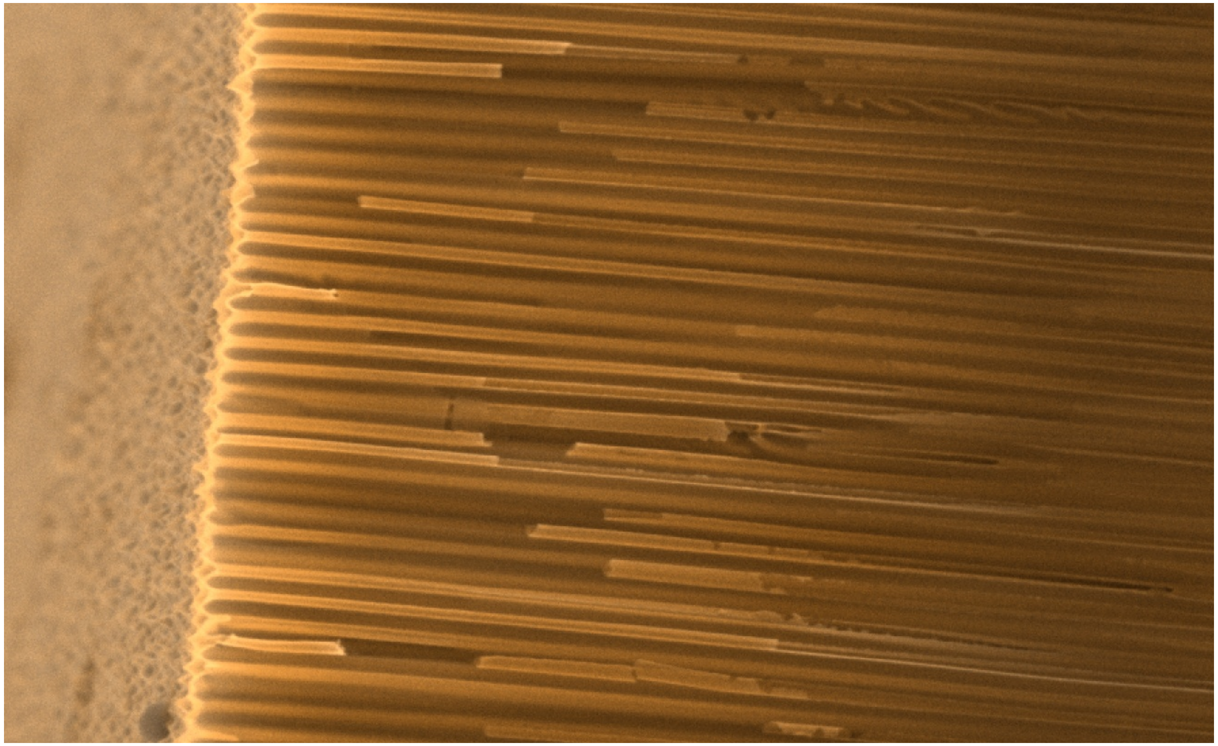
Platinum ALD from $Pt(acac)_2$ and O_3: Growth mechanism and electrocatalytic applications

Johannes Schumacher, Loïc Assaud, Alexander Tafel, Julien Bachmann
Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg

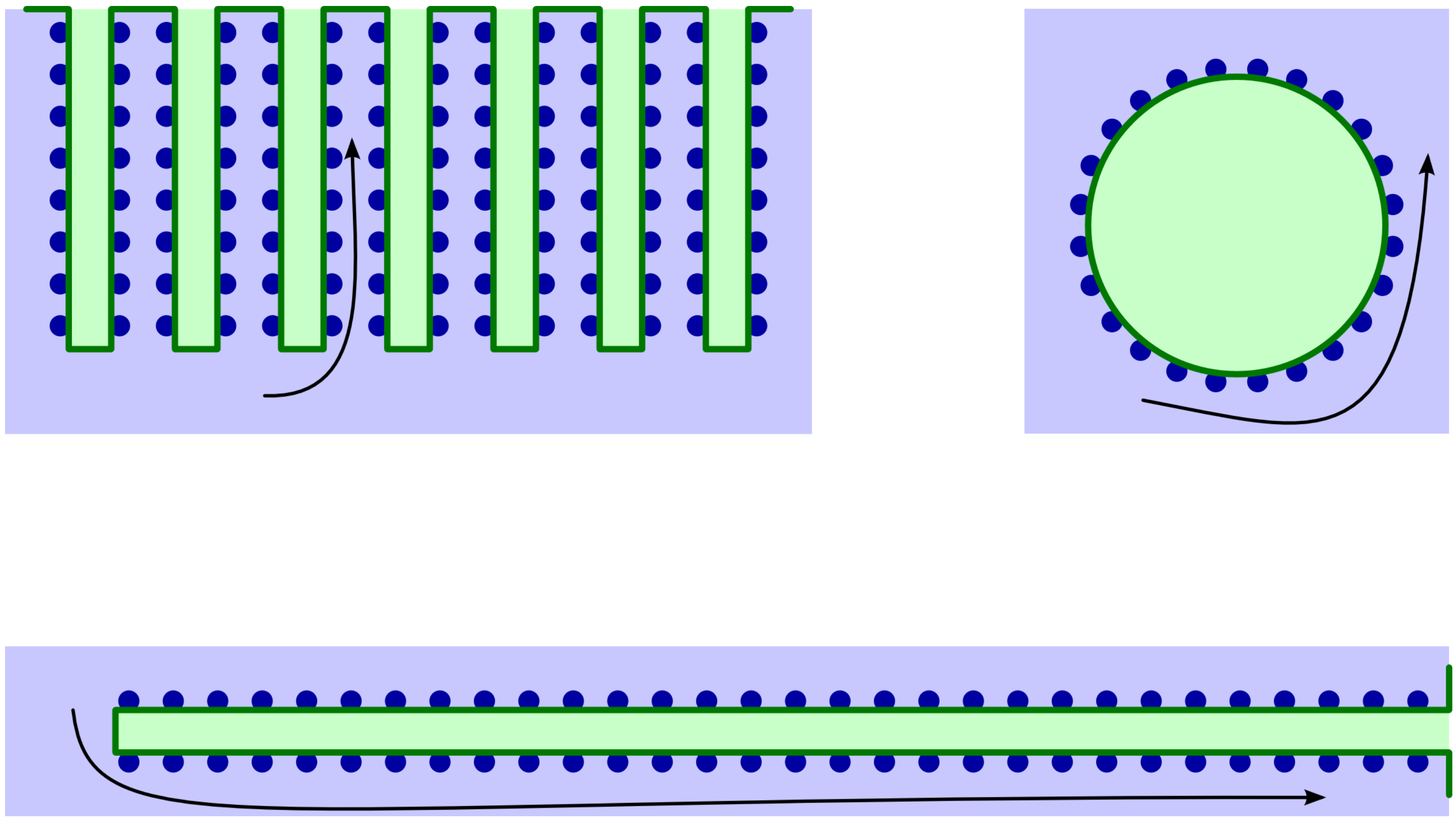


Energy conversion: Reactions at surfaces

Nanostructures: Control of specific surface area and diffusion paths

Energy conversion: Electrons and holes across interfaces

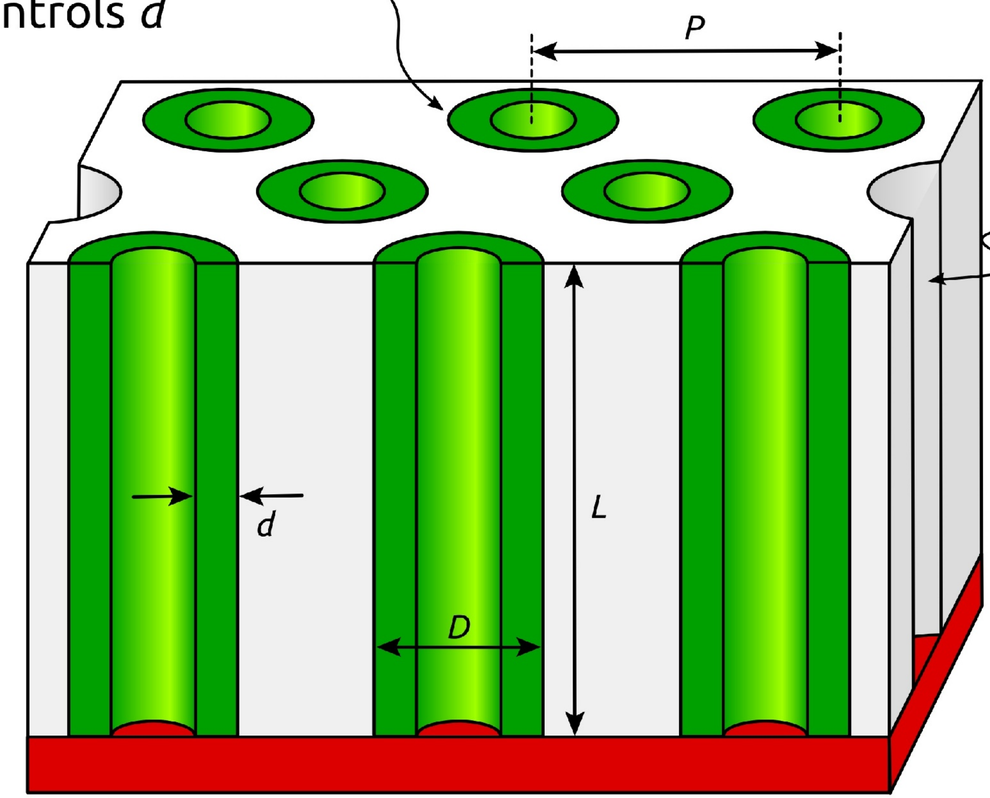
Nanostructures: Control of specific surface area and diffusion paths



Preparative strategy

Towards elongated nanostructures with tunable geometry

Conformal coating of functional material by **ALD or galvanic plating**: controls *d*



Porous template: **anodic alumina**: defines *L*, *P* and *D*

Sputtered electrical contact

Platinum

- Metallic Pt: Electrocatalyst for H_2 production from water and for ethanol oxidation (electrolysis, fuel cell)

- Standard ALD reaction:

  $MeCpPtMe_3 + O_2$ — 0.30-0.48 Å/cycle @ 200-300°C

  Aaltonen, Ritala, Sajavaara, Keinonen, Leskelä, *Chem. Mater.* **2003**, *15*, 1924-1928
  Aaltonen, Ritala, Tung, Chi, Arstila, Meinander, Leskelä, *J. Mater. Res.* **2004**, *19*, 3353-3358

- Costs of Pt ALD precursors (Strem):

  $MeCpPtMe_3$: € 231 / 0.5 g

  $Pt(acac)_2$: € 115 / 1 g

- Conceivable alternative:

  $Pt(acac)_2 + O_3$ — PtO_x @ ≤130°C, Pt @ ≥140°C

  Hämäläinen, Munnik, Ritala, Leskelä, *Chem. Mater.* **2008**, *20*, 6840-6846

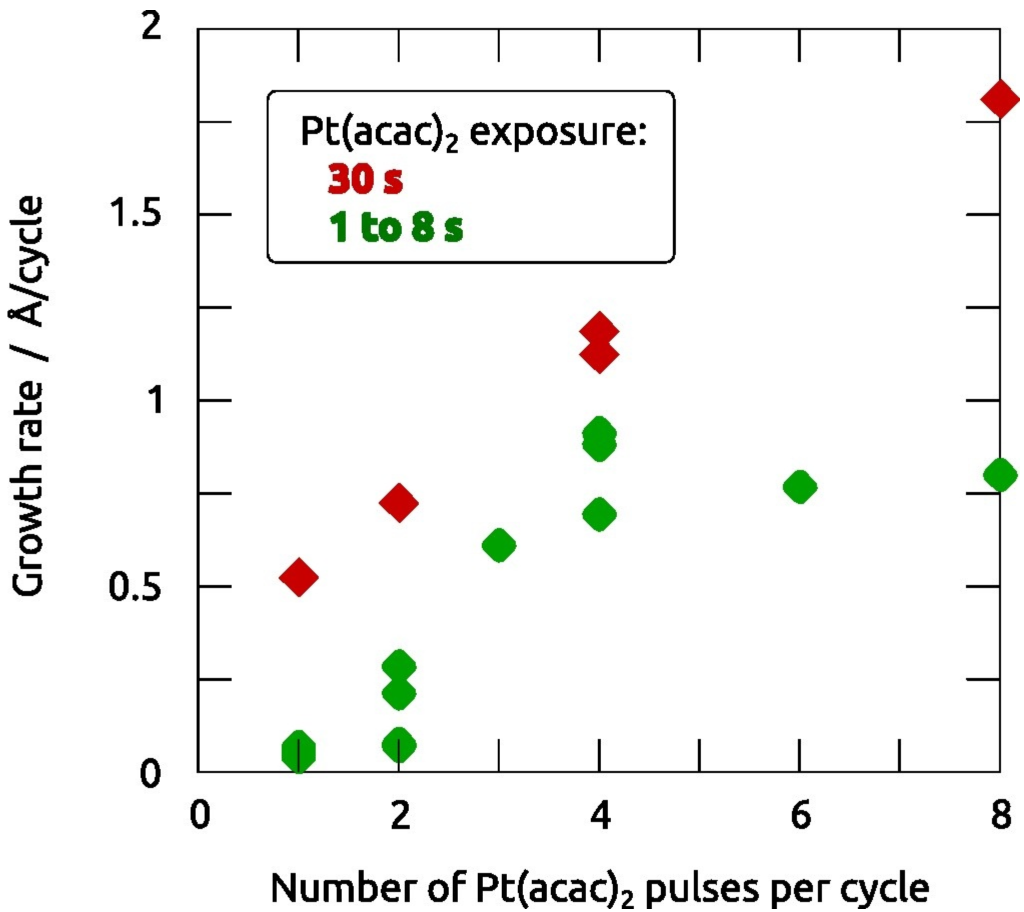
A. Reaction mechanism investigation of $Pt(acac)_2 + O_3$

- Arradiance GEMSTAR reactor, chamber at 130-150°C
- Piezoelectric microbalance SQL-310 from Inficon
- **$GaPO_4$ piezoelectric crystal** (Inficon R-20)
- O_3 from BMT 803N generator
- $Pt(acac)_2$ @ 80°C, several 'boosted' pulses
- **$Pt(acac)_2$ dosage set by the number of pulses**

A. Reaction mechanism investigation of $Pt(acac)_2 + O_3$

- Arradiance GEMSTAR reactor, chamber at 130-150°C
- Piezoelectric microbalance SQL-310 from Inficon
- **GaPO$_4$ piezoelectric crystal** (Inficon R-20)
- O_3 from BMT 803N generator
- $Pt(acac)_2$ @ 80°C, several 'boosted' pulses
- **$Pt(acac)_2$ dosage set by the number of pulses**

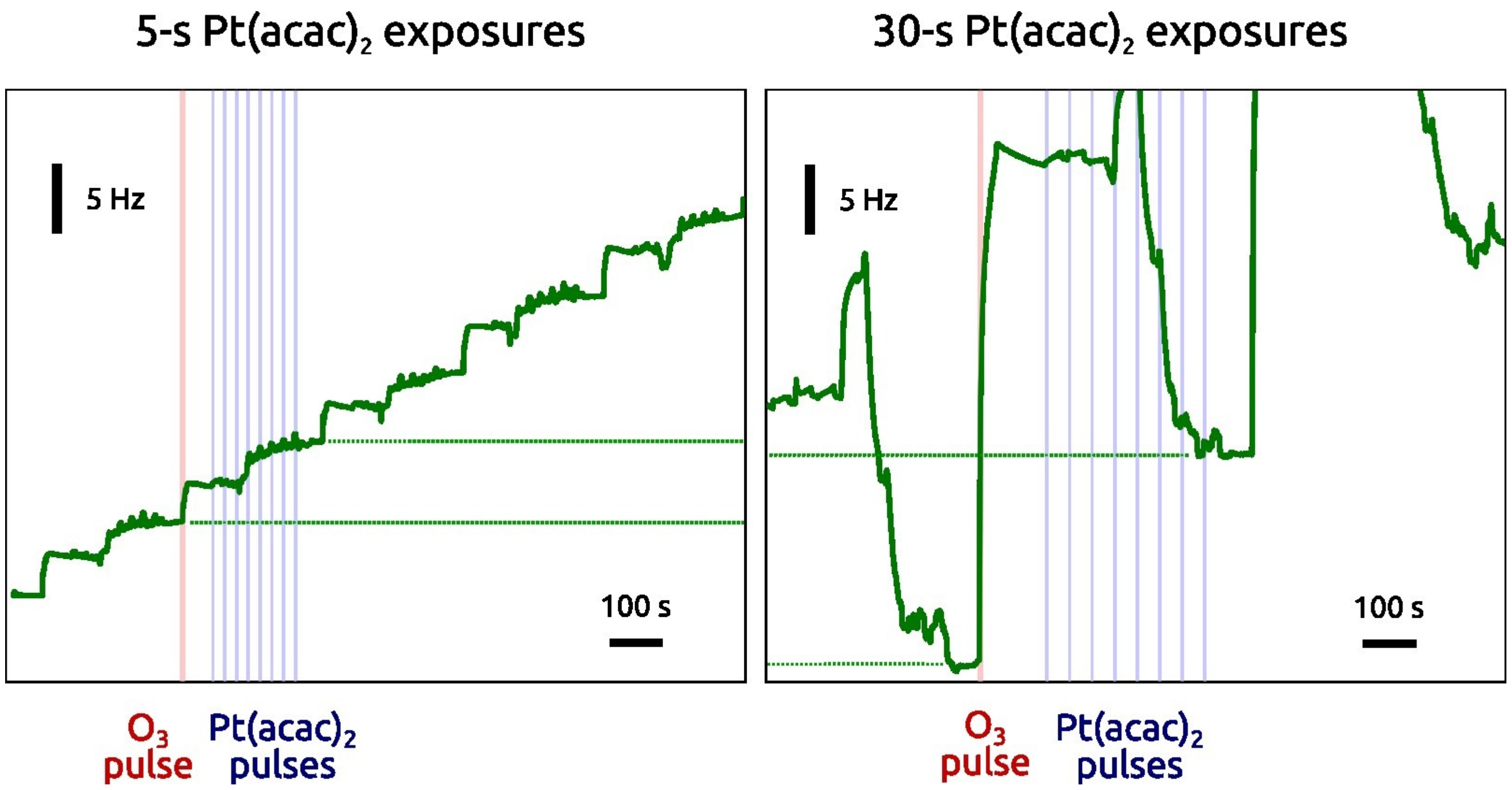
Growth rates at 150°C:



Long reaction durations: not self-limiting
Short reaction times: self-limiting

A. Reaction mechanism investigation of $Pt(acac)_2 + O_3$

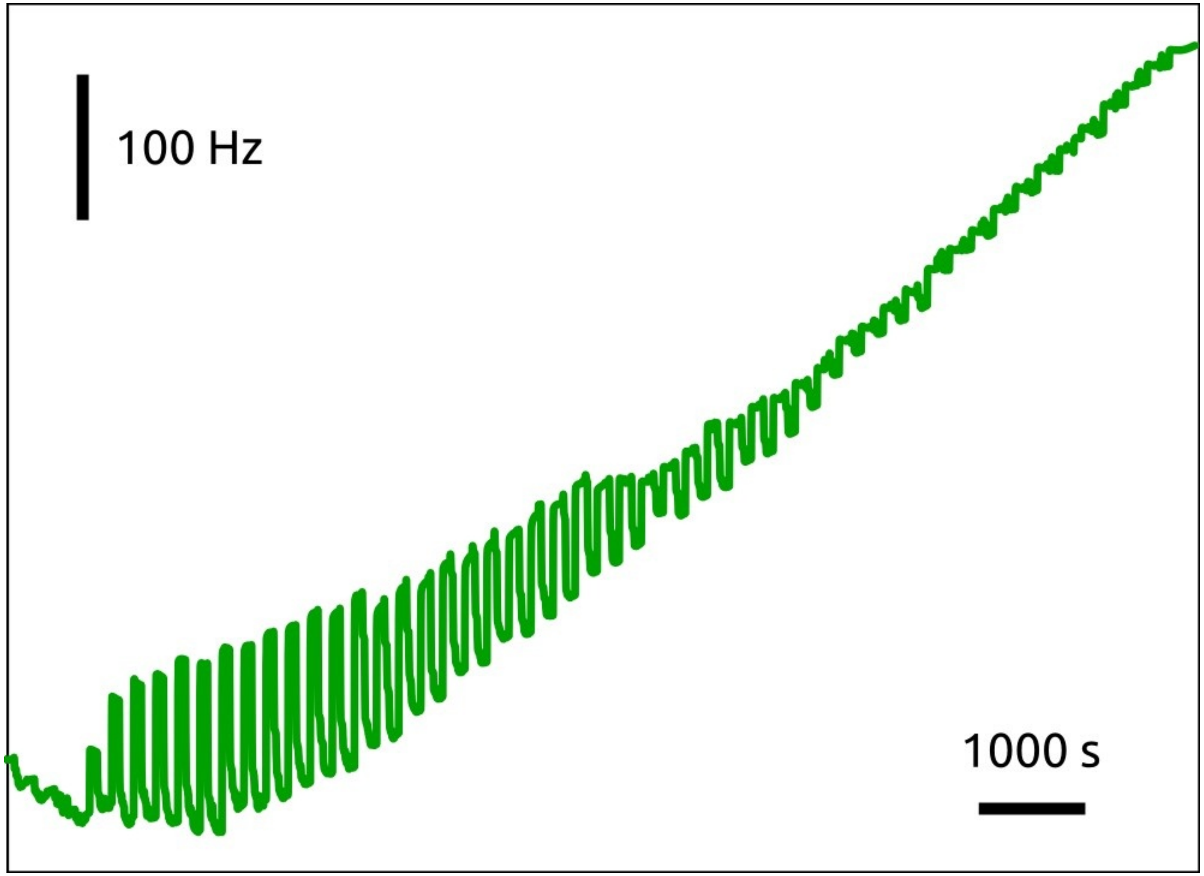
Comparison btw. short and long $Pt(acac)_2$ exposure durations:



- Mass increase at O_3 step: **Oxidation of metallic Pt**
- Large mass oscillations at long expo times: **'Deep' oxidation/reduction**

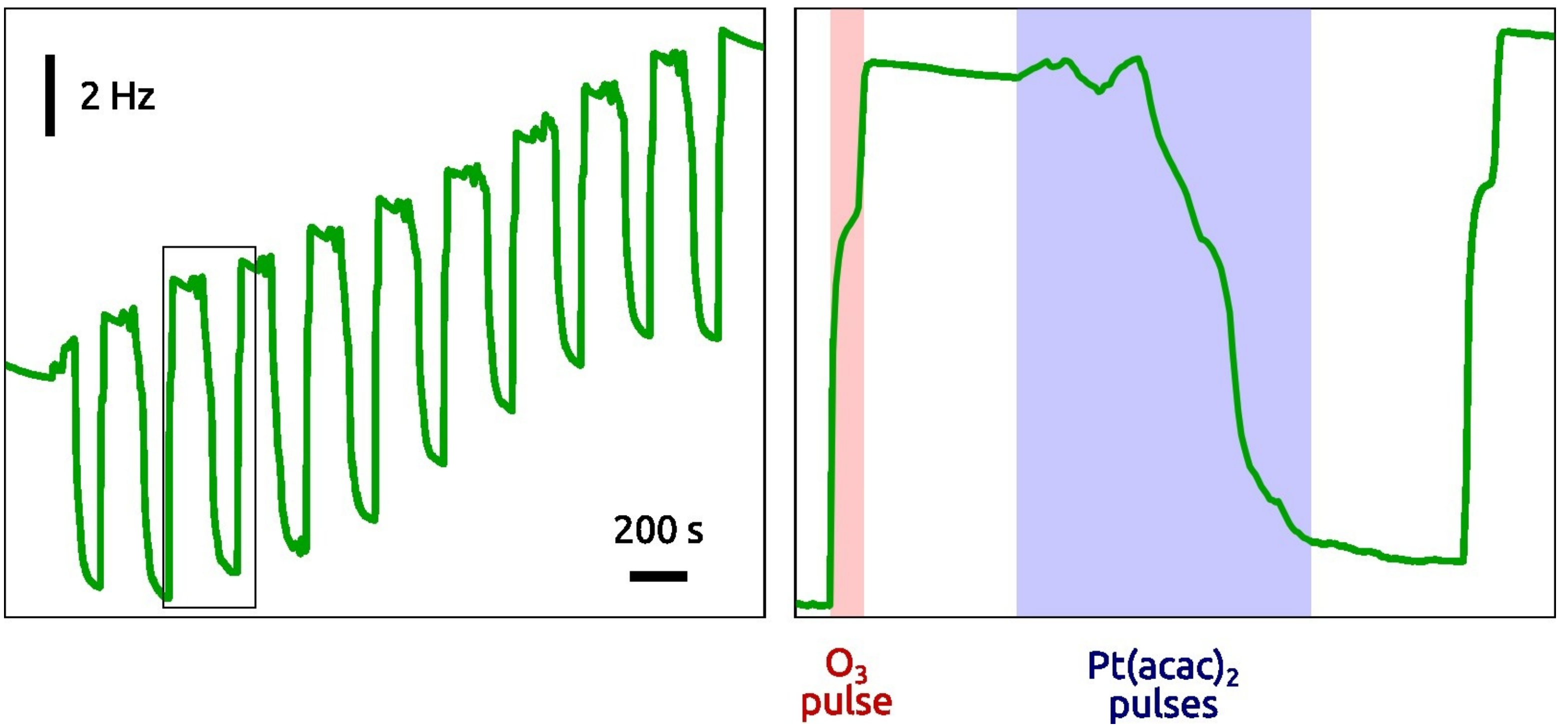
A. Reaction mechanism investigation of $Pt(acac)_2 + O_3$

- Al_2O_3 ALD performed before start of Pt ALD
- **Nucleation** (150°C, 4 $Pt(acac)_2$ pulses per cycle, 5 s exposure):



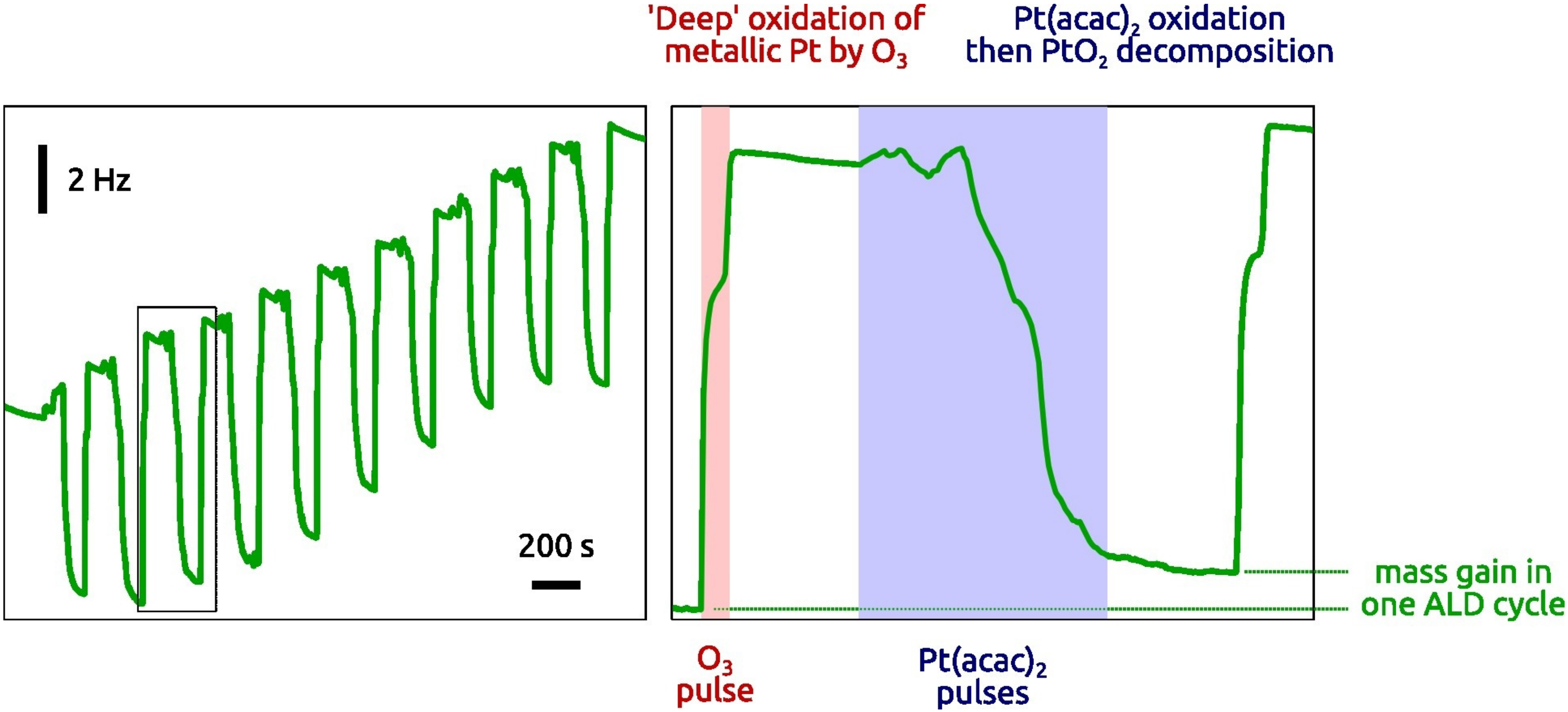
A. Reaction mechanism investigation of $Pt(acac)_2 + O_3$

Growth at 130°C (self-limited, 0.6 Å(cycle):



A. Reaction mechanism investigation of $Pt(acac)_2 + O_3$

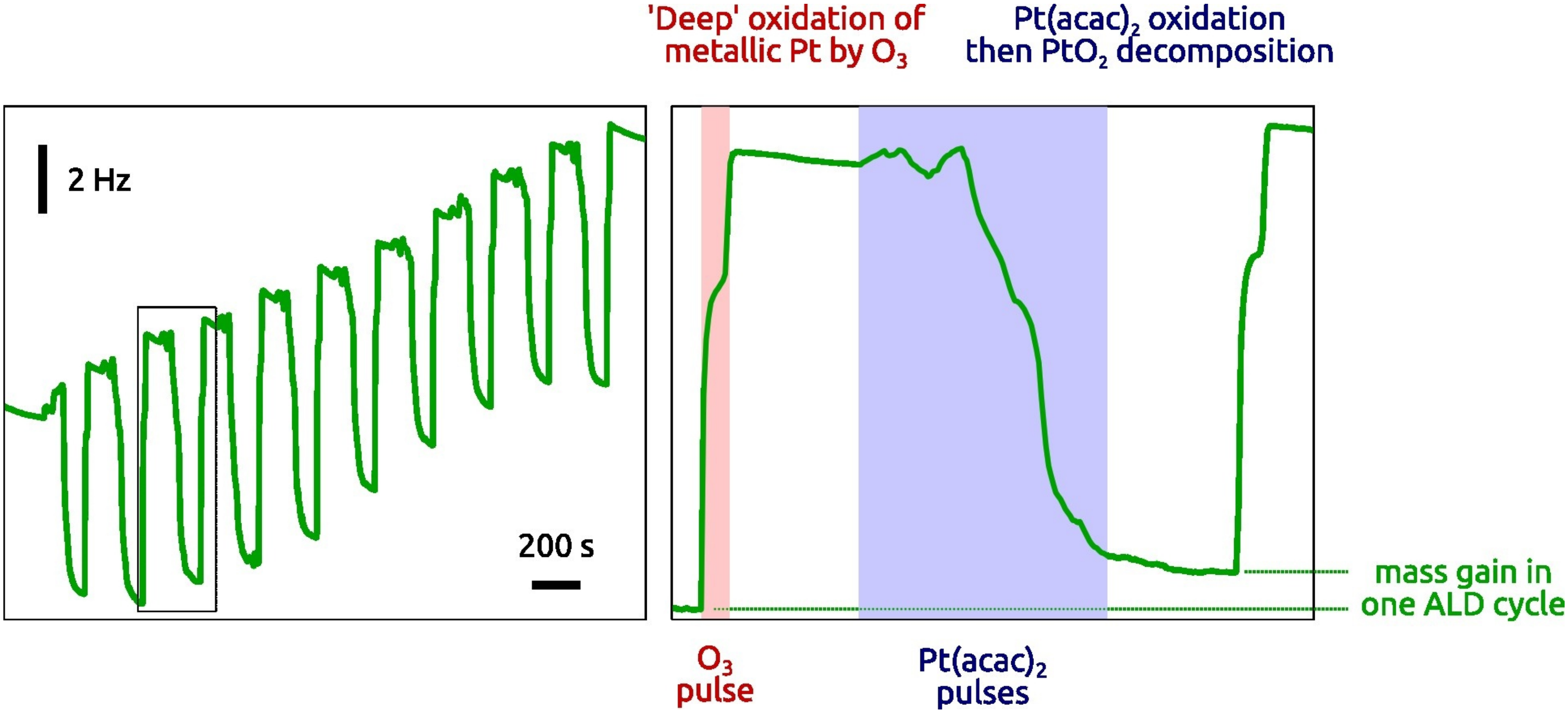
Growth at 130°C (self-limited, 0.6 Å(cycle):



A. Reaction mechanism investigation of $Pt(acac)_2 + O_3$

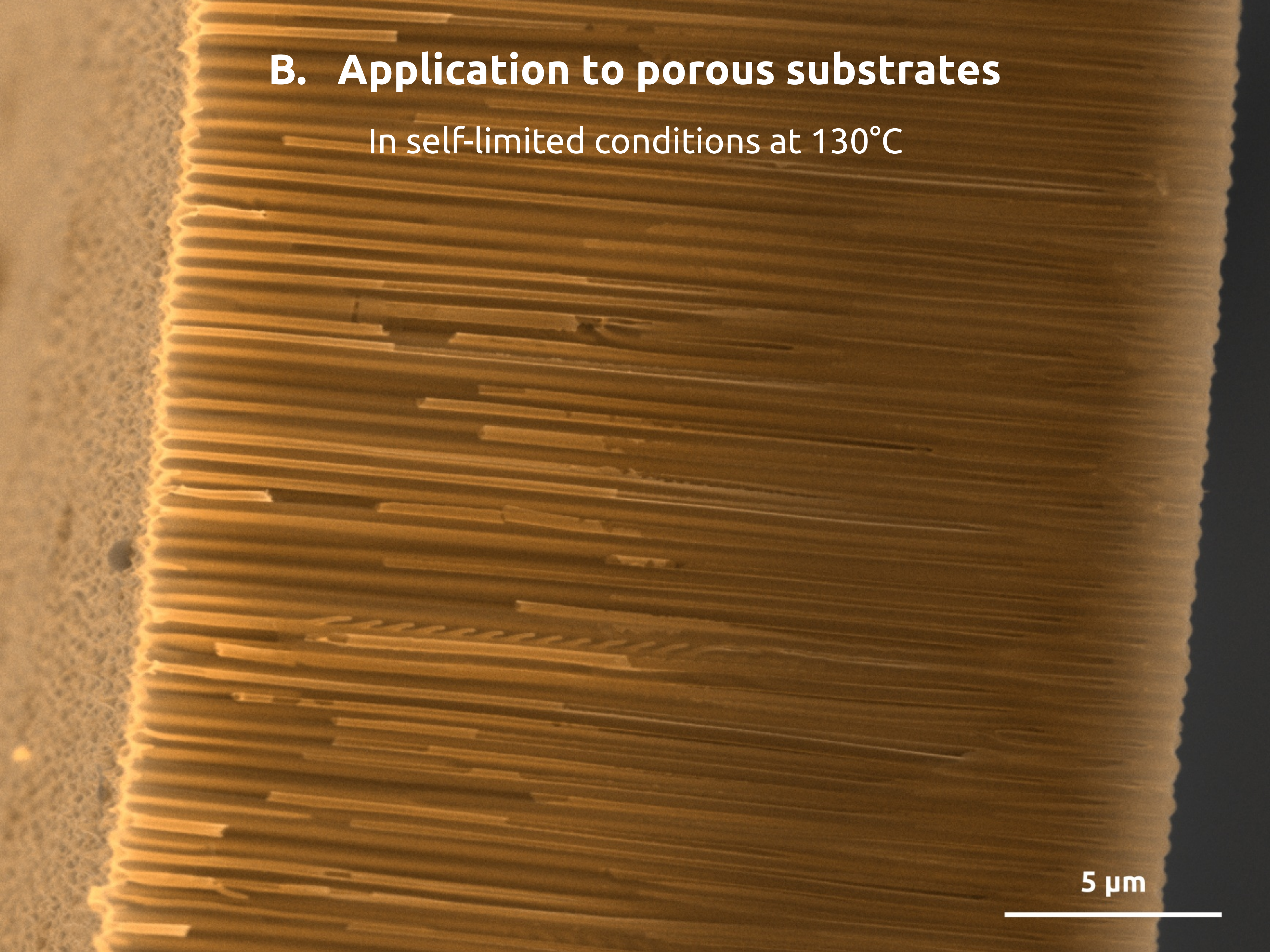
- **Metastable Pt oxide is a resting state during the ALD cycle**
- **Ozone oxidizes the metal in depth**
- Autocatalytic decomposition of oxide triggered by $Pt(acac)_2$
- Literature precedents: Ru ALD and Pt UHV studies

Saliba, Tsai, Panja, Koel, *Surf. Sci.* **1999**, *419*, 79-88
Methaapanon, Geyer, Lee, Bent, *J. Mater. Chem.* **2012**, *22*, 25154-25160



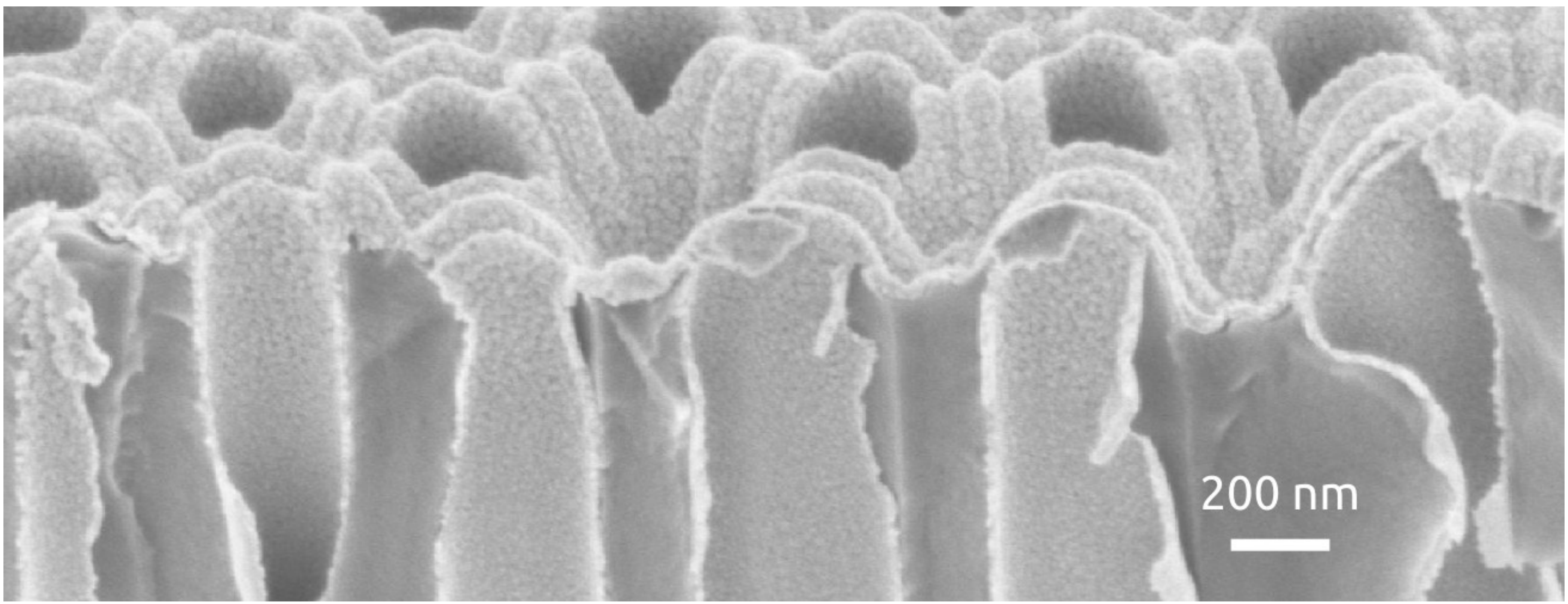
B. Application to porous substrates

In self-limited conditions at 130°C



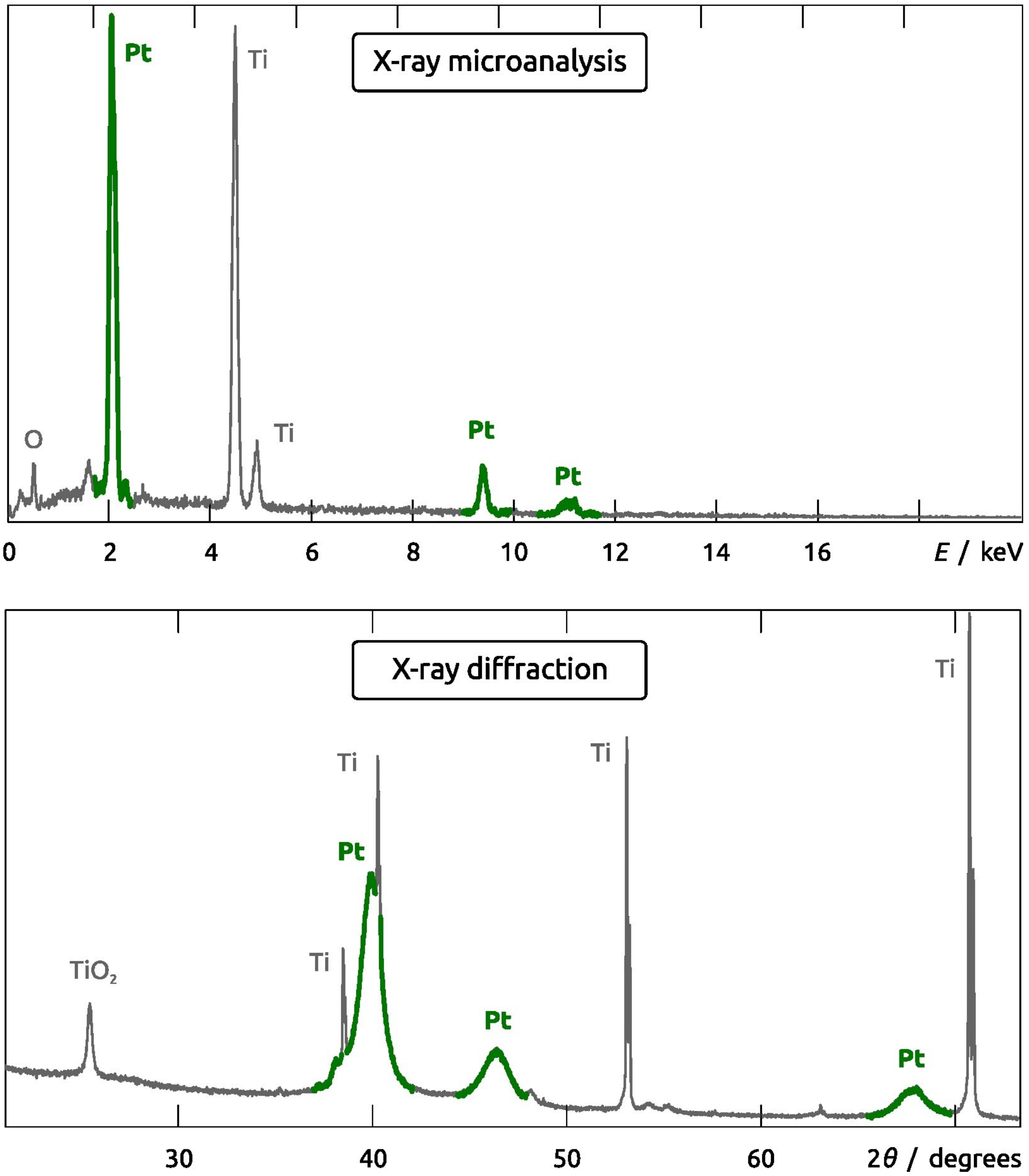
B. Application to porous substrates

In self-limited conditions at 130°C



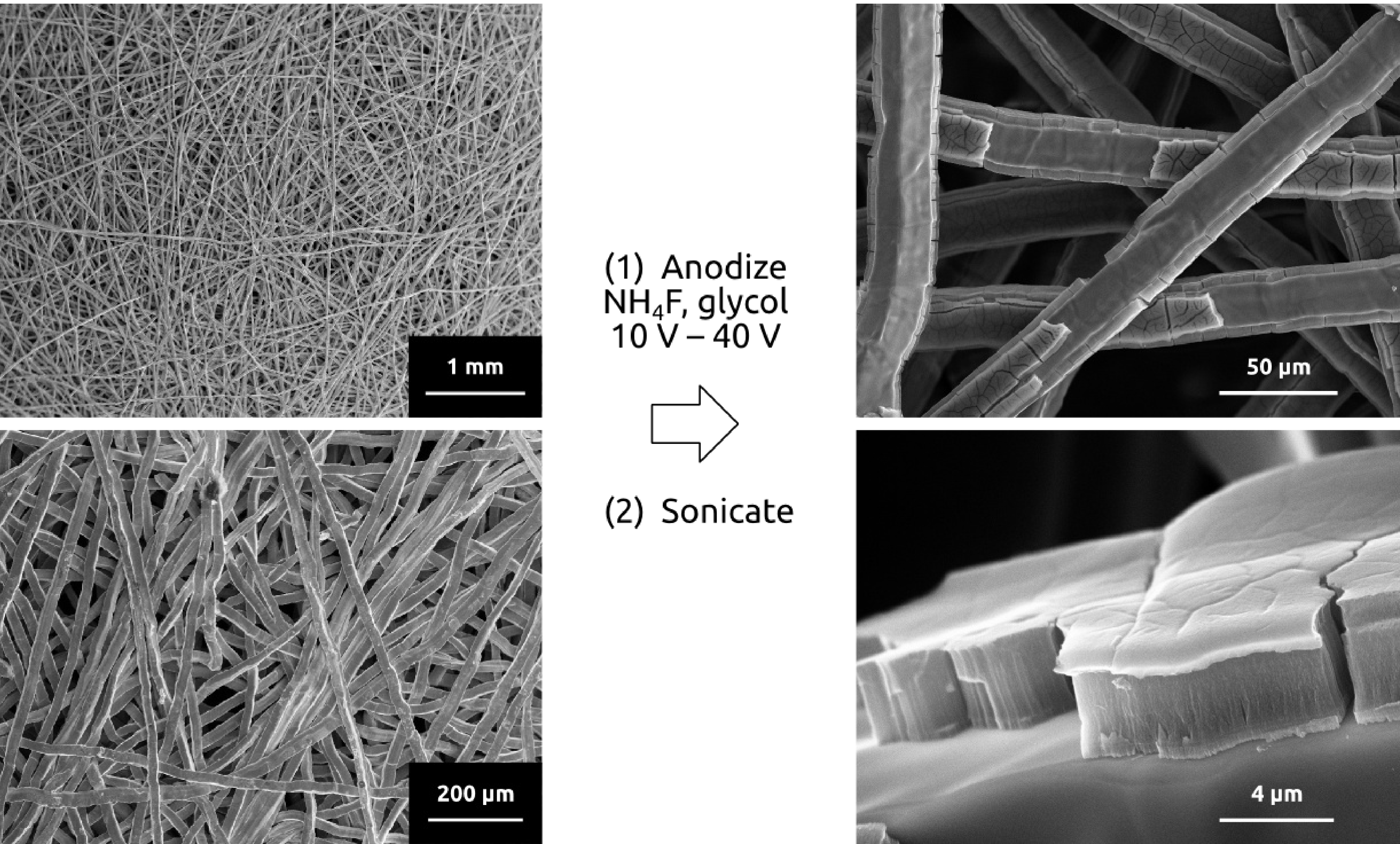
B. Application to porous substrates

Elemental and structural analyses on anodic TiO_2 tubes



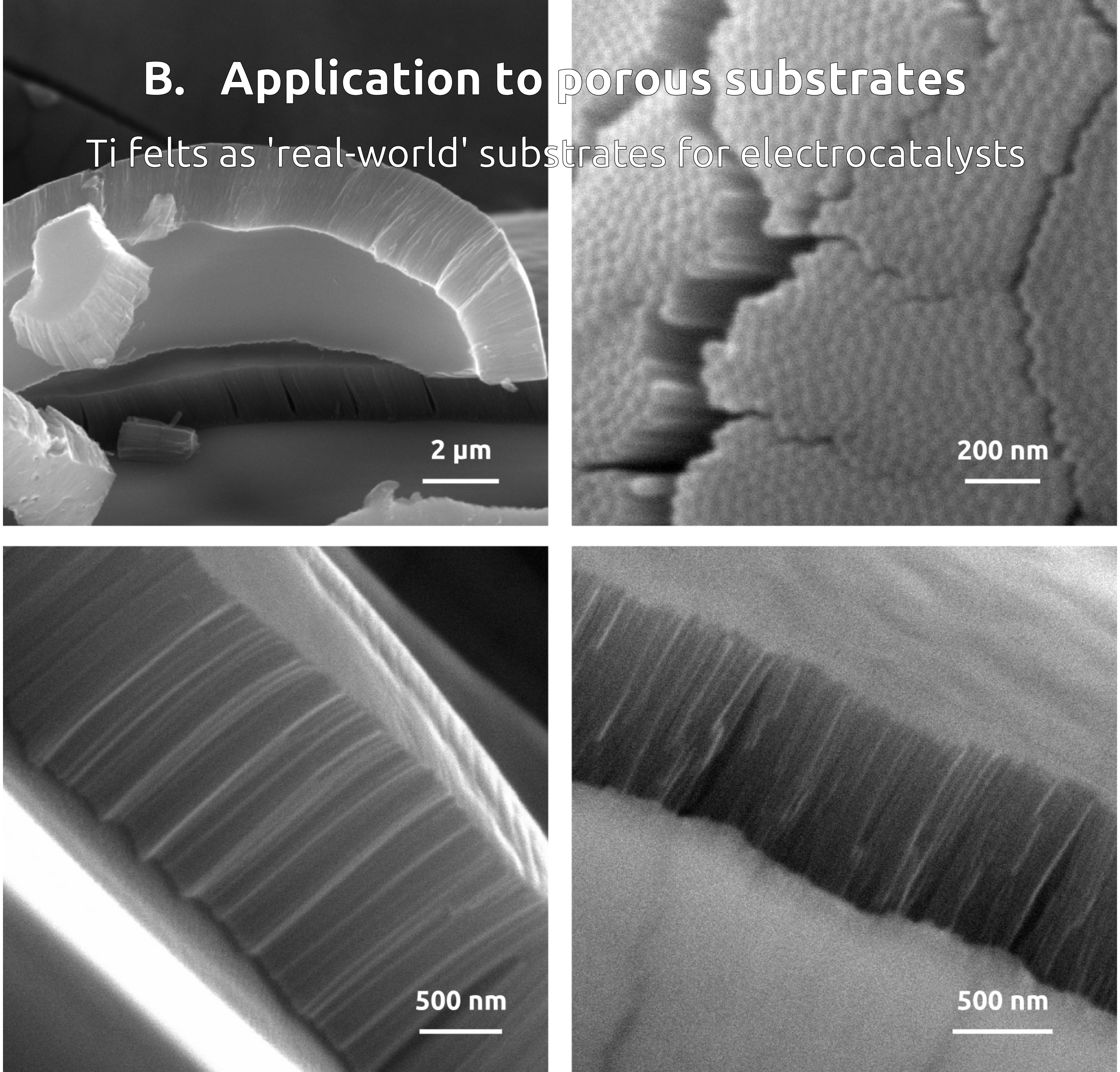
B. Application to porous substrates

Ti felts as 'real-world' substrates for electrocatalysts



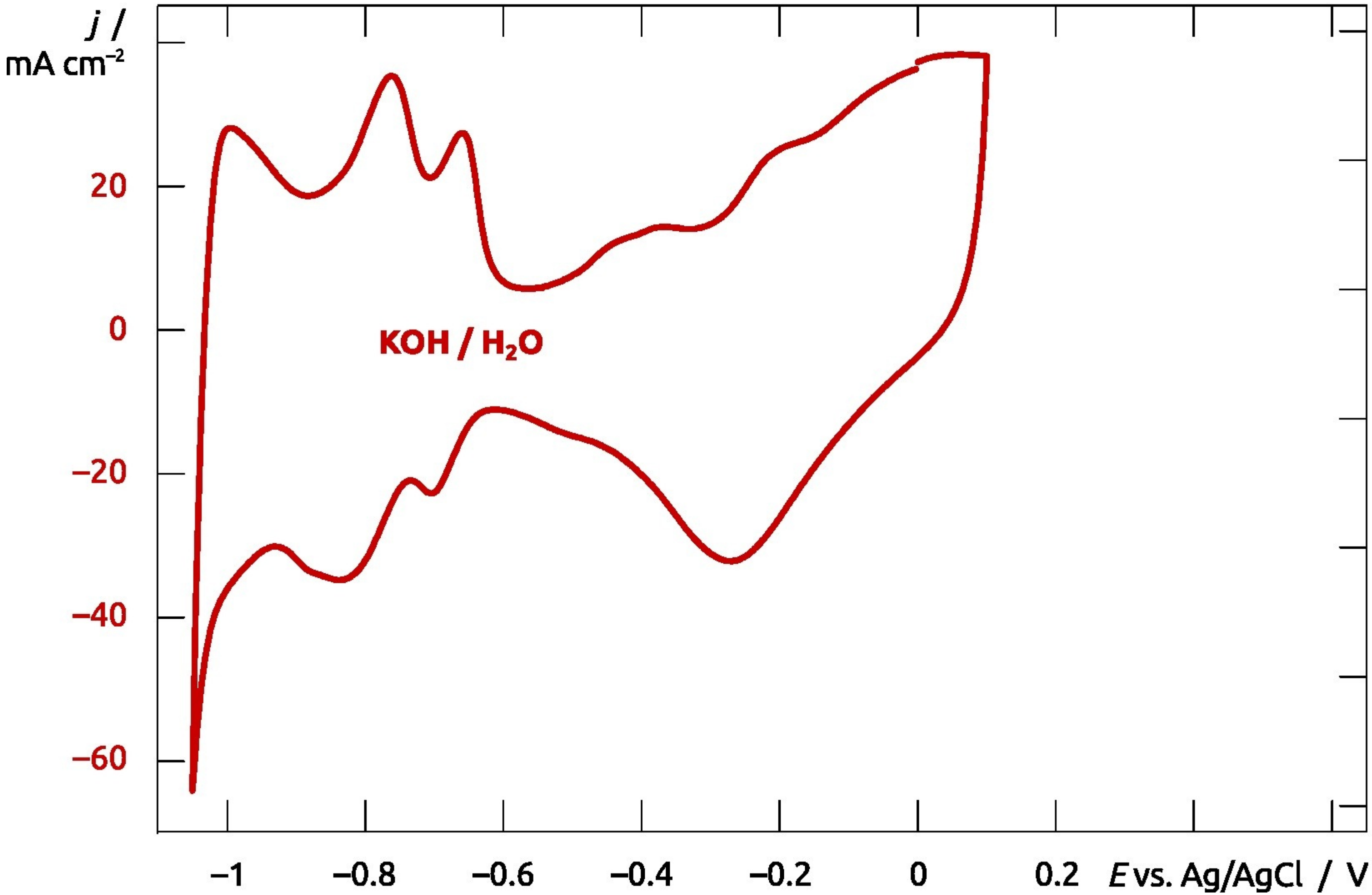
B. Application to porous substrates

Ti felts as 'real-world' substrates for electrocatalysts

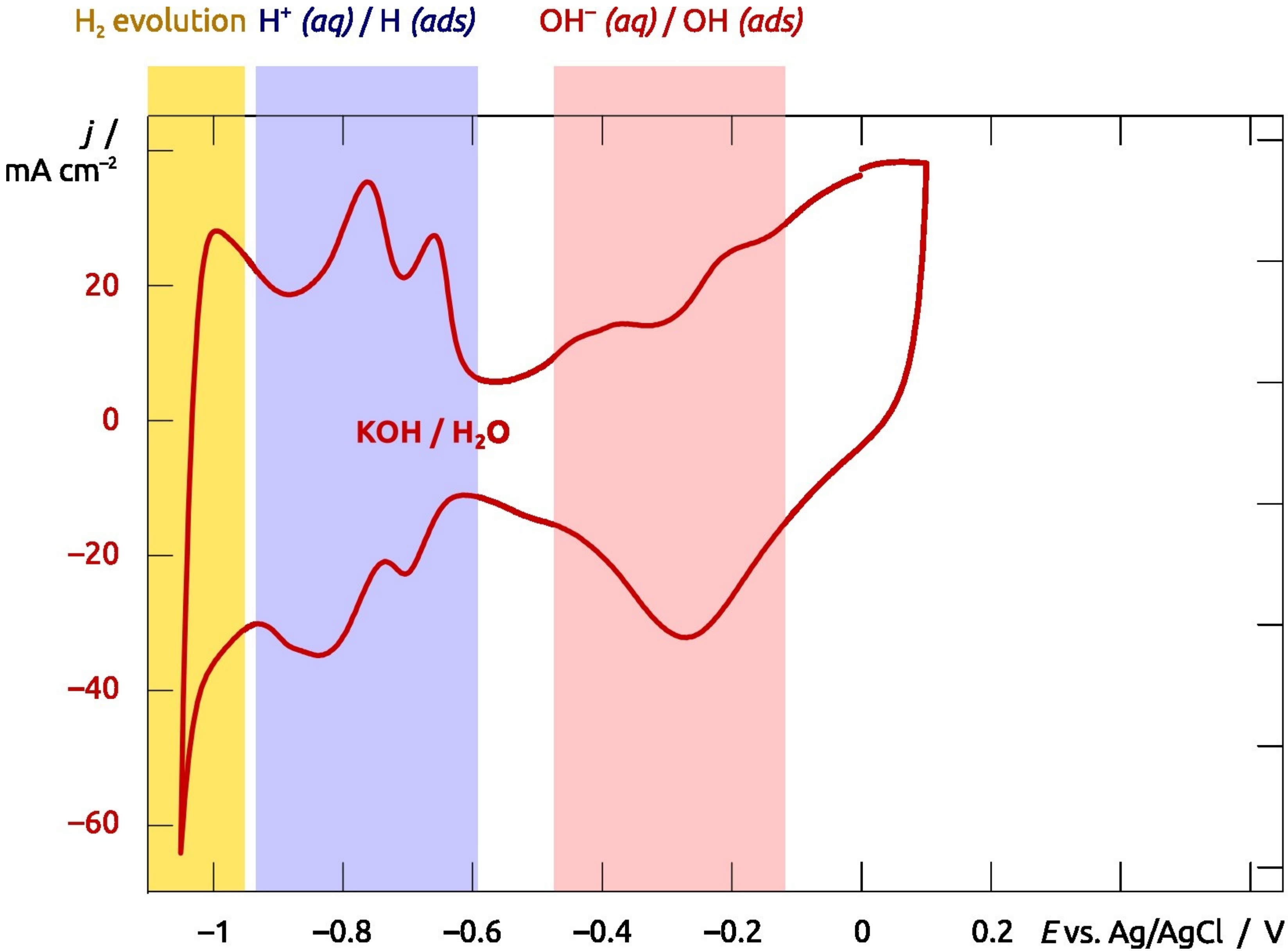


C. Electrocatalysis at nanoporous Pt / TiO_2 surfaces

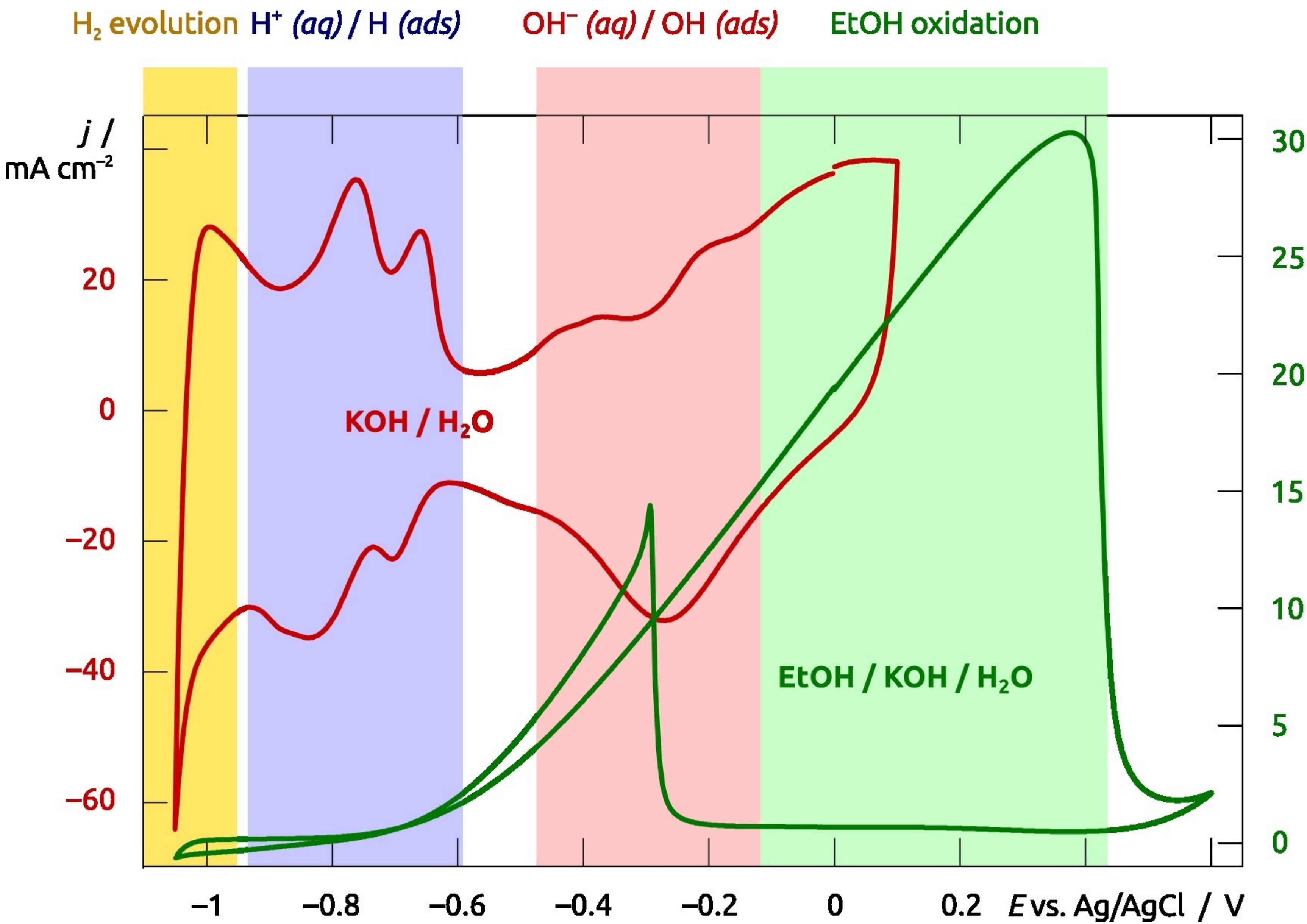
Planar anodized sample:



C. Electrocatalysis at nanoporous Pt / TiO_2 surfaces

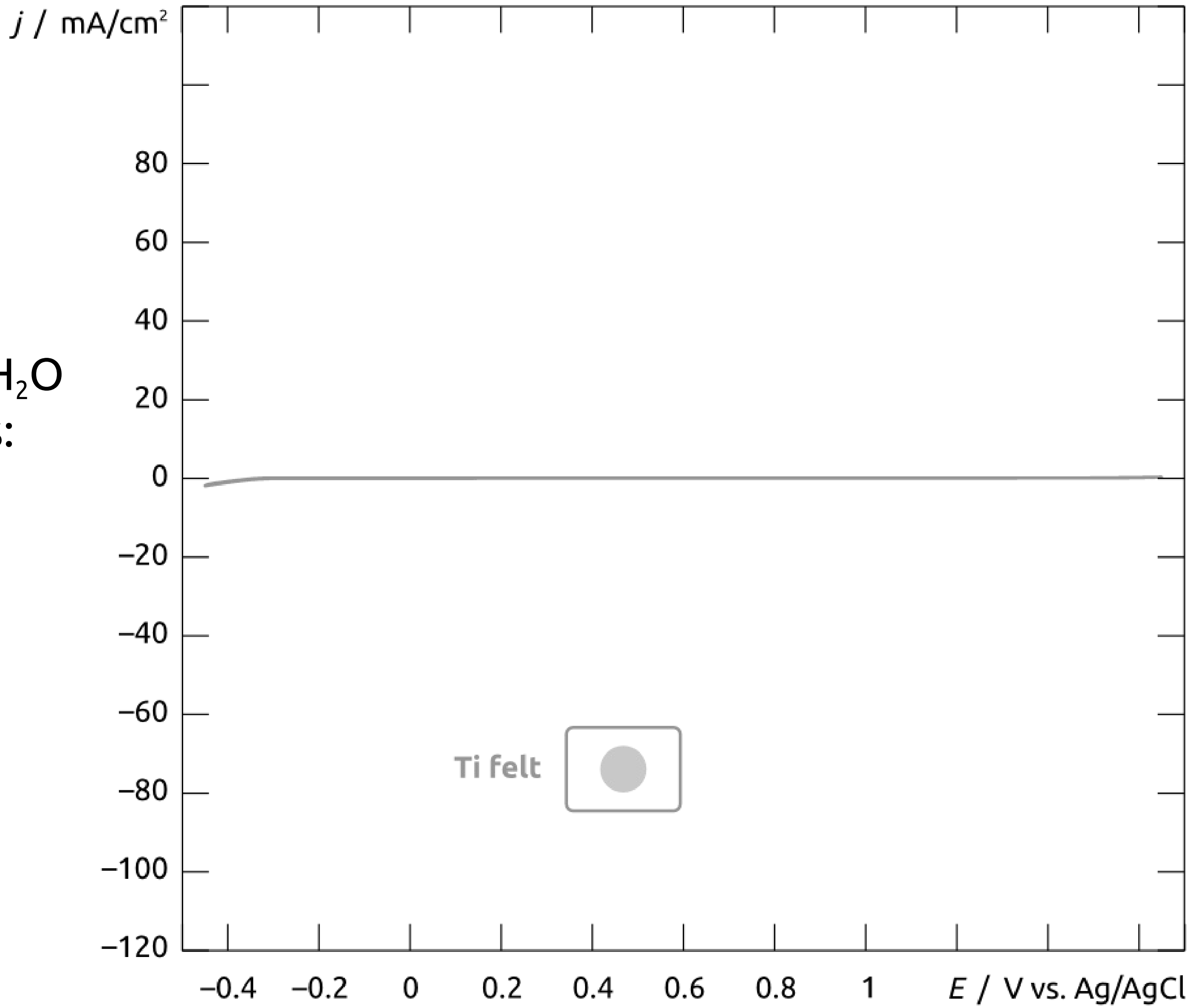


C. Electrocatalysis at nanoporous Pt / TiO_2 surfaces

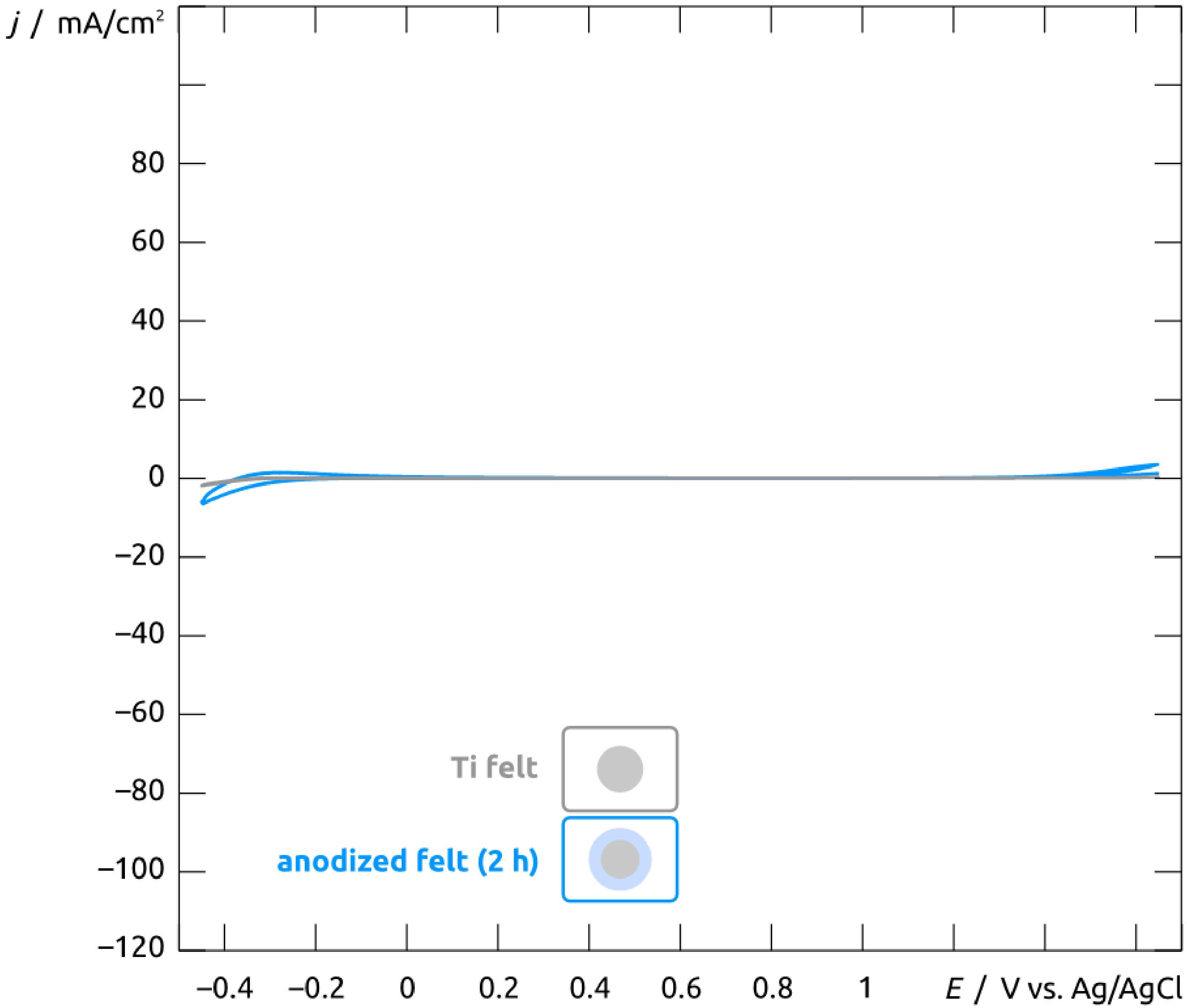


C. Electrocatalysis at nanoporous Pt / TiO_2 surfaces

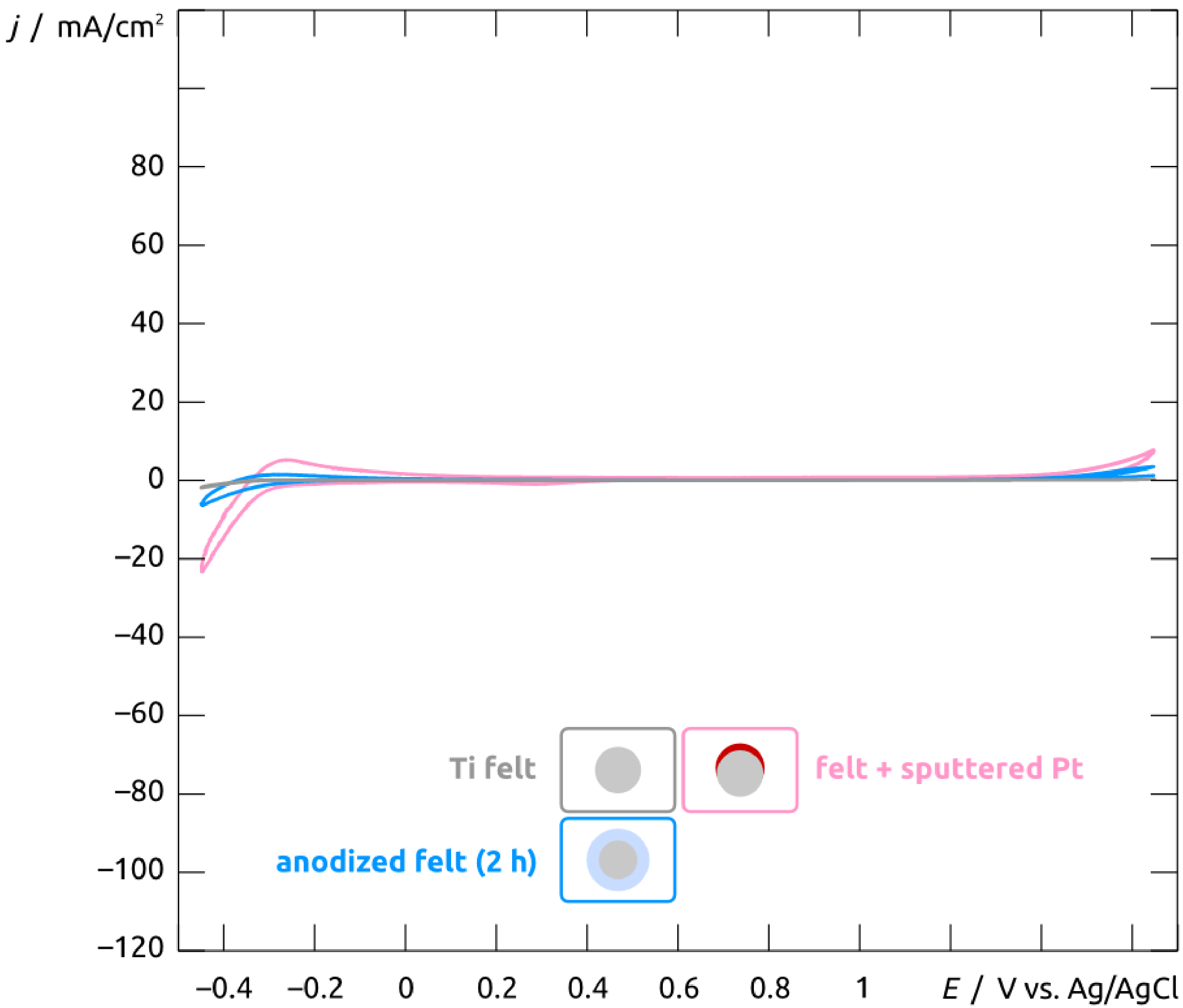
H_2SO_4/H_2O on felts:



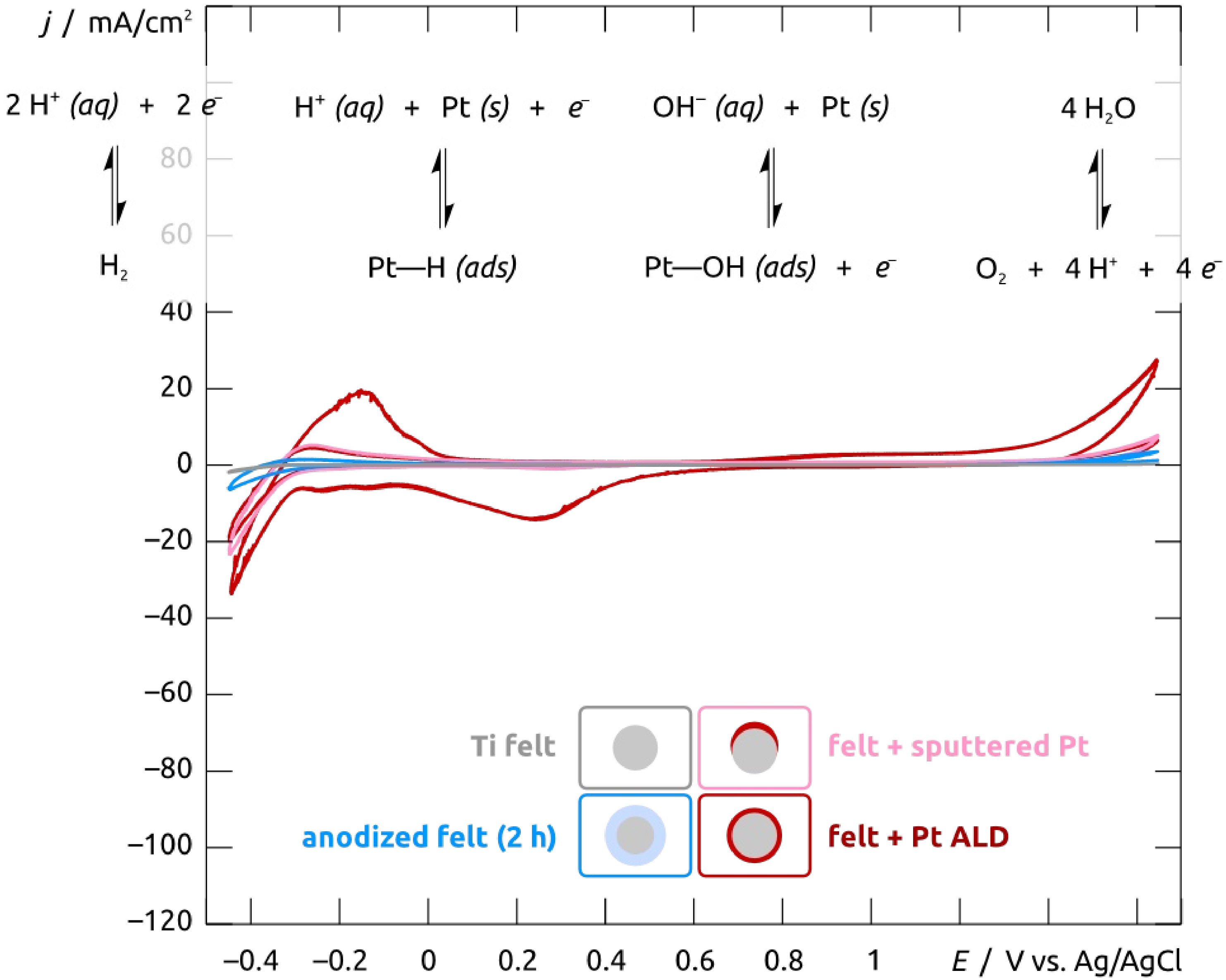
C. Electrocatalysis at nanoporous Pt / TiO_2 surfaces



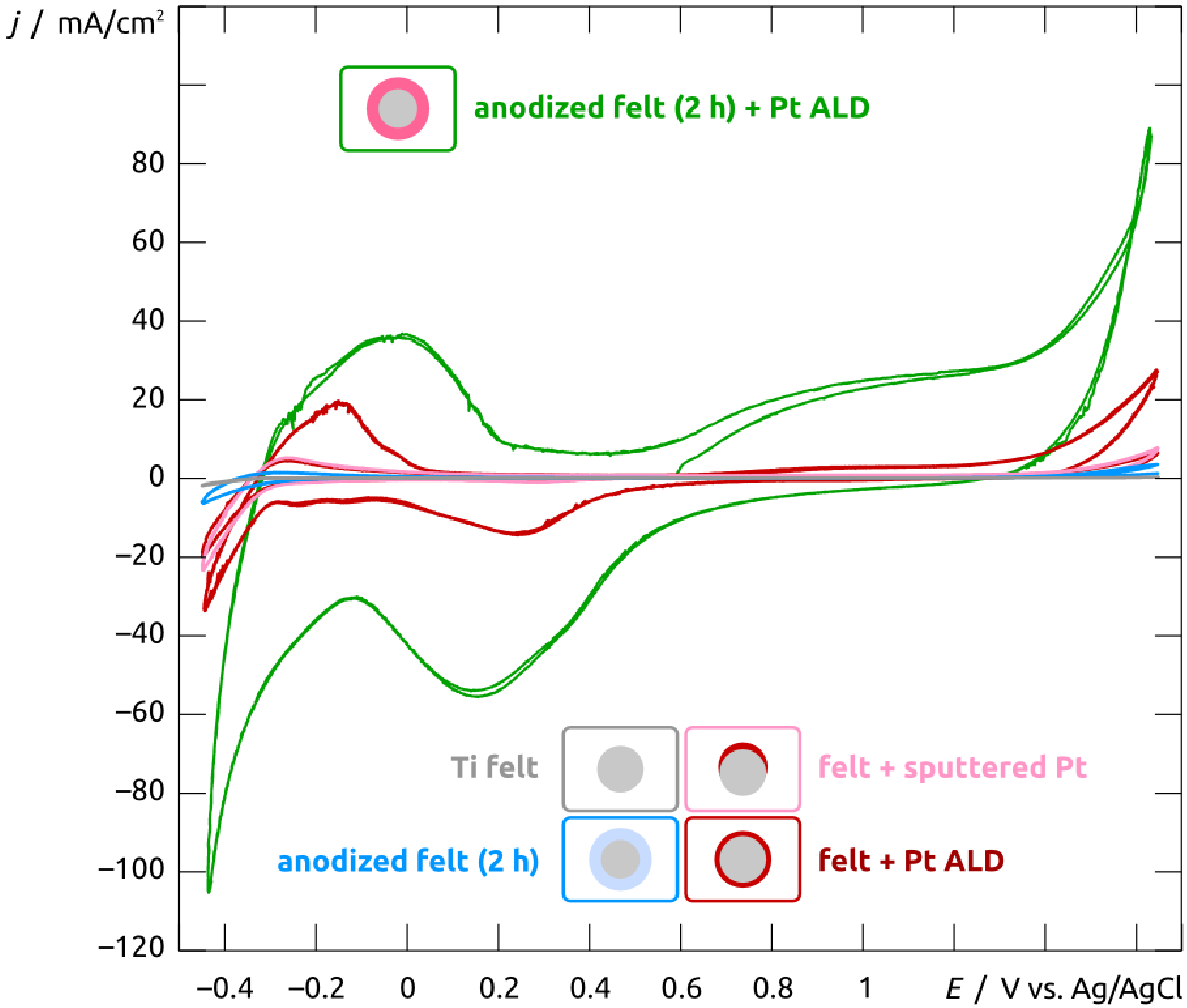
C. Electrocatalysis at nanoporous Pt / TiO_2 surfaces



C. Electrocatalysis at nanoporous Pt / TiO_2 surfaces



C. Electrocatalysis at nanoporous Pt / TiO_2 surfaces

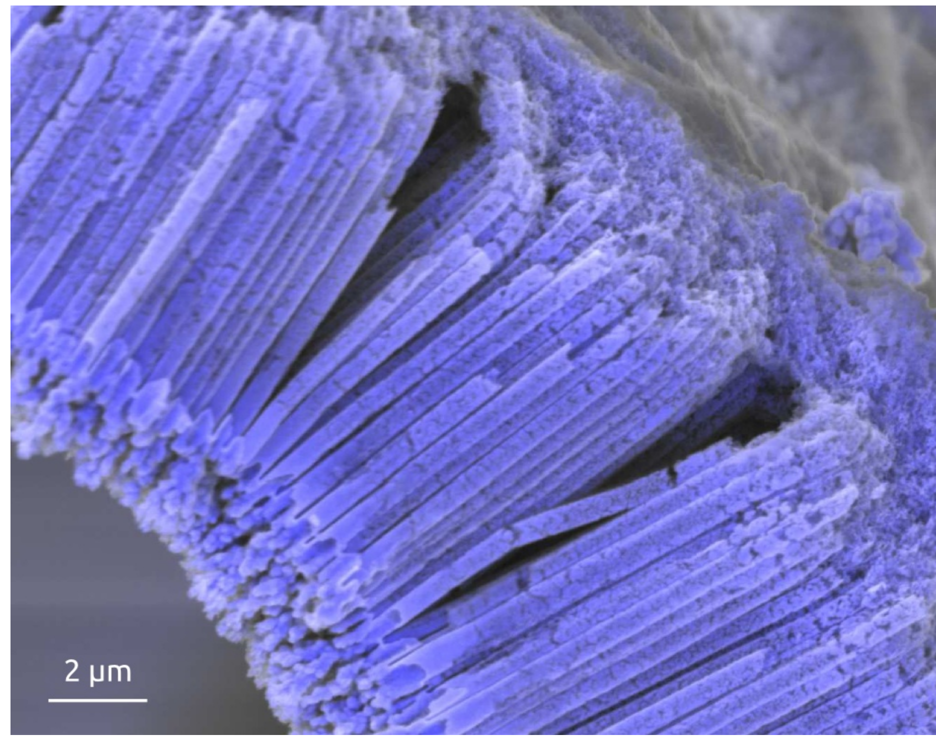


Conclusions

- Surface chemistry of $Pt(acac)_2$ at oxidized Pt surface can be self-limiting at 130-150°C — dosage is crucial
- Optimization of electrocatalytic performance by nanostructuring

Conclusions

- **Surface chemistry of Pt(acac)$_2$ at oxidized Pt surface can be self-limiting at 130-150°C — dosage is crucial**
- **Optimization of electrocatalytic performance by nanostructuring**



- Similar results obtained with galvanically deposited Pt

Roscher, Licklederer, Schumacher, Reyes Rios, Hoffmann, Christiansen, Bachmann, *Dalton Trans.* **2014**, *43*, 4345-4350

Acknowledgements

FAU FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

tubulAir±

ENERGIESPEICHER Forschungsinitiative der Bundesregierung

EAM ENGINEERING OF ADVANCED MATERIALS

BMBF (project TubulAir±)

Johannes Schumacher

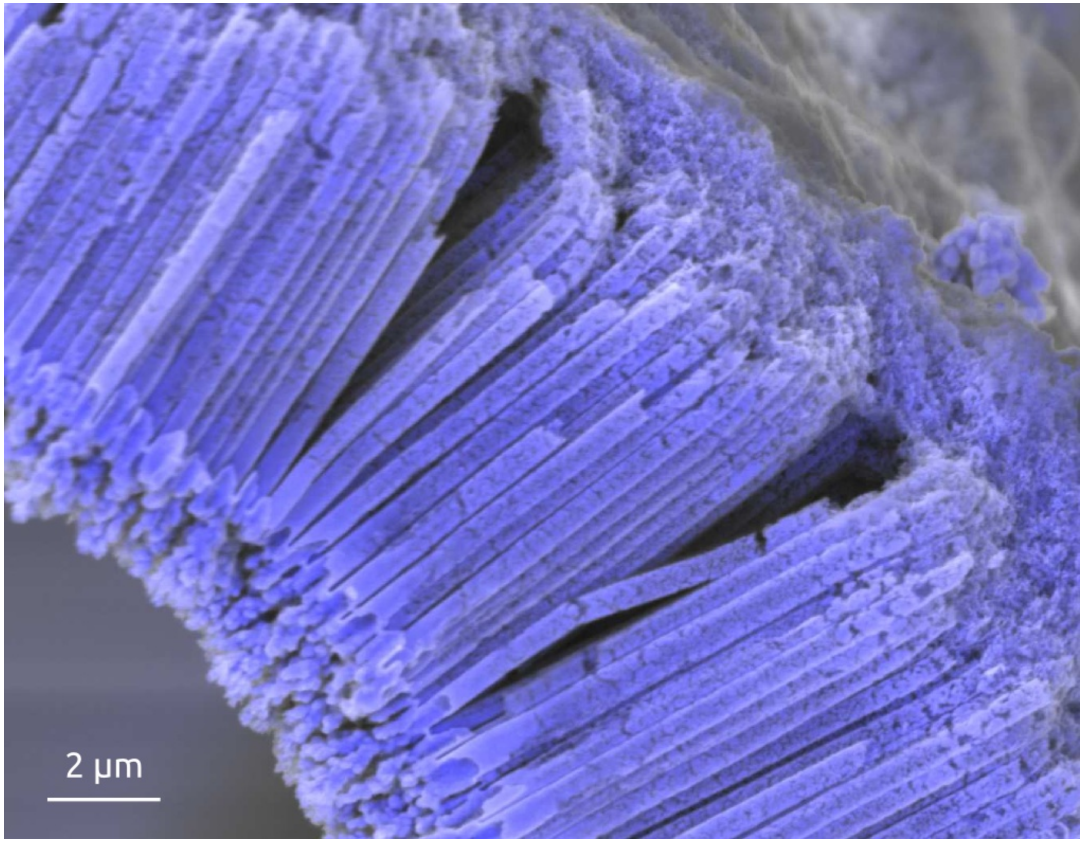
Dr. Loïc Assaud

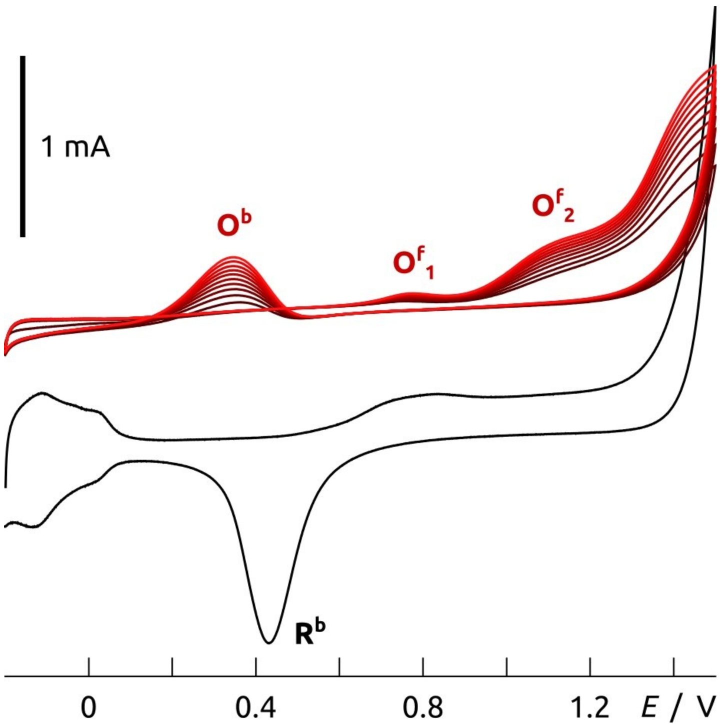
Alexander Tafel

XRD: S. Bochmann (FAU inorganic chemistry), Prof. W. Peukert (FAU materials science)
FE-SEM: Dr. S. Christiansen (MPI for the Science of Light, Erlangen)

Electrodeposited, structured Pt electrode surfaces

Nanotubular Pt surface:
electrochemically active in **acidic** and **ethanolic** solution





Transport effects at structured electrode surfaces

Steady-state electrolytic currents at Pt, various lengths L:

- **Hexacyanoferrate oxidation**: fast reaction, diffusion-limited
- **Proton reduction**: slow reaction, surface-limited
- **Ethanol oxidation**: slow reaction, surface-limited