RANEY-NI ELECTRODES FOR THE ALKALINE ELECTROLYSIS OF WATER

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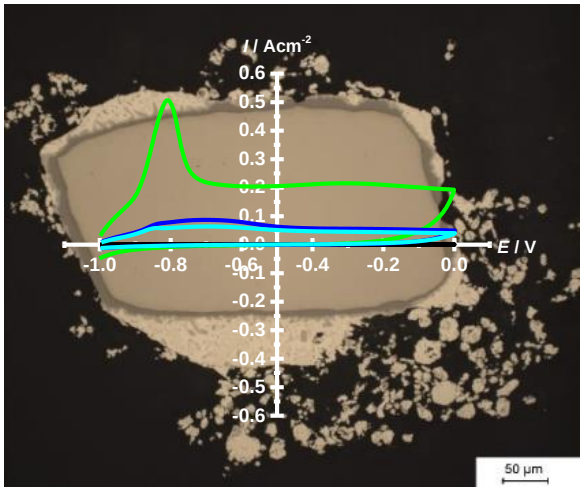
ICE 2017
International Conference on Electrolysis



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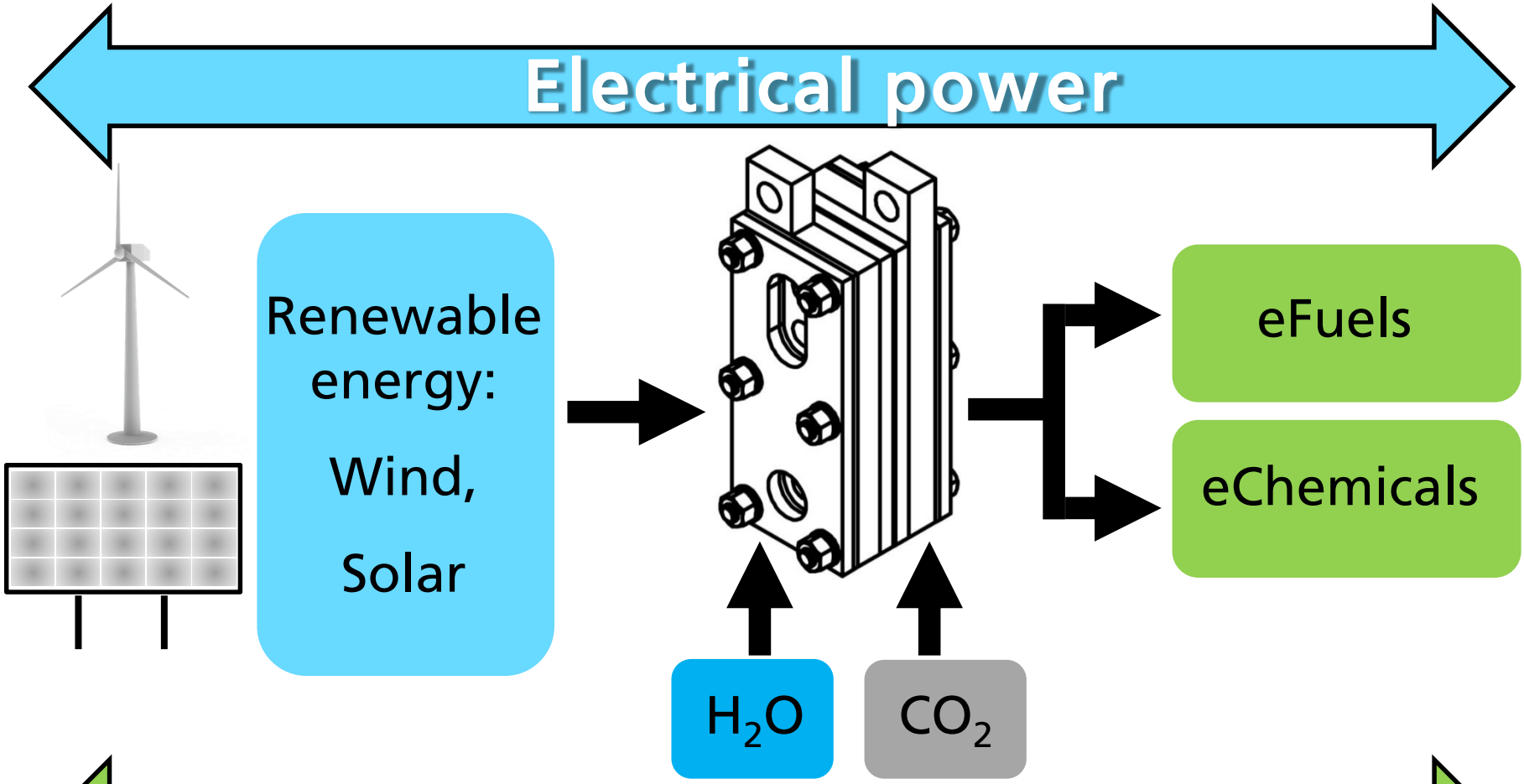
Motivation


Electrical power
Renewable energy:
Wind,
Solar
eFuels
eChemicals
H_2O
CO_2
Chemical energy carrier

Electrode Materials for AEL

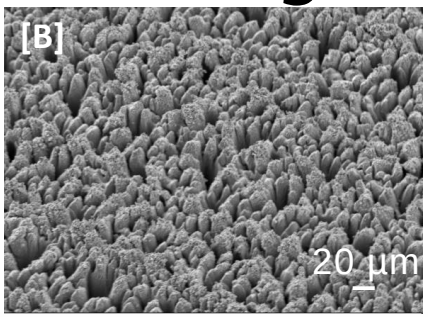
- **Low Voltage** at a **High Current Density**
  - ↳Energy
  - ↳H_2-production rate

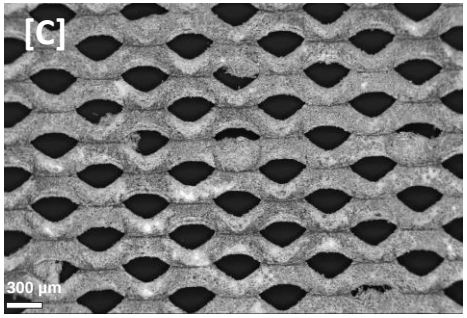
- Demands
  - **Stability**
    - Degradation < 3 µV/h[A]
    - Life-Time Stack > 90 000 h (10 a)
  - **Electrochemical Activity**
    - Cell-voltage 1.8 – 2.2 V (< 0.6 A/cm²) [A]
  - **Costs**
    - Investment costs of the system < 1000 €/kW_{el}[A]

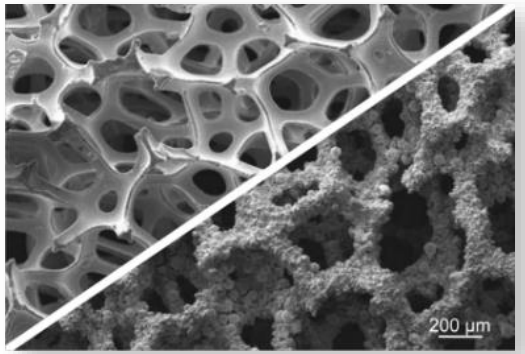
[A] Smolinka et al., NOW Studie, 2011.

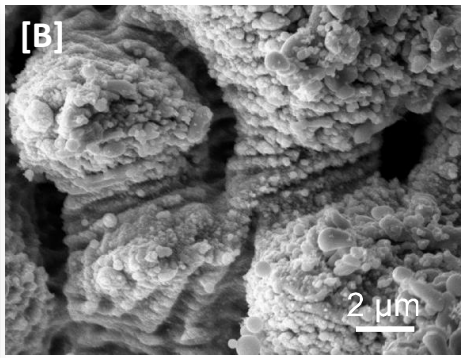
Hydrogen: Electrodes with a large surface area

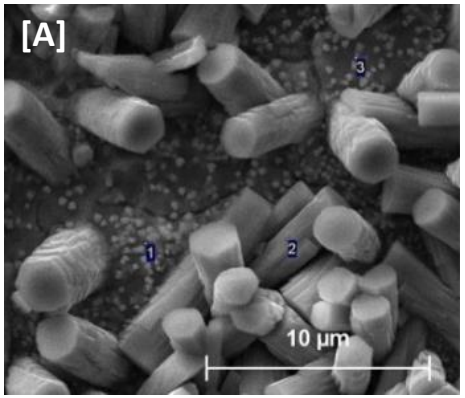
- Structuring the surface of flat and porous materials
- Structures in the range of 100 nm to 100 µm possible
- Surface enlargement up to 10000-fold possible

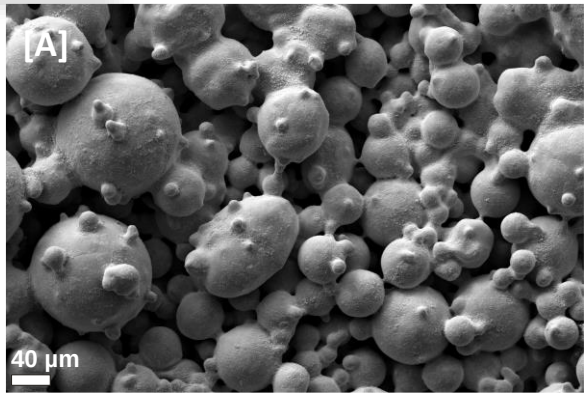








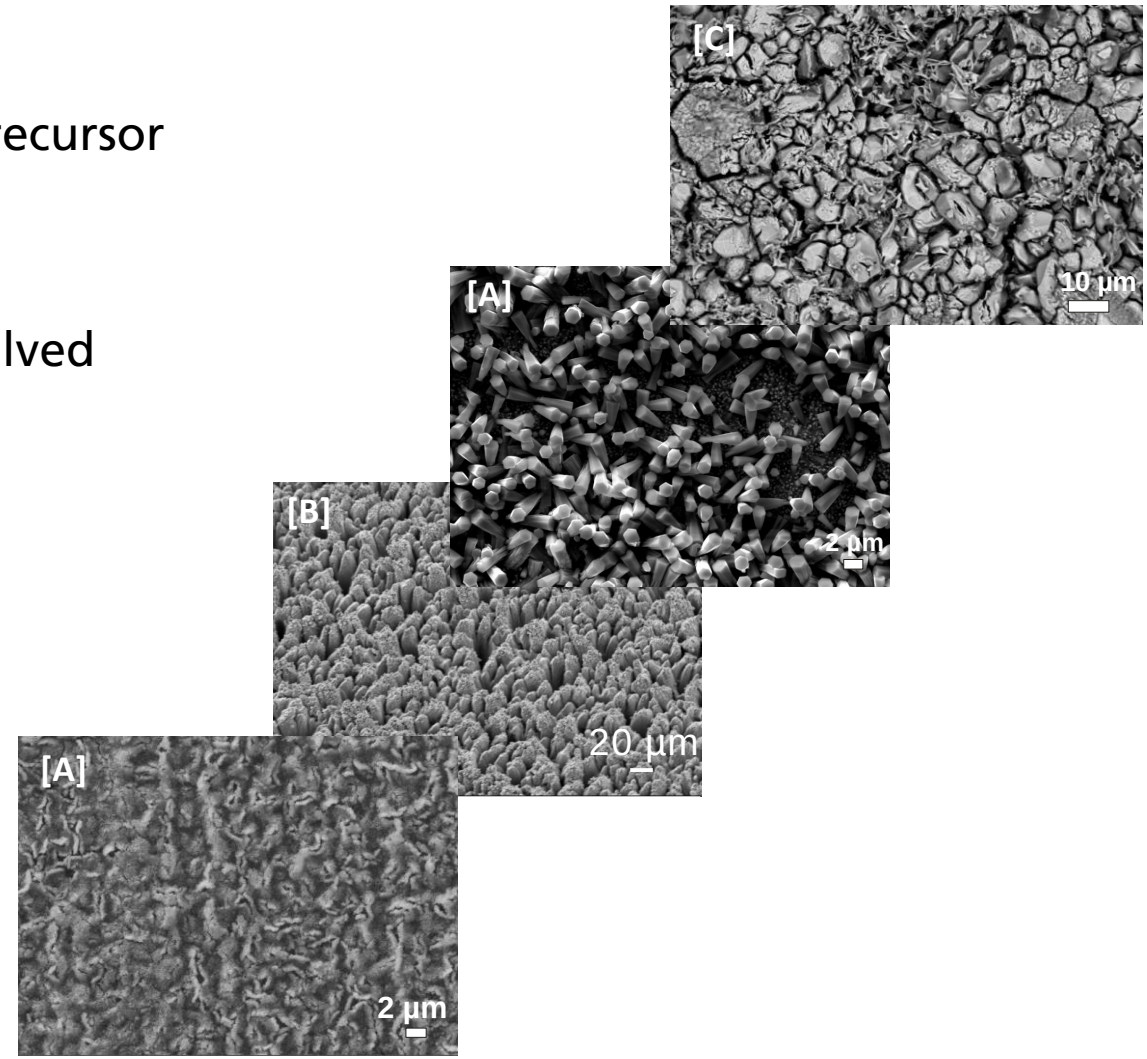




[A] AMORPHEL (0327899A), funded by the BWMi of the Federal Republic of Germany .
[B] Green-H2 (03ET6058), funded by the BWMi of the Federal Republic of Germany.
[C] ELYntegration, funded by FCH-JU under grant agreement No 671458, FCH-JU receives support from the European Union's Horizon 2020 program.

Hydrogen: Electrode production techniques

- Powder metallurgical route
  - Sintering of a powdery precursor
- Electroplating
  - Electrodeposition of dissolved species
- Laser ablation process
  - Femto-second pulse process
- Rapid quenching technique
  - Amorphous ribbons



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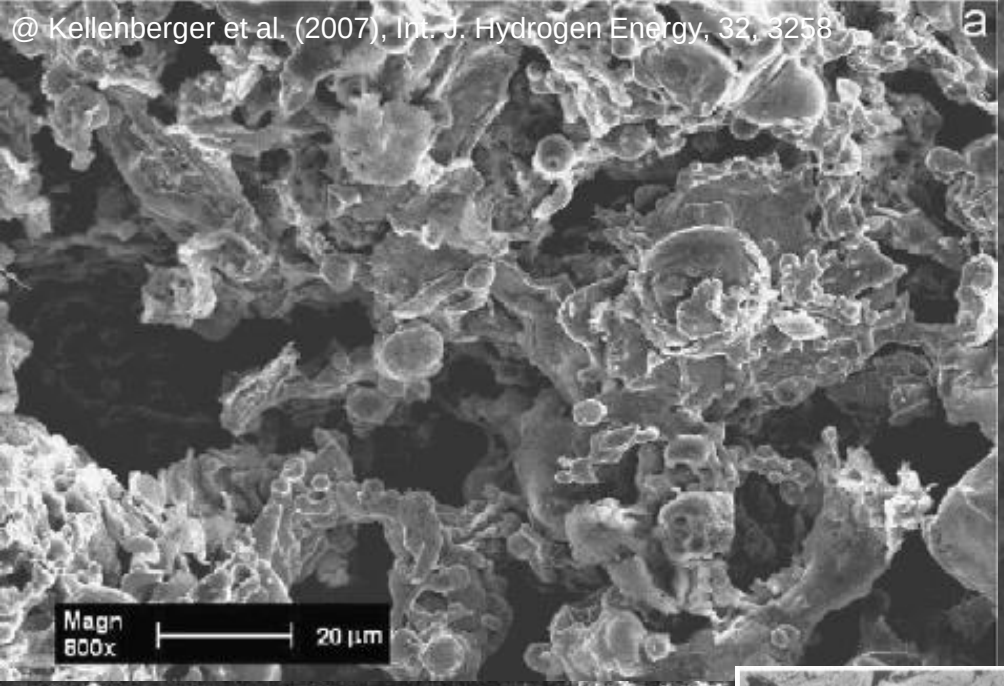
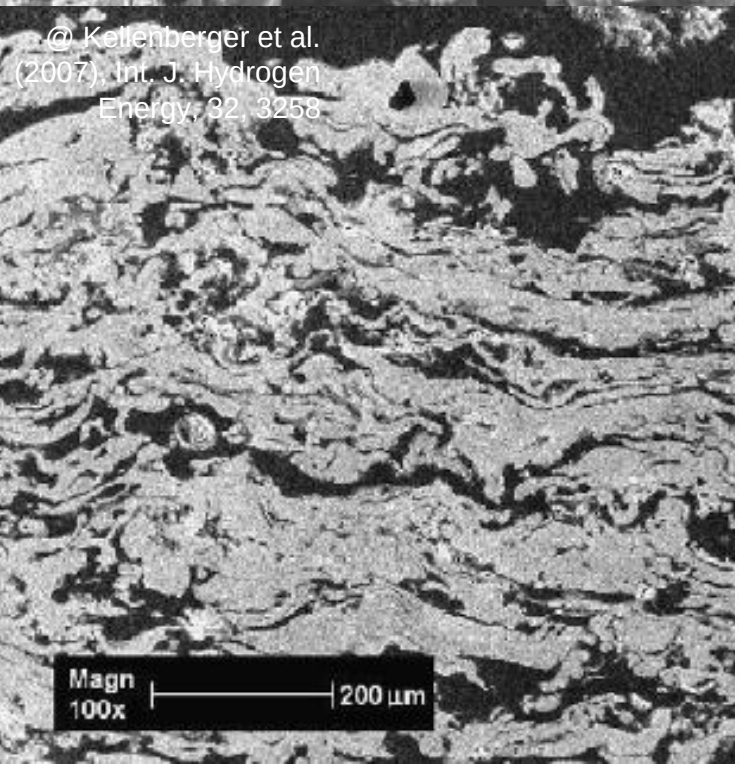


@ Kellenberger et al. (2007), Int. J. Hydrogen Energy, 32, 3258

@ Rausch et al. (1996), J. Electrochem. Soc., 143, 2852.



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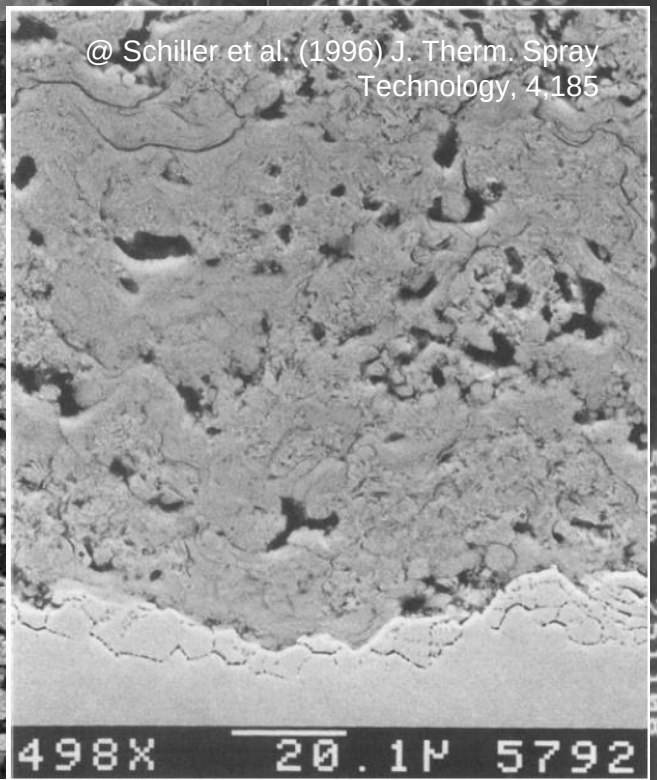
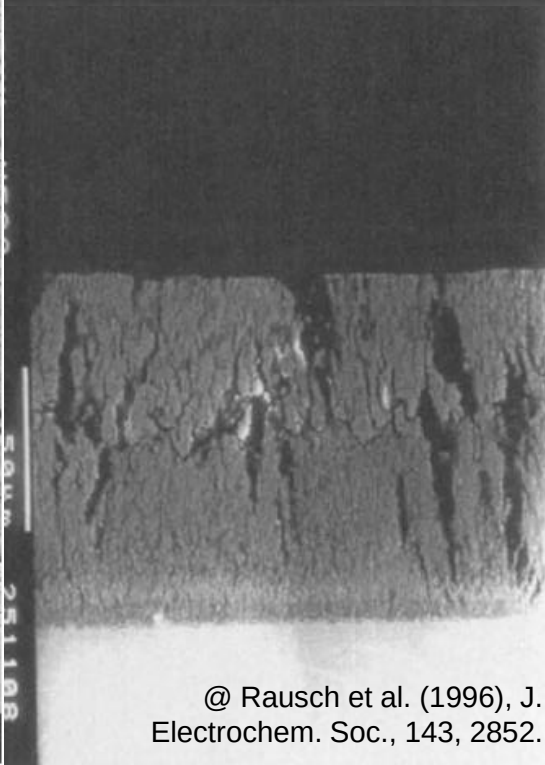


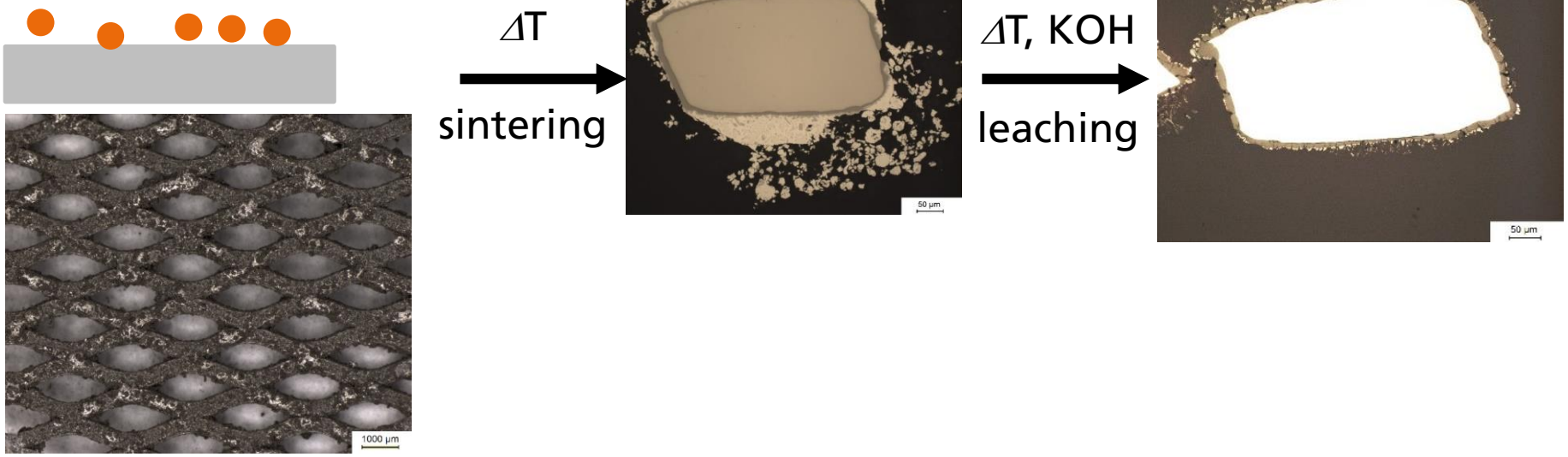
@ Schiller et al. (1996) J. Therm. Spray Technology, 4,185



@ Rausch et al. (1996), J. Electrochem. Soc., 143, 2852.

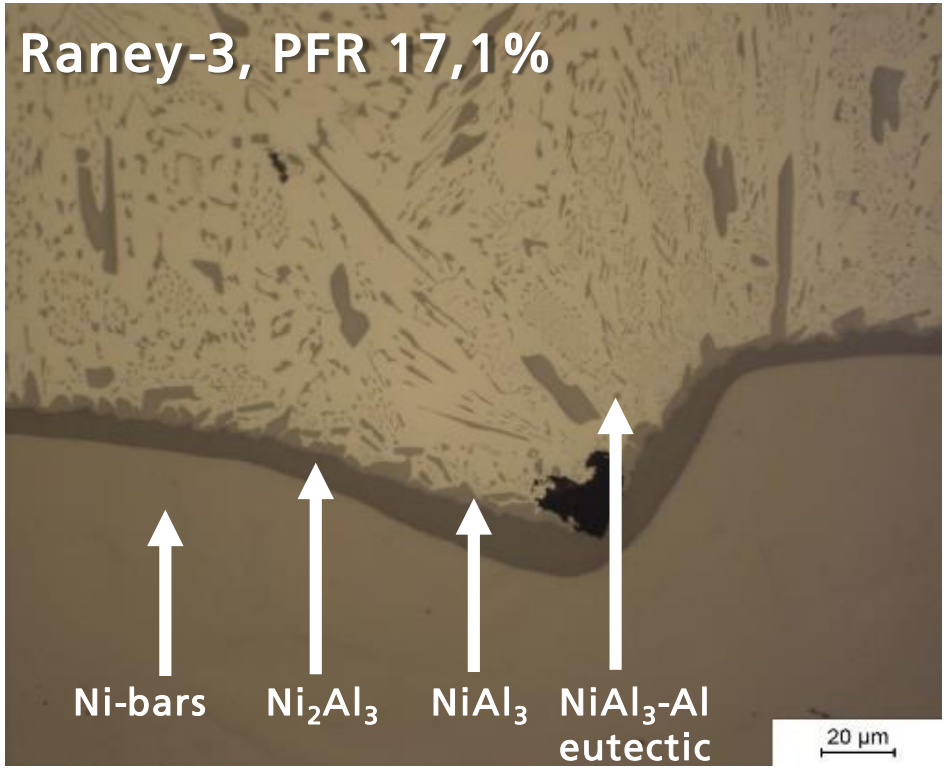
Synthesis of Raney-Ni electrodes

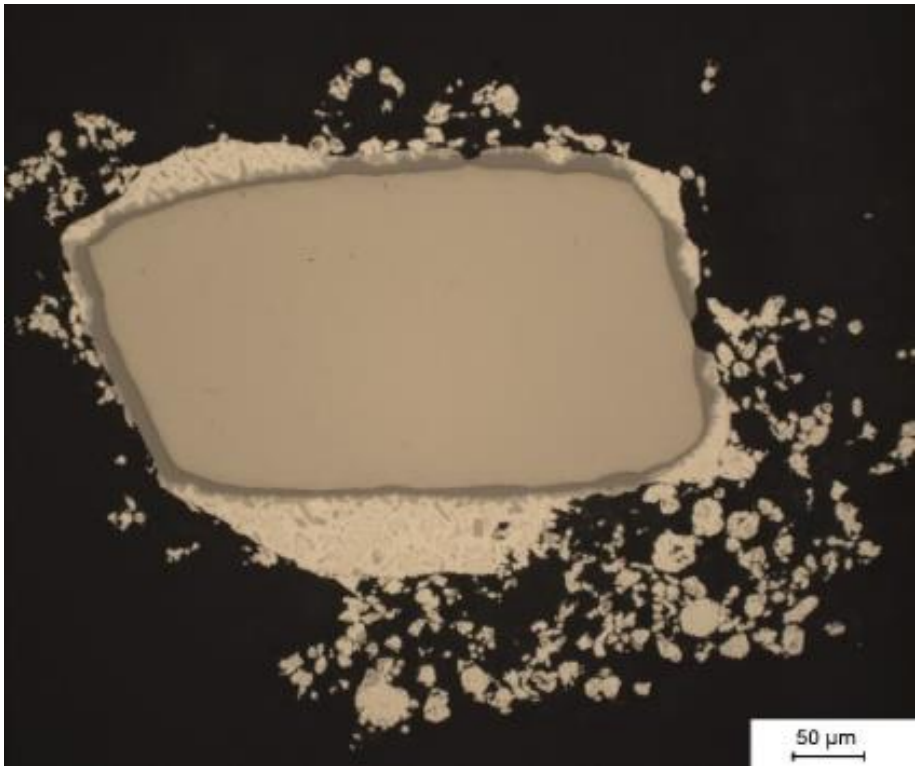
- State of the art:
  - Electroplating (NiZn) → batch process, doping difficult
  - VPS (NiAl) → batch process
- Approach: sintering → scalable (continuously produced), different alloy compositions possible, stable connection of catalyst to substrate
  - → costs < 300 €/m²



Sintered Raney-Ni electrodes (Raney-3)

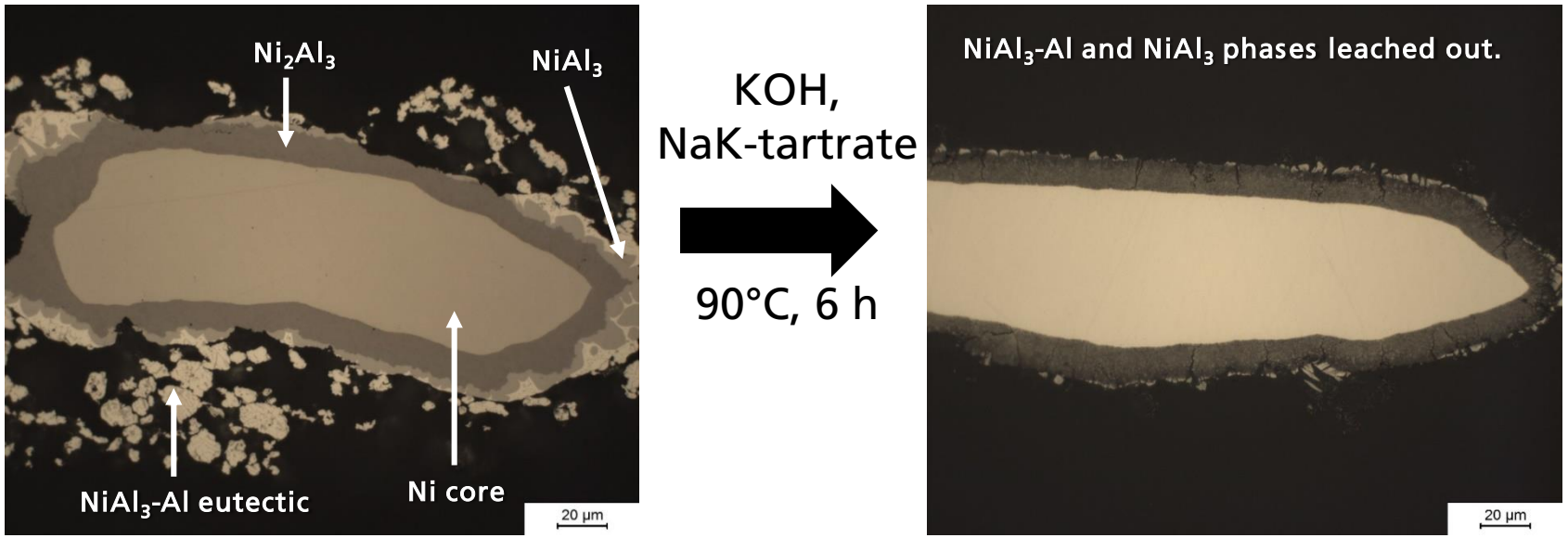
- Substrate Ni-mesh (Dexmet)
  - Al-powder-mesh-ratio (PMR): 17.1 % (calculated after sintering)
  - Ni-mesh perfectly surrounded by NiAl-phases





Ni-mesh: enlarging the surface area

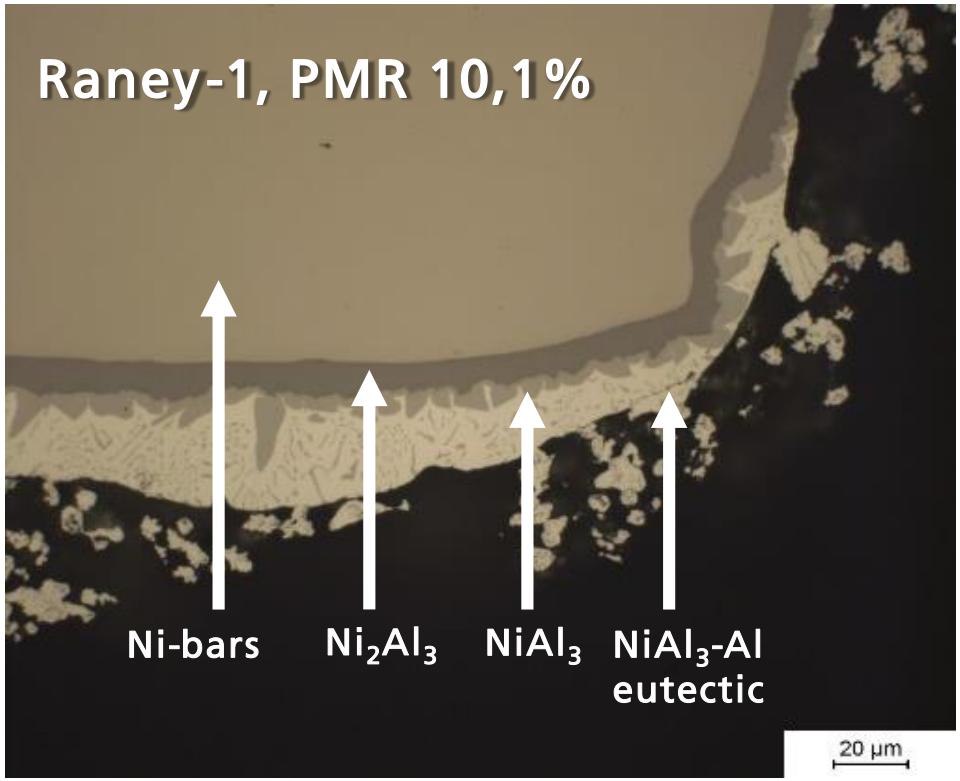
- Raney-Ni production via a powder metallurgical and a chemical process



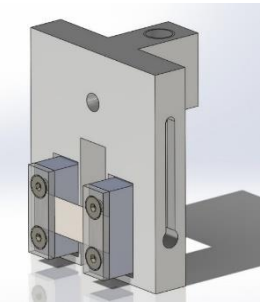
- Porous layer is formed → strongly increased surface area
- No delamination of the Ni_2Al_3-phase detectable, due to the sintering process → good stability

Sintered Raney-Ni electrodes (Raney-1)

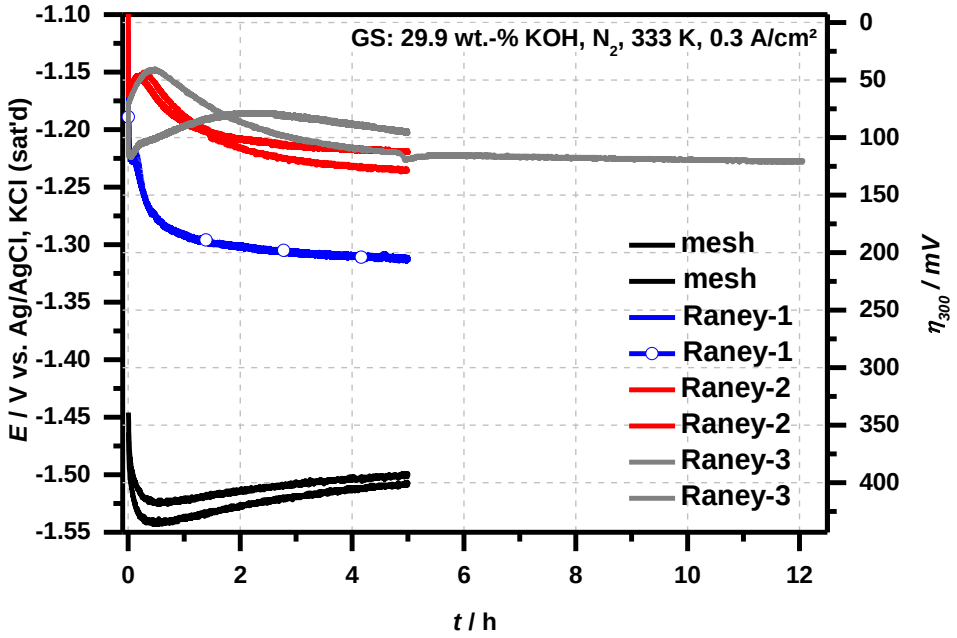
- Substrate Ni-mesh (Dexmet)
  - Al-powder-mesh-ratio (PMR): 10.1 % (calculated after sintering)
  - Ni-mesh perfectly surrounded by NiAl-phases

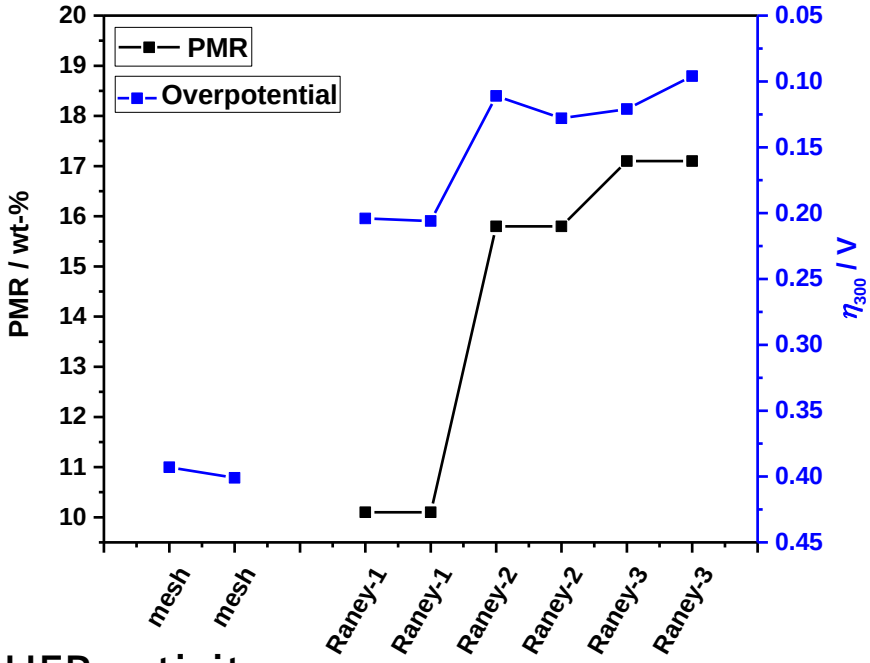


HER activity of sintered Raney-Ni electrodes



- Raney-1: 10.1 % PMR
- Raney-2: 15.8 % PMR
- Raney-3: 17.1 % PMR

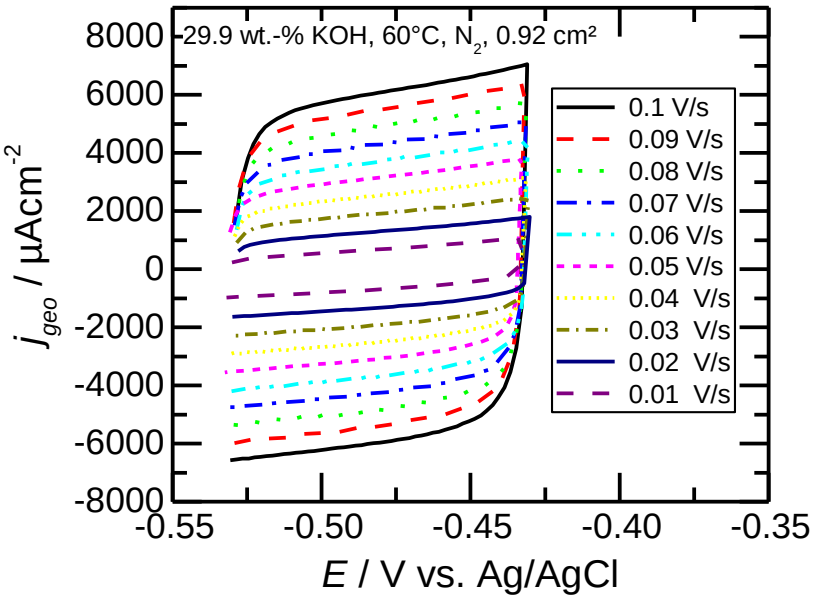


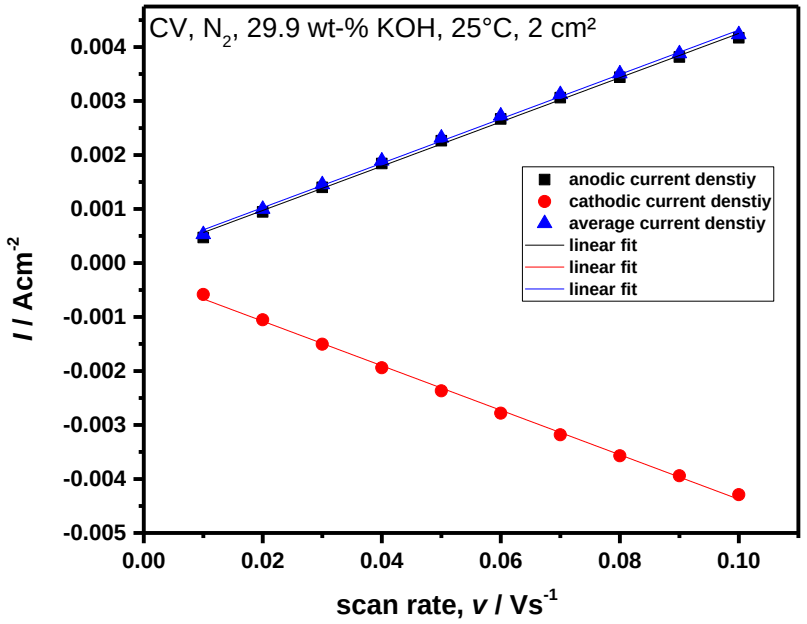


- Raney-Ni layer has a strongly increased HER activity
- Higher PMR value causes a higher HER-activity

Electrochemical surface area

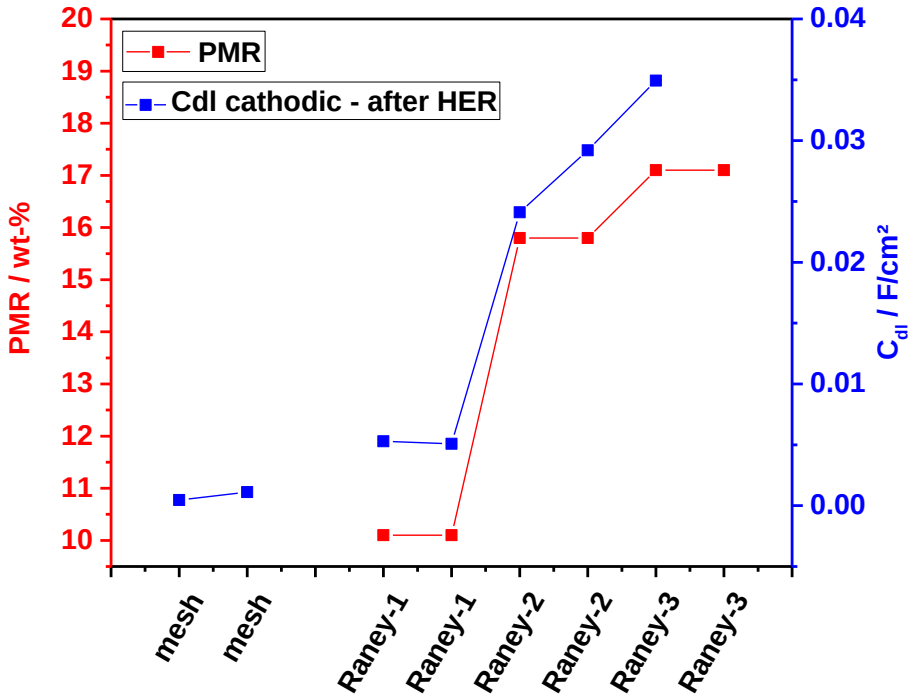
- Determining the double layer capacity C_{dl} → $i_c = C_{dl} \times v$
  - CV-pretreatment, in order to remove H-ad and M-H
  - C_{dl} determined at the OCP (-400 to -600 mV)

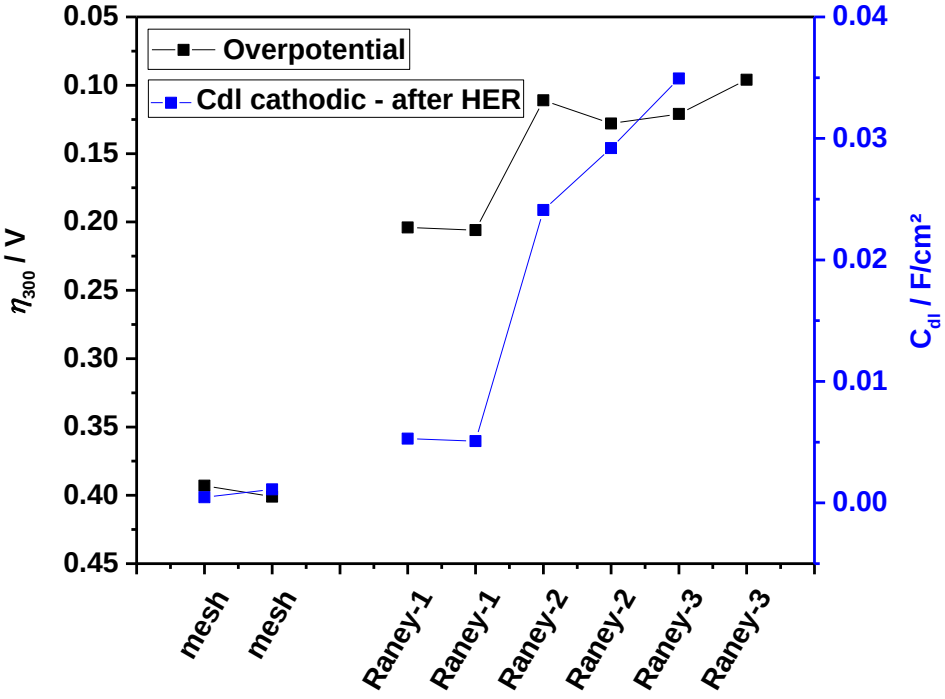




Electrochemical surface area

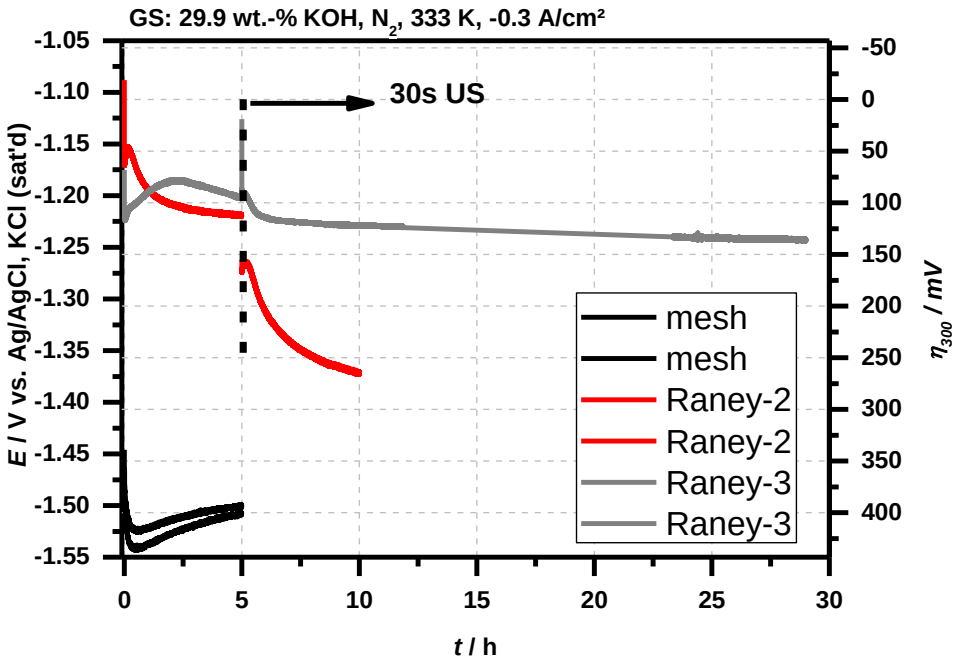
- Correlation between PMR and C_{dl}
- Correlation between η_{300} and C_{dl}
  - →Main effect: enlarged surface area
  - →Minor effect: increased intrinsic activity

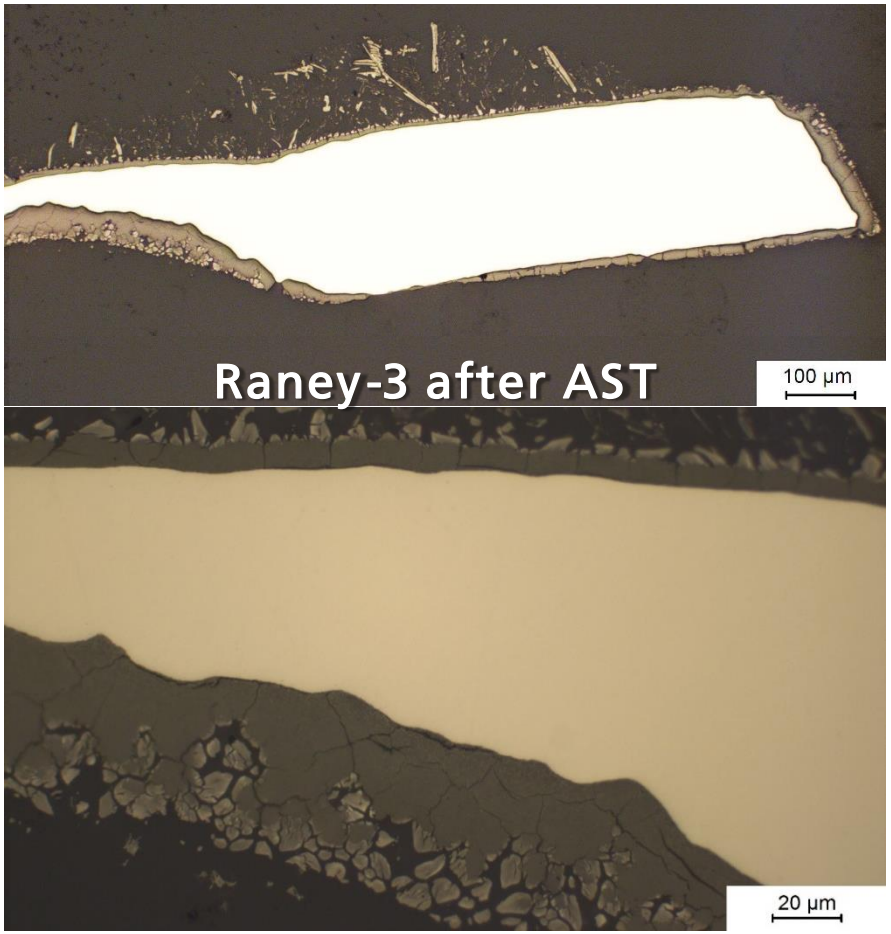




Accelerated stress test using ultrasonic treatment

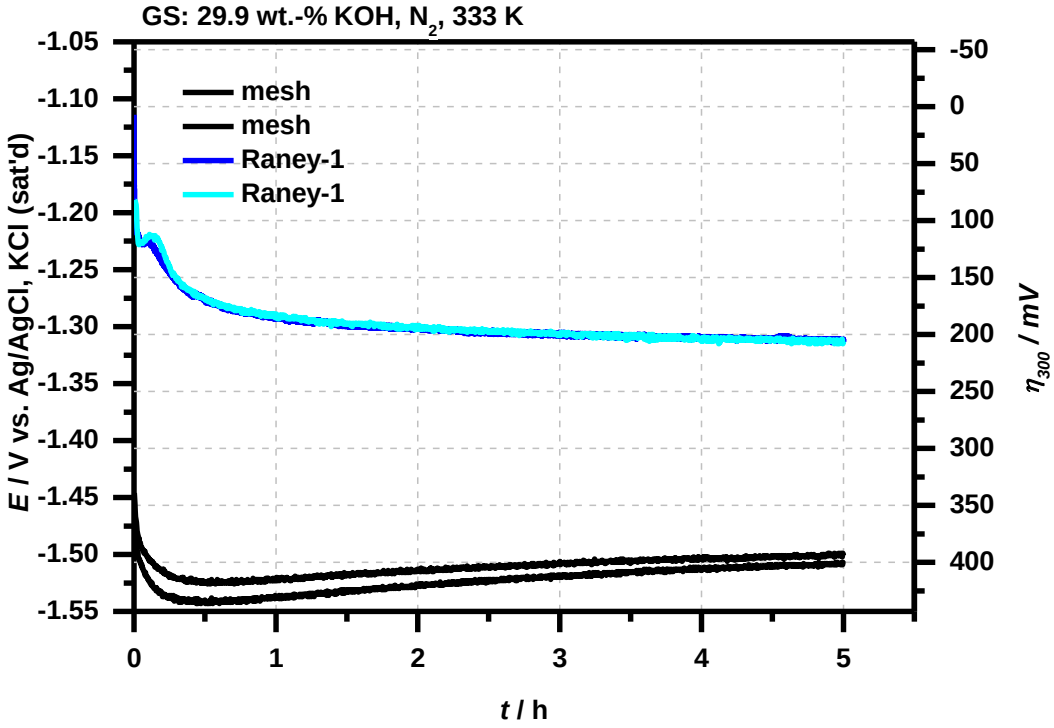
- Accelerated Stress test (AST)
  - GS @0.3 A/cm²
  - Ultra sonic treatment for 30 s
  - GS @0.3 A/cm²

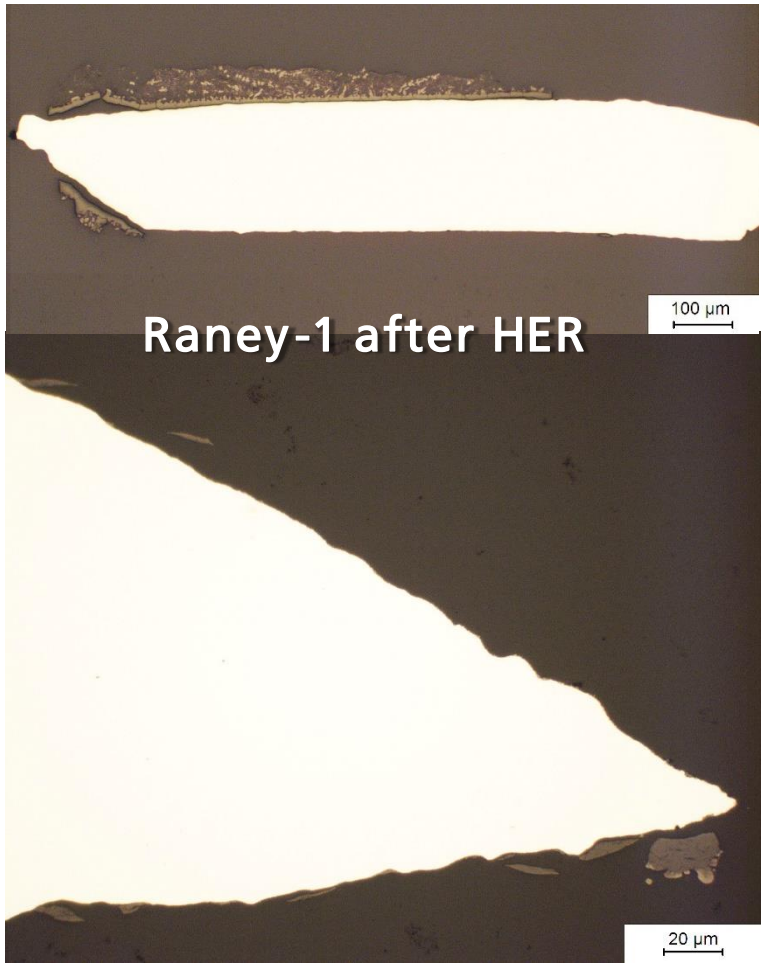




Raney-1 (lowest PMR)

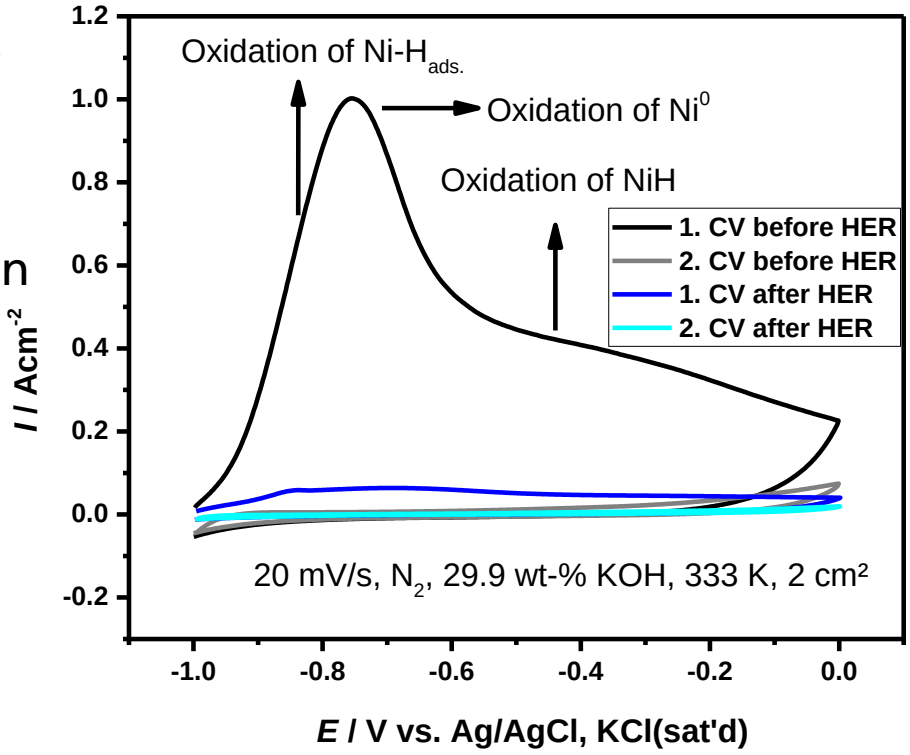
- Degradation detectable
- delamination of Raney-catalyst
  - Due to eruptive gas bubble evolution
  - Due to M-H formation



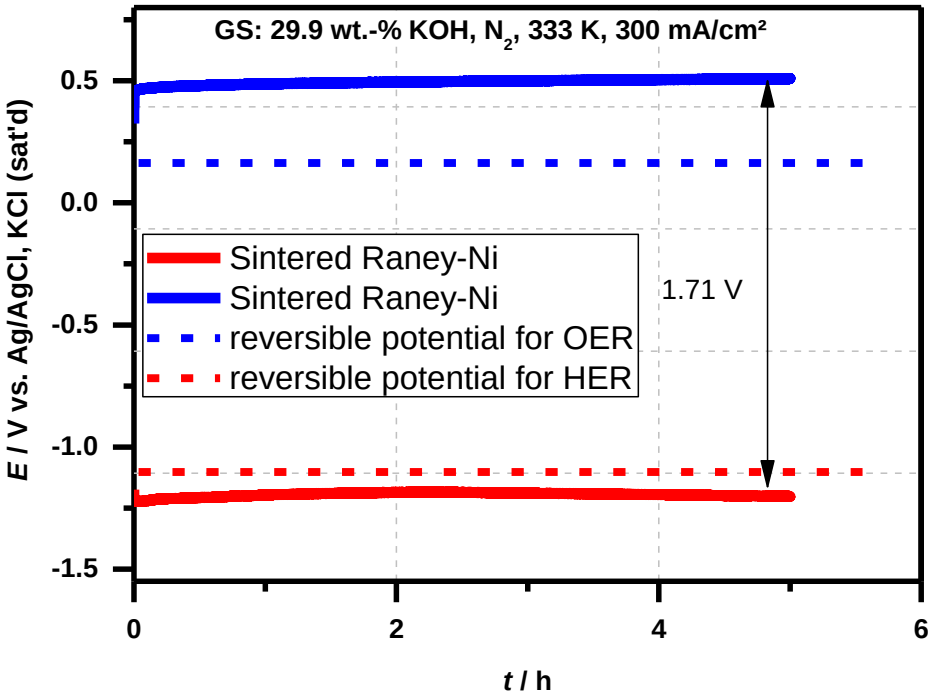


Cyclic voltammetry

- Formation of Ni-H_{ads} and Ni-H (Nickelhydride) before and after HER
  - self-ignition of leached Raney-Ni due to Ni-H_{ads} and Ni-H formation!
  - Formation of Ni-H is accompanied by a volumetric expansion of the phase → delamination
    - Potential shift of the cathode above -0.8 V should be prevented during down time of ELY!
  - No peak observable for the second scan
    - Deactivating of leached electrodes



HER + OER



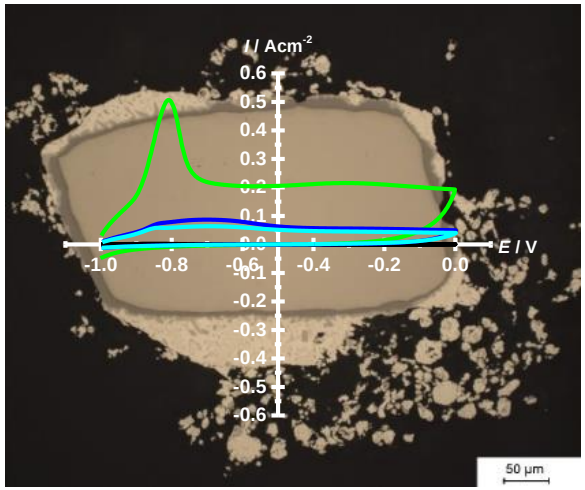
- Calculate cell voltage (only electrode overpotential) around 1.71 V @ 0.3 A/cm²
- @3000 A/m² → 1.684 V (cell voltage)
- 45,8 kWh/kg_{H2} → 4.58 €/kg_{H2} (0.1 €/kWh electricity costs)

Summary

- Raney-Ni electrodes developed using sinter technology
  - Higher PMR beneficial for HER-activity
  - Main degradation due to delamination of Raney-Ni layer
    - Caused by formation of Nickel-hydride (volumetric expansions)
    - → Potential shift of the cathode above -0.8 V should be prevented during down time of ELY
    - CV can be used to deactivate the leached electrode for safe handling
    - Calculate cell voltage (only electrode overpotential) around 1.71 V @ 0.3 A/cm²

Acknowledgement

elyntegration



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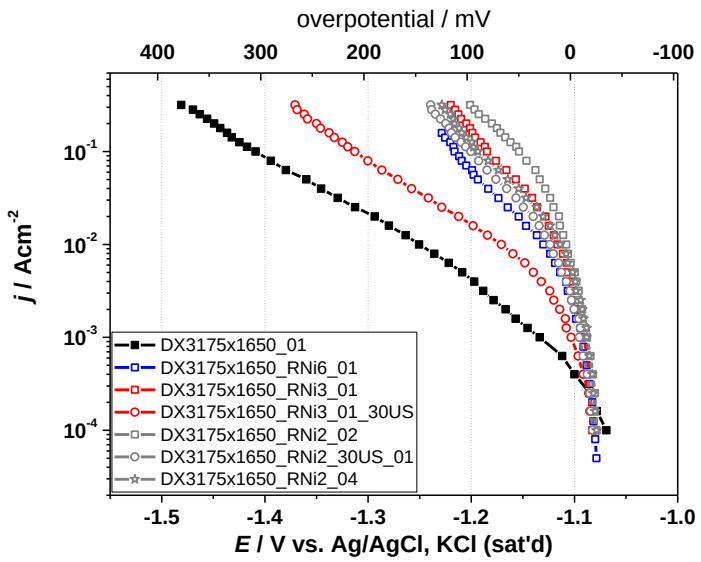
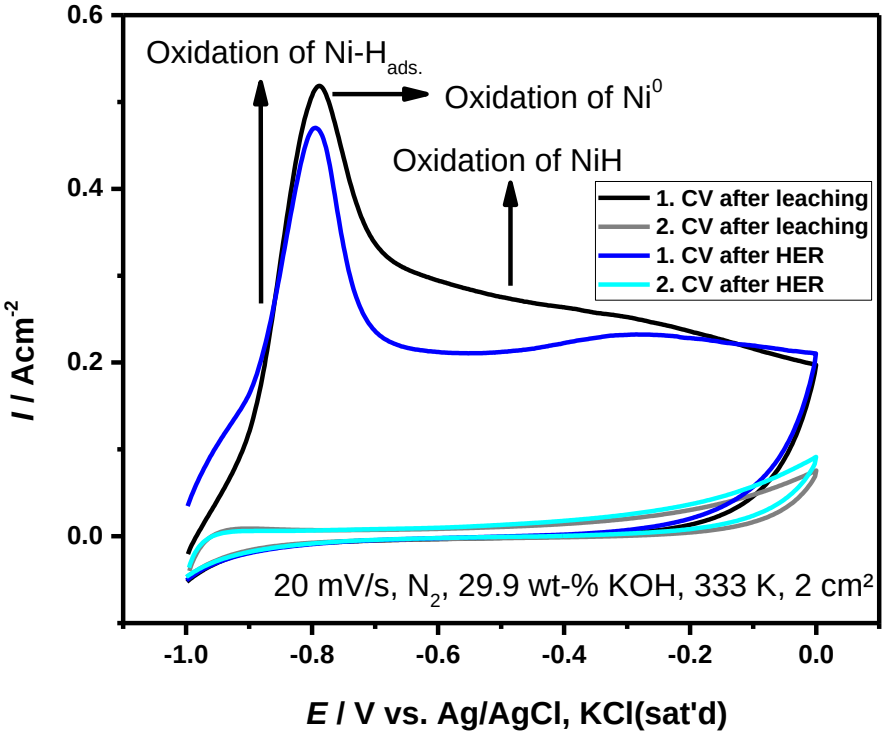
Thank you
for your
kind attention!
10 µm


overpotential / mV
400
300
200
100
0
-100
j / Acm-2
10-1
10-2
10-3
10-4
DX3175x1650_01
DX3175x1650_RNi6_01
DX3175x1650_RNi3_01
DX3175x1650_RNi3_01_30US
DX3175x1650_RNi2_02
DX3175x1650_RNi2_30US_01
DX3175x1650_RNi2_04
-1.5
-1.4
-1.3
-1.2
-1.1
-1.0
E / V vs. Ag/AgCl, KCl (sat'd)


0.6
0.4
0.2
0.0
I / Acm-2
Oxidation of Ni-Hads.
Oxidation of Ni0
Oxidation of NiH
1. CV after leaching
2. CV after leaching
1. CV after HER
2. CV after HER
20 mV/s, N2, 29.9 wt-% KOH, 333 K, 2 cm²
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
E / V vs. Ag/AgCl, KCl(sat'd)