

In situ Fe³⁺ Incorporation vs. Compounded Fe Doping of NiO and Ni(OH)₂ Catalysts for the Alkaline Oxygen Evolution Reaction

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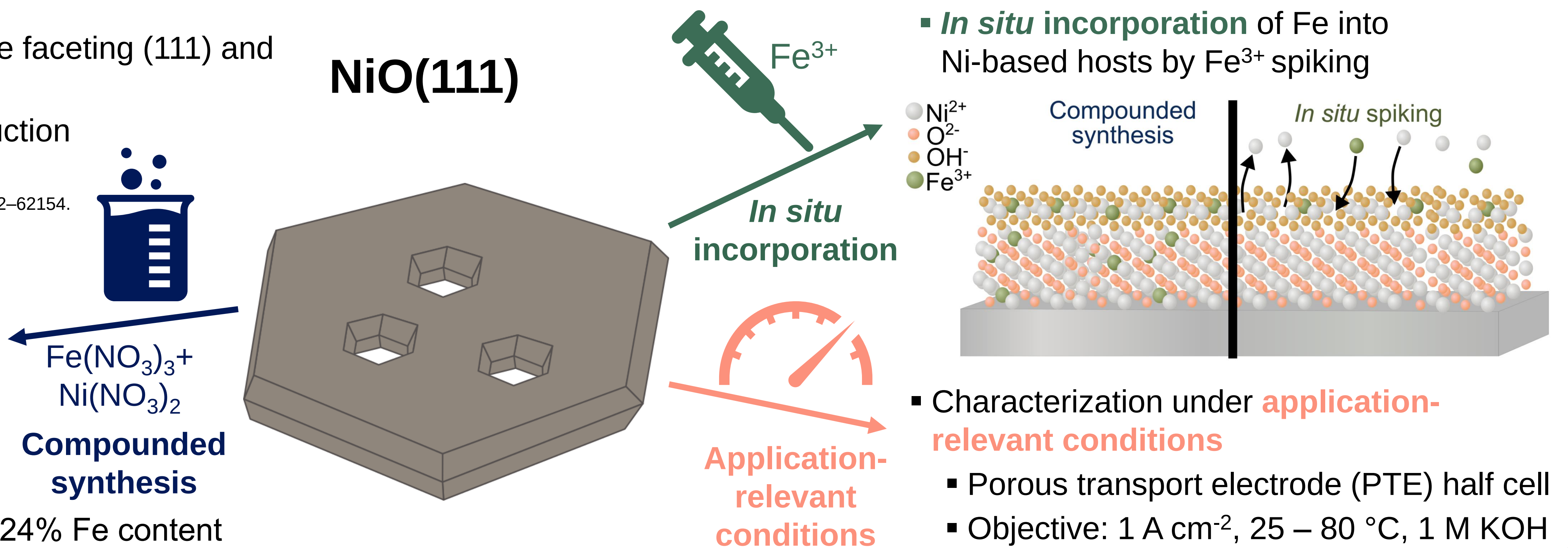
Faceted Catalysts as Platform

- Microwave synthesis route to achieve faceting (111) and doping of NiO
- Investigation of precatalyst reconstruction dependent on dopant (Co, Mn, Fe)

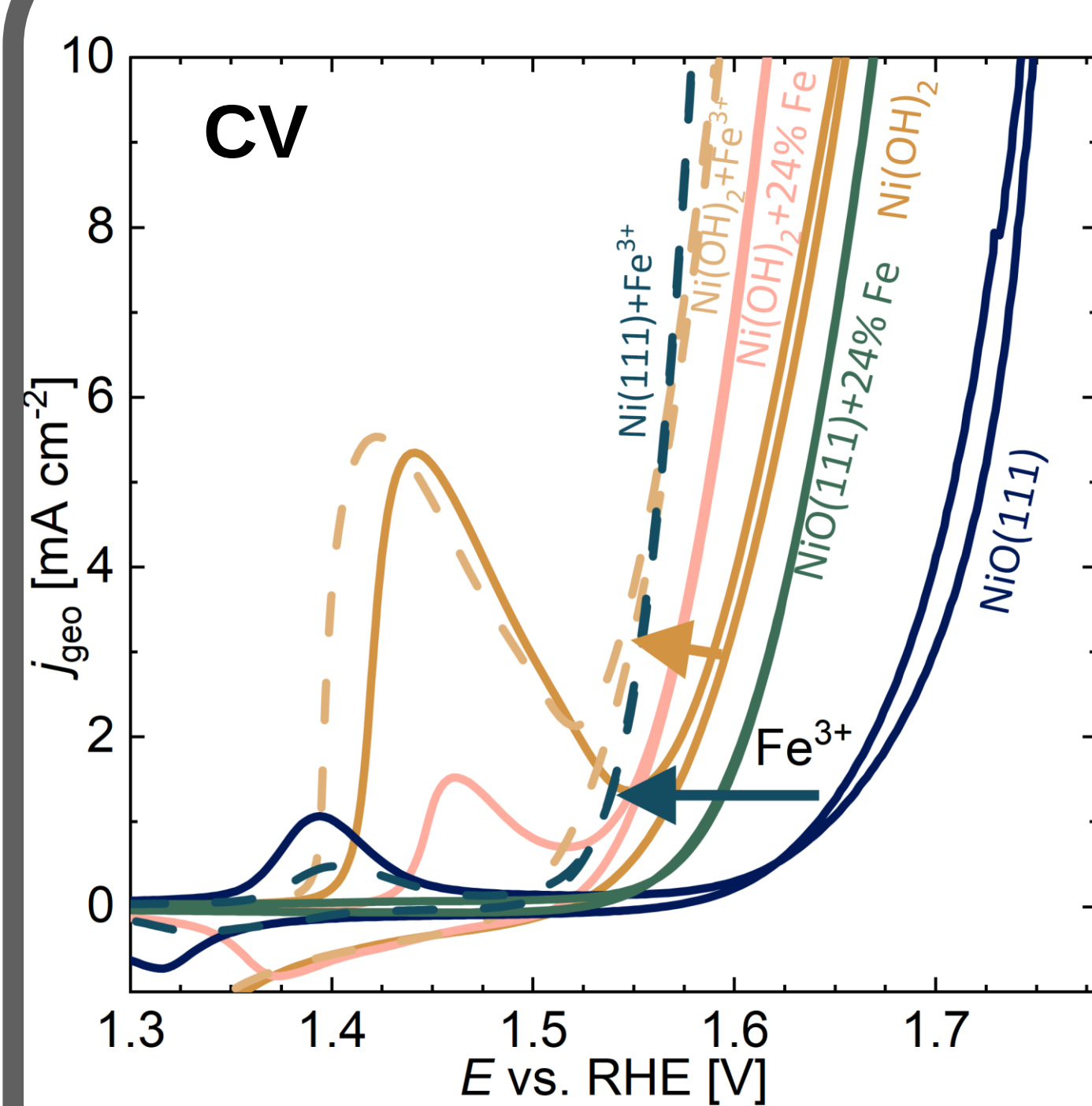
D. H. Taffa et al. ACS Appl. Mater. Interfaces 2024, 16, 45, 62142–62154.
K. Rücker et al. J. Phys. Chem. C 2025, 129, 20, 9341–9355.

- **Compounded synthesis** of Ni/Fe materials required adaptation

- Synthesis time
- pH control of precursor
- Preparation of Ni/Fe-materials with 1-31% Fe content
- XRD reveals impurity Fe-phase for ≥24% Fe content

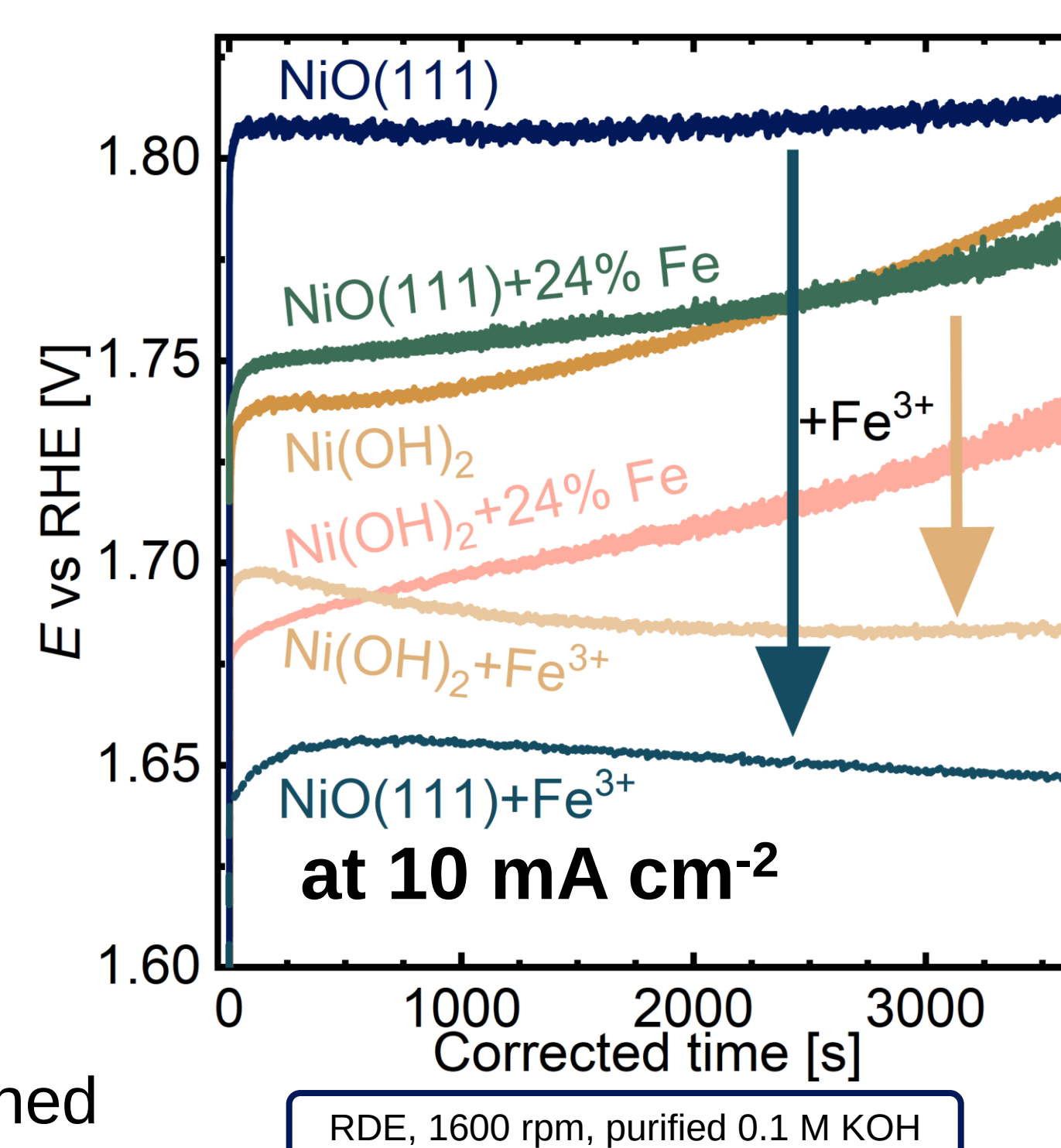


RDE Study of Fe Doping



Cyclic voltammetry (CV):

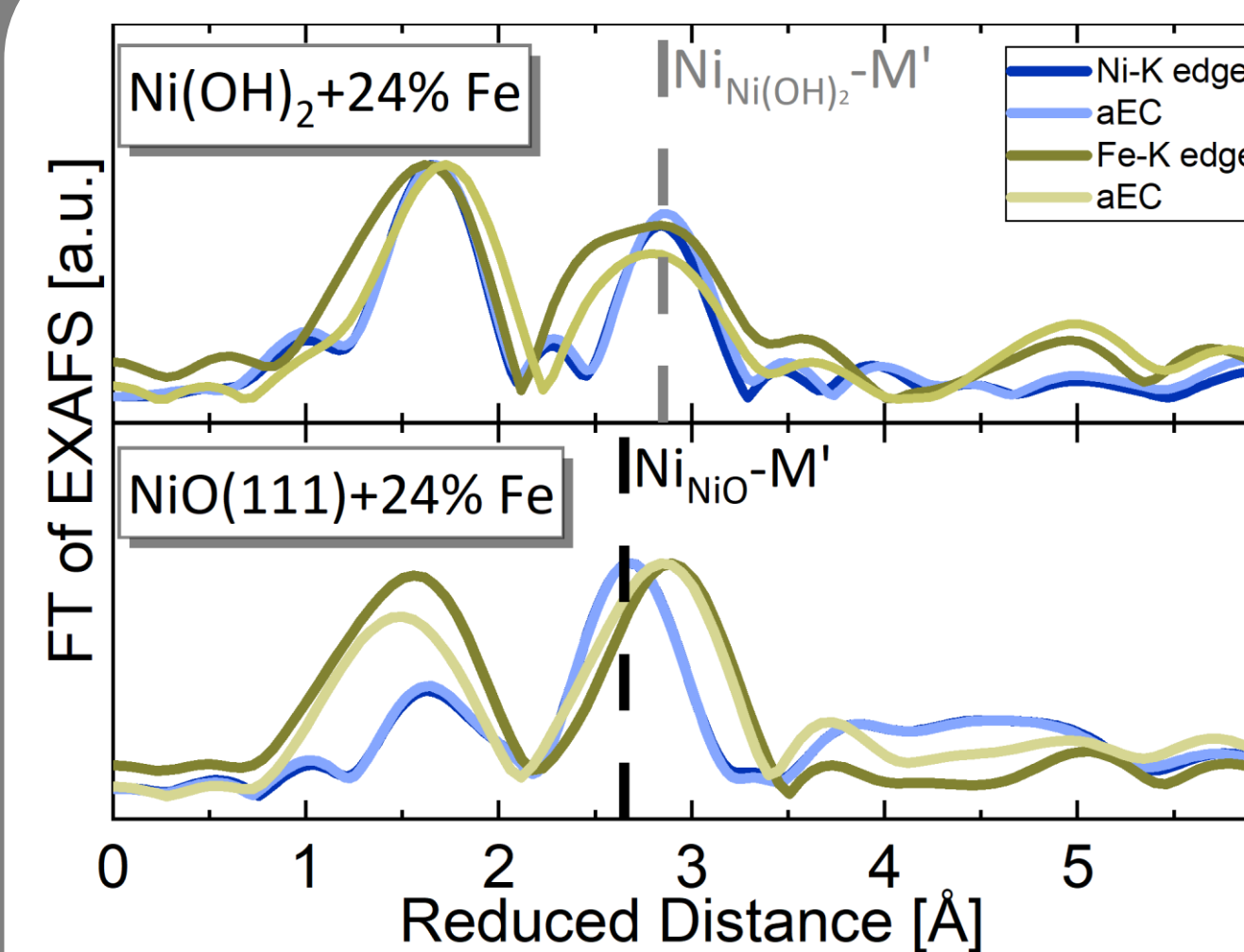
- Drastic activation due to Fe³⁺ spiking
- Activity after **in situ incorporation** surpasses **compounded** Ni/Fe materials
- **150 mV** overpotential decrease for **NiO(111)** sample after Fe³⁺ spiking
- Ni^{II}/Ni^{III} oxidation peak unproportionally suppressed relative to the Fe content



Galvanostatic performance:

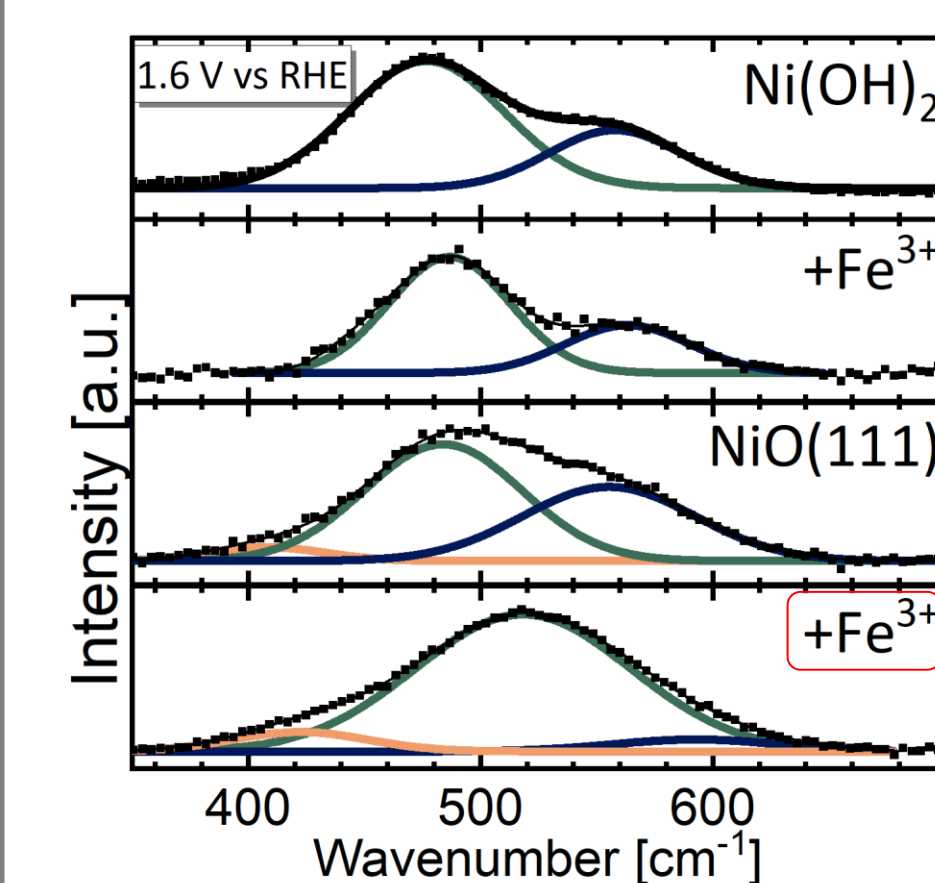
- Activity trends similar to CV
- Overpotentials higher (capacitance free)
- Most **compounded** samples exhibit deactivation during galvanostatic hold
- **In situ incorporation** promotes activation during hold
- Fe incorporation surface confined

Spectroscopic Effect of Fe Doping

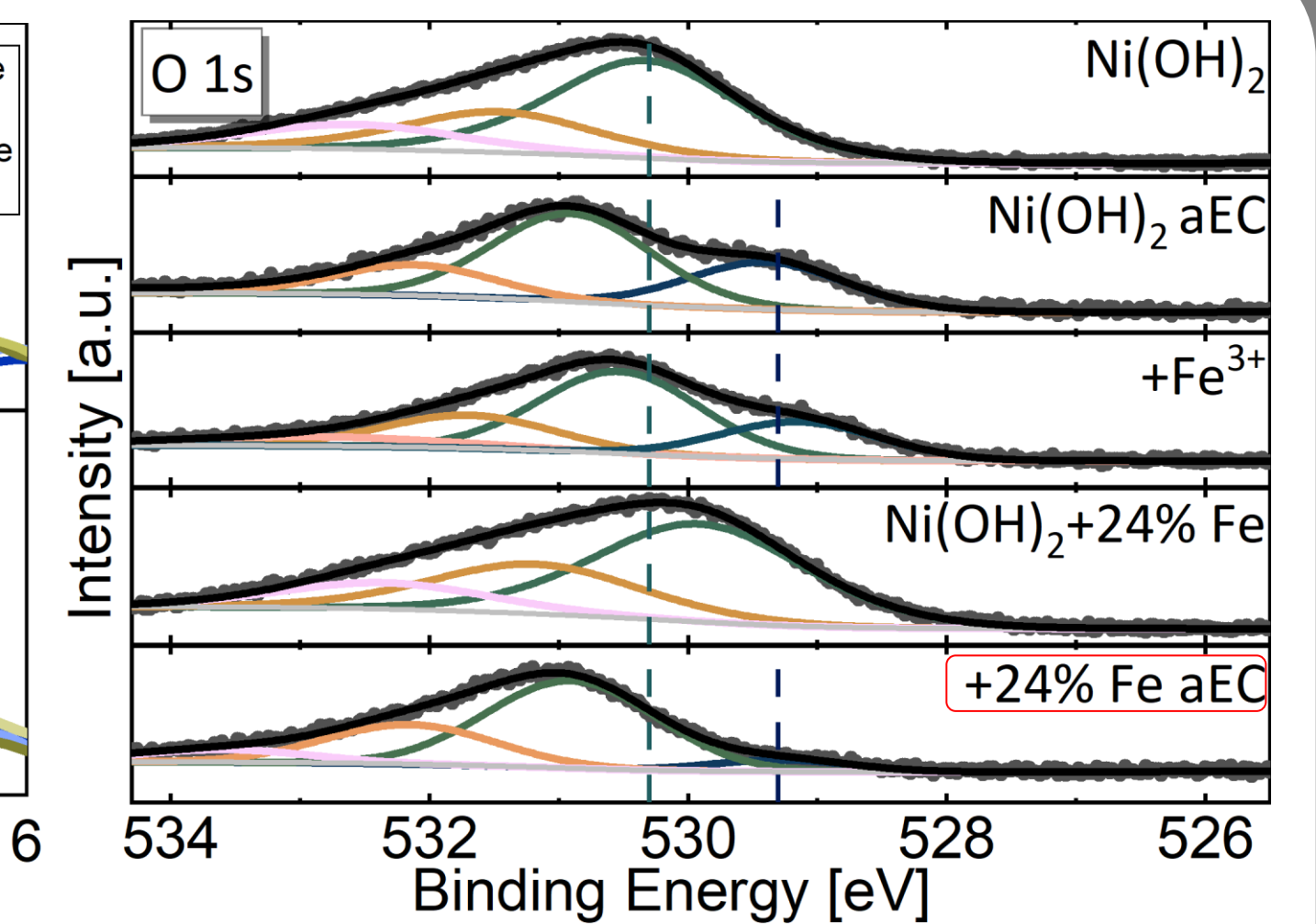


Ex Situ XAS:

- Incorporation of Fe³⁺ detected
- EXAFS suggests separate Fe-phase for **compounded** samples
- Different M-M' distances between **Ni** and **Fe-K** edge



In situ cell, 1.6 V vs RHE, purified 0.1 M KOH



Ex situ XPS:

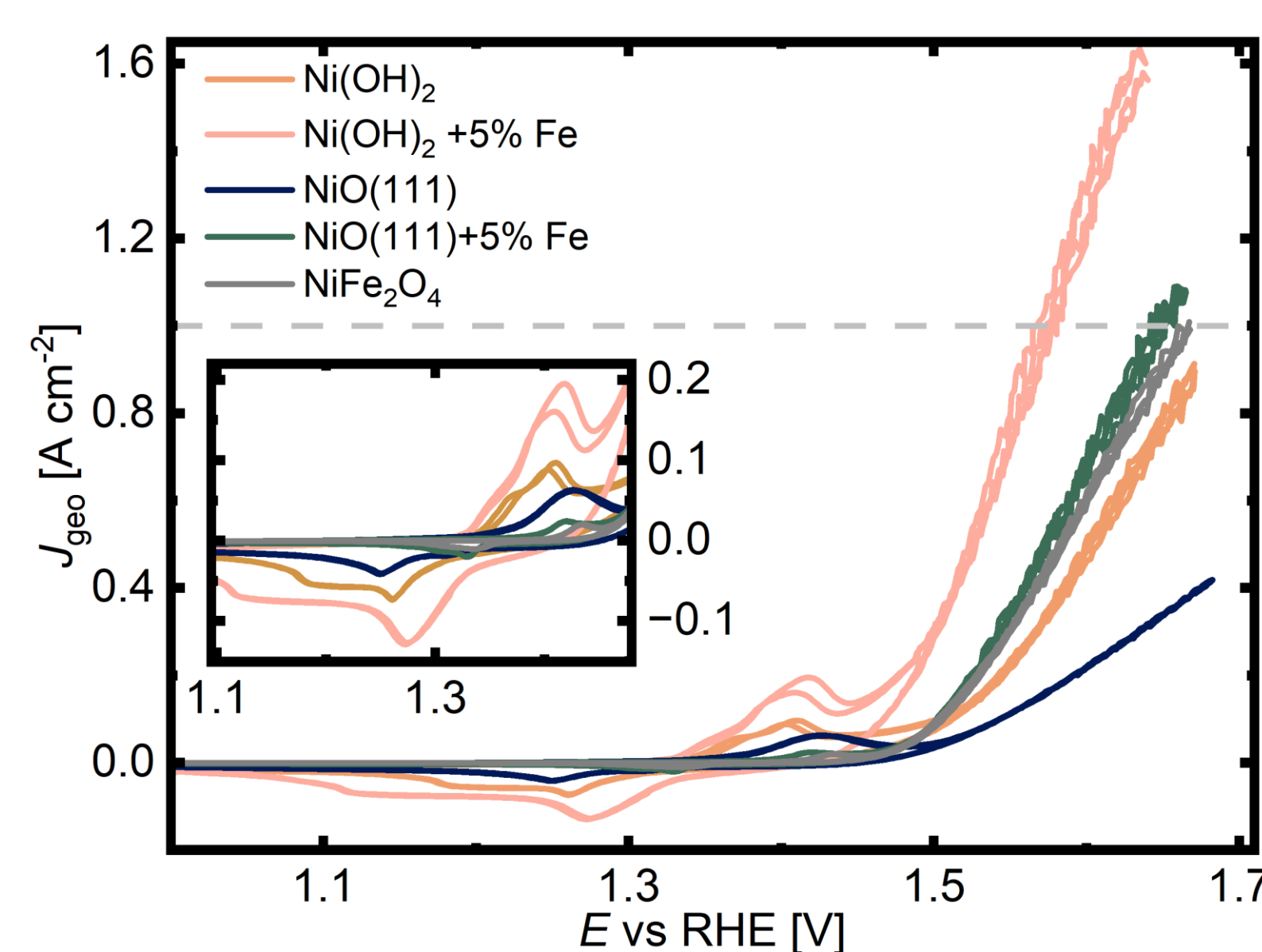
- O 1s of Ni(OH)₂ samples reveals different **NiOOH** formations for the Fe-**compounded** samples
- +24% Fe with least conversion to **NiOOH**
- O 1s of NiO(111) samples with minor changes

In situ Raman (1.6 V vs RHE):

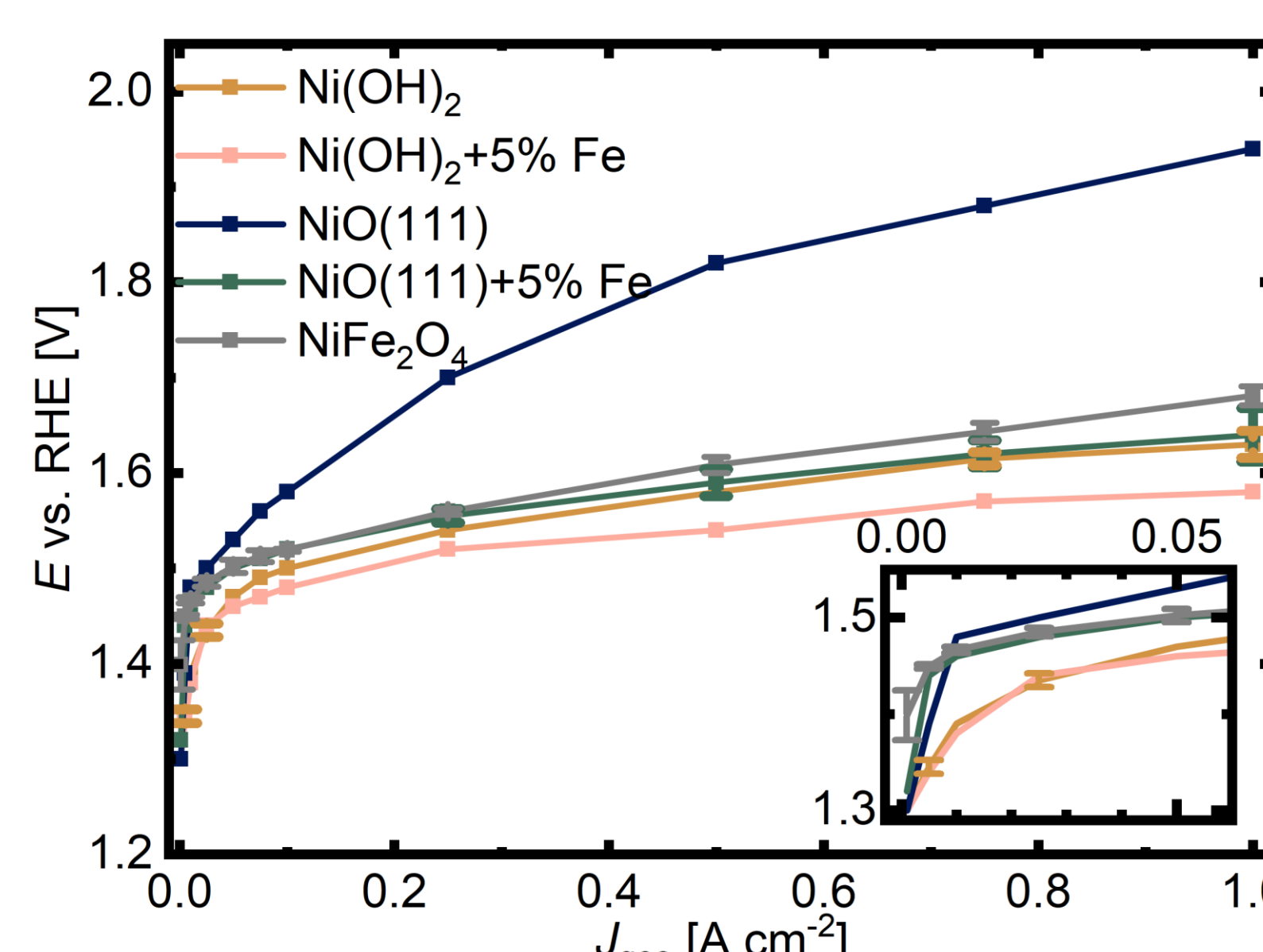
- Suggests **lower NiOOH** formation with Fe in **both** doping approaches
- NiO(111)+Fe³⁺ sample shows minimal **NiOOH** peak
- The **NiO** peak at 390 cm⁻¹ remains unchanged for oxides⁴

PTE Half-Cell

- FlexCell-based PTE half-cell was able to reach current densities up to 1 A cm⁻²
- Circulation of electrolyte for bubble removal
- Stable experiments until 1 A cm⁻² at 60°C in 1 M KOH
- Highest and lowest overpotentials achieved with Ni(OH)₂+5% Fe and NiO(111), respectively
- Activity trends are in agreement with the RDE experiments



PTE half cell, 10 mV s⁻¹, 60°C, 1 M KOH



PTE half cell, 60°C, 1 M KOH

Conclusion & Outlook

- **In situ spiking** exceeds activity of **compounded synthesis** of Fe into Ni(OH)₂ and NiO(111)
- Surface confined Fe incorporation from **in situ spiking** more efficient than synthetic approach
- Fe inhibits surface reconstruction of pre-catalyst
- Measured by **in situ** Raman and XPS
- Amount of Fe too low for surface analytics (XPS)
- High surface area pre-catalyst could help
- Establishing novel half-cell for testing under **application-relevant conditions**
- 60°C and 1 A cm⁻² in 1 M KOH achieved
- Comparability to MEA needs to be tested

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