Electrochemistry in LP-EM & Effects Induced by Irradiation of Metal Electrodes

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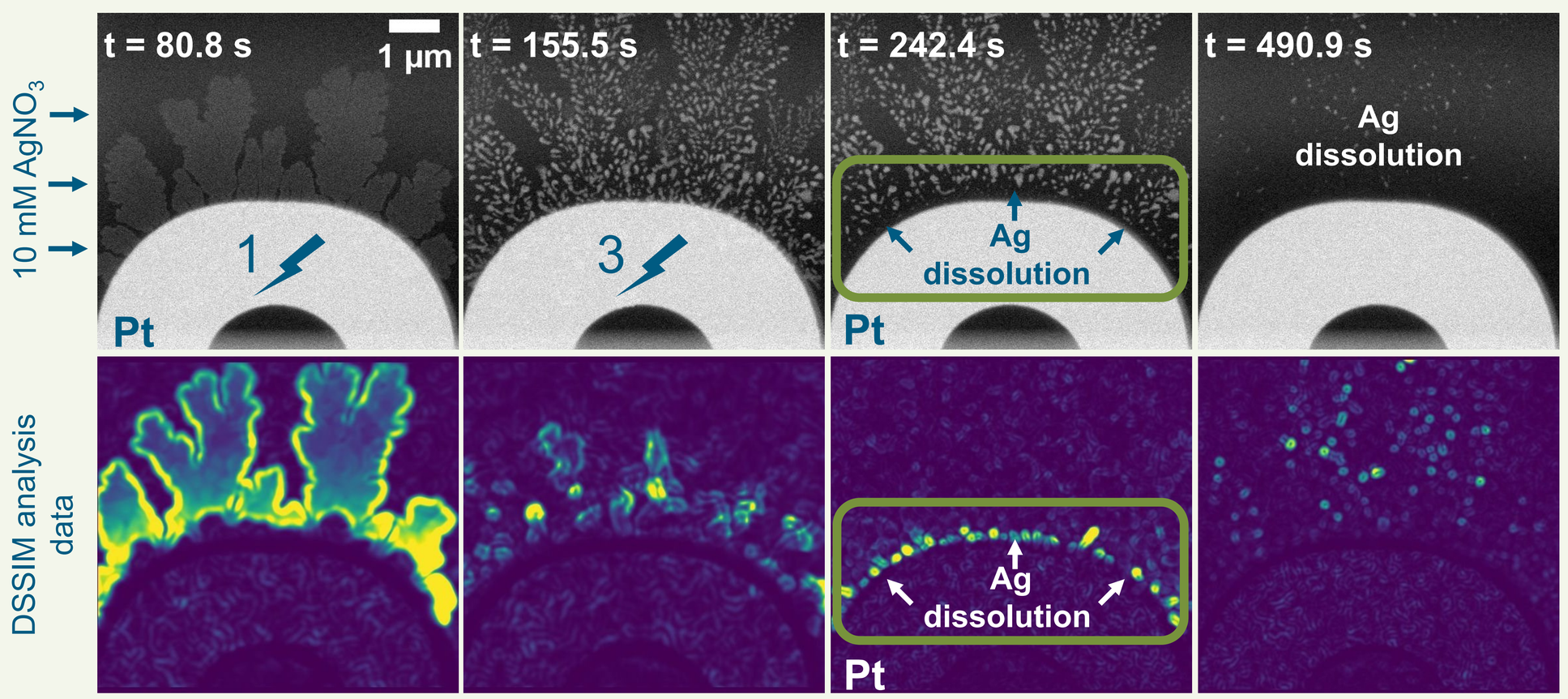
In-situ electrochemical growth of Ag dendrites

Talos F200i @ 200 keV
Beam current 533 pA
HAADF STEM
DENSsolution Stream
Flowrate 0.8 µL/min

Beam effects when closer to electrodes?

Accelerated Ag dissolution closer to Pt working electrode (WE)



$AgNO_3$ radiolysis → **Reductive species (e_h^-, $H^\cdot$)** **Oxidative species (O_2)**

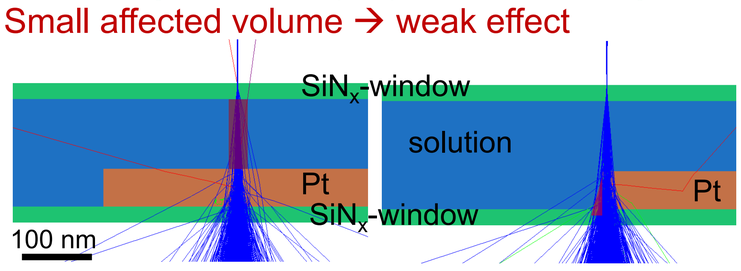
But… Why Ag dissolves faster closer to Pt WE?

Tested hypotheses:

SE emission

- CASINO simulations [1]
- Determines SE value

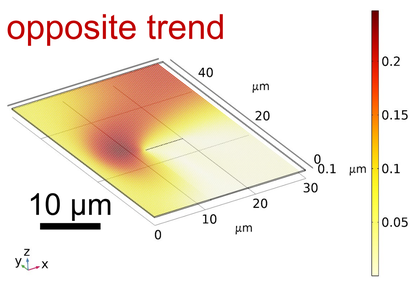
- e⁻ scattering @ Pt WE
- ✓ Secondary electrons (SE) enhance radiolysis
- x Small affected volume → weak effect



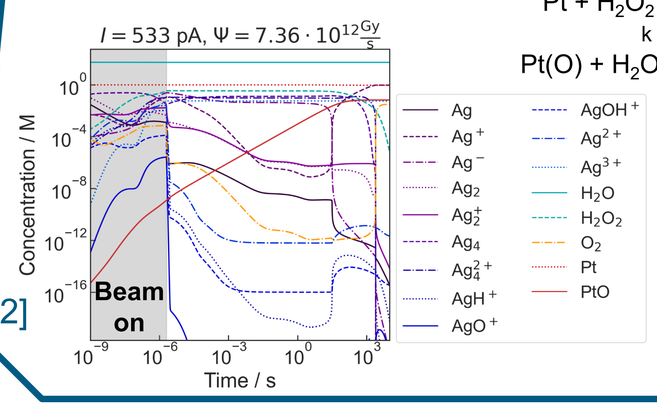
Flow speed

- Influences radiolysis chemistry → chemical environment
- COMSOL simulations
- Estimates flow velocity

- Fast flow → growth / Slow flow → etching [2]
- ✓ Flow @ Pt WE fast
- x Growth expected → opposite trend



Catalytic Pt



[2]

k = 0.0028 mol L^{-1} s^{-1}

$Pt + H_2O_2 \longrightarrow H_2O + Pt(O)$

k = 0.038 mol L^{-1} s^{-1}

$Pt(O) + H_2O_2 \longrightarrow Pt + O_2 + H_2O$

- Pt catalyzes H_2O_2 to O_2
- ✓ Oxidative environment (O_2)
- x Pt bad catalyst for oxygen evolution reaction (OER) → slow effect

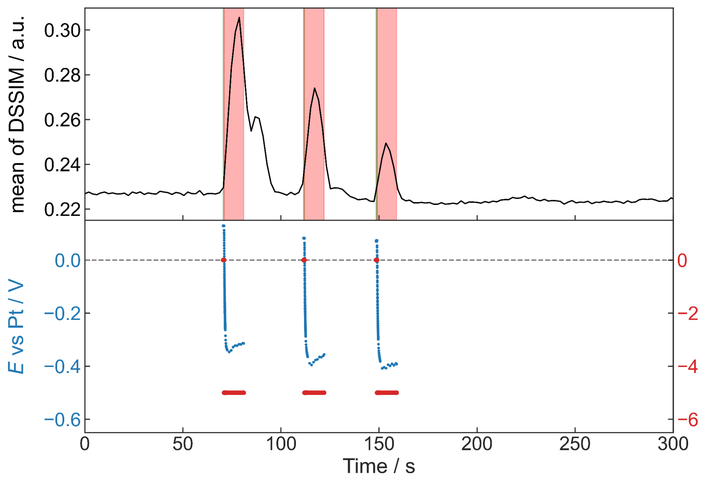
Structural Dissimilarity Metric (DSSIM) [3]

- Metric to show regions of change
- The brighter the spots, the bigger the change
- Dissolution rate faster when closer to the electrode

Galvanic replacement reaction [4]

- Pt nobler than Ag
- corrosion potential = open circuit potential (OCP)

+OCP = unlikely to corrode
-OCP = likely to corrode



1. Pt → +OCP
2. ⚡ hold x3 → Ag grows
3. Pt OCP drops x3
4. ⚡ holds stop → Pt OCP increases again → Pt back to initial state
5. Ag closer to Pt WE starts etching → Ag galvanic corrosion

References:
[1] Drouin et al., Scanning, 29, 2007, 92-101. DOI: 10.1002/sca.20000
[2] Körner *et al.*, Submitted, PrePrint. DOI: 10.2139/ssrn.4891103
[3] Mulvey *et al.*, Ultramicroscopy 257, 2024, 113894. DOI: 10.1016/j.ultramic.2023.113894
[4] Papavinasam, Techniques for Corrosion Monitoring; Elsevier, 2008; pp 49–85. DOI: 10.1533/9781845694050.1.49

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