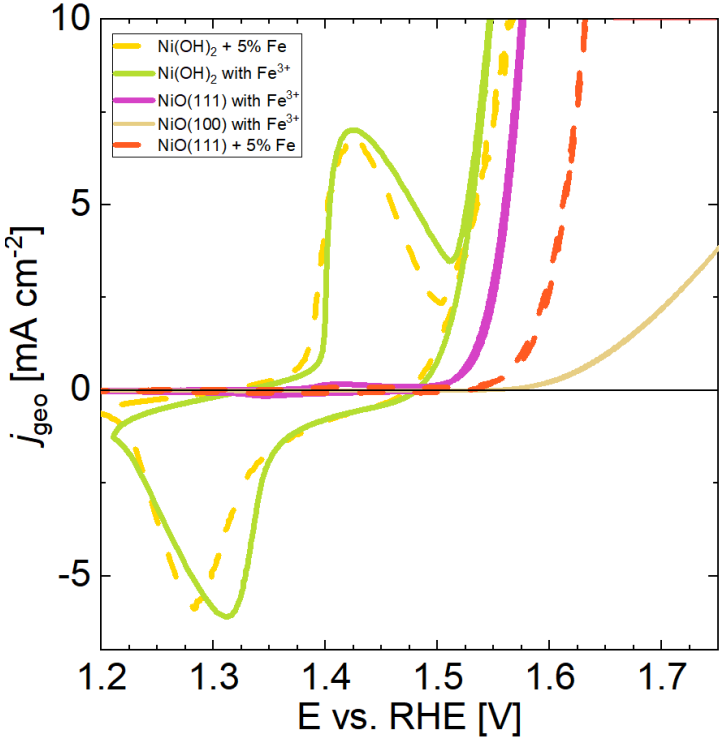


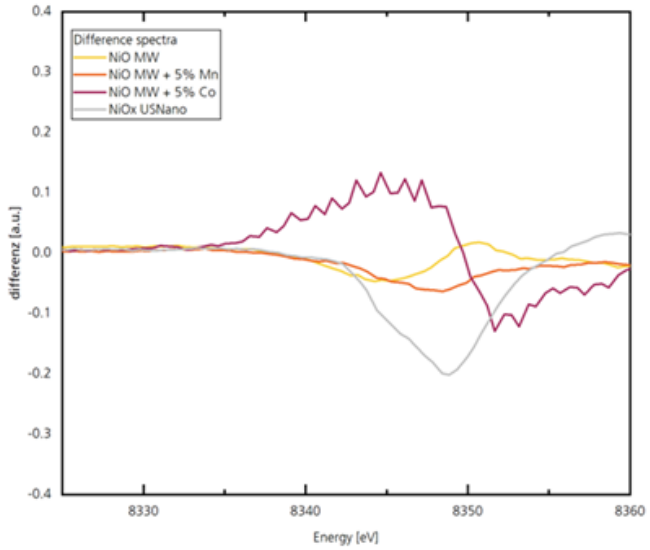
- In situ Fe^{3+} doping by exceeds compounded doping
- Influence of host structure on OER activity after Fe^{3+} doping



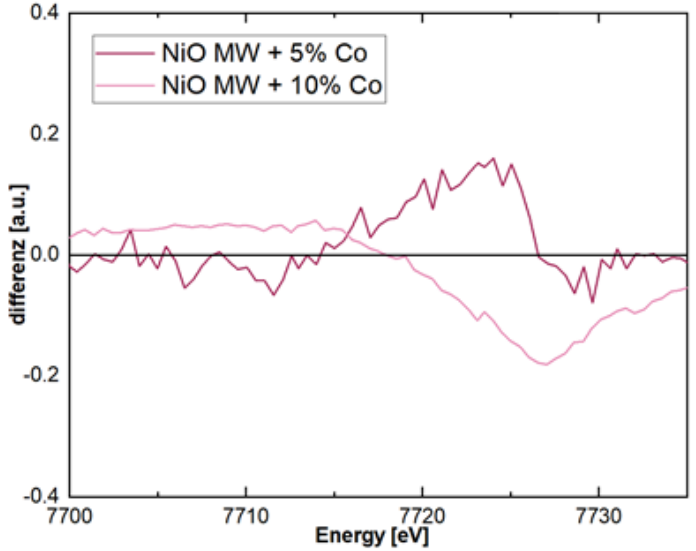
Supporting Slide: Compounded doping of Co and Mn into faceted NiO(111) – After EC

- Difference plots of XANES spectra

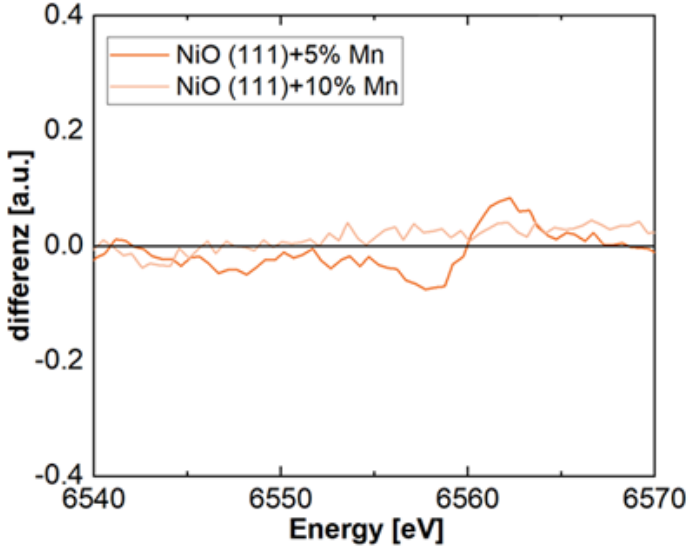
Ni-K edge



Co-K edge



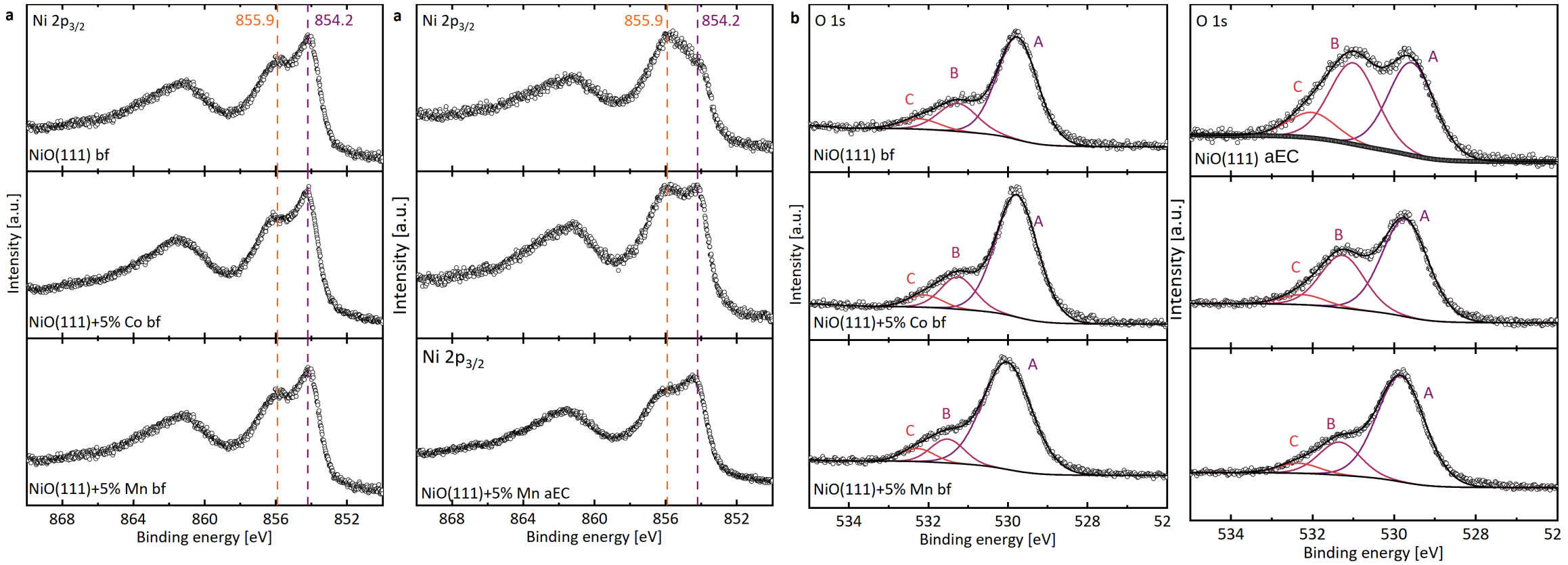
Mn-K edge



- ➢ Ni oxidation for Co-doped and Ni reduction Mn-doped samples
- ➢ Co oxidation (5%) and reduction (10%)
- ➢ Rather no oxidation state changes in case of Mn samples

Supporting Slide: Compounded doping of Co and Mn into faceted NiO(111) – After EC

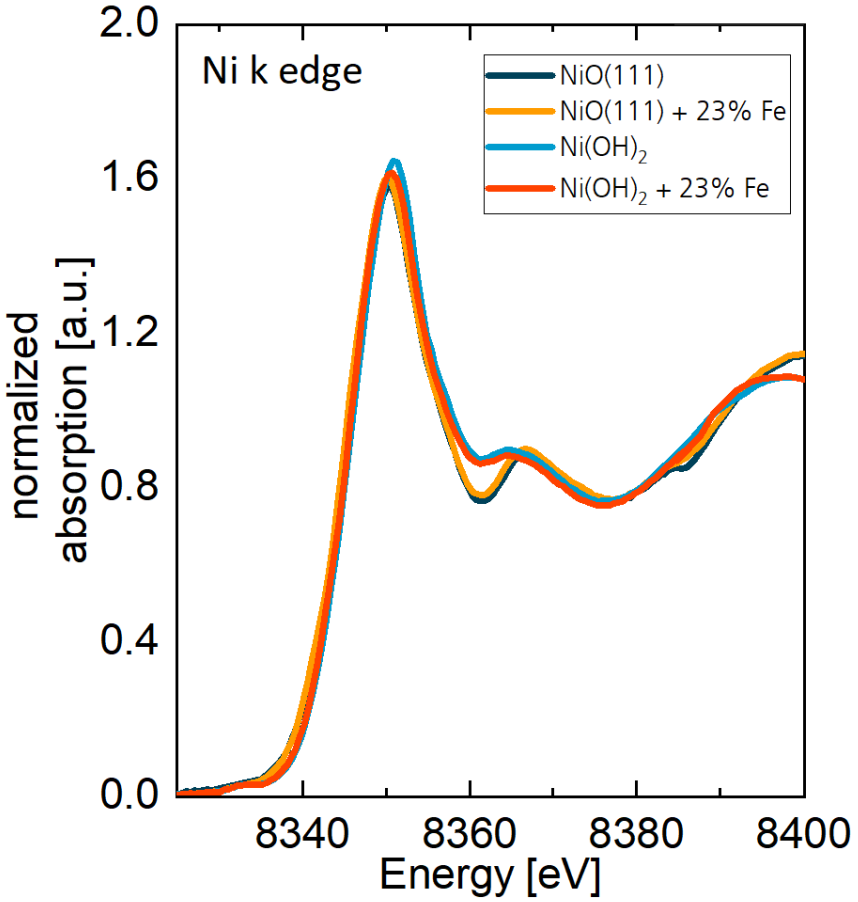
- Changes of the NiO(111) surfaces for pure and doped samples

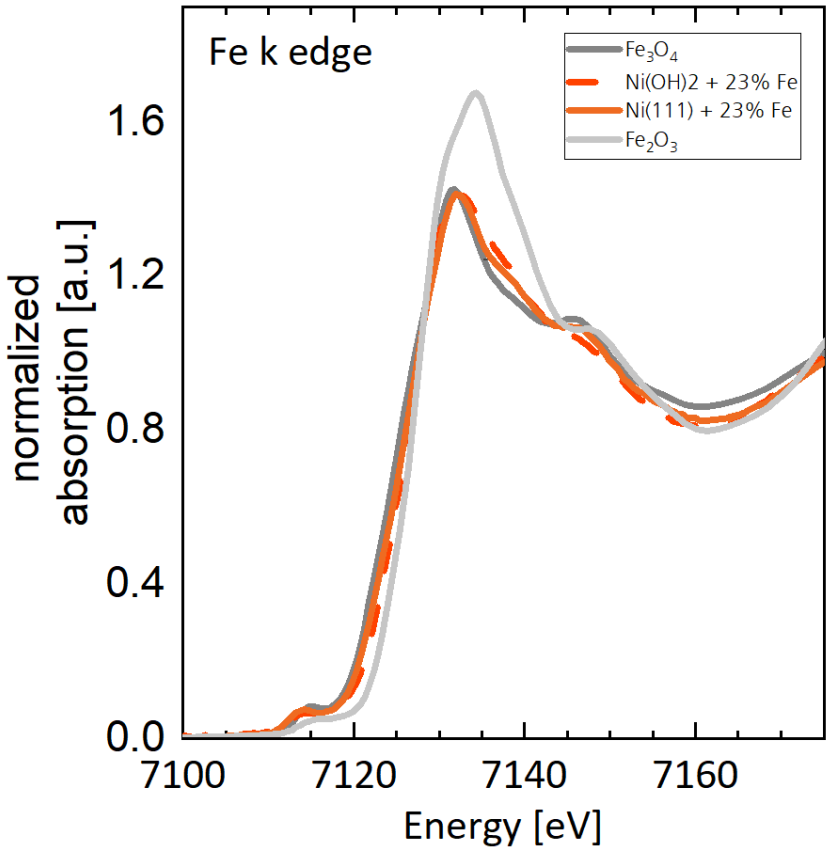


Supporting Slide: Compounded Fe doping of NiO(111) and $Ni(OH)_2$

- Edge energy ~ oxidation state

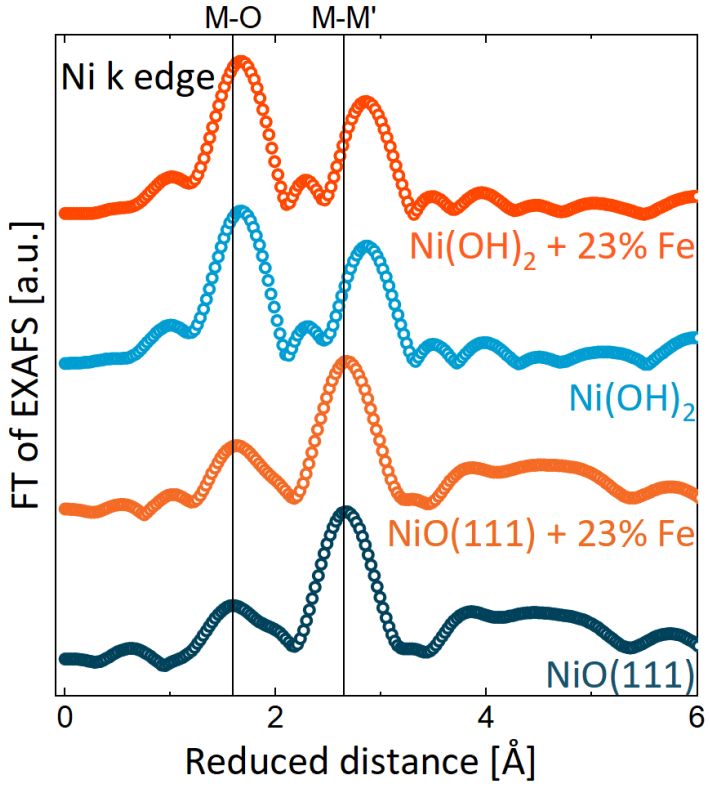
- Ni k edge of iron doped materials similar to pure samples
- Fe k edge reveals oxidation state close to Fe_3O_4
  - ~ +2.6 (Fe^{+II},2 Fe^{+III})





Supporting Slide: Compounded Fe doping of NiO(111) and $Ni(OH)_2$

- Ni k edge scattering of doped samples compareble to pure samples



- Fe k edge more interesting
  - Both show features close to Fe_2O_3 (contrast to ox state)
  - Main M-M‘ feature similar to Ni k edge distances
  - Shoulder in hydroxide
    - Propably second hydroxide phase
    - No other explanation so far