SVET measurements combined with in-situ scratching approaches

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Research motivations

The generation of **defects through coatings** are inevitable ...

The time-response of corrosion/inhibition: difficult to predict! *M. F. Montemor, Surf. Coatings Technol. 258, 17 (2014)*

→ **timing** for defect analysis?

→ **early stages of corrosion** after coating failure?

H. S. Isaacs et al., Corros. 52, 163 (1996)
M. E. McMahon et al., Front. Mater. 6, 1 (2019)
W. Kautek et al., Electrochim. Acta 48, 3249 (2003)

- Scribed surfaces studied by SVET:

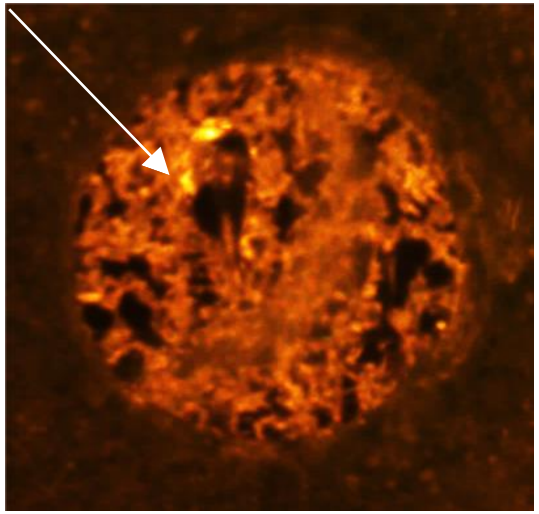
→ **time-related aspects** of inhibition, self-healing, cathodic activation of Mg

A. S. Gnedenkov et al., Corros. Sci. 102, 269 (2016)
N. Wint et al., Corros. Sci. 158, 108073 (2019)
S. Rossi et al., Comptes Rendus Chim. 11, 984 (2008)
D. Snihirova et al., Electrochim. Acta 322, 134761 (2019)
E. Michailidou et al., J. Electrochem. Soc. 165, C195 (2018)

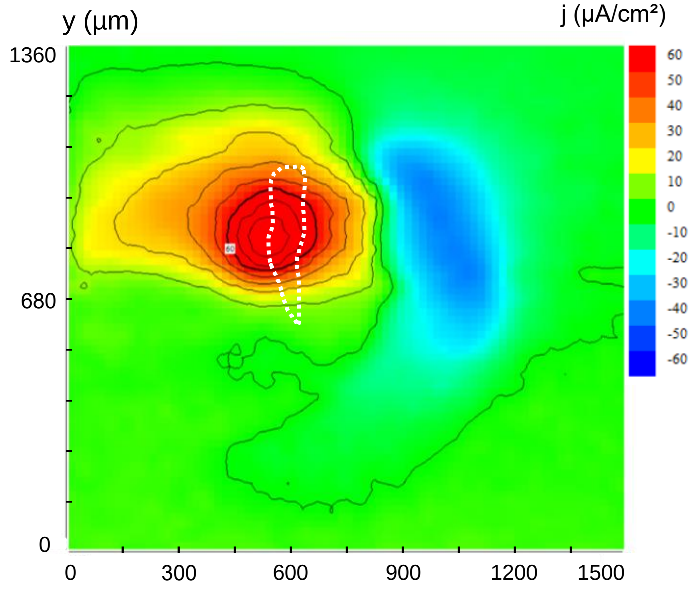
→ High activities from the first possibly executed scans

J. J. Santana et al., Corros. Sci. 52, 3924 (2010)
S. Neema, et al., J. Appl. Polym. Sci. 127, 740 (2013)

ex-situ scratching



"empty" time slots



L. B. Coelho et al., Corros. Sci. 175, 108893 (2020)

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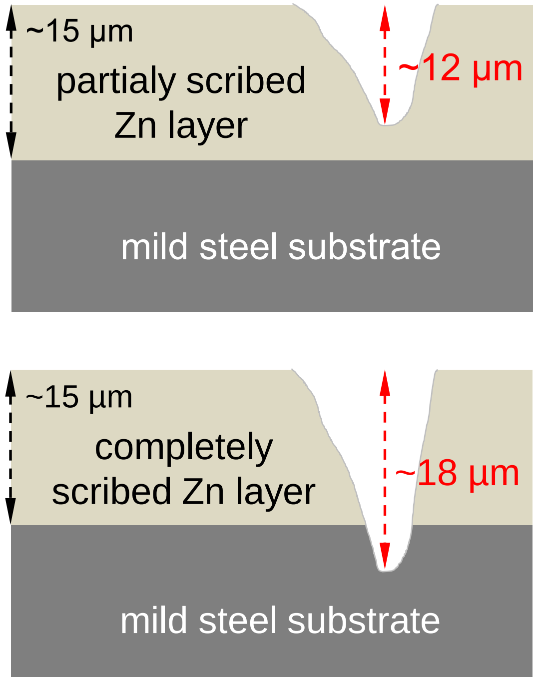
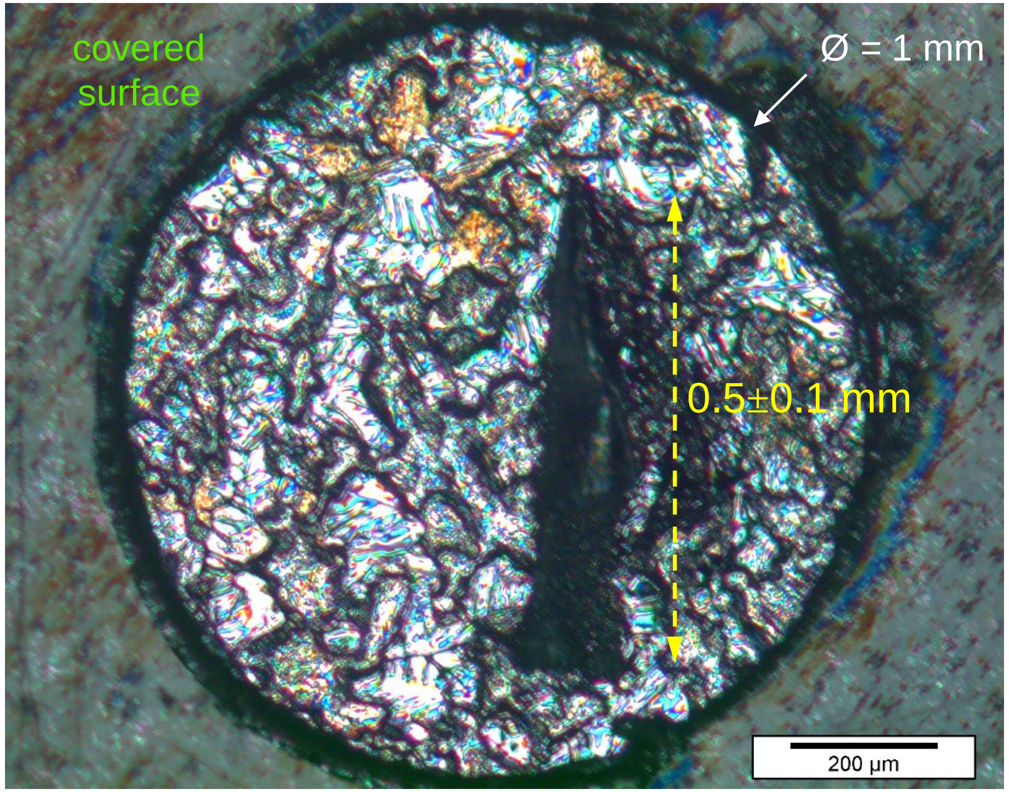
Research motivations

- Defect-related SVET investigations: low reproducibility!

Cross-sections of scribed HDG surfaces:





L. B. Coelho et al., Corros. Sci. 175, 108893 (2020)

- Open issues:

- geometry/area/number of defects?

- multiple damaging events?

M. F. Montemor, Surf. Coatings Technol. 258, 17 (2014)

→ **combination of local experimental tools** for advancement of anti-corrosion systems!

Unique setup for quasi-simultaneous monitoring of current density and pH.

S. V. Lamaka et al., Electrochem. Commun. 13, 20 (2011)

Combination of local electrochemical techniques with in-situ scratching?

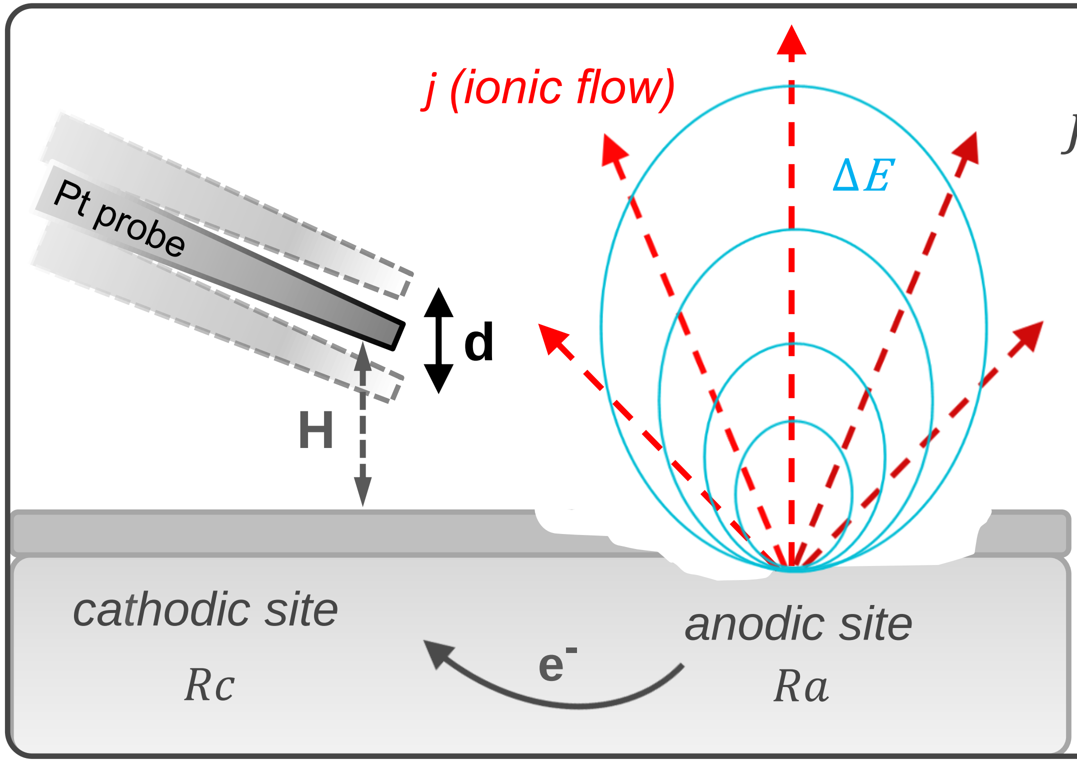
P. Schmutz et al., J. Electrochem. Soc. 145, 2295 (1998)
Y. Zhu et al., J. Electrochem. Soc. 144, L43 (1997)

New SVET approaches for assessing the corrosion activity of defects created in-situ.

Scanning Vibrating Electrode Technique

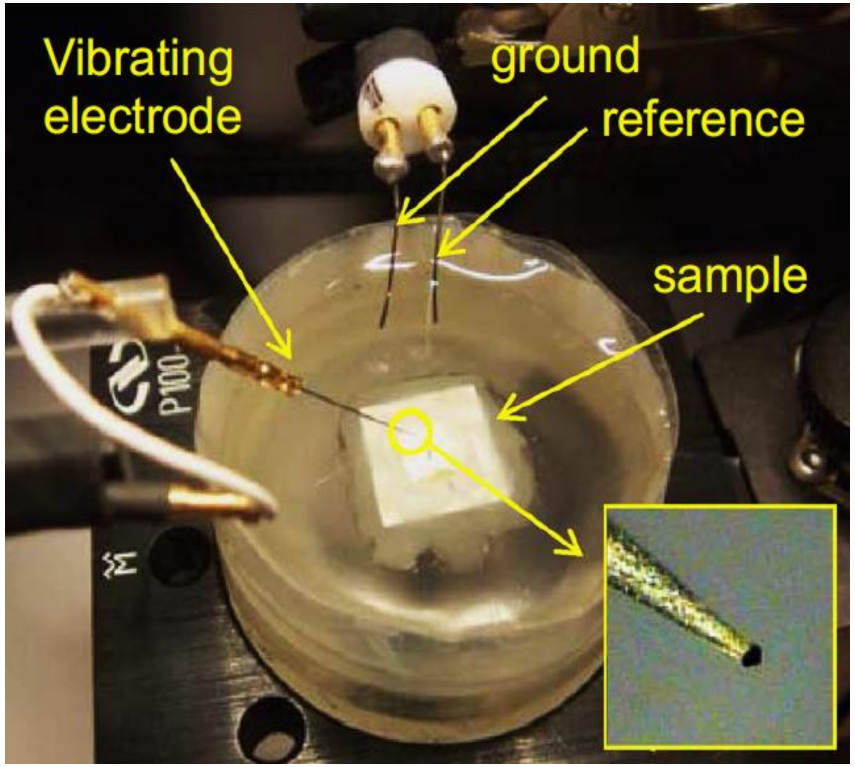
SVET: local characterisation of corrosion activity under free corrosion conditions

Working principle: measurement of **electric potentials** generated due to the flux of **ionic currents** related to the **electrochemical reactions** → ΔE detected using a **vibrating probe**



$$j = \frac{\Delta E}{\sum R_{\Omega} + Ra + Rc}$$

$$j = -\Delta E \frac{k}{d}$$



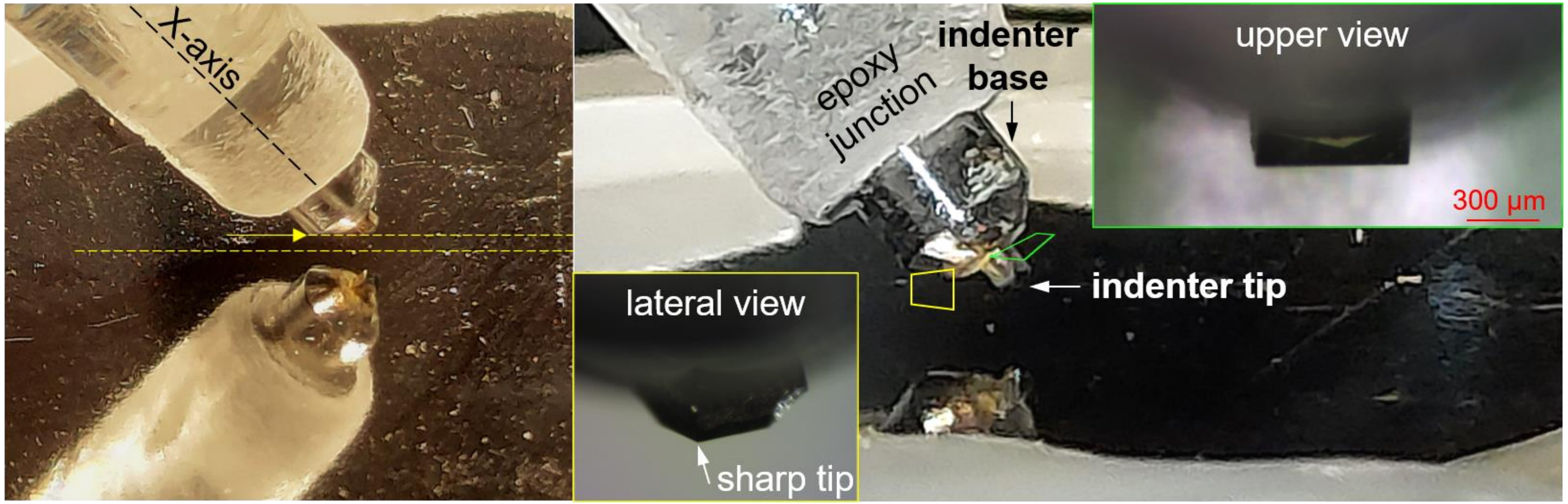
R.M. Souto, Y. González-García, A.C. Bastos, A.M. Simões, Corros. Sci. 49 (2007) 4568–4580

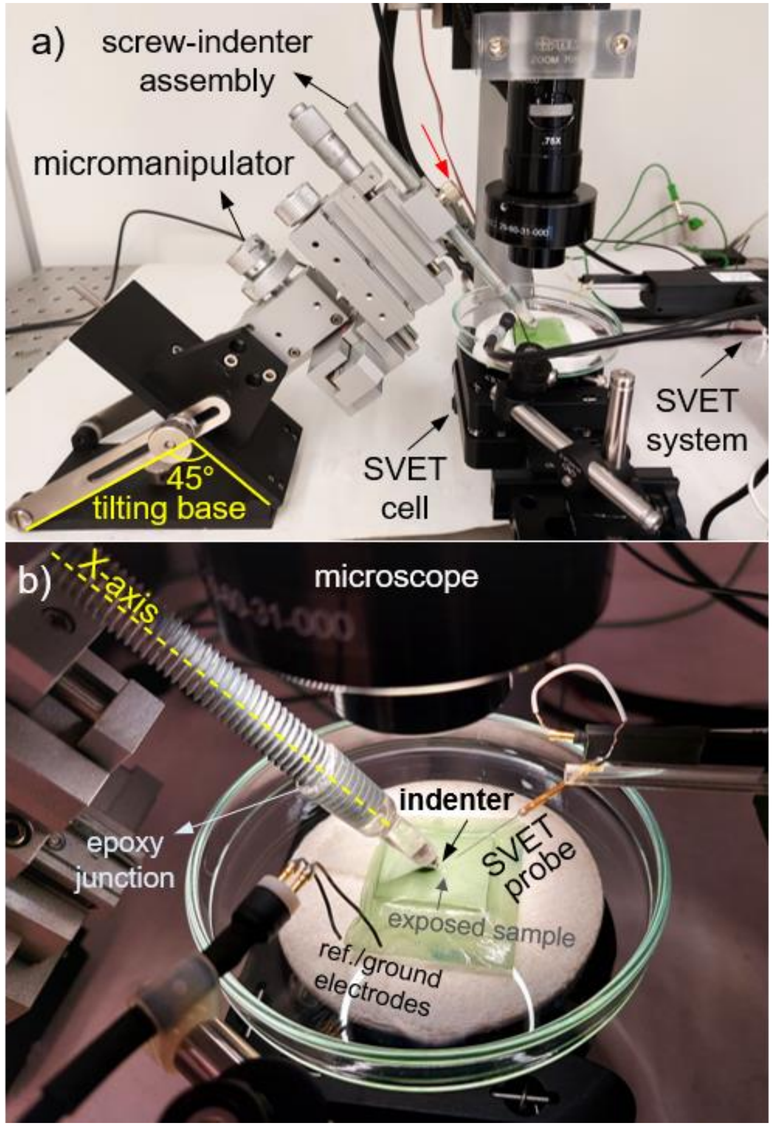
S.V. Lamaka, M. Taryba, M.F. Montemor, H.S. Isaacs, M.G.S. Ferreira, Electrochem. Commun. 13 (2011) 20-23

A.C. Bastos et al. J. Electrochem. Soc. 164 (2017) C973–C990

Scratching assembly

Berkovich indenter (Synton-MDP) assembled to a metallic screw beam, fixed in a manual **micromanipulator** attached to a **tilting base** (tilted at ~45° with the horizontal plane).





Displacement control:

- 10 µm in the **X-axis** (**vertical/horizontal control of 7.07 µm**)
- 0.1 mm in the Y/Z axes

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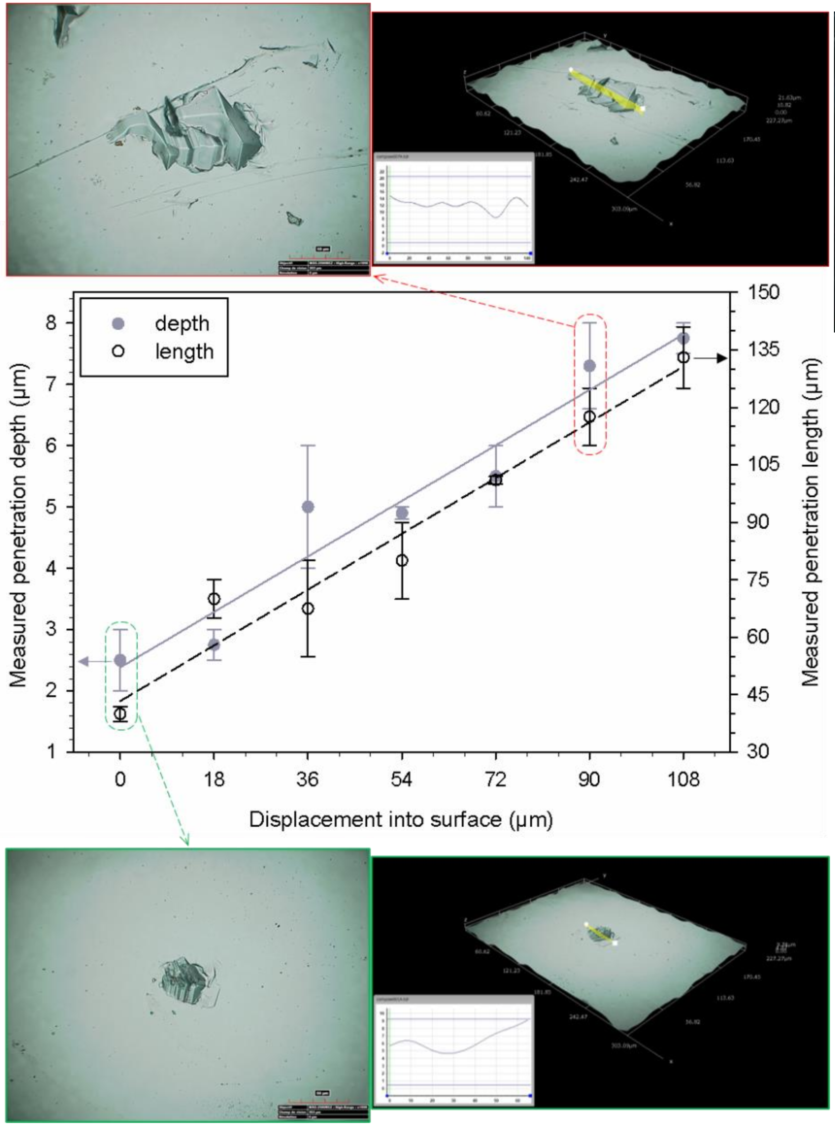
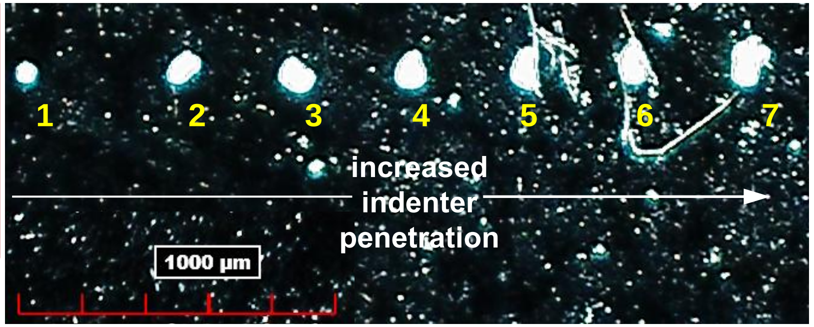
Materials

316L stainless steel (electropolished): reproducibility of scratching

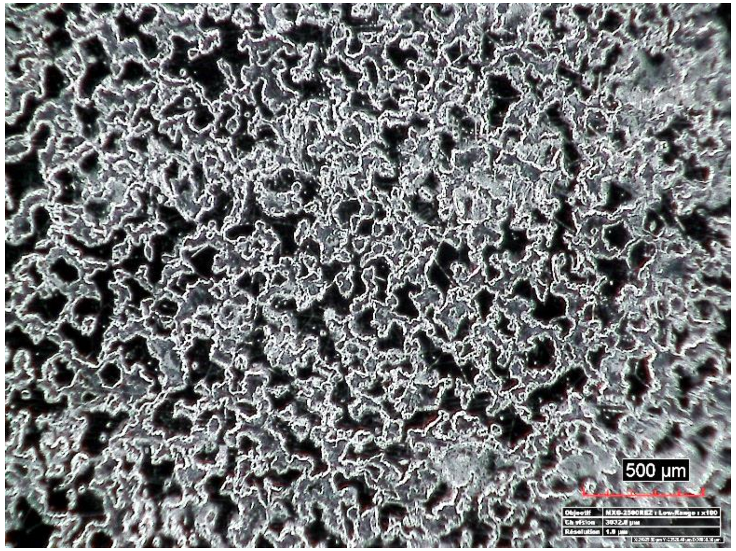


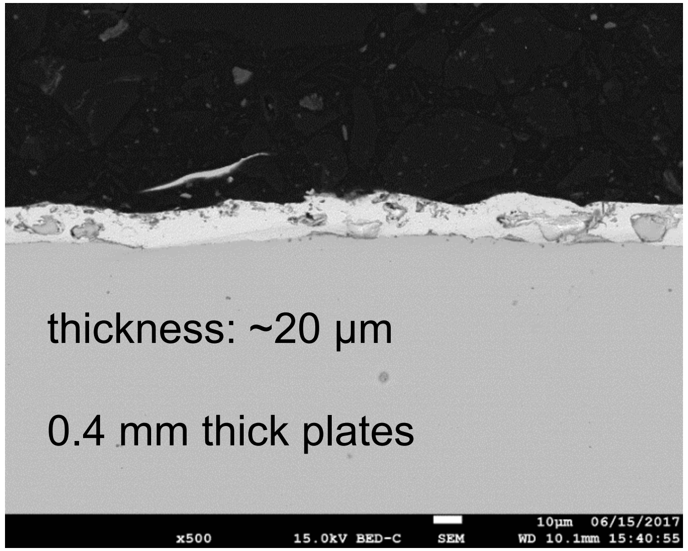


Hot-dip Galvanised Steel:

testing specimen

Extragal® Z100 (Arcelormittal),
skin-passed surface



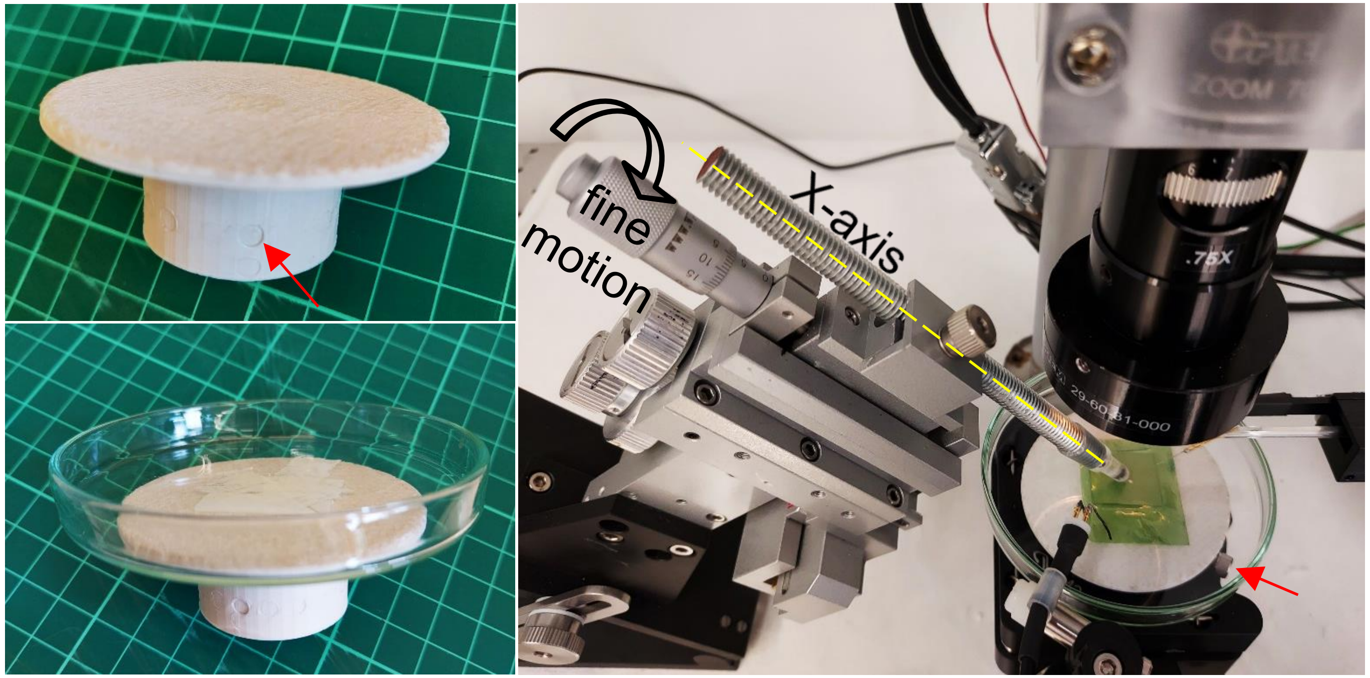


Electrochemical testing: **industrial structure was preserved**!

Sample preparation

Hot-dip galvanized steel

- surface preparation: ultrasonic/acetone degreasing + washing + air drying;
- surface entirely covered by protective insulating tape (except on the **1 mm diameter testing area**).



Scratches produced in-situ:

- **in air**
- **in solution**

Indenter displacement = 18-36 µm

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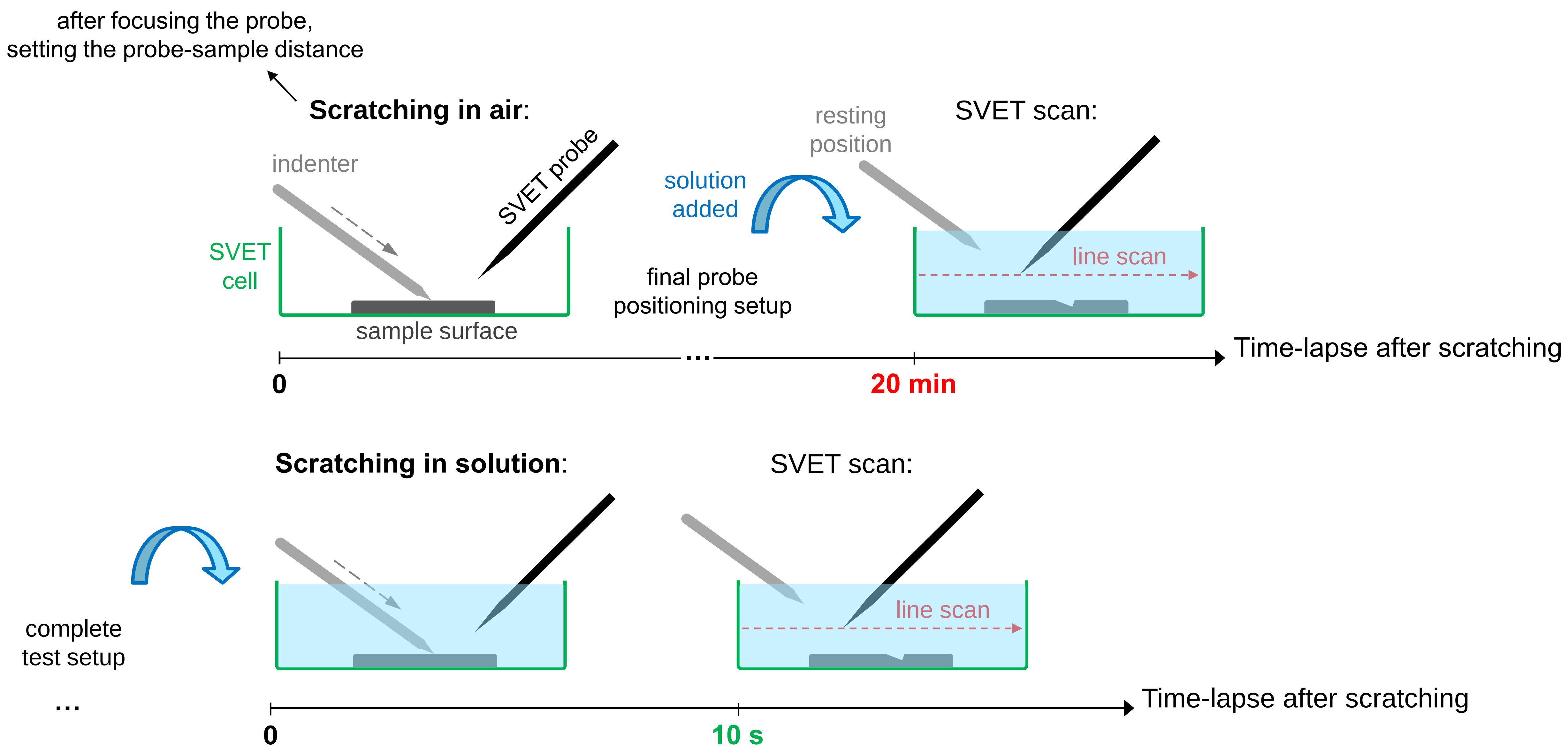
Production of in-situ scratches



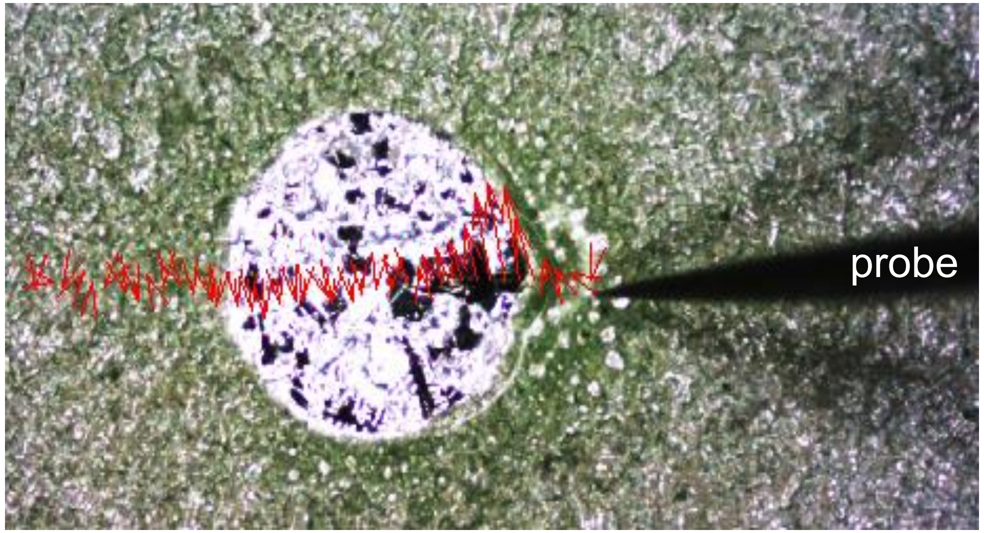
Line scans across the defect

1) Scratching in air *Vs* **in solution (0.05 M NaCl)**

1 min line scans (~1250 µm length, 51 points)

2) Repetitive scratching in 0.05 M NaCl + 5 mM Na_2MoO_4

30 s line scans (~600 µm length, 11 points)



SVET parameters

Equipment: Applicable Electronics™

Software: Science Wares™

Pt-Ir probe: Microprobe, Inc

Pt black deposit (Ø ≈ 20 µm)

40 µm vibration amplitude (peak-to-peak)

probe-sample distance = 150 µm

→ **10 s** time-lag between **in-situ scratching and scanning**

j_Z **profiles continuously** (2 s time-lag) taken from the **same the location**

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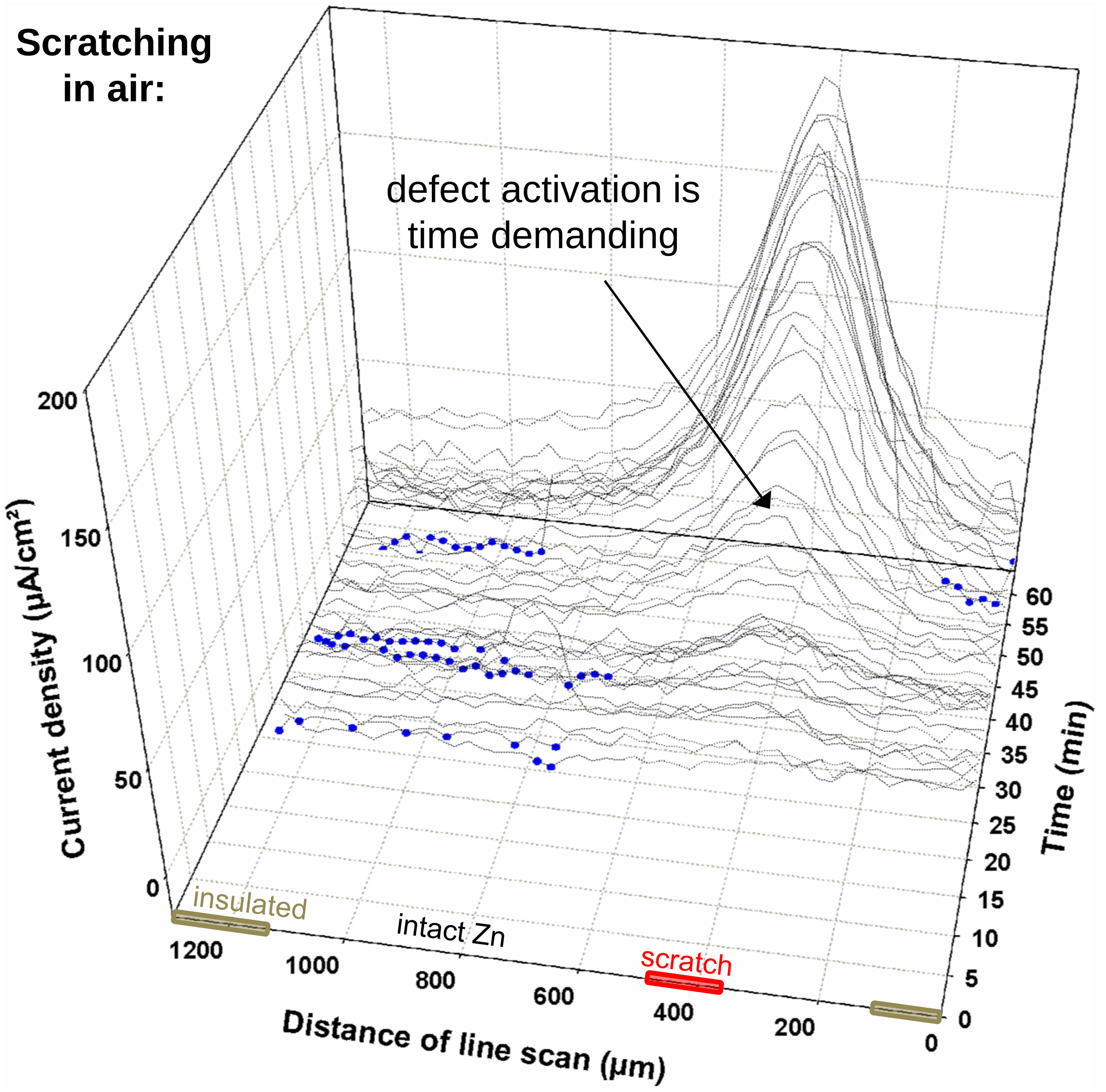
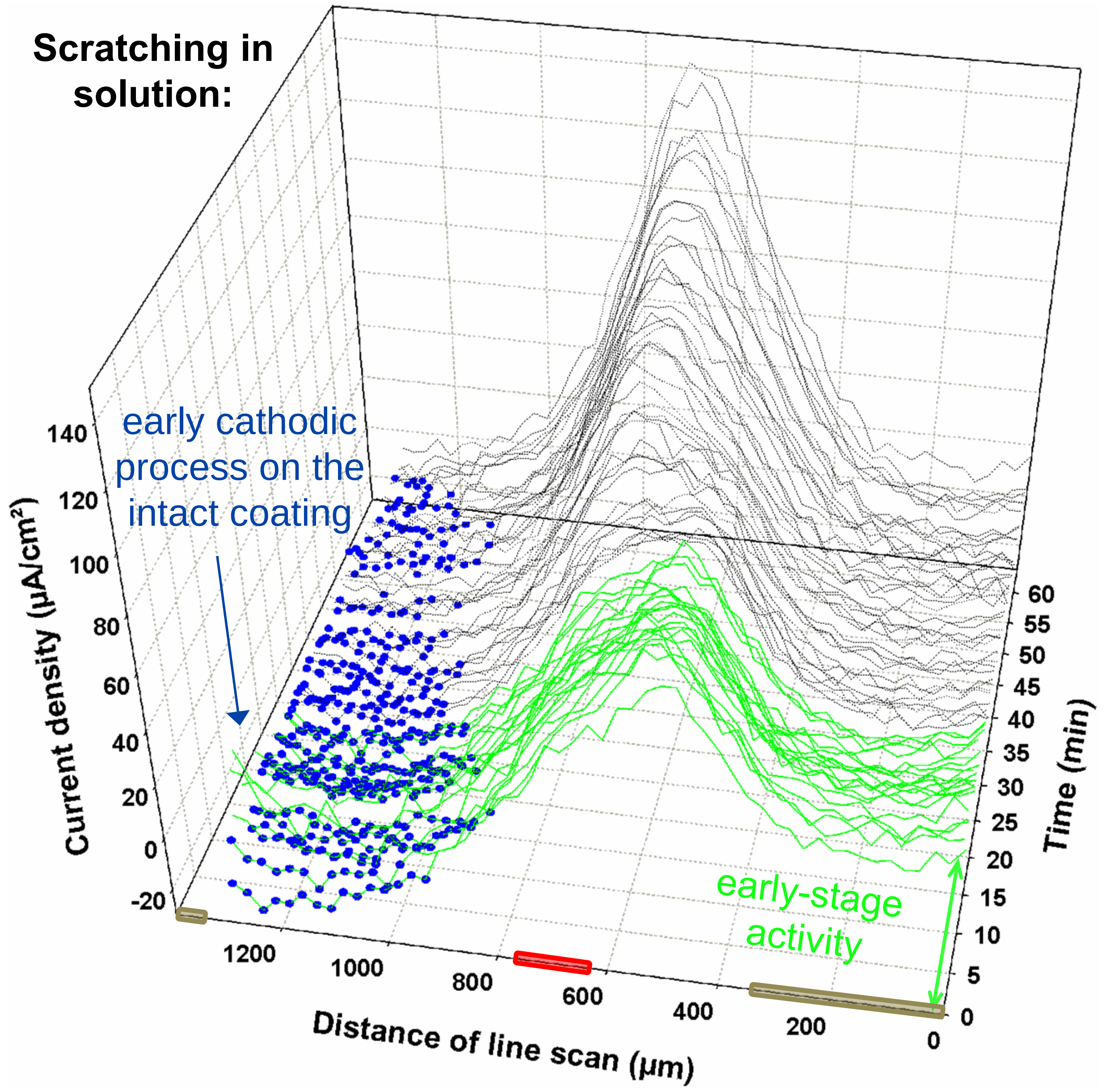
HDG scratched in air *Vs* in 0.05 M NaCl





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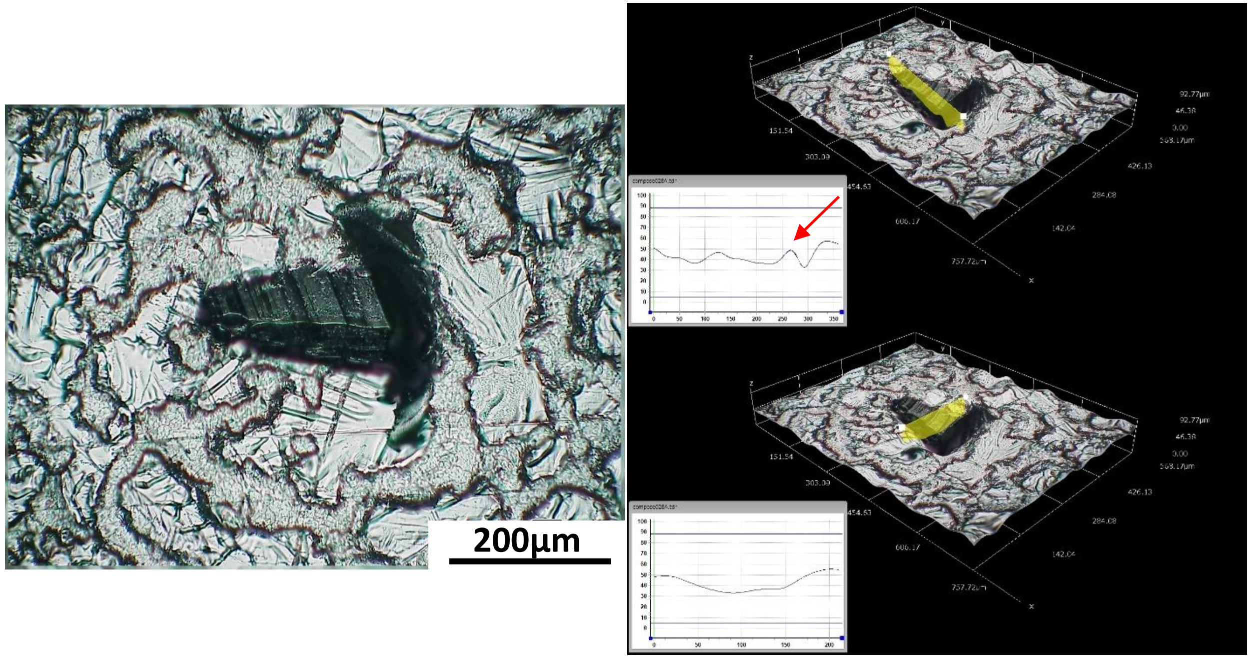
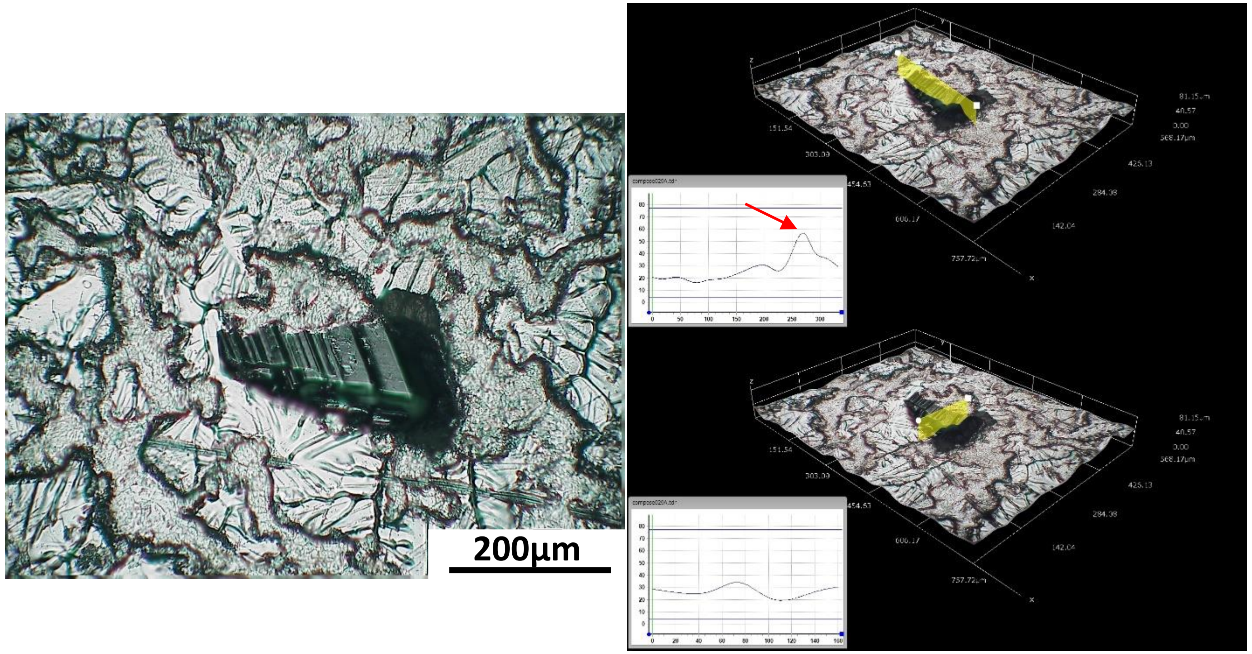
HDG scratched in air *Vs* in 0.05 M NaCl

Post-mortem analysis

Scratches produced in air:



Scratches produced in solution:



~277 µm length , ~15 µm depth, ~24 µm wide

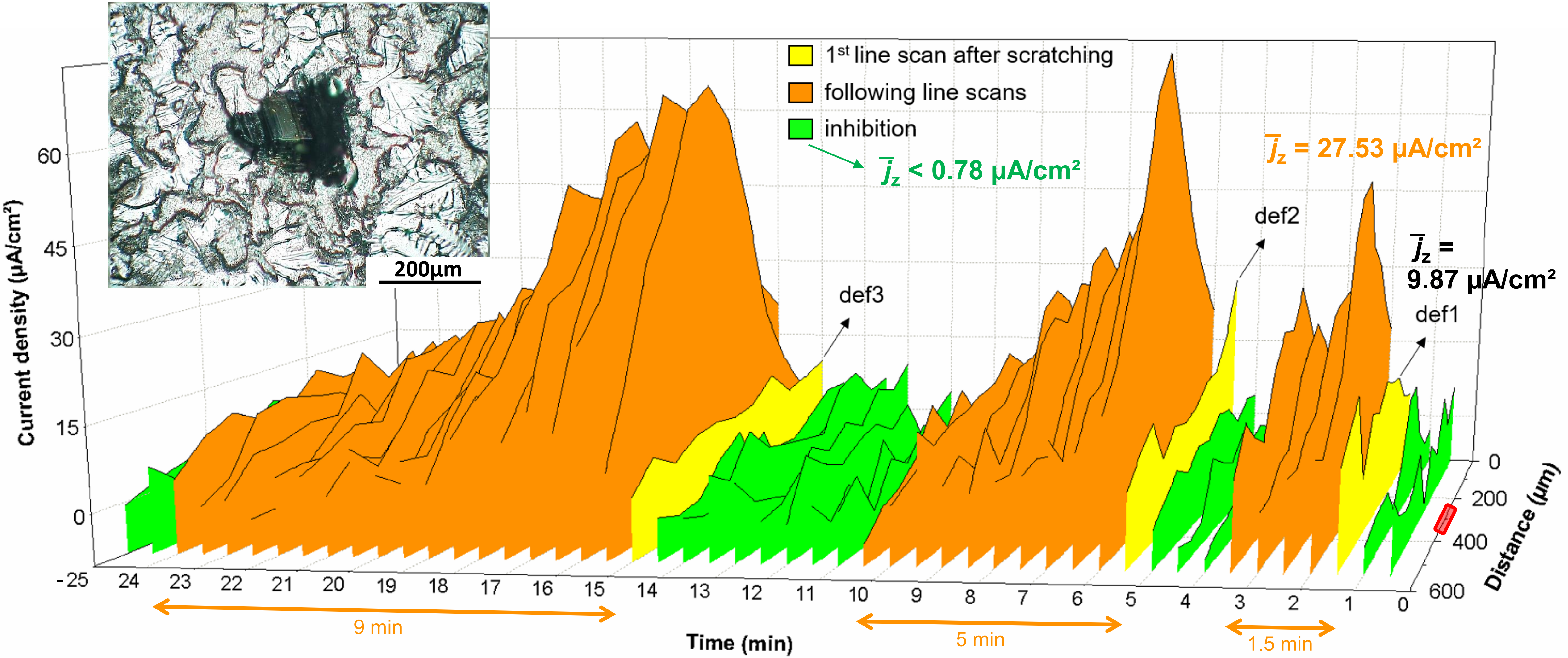
~267 µm length, ~16 µm depth, ~24 µm wide

→ **similar dimensions**

→ corrosion products build-up

Multiple scratching in 0.05 M NaCl + 5 mM Na_2MO_4

→ time for activation ≥ 30 s



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Context

- The development of **anti-corrosion technologies** depends on:

- the understanding of **corrosion/inhibition processes related to microdefects**;
- novel experimental designs combining local tools with in-situ protocols for creating defects.

Conclusions

- The **combination of SVET with in-situ scratching** is a powerful and **easy-to-implement** approach for **early investigation of defect-driven corrosion** (HDG).
- **Scratching in air** *Vs* **in 0.05 M NaCl**: different **behavior!**
- **Repetitive scribing** in 0.05 M NaCl + 5 mM Na_2MO_4: assessment of **time-related aspects of inhibition** (dynamic behavior).

Perspectives

- **Quantitative information could be derived** (kinetic aspects of depassivation/inhibition).
- Promising for tracking **the release of inhibitors in self-healing** systems (rates, long-term effectiveness).

Thanks for your attention!

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