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NATURWISSENSCHAFTLICHE FAKULTÄT

Cobalt—Iron (Oxy)hydroxide Oxygen Evolution Electrocatalysts: The Role of Structure and Composition on Activity, Stability, and Mechanism

Michaela S. Burke, Matthew G. Kast, Lena Trotochaud, Adam M. Smith, Shannon W. Boettcher
Soheila Naridi, Alexey Saushev
Friedrich-Alexander University of Erlangen-Nuremberg
30. Januar 2017

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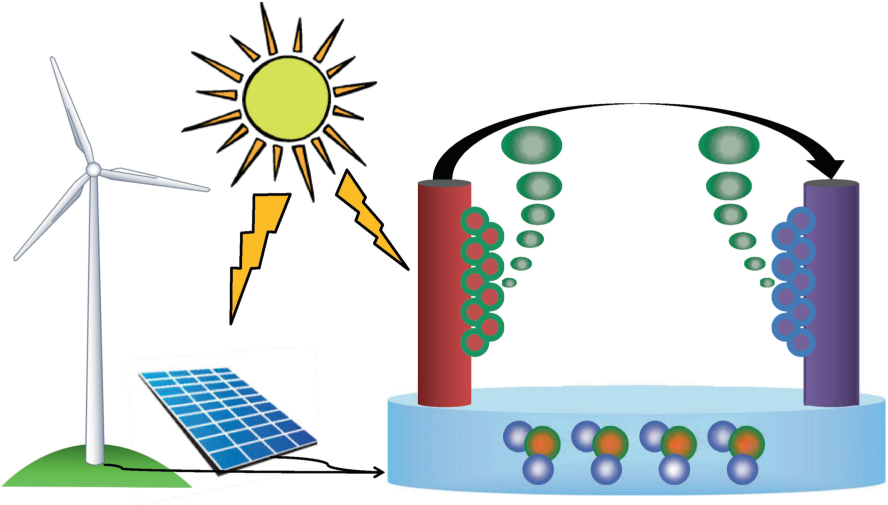
Slide 1



Schematic representation of the splitting of water via electrolysis, utilizing electricity derived from renewable sources such as wind and solar, and photoelectrolysis

Slide 2

The overall water electrolysis can be described by the following equation:

$$2\mathrm{H_2O} \rightarrow 2\mathrm{H_2} + \mathrm{O_2}$$

In alkaline solutions ($\mathrm{pH} = 14$), the corresponding cathode and anode reactions are:

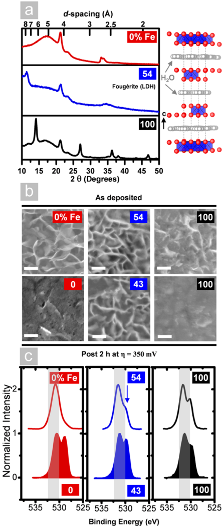
$$\begin{aligned} 4\mathrm{H_2O} + 4e^- &\rightarrow 2\mathrm{H_2} + 4\mathrm{OH^-} & E^\circ &= -0.826\mathrm{V} \\ \mathrm{O_2} + 2\mathrm{H_2O} + 4e^- &\rightarrow 4\mathrm{OH^-} & E^\circ &= 0.404\mathrm{V} \end{aligned}$$

In acid solutions ($\mathrm{pH} = 0$),

$$\begin{aligned} 4\mathrm{H^+} + 4e^- &\rightarrow 2\mathrm{H_2} & E^\circ &= 0\mathrm{V} \\ \mathrm{O_2} + 4\mathrm{H^+} + 4e^- &\rightarrow 2\mathrm{H_2O} & E^\circ &= 1.23\mathrm{V} \end{aligned}$$

In neutral conditions ($\mathrm{pH} = 7$),

$$\begin{aligned} 4\mathrm{H_2O} + 4e^- &\rightarrow 2\mathrm{H_2} + \mathrm{OH^-} & E^\circ &= -0.413\mathrm{V} \\ \mathrm{O_2} + 4\mathrm{H^+} + 4e^- &\rightarrow 2\mathrm{H_2O} & E^\circ &= 0.817\mathrm{V} \end{aligned}$$



(a) GIXRD of as-deposited films

(b) SEM images of samples as-deposited (top) and after 2 h of anodic polarization at $\eta = 350\mathrm{mV}$ (bottom)

(c) O 1s XP spectra of samples as-deposited (top) and after 2 h of anodic polarization (bottom)

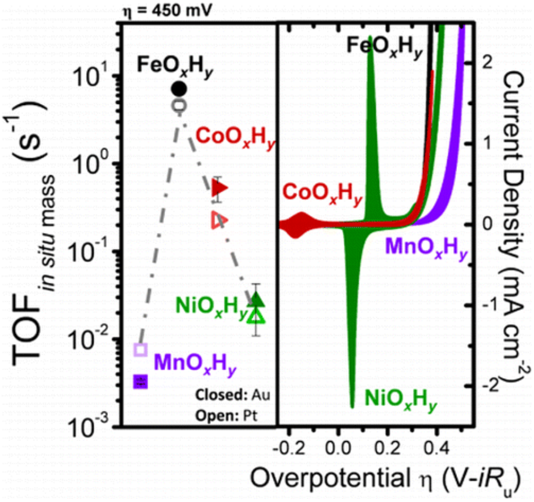
Motivation

Why Co-Fe (oxy)hydroxide:

- abundance (price);
- stability;
- conductivity;
- “self-repair”.

Problems:

- conflicting reports on activity;
- unknown active sites;
- stability.



Workflow

Sample preparation:

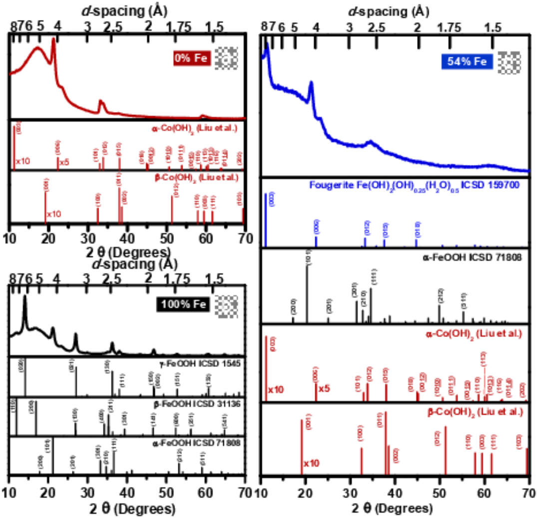
- initial rinse (XXX: cleaning QCM electrode?)
- cathodic deposition
- final rinse (XXX: washing QCM electrode holder?)

"As-deposited" sample.
Electrochemical testing:

- preliminary cycles
- constant potential, 2 h
- main part

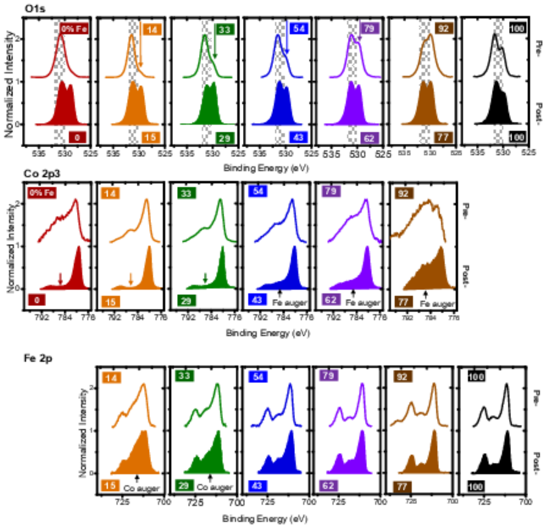
Final sample.

Grazing Incidence X-Ray Diffraction (GIXRD)



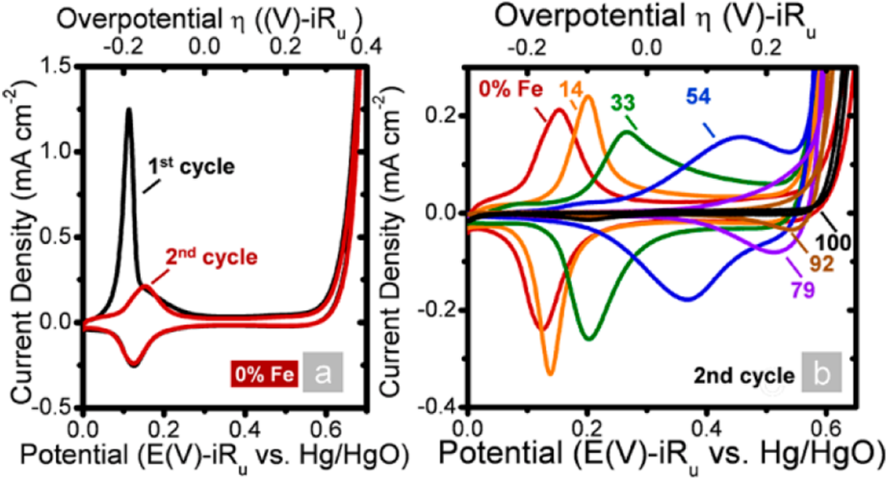
No substrate (Au–Ti) reflections.

X-Ray Photoelectron Spectroscopy (XPS)

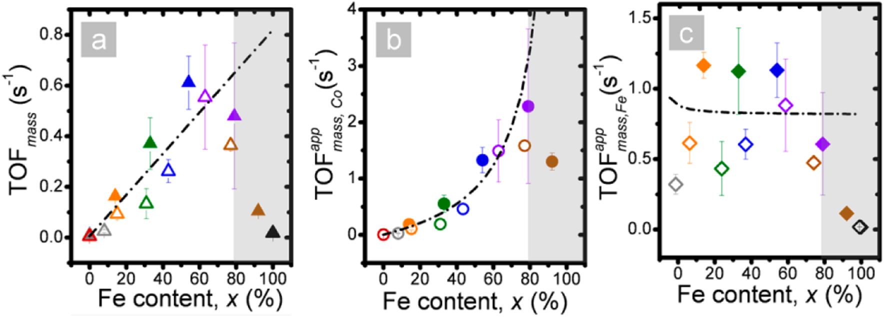


Scanning Electron Microscopy (SEM)

Cyclic Voltammetry (CV)

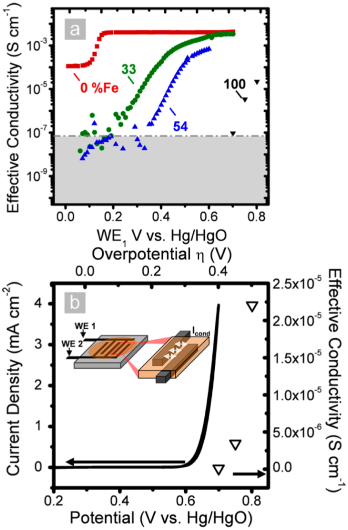


Turnover Frequency (TOF)

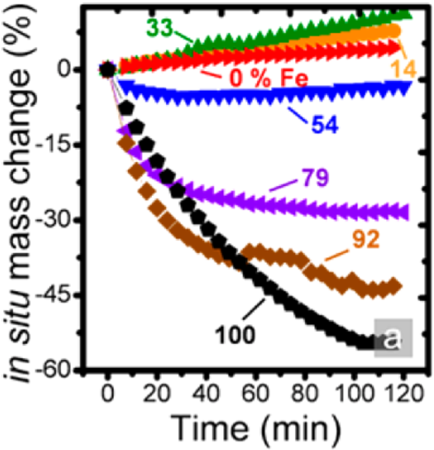


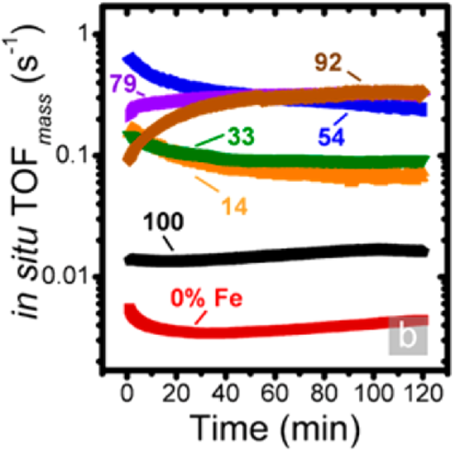
$$
\begin{aligned}
\mathrm{TOF}^{\mathrm{app}}_{\mathrm{mass,Co}} &= \mathrm{TOF}_{\mathrm{mass}}/(1-x) \\
\mathrm{TOF}^{\mathrm{app}}_{\mathrm{mass,Fe}} &= \mathrm{TOF}_{\mathrm{mass}}/x \\
\mathrm{TOF}_{\mathrm{mass}} &= (1-x)\cdot \mathrm{TOF}^{*}_{\mathrm{Co}} + x\cdot \mathrm{TOF}^{*}_{\mathrm{Fe}}
\end{aligned}
$$

Conductivity



Dissolution





Conclusion

- Fe incorporation enhances OER activity by $\approx$100-fold.
- Fe impurities are incorporated into CoOOH
- FeOOH has higher intrinsic OER activity than CoOOH
- FeOOH is insulator
- FeOOH is chemically unstable under OER conditions
- strong dependence of $Co^{3+/2+}$ potential on Fe content
- CoOOH is conductive, chemically stable, porous/permeable host
- Fe serves as the (most) active site for OER catalysis