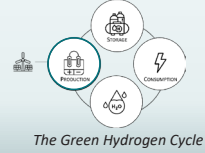


## Abstract

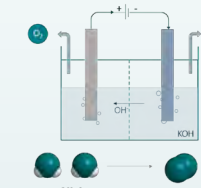
Decarbonizing energy and addressing climate change are crucial goals in our society. However, the intermittent nature of renewable energies poses a challenge and emphasizes the need of a reliable energy storage system. **Hydrogen**, produced through water **electrolysis**, is promising as such an **energy carrier**. (Green hydrogen cycle) Currently, hydrogen production heavily relies on fossil fuel-based steam reforming for economic reasons. To make electrolysis more appealing and competitive for large-scale hydrogen production, efficiency and cost improvements are vital. This has sparked significant interest in developing highly efficient and cost-effective **catalysts for hydrogen production**.

This thesis concentrates therefore on the electrochemical, structural and chemical investigation of non-noble metallic materials and their catalytic behavior towards the **hydrogen and oxygen evolution reaction**. The ultimate aim of the conducted studies within this thesis is to gain fundamental insights into electrode processes and material alterations. The understanding of those fundamental processes and the deep understanding of catalyst activity influences is of uttermost interest for successful catalyst design and application.



## H<sub>2</sub> Production

### Alkaline water splitting

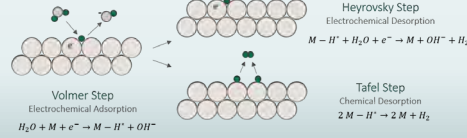


**Sluggish kinetics** due to either:

- slower transport of OH<sup>-</sup> than H<sup>+</sup> in solutions;
- stronger O-H bond in water molecules than in hydrated protons;
- adsorption ability of hydrogen on surface

### Hydrogen evolution reaction mechanism in alkaline media

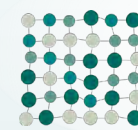
**Volmer Step:** reduction of H<sub>2</sub>O<sub>ads</sub> to H<sub>ads</sub>  
**Heyrovsky Step:** reaction with another H<sub>2</sub>O  
**Tafel Step:** recombination of two H<sub>ads</sub>



**Chemical tuning:** composition, alloying elements, oxidation

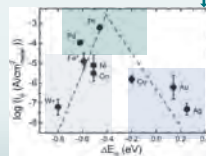
**Physical tuning:** surface area increase, structuring of surfaces

### High Entropy Alloys (HEA)



- min. 5 elements  
 - solid solution  
**Effects in HEAs**  
 High-entropy effect  
 Sluggish diffusion effect  
 Severe lattice distortion  
 Cocktail effect

### Catalyst Efficiencies



### Efficiency dependencies:

- inherent surface properties
  - M-H bond strength
  - Gibbs free energy of hydrogen adsorption
- Interaction between adsorbates
  - H<sub>ads</sub>
  - OH<sub>ads</sub>
- Double-layer environment
  - Transport of species (especially OH<sub>ads</sub>)

## Processes

### 1. Electrode Production



HEX series Compact Thin Film Deposition System by Korvus Technology

**Thin films**

- magnetron sputter deposition
- low roughness
- nanocrystallinity

**Nanoparticles**

- magnetron sputter deposition
- dewetting

**Process Parameters:**

- Temperature
- Chamber pressure
- Deposition Power
- Co-deposition

**Bulk electrodes**

- arc melting
- dealloying
- anodization

### 2. Material Characterization

**Electrode Material**

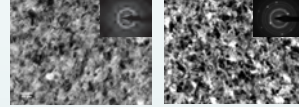
Ni NiMo FeCoNiMo FeCoNiMo(Cu)-Pd

Illustration of sputter deposited low roughness thin film electrode on support.

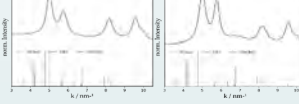
**Adhesion optimization**  
Thin film adhesion to the substrate is crucial for reliable and reproducible data.

### Sputter deposited nanocrystalline Ni surfaces as HER catalyst materials

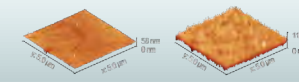
as deposited 100 cycles



TEM imaging of sputter deposited nanocrystalline thin films before application and after 100 cycles of hydrogen evolution reaction



Diffraction peaks obtained by azimuthal integration of the SAED patterns using PASAD



AFM topography investigation for roughness estimation.

### 3. Electrochemical Evaluation

### 4. Evaluation of Electrode Changes

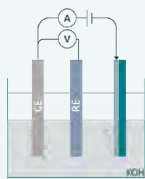
- HER Overpotentials
- Tafel analysis
- Determination of ECSA
- Electrochemical oxidation of metallic samples
- Long term stability

### Electrochemical Setup

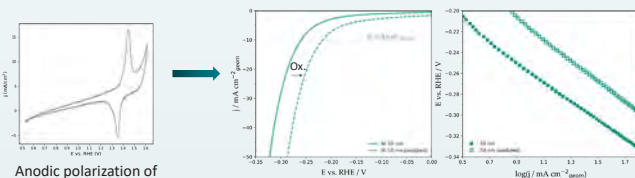
3-Electrode Setup

RE: Hg/HgO  
 CE: Pt coil  
 WE: thin film

Electrolyte: 1M KOH

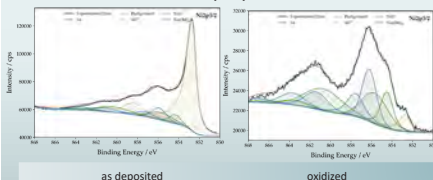


### In situ electrochemical oxidation of Ni thin films



Anodic polarization of the working electrode Oxidation

Builtup of defined Ni, NiO and Ni(OH)<sub>2</sub> surface (XPS)



- Boost of HER
- Lowering of overpotential (η)
- Improvement of stability
- Influence of film thickness
- Comparability with theoretical calculations (DFT)

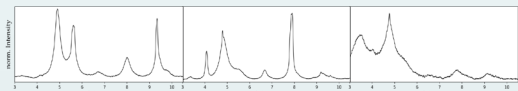
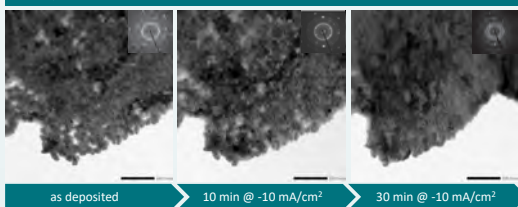
### Identical location investigation of NiMo low roughness thin films

Sputter deposition of thin films on electropolished Cu TEM substrates



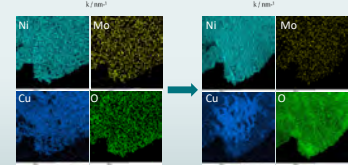
Structural investigation of changes upon the application of a constant current.

### Identical location TEM investigation of Ni<sub>0.9</sub>Mo<sub>0.1</sub> upon constant current at -10 mA/cm<sup>2</sup>



Diffraction peaks obtained by azimuthal integration of the SAED patterns using PASAD

Identical location studies aim a structural detection of Mo leaching from the electrode material to the electrolyte during application.



EDS analysis of the selected area of an as-deposited sample and after 30 minutes at -10 mA/cm<sup>2</sup>

## Catalyst Activity

## Durability

## Identical location TEM