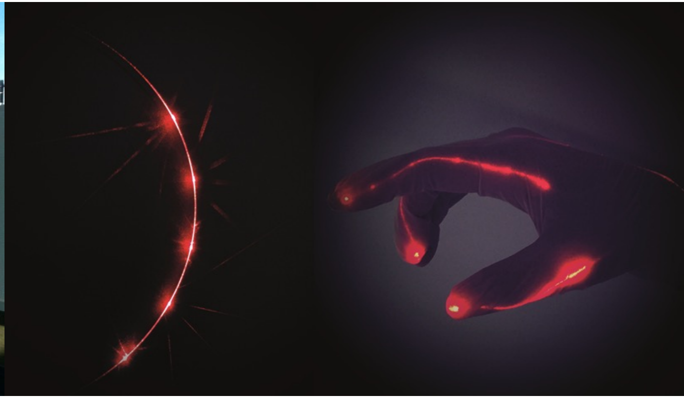
Femtosecond laser for surface structuring of new electrode materials

Fraunhofer HHI Goslar



Wolfgang Schade

TU Clausthal
Clausthal University of Technology

Fraunhofer
HHI

Our New Energy World

Hydrogen generation and energy storage

Needs efficient generation of H_2

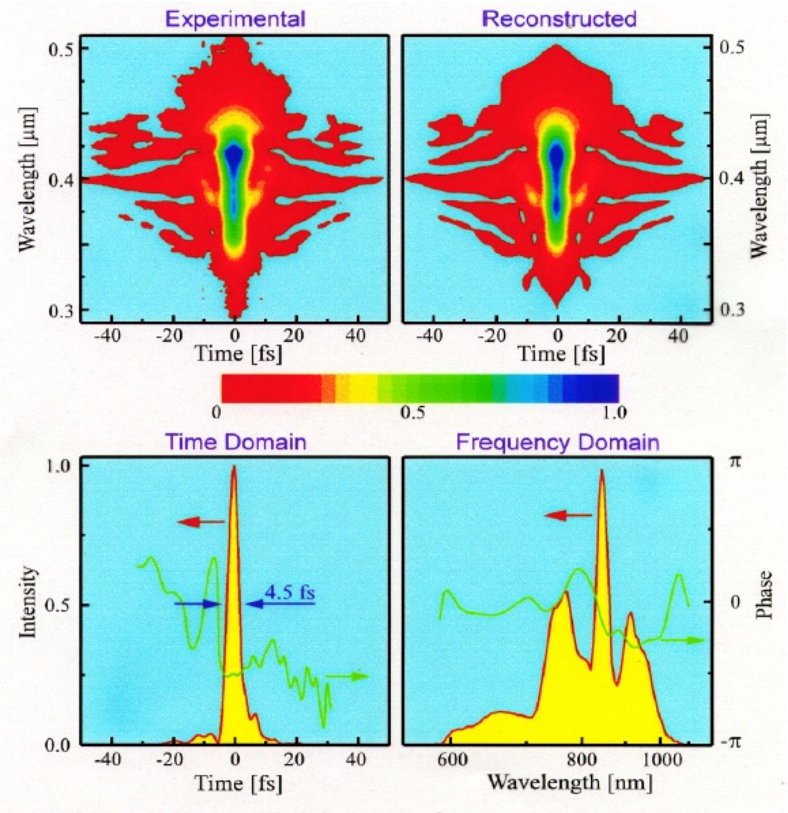
→ Electrolysis

→ Optimization of electrodes

Rechargeable Zn-Air batteries

→ New electrode materi

Our working tool – femtosecond lasers pulses



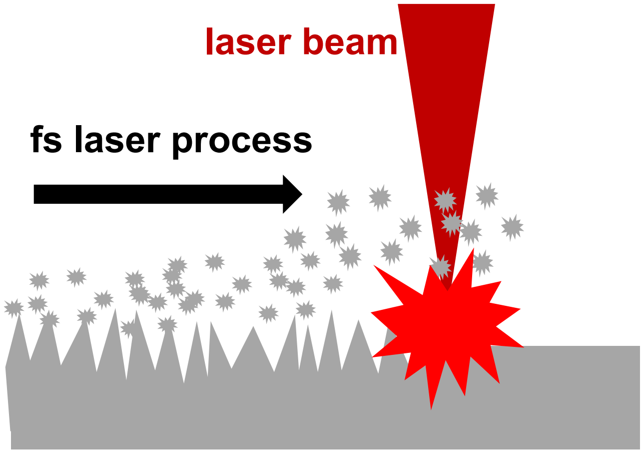
1 femtosecond = 10^{-15} s

= 0,000000000000001 s

… with amazing characteristics …

Femtosecond Laser Surface Structures

Structure Development



Number of laser pulses per spot on the surface[1]:

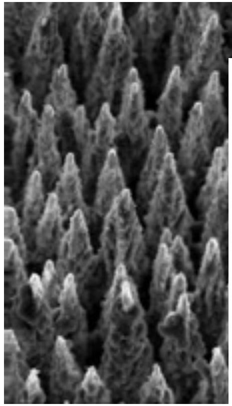
N = 1 – 10 → 10 – 25 → 25 – 50 → 50 – 100 → **100 – 250** → >> 1000

LIPSS → ripples → grooves → cones → **<u>cones</u>** (10 µm) → **?**

surface enlargement

[1] for J ~ 1 J/cm² @1 - 10 kHz
See e.g. B. N. Nayak, M. C. Gupta, *Opt. Laser. Eng.* **2010**, *48*, 966 - 973. DOI: 10.1016/j.optlaseng.2010.05.009

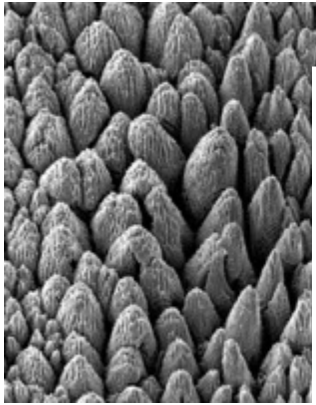
SurfaceLab – Femtosecond Laser Surface Processing



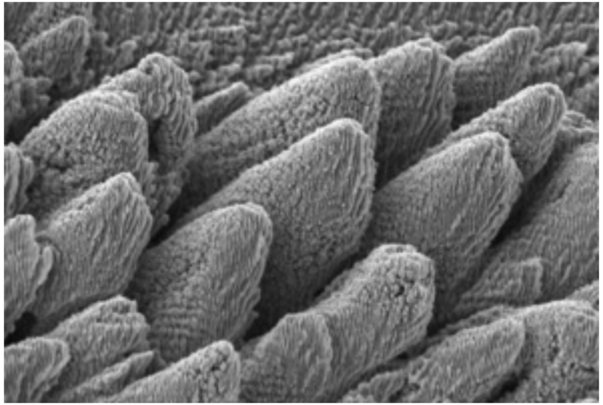
silicon

aluminium

polymer



titanium



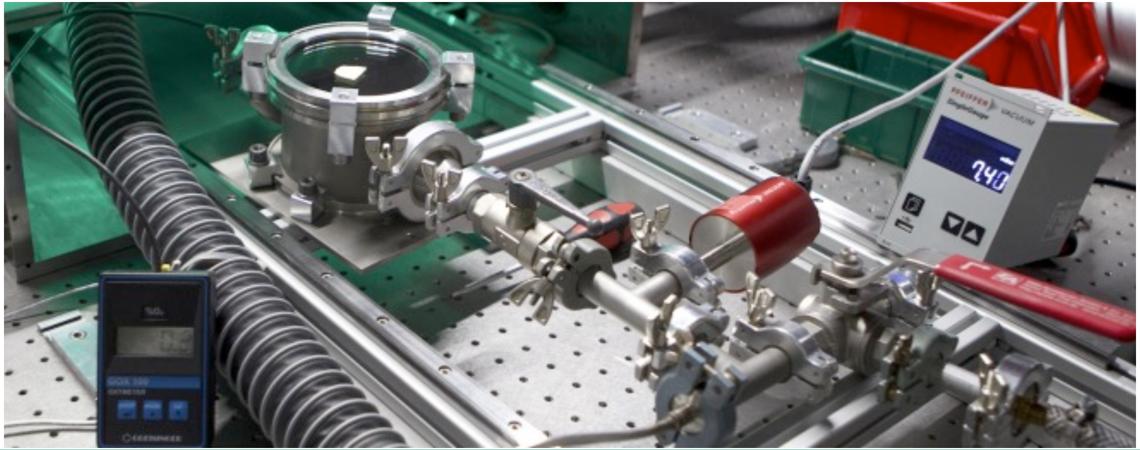
nickel

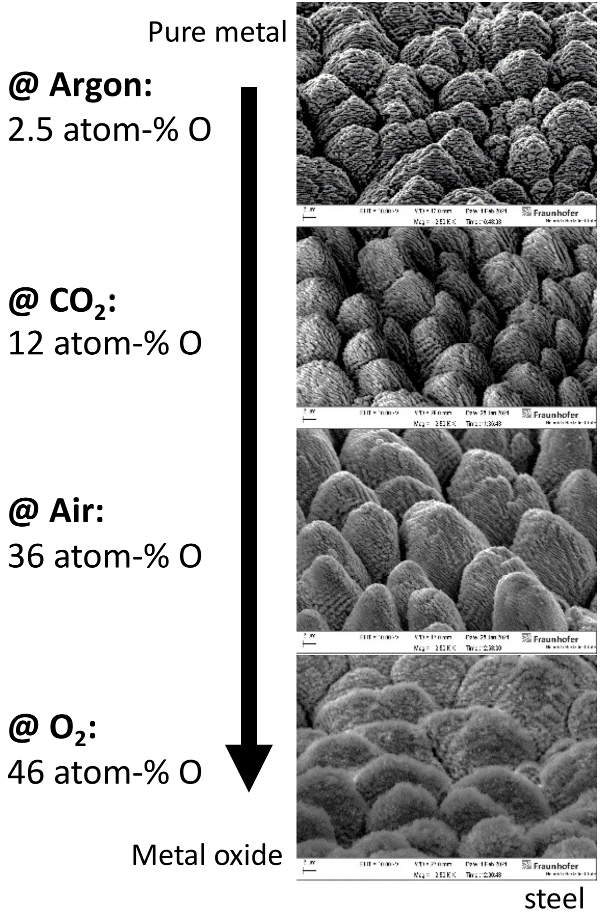
… zinc, silver, ceramic, copper, graphite, …

Femtosecond Laser Surface Structures

Controlling Surface Chemistry

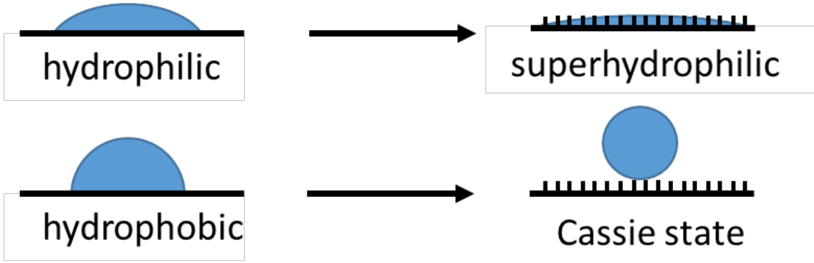
- To control wettability
- Optimized stoichiometry for catalysts
- Ar, N_2, CO_2, O_2, Cl_2, Br_2, I_2,





[1] R. Fedorov, F. Lederle, M. Li, V. Olszok, K. Wöbbeking, W. Schade, E. G. Hübner, *ChemPlusChem* **2021**, *86*, 1231 - 1242.
DOI: 10.1002/cplu.202100118

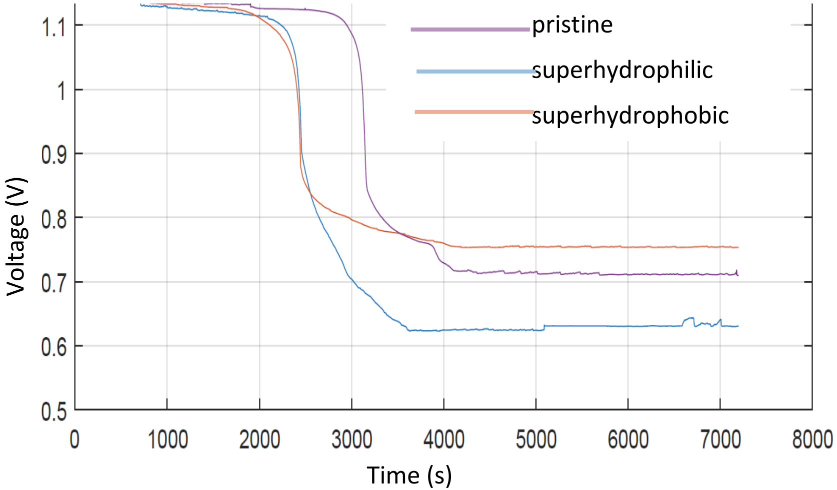
Femtosecond Laser Surface Structures

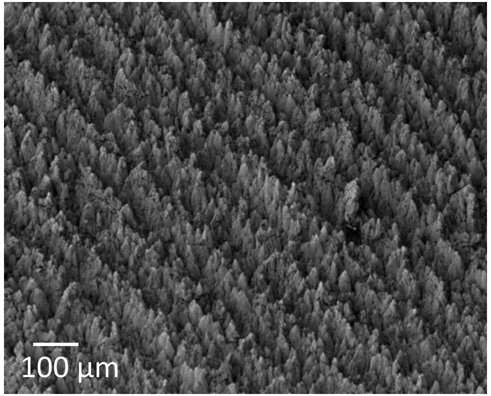


Controlling Wettability

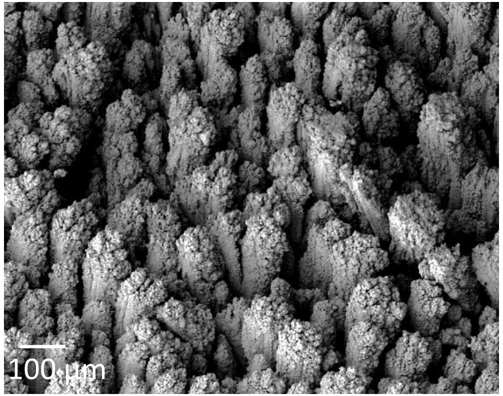
- Rechargeable zinc-air battery
- GDE water contact angle: 0° vs. 130° (pristine) vs. 180°
- Improved oxygen consumption

➢ Cell voltage - 0.1 V (0°) → + 0.05 V(180°)





Θ → 0°



Θ → 180°

Femtosecond Laser Surface Structures

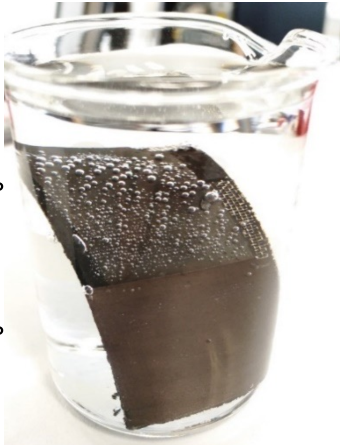
Zinc-air Batteries

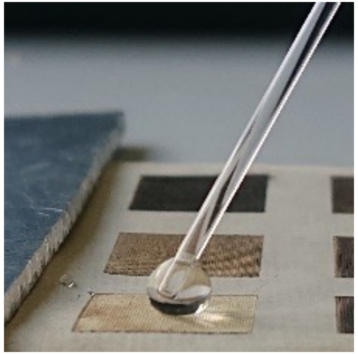
GEFÖRDERT VOM
Bundesministerium für Bildung und Forschung

- Rechargeable zinc-air battery
- Key part: (bifunctional) gas diffusion electrode (GDE)
  - Ag/AgO (Co_3O_4) and hydrophobic binder
- Femtosecond laser structuring to optimize surface structure and wettabiliy

$\Theta \rightarrow 180°$

$\Theta \rightarrow 0°$

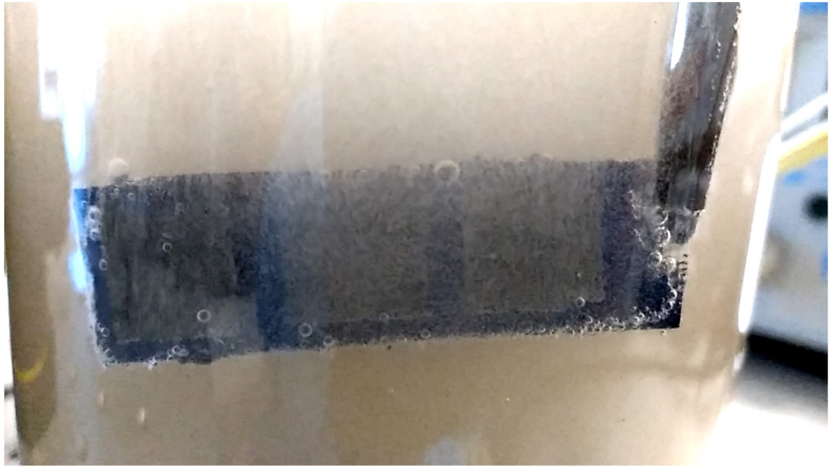




$\Theta \rightarrow 180°$

$\Theta \rightarrow 0°$

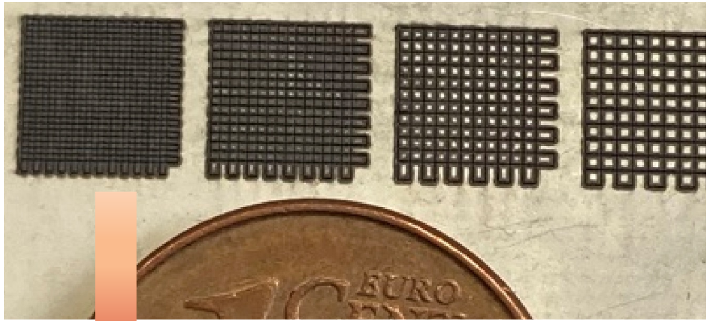
Video: Oxygen evolution

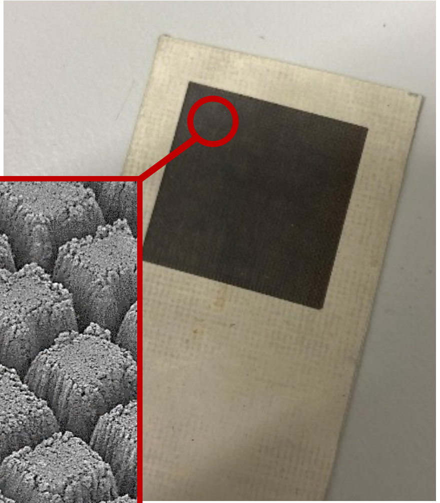


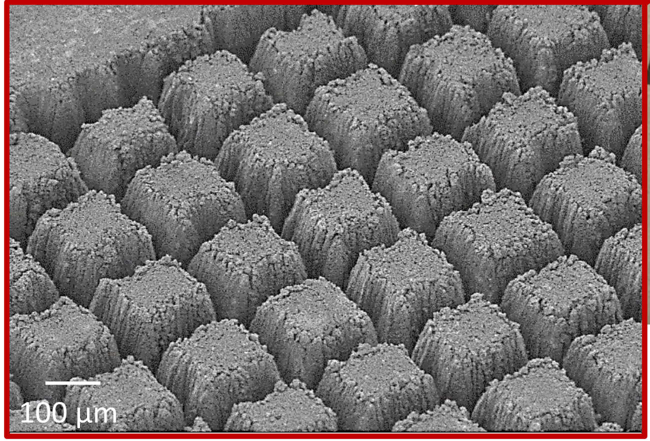
Femtosecond Laser Surface Structures

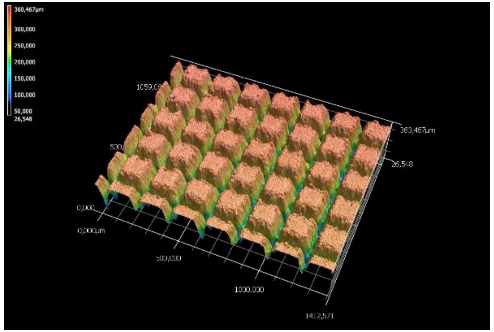
Zinc-air-Batteries

- Bifunctional electrode must be optimized for oxygen consumption and evolution
- Porous electrode → significant contact area inside
    - ➢ Grid-like macroscopic surface structuring
    - ➢ 40 µm focus spot ($1/e^2$), 100 µm grid
    - ➢ Optimized mass transport phenomena









Project: **ZILsicher** (BMBF)

Femtosecond Laser Surface Structures

GEFÖRDERT VOM Bundesministerium für Wirtschaft und Energie

Gefördert durch: Niedersächsisches Ministerium für Wissenschaft und Kultur

Hydrogen: Electrodes for Alkaline Water Electrolysis (AEL)

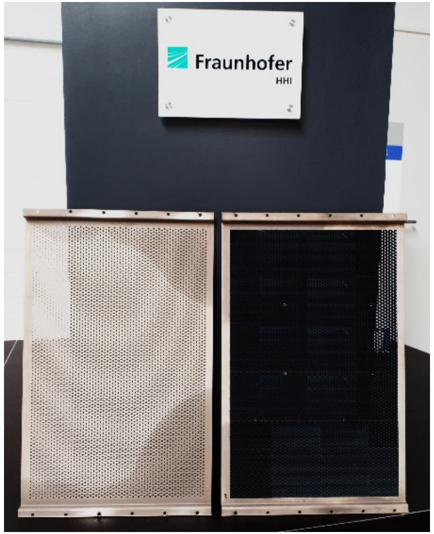
- Key Factor: Overpotential reduction
  - ➢ Recent reviews define major aspects[1]:
    - Specific surface area (Tafel equation: overpotential η (V) ~ current density i (A/cm^2))
    - Presence of gas bubbles on the surface of the electrode
    - Electrocatalytic materials
- Surface enlargement | Superhydrophilicity | Nickel oxides
  - ➢ Porosity

N pulses >1000 ⟷ N pulses >250 processing at oxygen/air ⟷ processing at oxygen/air

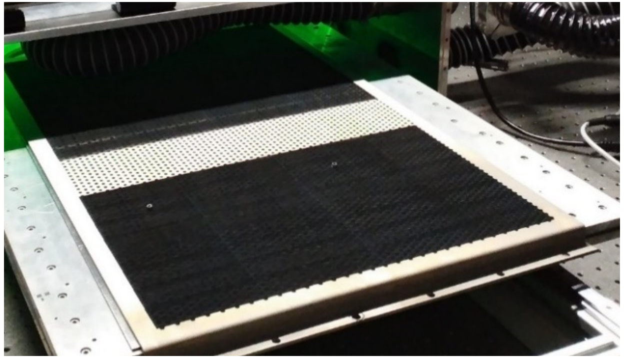
[1] see e.g. M. David, C. Ocampo-Martínez, R. Sánchez-Peña, *J. Energy Storage* **2019**, *23*, 392 - 403.
DOI: 10.1016/j.est.2019.03.001
Projects: **GreenH2** (BMWi), **InnoEly** (state of lower saxony)

Femtosecond Laser Surface Structures

Large Scale Electrodes[1]

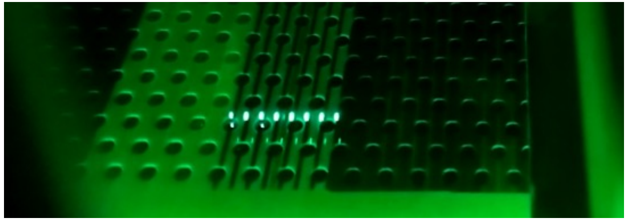


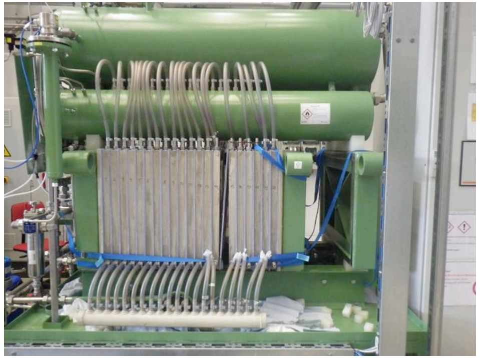
- Base material: Steel coated with approx. 300 µm nickel (MTV)
- 0.66 x 0.41 m^2 structured on both sides (0.54 m^2 per electrode)
- N pulses ~20 x 2000[2]
- Processed at air
  - ➢ Porous microcones, nickel oxides, superhydrophilic surface



processing time: ~ 150 h / electrode

8-fold beam via diffractive element





[1] C. I. Bernäcker, T. Gimpel, A. Bomm, T. Rauscher, M. Li, E. G. Hübner, W. Schade, T. Weißgärber, L. Röntzsch, *Sources*, to be submitted.
[2] for J ~ 0.1 J/cm² @ 1 MHz

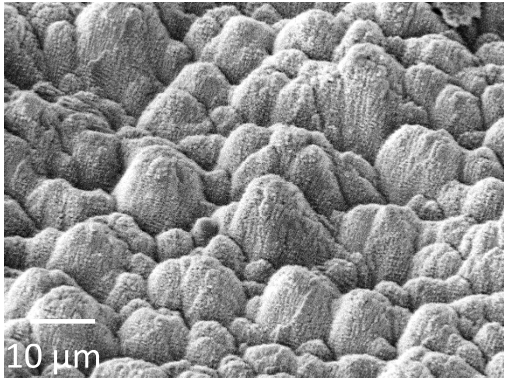
J. Power

Electrolyzer: Christian I. Bernäcker, IFAM Dresden

Femtosecond Laser Surface Structures

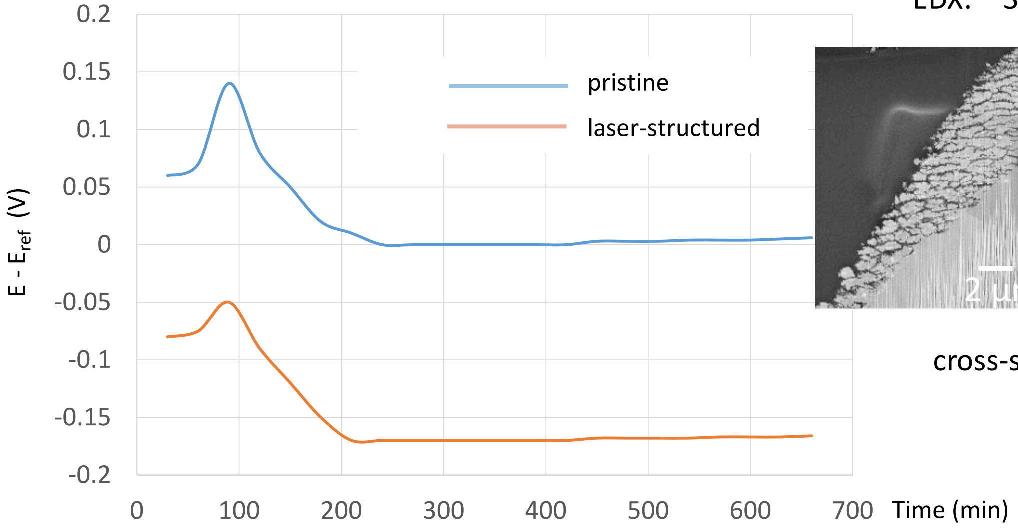
Electrodes for Alkaline Water Electrolysis (AEL)

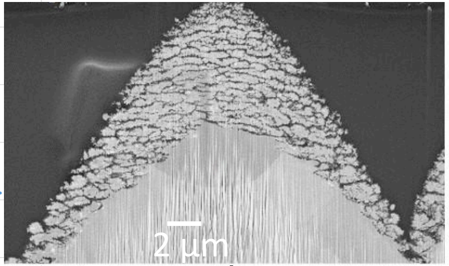
- Surface enlargement ~100x (BET)
- Operation of electrodes at realistic conditions (Fraunhofer IFAM)
- 4 Electrodes laser-structured (both sides) vs. 4 pristine electrodes



EDX: ~ 30 atom-% O

- ➢ 750 A per electrode
- ➢ Overpotential reduced
- ➢ Process efficiency increased approx. 10 %





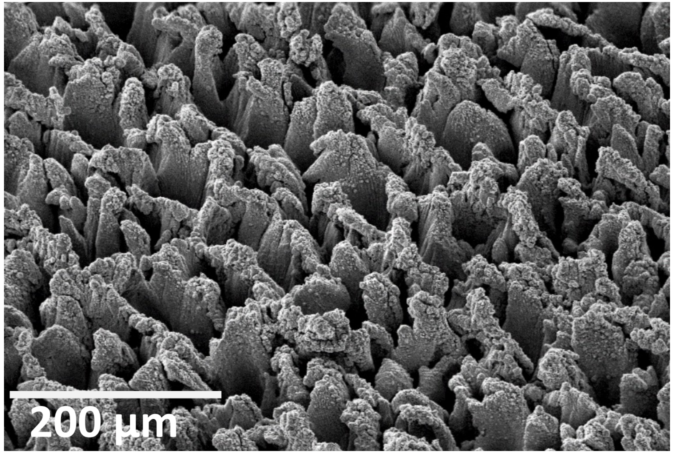
cross-section[2]

[1] C. I. Bernäcker, T. Gimpel, A. Bomm, T. Rauscher, M. Li, E. G. Hübner, W. Schade, T. Weißgärber, L. Röntzsch, *J. Power Sources*, to be submitted.
Project: **GreenH2** (BMWi)
[2] cross-section: Christian I. Bernäcker, IFAM Dresden

Fem2Nano

Self-organized Structure Formation

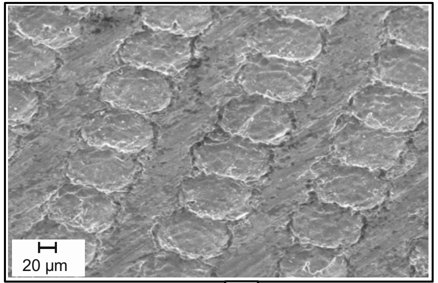
- Microcones and related structural motifs
  - ➢ By physical and chemical ablation processes
  - ➢ Initiated by energy input (laser light) on the surface



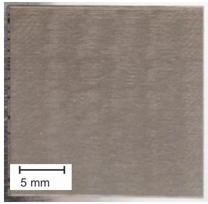
Fem2Nano

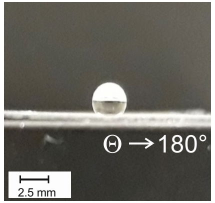
Transfer from Femtosecond to Nanosecond Laser Pulses

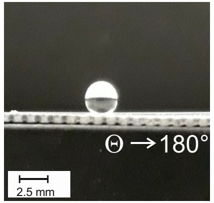
- Assisted by chemical ablation („etching“)

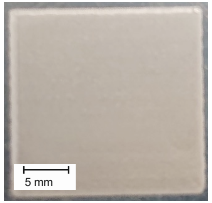


α = 77 %





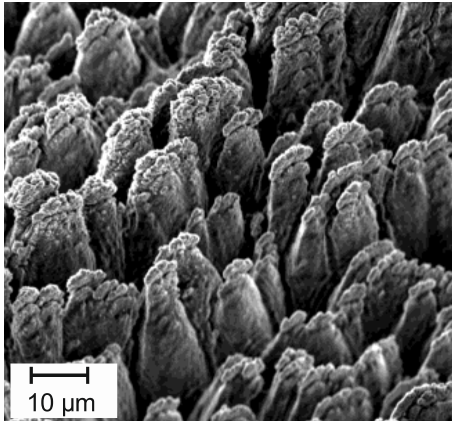




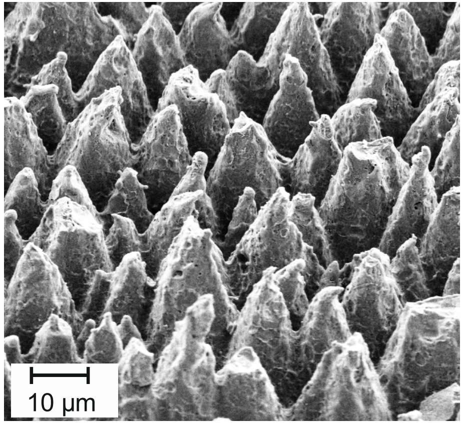
α = 56 %

Process parameters:

- τ = 60 fs
- J = 2.6 J/cm²
- N = 250 pulses
- N_2-atmosphere



vs.



J = 9.8 J/cm²

N = 512 pulses

iodine/reduced pressure

EDX [atom-%]: 97 % Al, 3 % O 98 % Al, 2 % O

TU Clausthal
Clausthal University of Technology

[1] S. Rauh, K. Wöbbeking, M. Li, W. Schade, E. G. Hübner, *ChemPhysChem* **2020**, *21*, 1644 - 1652.
DOI: 10.1002/cphc.202000418

[2] K. Wöbbeking, M. Li, E. G. Hübner, W. Schade, *RSC Advances* **2019**, *9*, 37598 - 37607.
DOI: 10.1039/c9ra05918k

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Summary

Fraunhofer-Institut für Nachrichtentechnik
Heinrich-Hertz-Institut
HHI

Abteilung:
Faseroptische Sensorsysteme

https://www.youtube.com/watch?v=i9LskwHnCEo