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: Electro catalyst for H\textsubscript{2} production from water and for ethanol oxidation (electrolysis, fuel cell)

• Standard ALD reaction:
  \[
  \text{MeCpPtMe}_3 + O_2 \rightarrow 0.30-0.48 \text{ Å/cycle @ 200-300}^\circ\text{C}
  \]

• Costs of Pt ALD precursors (Strem):
  MeCpPtMe\textsubscript{3}: \(\varepsilon\) 231 / 0.5 g
  Pt(acac)\textsubscript{2}: \(\varepsilon\) 115 / 1 g

• Conceivable alternative:
  \[
  \text{Pt(acac)}_2 + O_3 \rightarrow \text{PtO}_x \leq 130^\circ\text{C}, \text{Pt} \geq 140^\circ\text{C}
  \]
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**
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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:

- **5-s Pt(acac)$_2$ exposures**
  - Mass increase at O$_3$ step: Oxidation of metallic Pt
  - Large mass oscillations at long expo times: 'Deep' oxidation/reduction

- **30-s Pt(acac)$_2$ exposures**

![Graphs showing mass changes over time](image)
A. Reaction mechanism investigation of Pt(acac)$_2$ + O$_3$

- Al$_2$O$_3$ 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

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

(1) Anodize
NH₄F, glycol
10 V – 40 V

(2) Sonicate
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

$H_2$ evolution  $H^+ (aq) / H (ads)$  $OH^- (aq) / OH (ads)$

$j / mA \text{ cm}^{-2}$

KOH / H$_2$O

$E_{vs.\ Ag/AgCl} / V$
C. Electrocatalysis at nanoporous Pt / TiO$_2$ surfaces

- H$_2$ evolution
- H$^+$ (aq) / H (ads)
- OH$^-$ (aq) / OH (ads)
- EtOH oxidation

Graph showing current density ($j$) vs. potential (E vs. Ag/AgCl) for different reactions.
C. Electrocatalysis at nanoporous Pt / TiO$_2$ surfaces

$j / \text{mA/cm}^2$

$E / \text{V vs. Ag/AgCl}$

$\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ on felts:
C. Electrocatalysis at nanoporous Pt / TiO$_2$ surfaces
C. Electrocatalysis at nanoporous Pt / TiO$_2$ surfaces

![Graph showing electrocatalysis at nanoporous Pt / TiO$_2$ surfaces with different samples: Ti felt, felt + sputtered Pt, and anodized felt (2 h).]
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
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Similar results obtained with galvanically deposited Pt

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