In Situ Visualization of Pitting Corrosion on Stainless Steel in Seawater

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Physics & Atmospheric Science, Dalhousie University

- Introduction: From pattern formation to wild fires to corrosion
- A simplified model for corrosion
- *In situ* imaging techniques to observe pitting corrosion: Ellipsomicroscopy, contrast enhanced microscopy
- Results

Workshop: Durability of Cables & Moorings in Tidal Flows, Halifax, March 31, 2016

Patterns Forming on a Sandy Beach

H H R , Verh. d. GDNÄ 123, S. Hirzel Verlag, Stuttgart, 69-88 (2005)

Permafrost Rock Formations at Svalbart

Mark Kessler and B. Werner, Science 299, 380, (2003)

C. Punckt et al., J. Chem. Edu., 10.1021/ed500714f 2015

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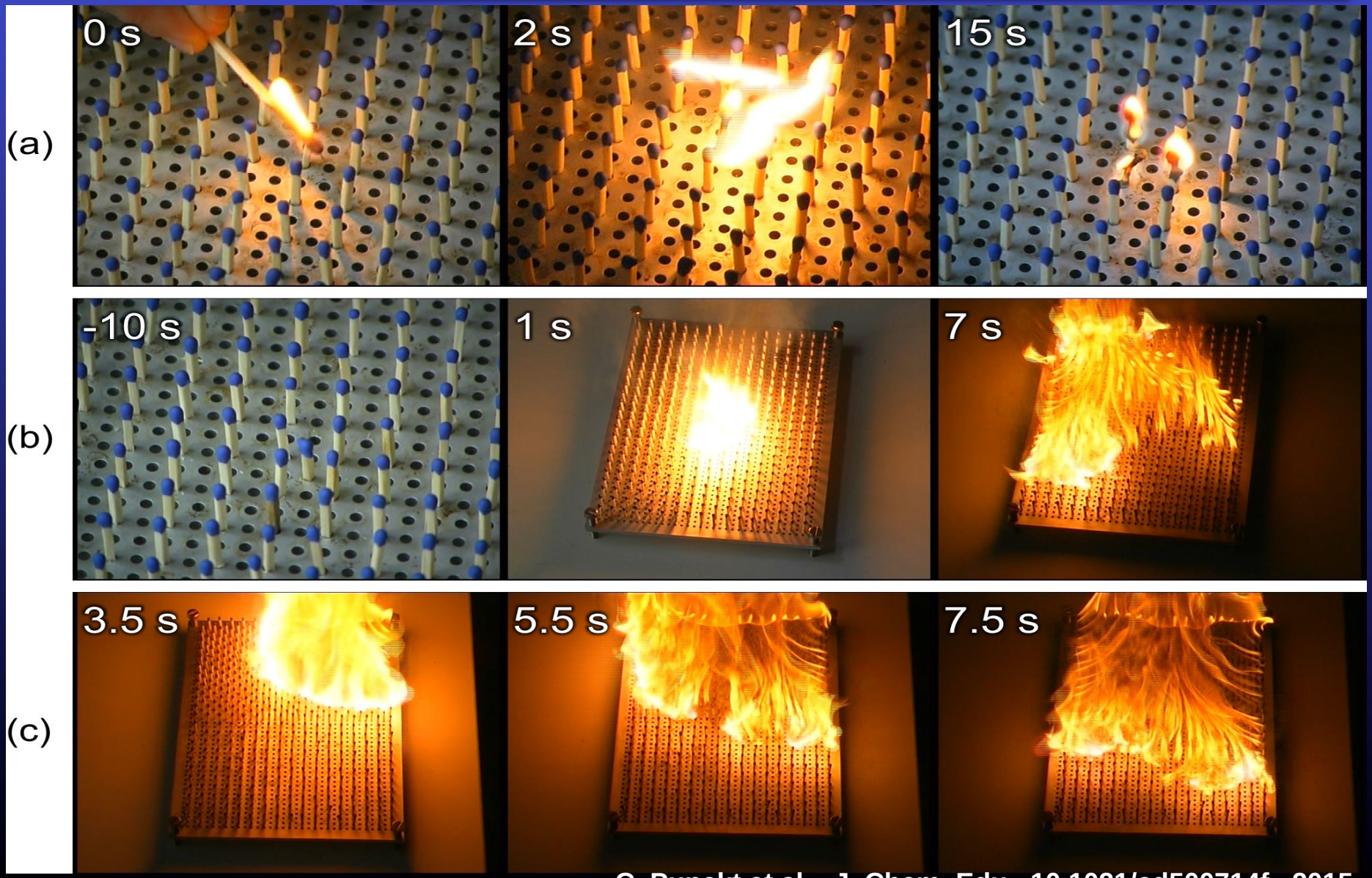
Excitable Media: Match Stick Fires



C. Punckt et al., J. Chem. Edu., 10.1021/ed500714f 2015

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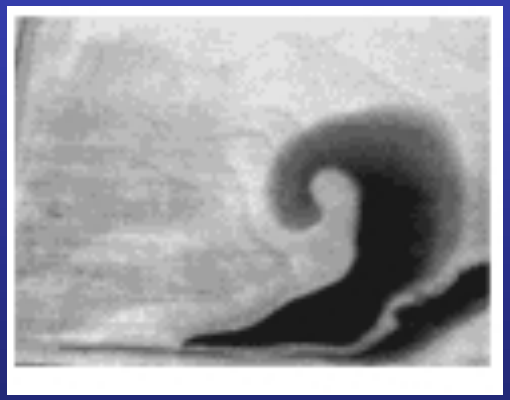
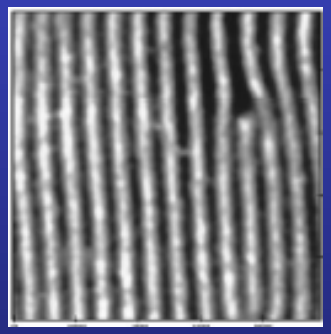
Cooperative Phenomena

Corrosion



Agladze and Steinbock , J. Phys. Chem. A **2000, 104, 9816-9819**

Electropolishing



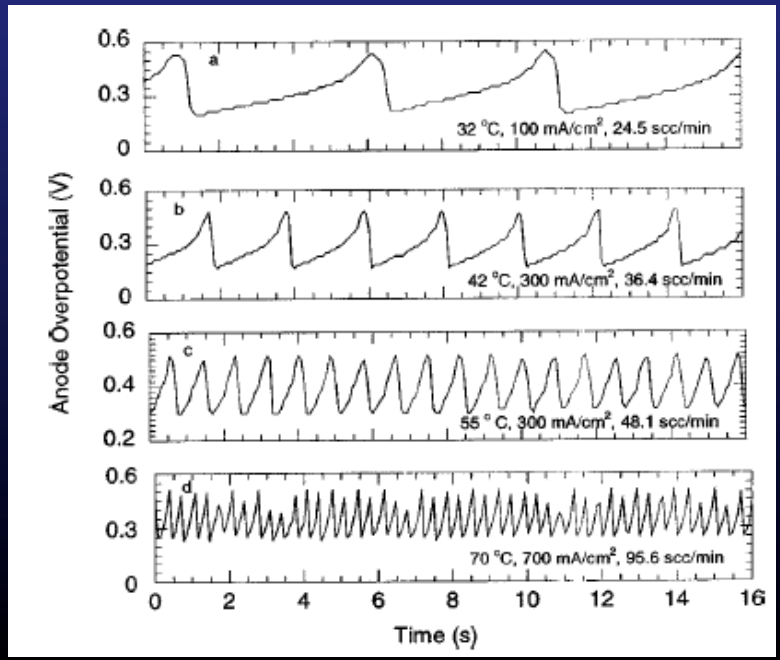
Yuzhakov et al.
PRB 56 (1997) 12608

Electroplating

Krastev and Koper,
Physica A 213,
199 (1995)

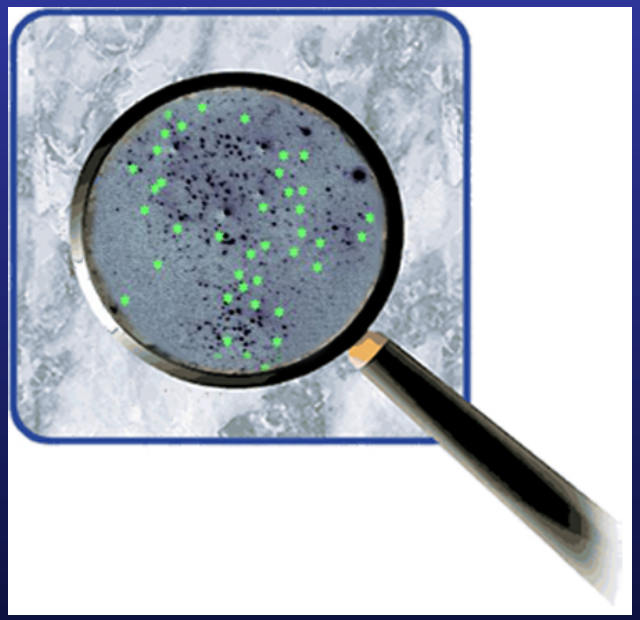
Fuel Cells

Zhang and Datta,
J. Electrochem Soc.
149,A1423 (2002)



Outline of Our Approach

Pitting corrosion is a non-equilibrium critical process.



What is pitting corrosion?

Concepts and modelling

Experimental methods and results

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Corrosion Studies in the environment

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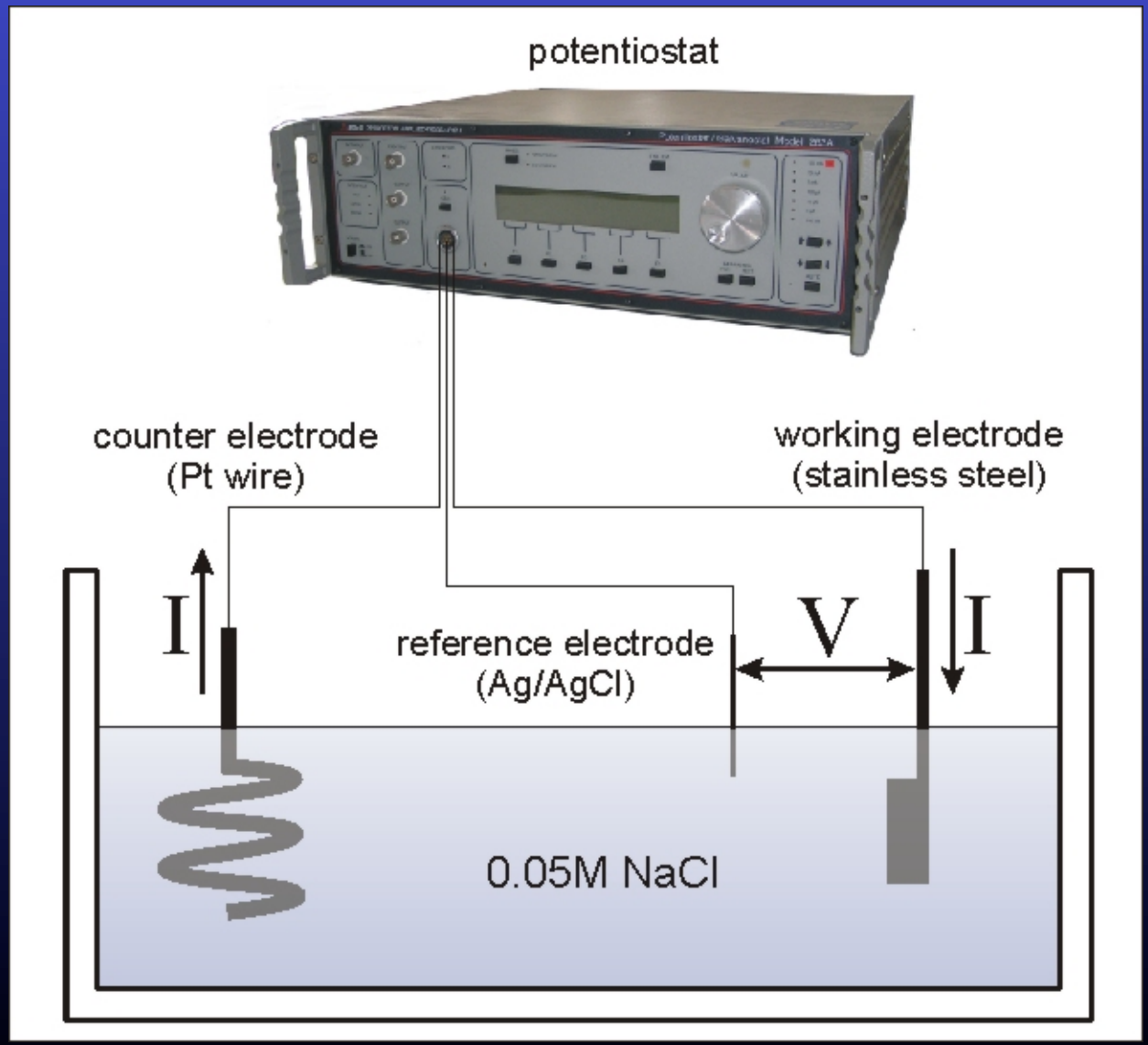
Electrochemical System

stainless steel (AISI 316):

18.18 % Cr
12.25 % Ni
2.40 % Mo
1.75 % Mn
0.38 % Cu
0.35 % Si
0.31 % Co
0.13 % C
0.01 % S

balance Fe:

64.23 %



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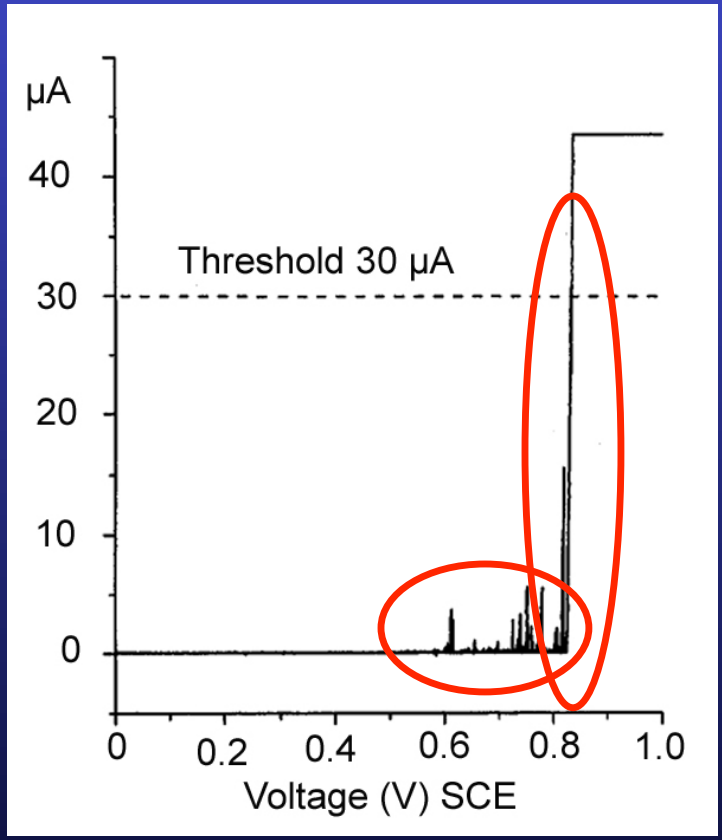
Sudden Onset of Corrosion

small parameter variations:

- abrupt transition to higher corrosion rates
- strong increase of current
- strong increase of number of pits



WHY?

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Pitting Corrosion

- Each pit gives rise to a tiny spike of electrical current, that can be measured.
- Electrical potential between the metal and the environment is an important parameter of the system.
- Increasing potential V has a similar effect as increasing the concentration of the electrolyte or temperature.
- Thus, electrical properties can be used both to control and to monitor the reaction.

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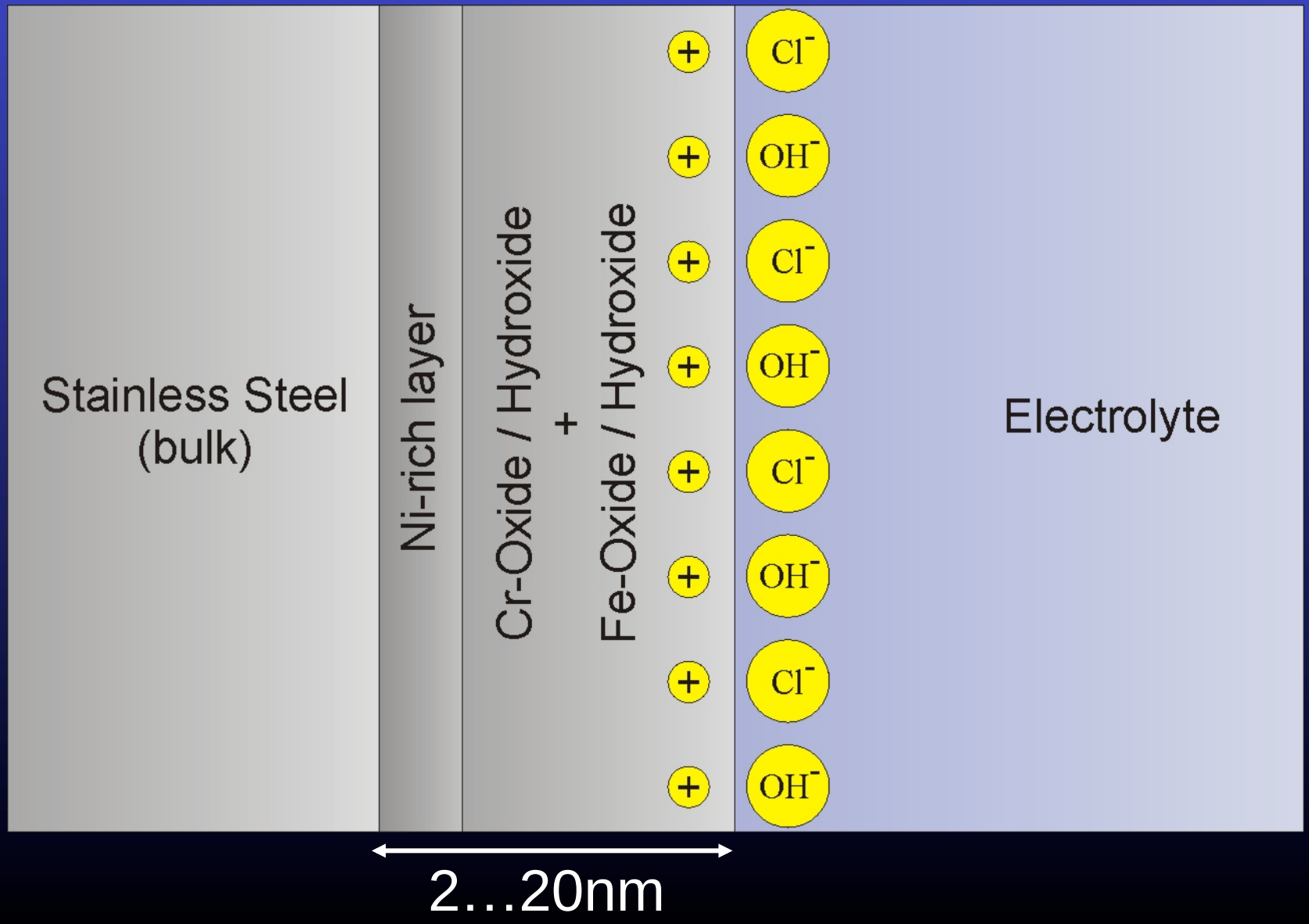
Metal-Electrolyte Interface



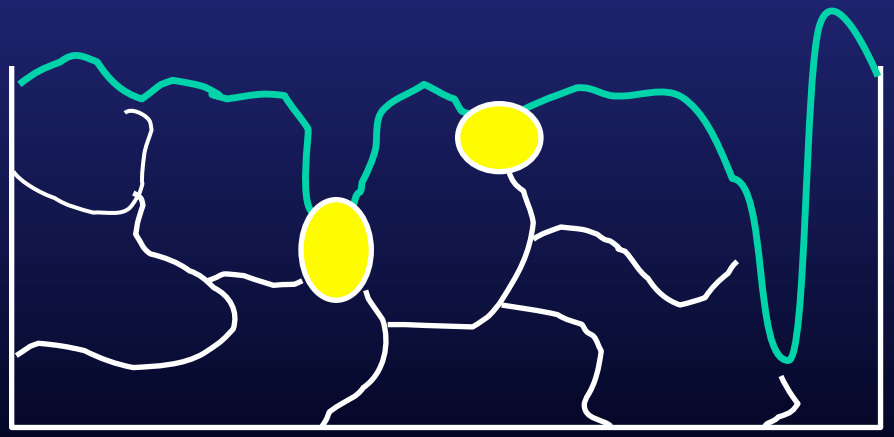
Nature of Metastable Pitting Sites

Physical or chemical inhomogeneities

(e.g. scratches or sulfide inclusions)

→ local imperfections of the passive film

→ increased susceptibility to attack of aggressive ions



Pistorius and Burstein, Philos. T. Roy. Soc. A 341, 531 (1992)

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Metastable Pits

- electrochemically active inclusions
- surface defects

- electrodissolution of metal cations
- migration of chloride into the depression

- activity stops
- protective oxide layer rebuilds

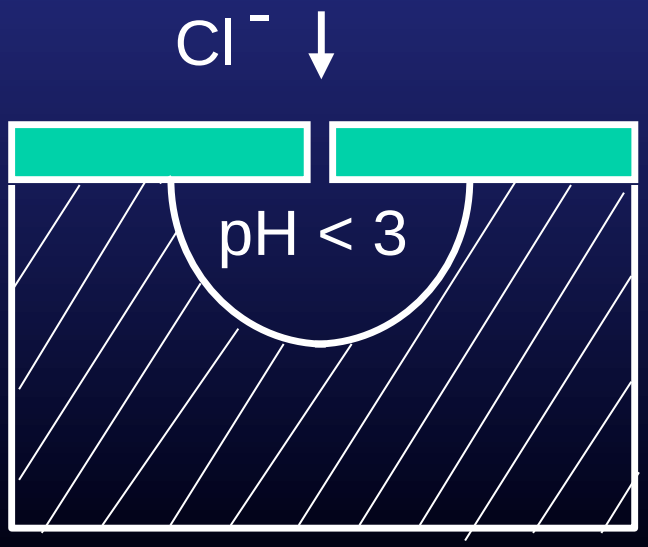
Pistorius and Burstein, Philos. T. Roy. Soc. A 341, 531 (1992)

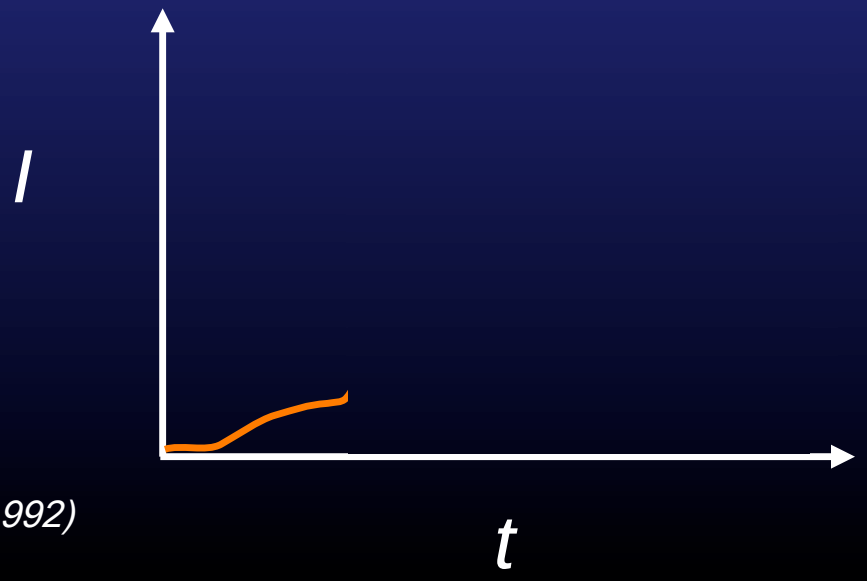
Metastable Pits: Growth and „Death“

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

$$Fe^{2+} + 2Cl^- \longrightarrow FeCl_2$$

$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 + 2HCl$$





Pistorius and Burstein, Philos. T. Roy. Soc. A 341, 531 (1992)

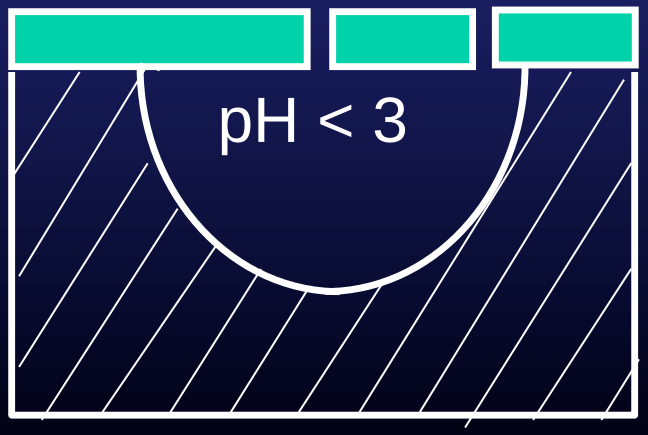
Metastable Pits: Growth and „Death“

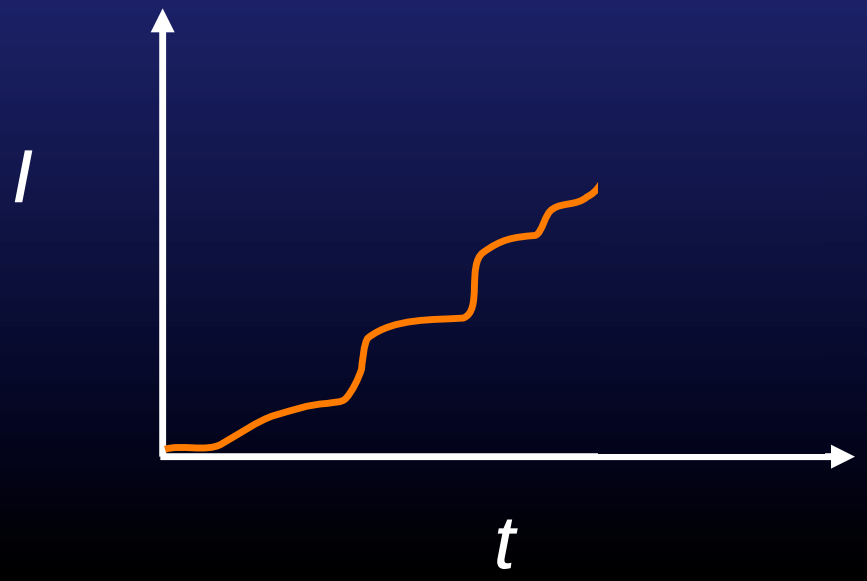
osmotic pressure leads to ruptures and holes

→ additional flaws

→ increased diffusion of ions

→ stepwise increase of the current

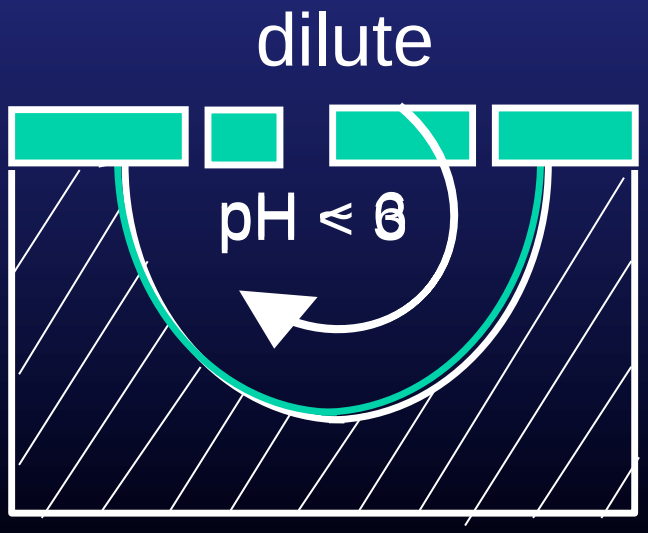


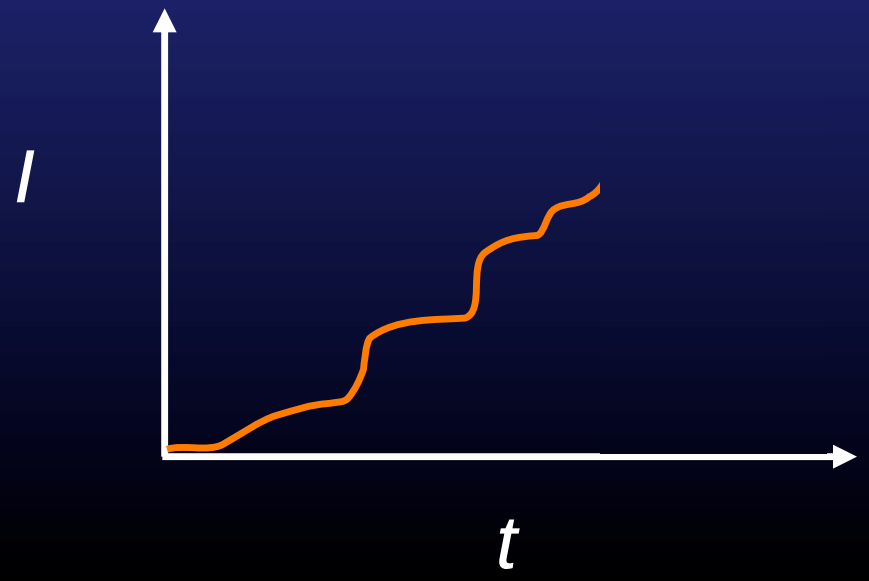


Metastable Pits: Growth and „Death“

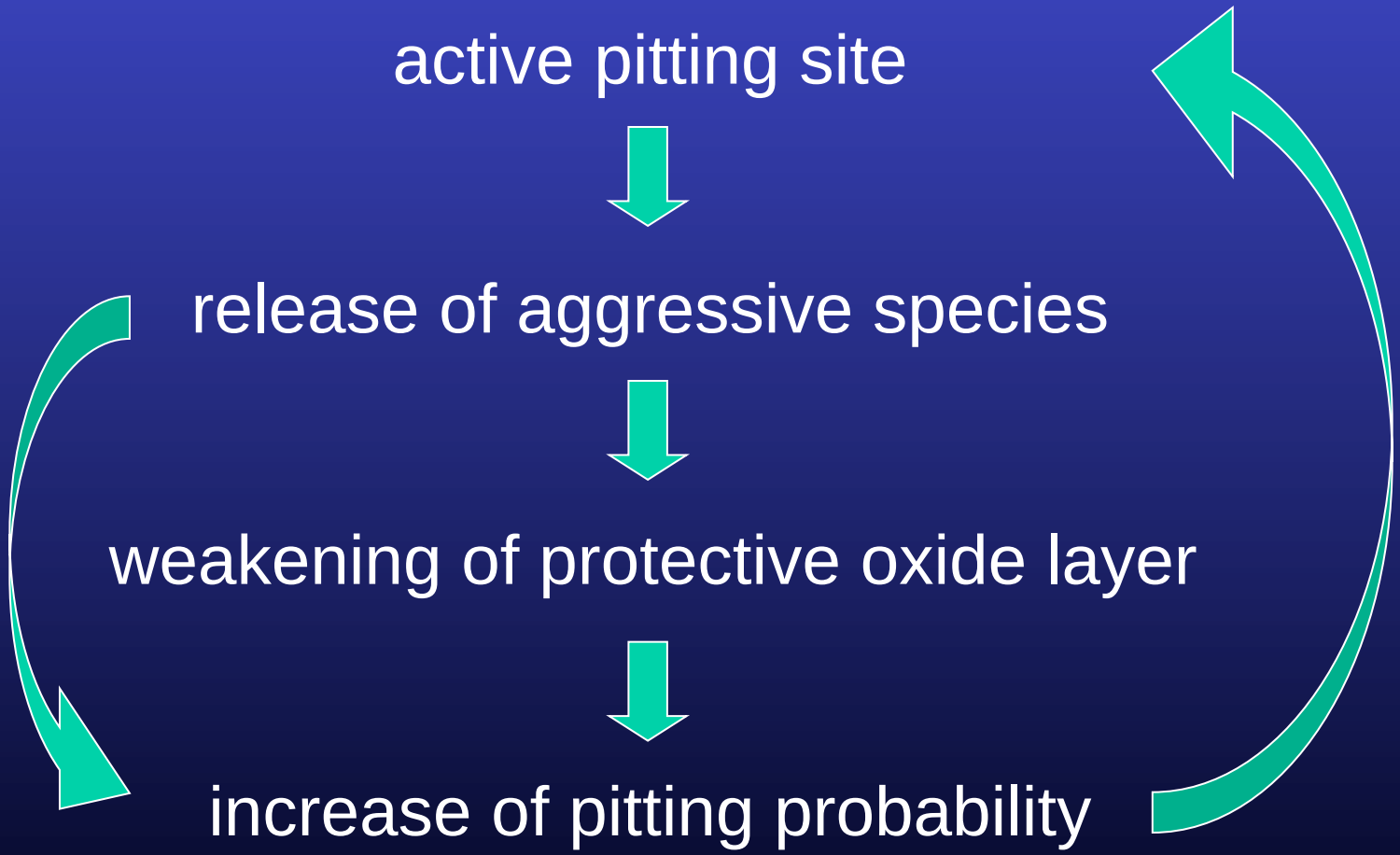
loss of pit cover:

- more rapid transport of ions
  → sharp increase of the current
- solution inside the pit dilutes
  →pH value increases
  →passivation and final sharp decrease of the current





New Model



B. Wu et al., J Electrochem. S., 144, 1614 (1997); T.T. Lunt et al., J Electrochem. S.149, B163 (2002); A.S. Mikhailov et al., Chaos 16, 37104 (2006); J.R. Scully et al., Corrosion Science 50, 316 (2008)

Modeling: New Concept: Interactions

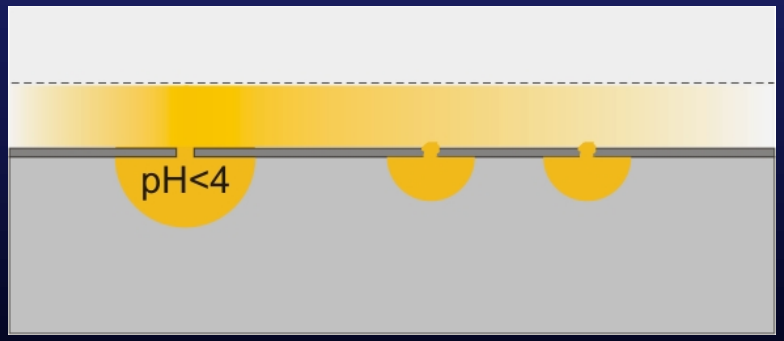
concentration of aggressive ions (c)

oxide film damage (s)

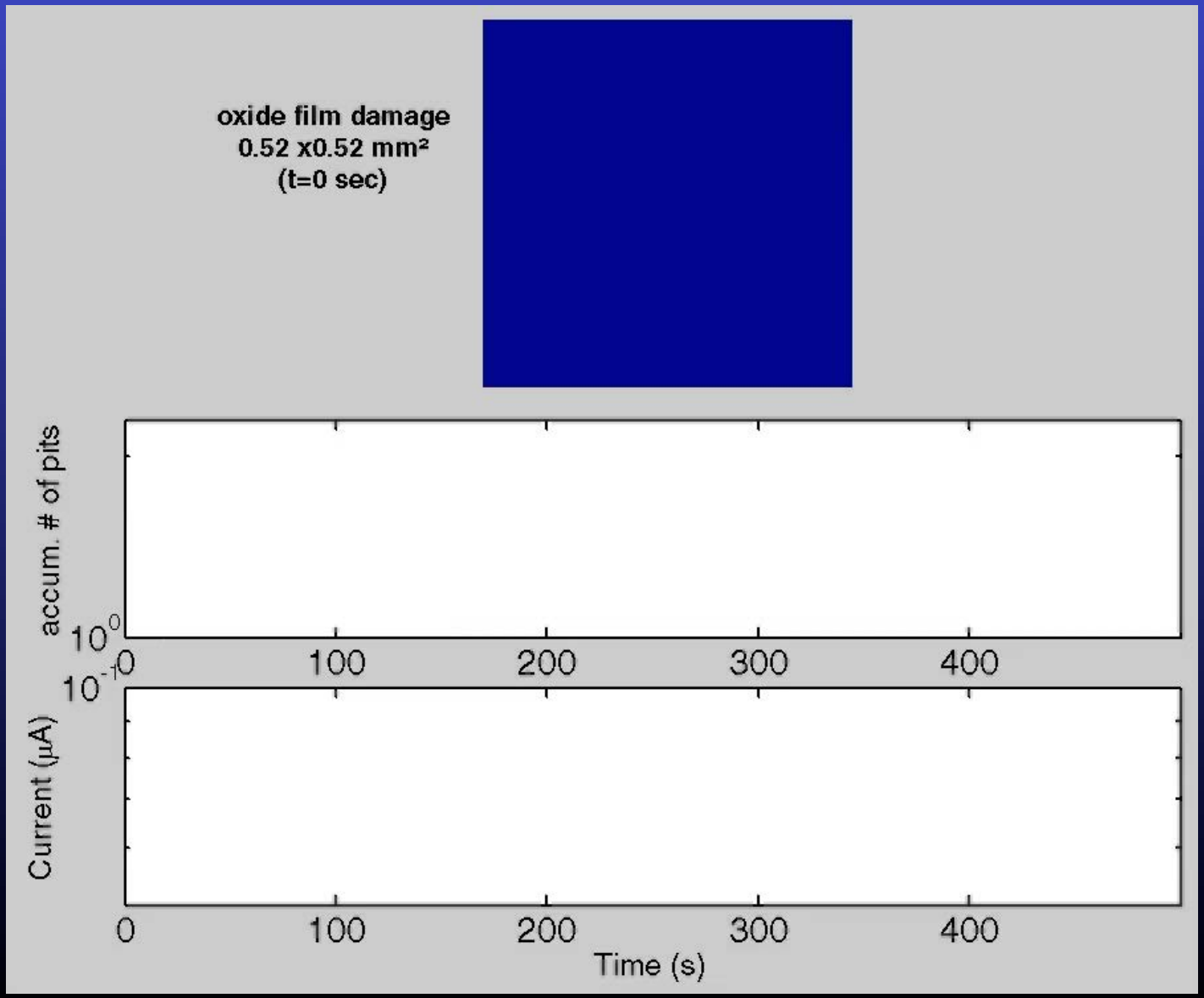
} activating

ohmic potential drop (Φ)

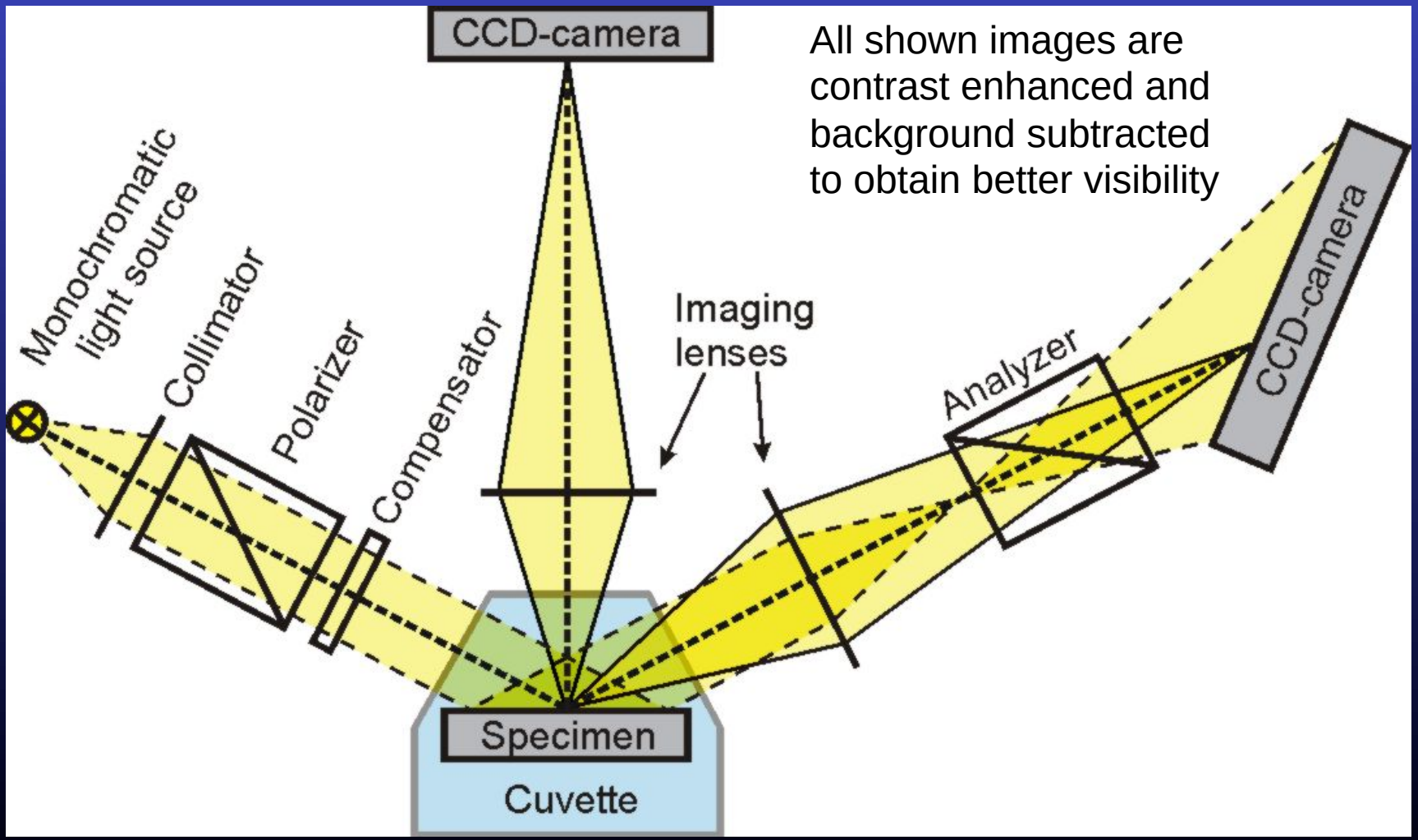
→ inhibiting



Numerical Simulations



Imaging Methods: Ellipso-Microscopy for Surface Imaging (EMSI) and Contrast Enhanced Microscopy



Punckt et al., Science 305, 1133 (2004)

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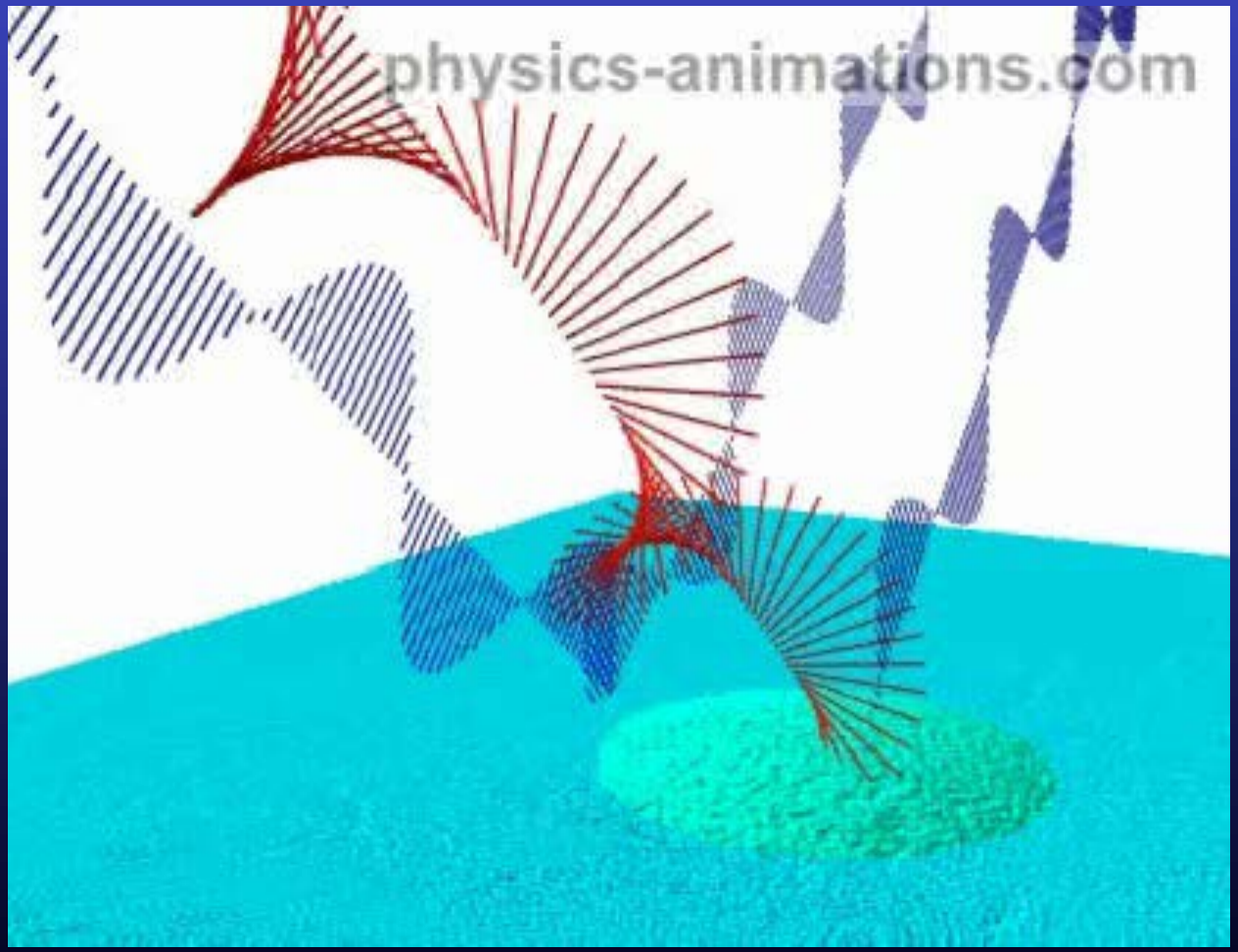
Imaging Method: EMSI
Ellipso-Microscopy for Surface Imaging



HHR et al., Science, 270, 608, (1995)
J. Dicke et al., Surf. Sci. 462, 90, (2000)

http://physics-animations.com/Physics/English/optics.htm

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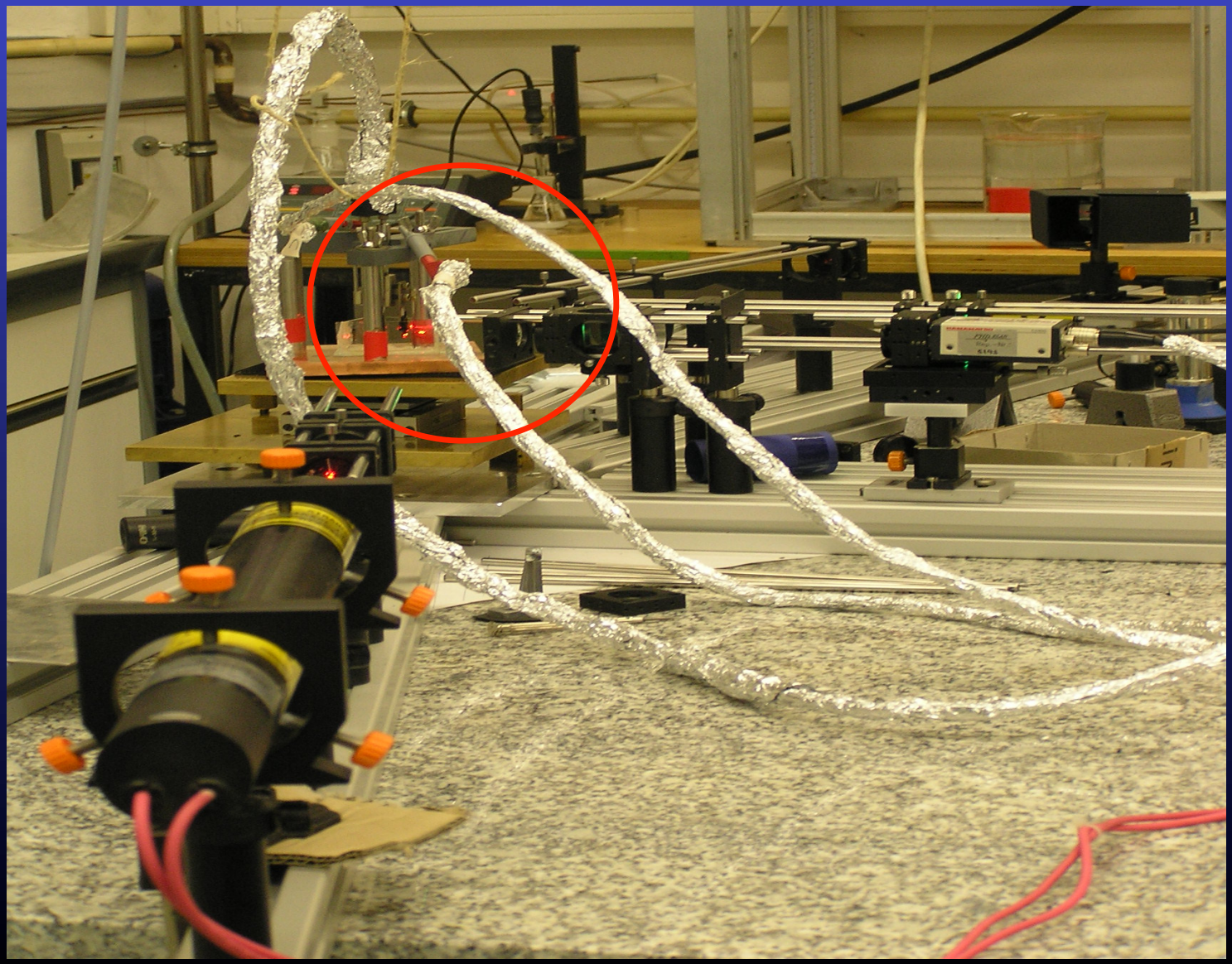
Experimental Realization



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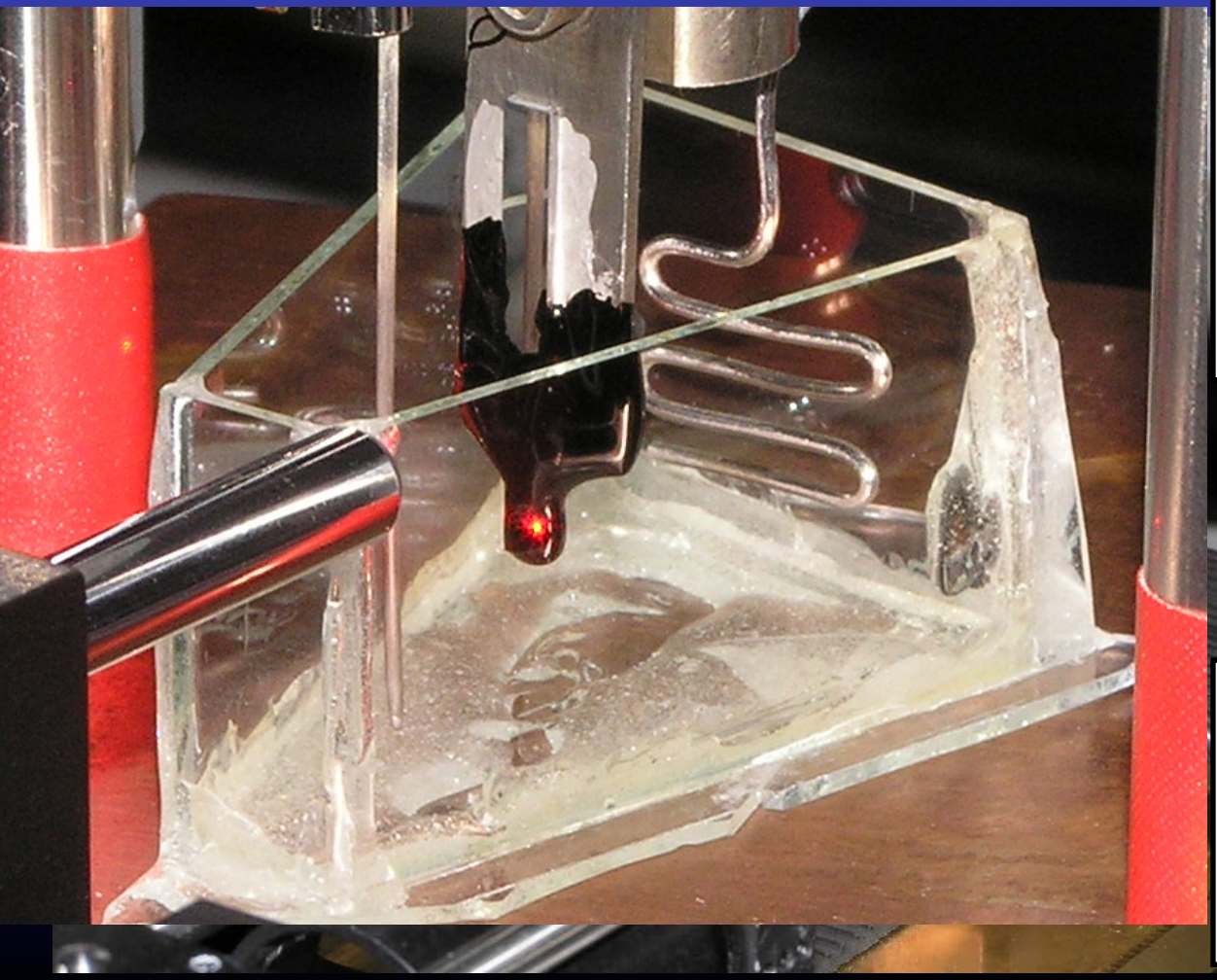
Electro-Chemical Cell



The sample (AISI 316):

1 µm diamond paste polish vertical configuration

Besides the imaged area of ~ ∅ 0.5 mm the rest of the sample and the connectors are covered with apiezon wax.

Ambient temperature ~ 22 C

Electrolyte: 0.05 Mol/l NaCl

Potential increased from -100 mV (NHE) at 1mV/s

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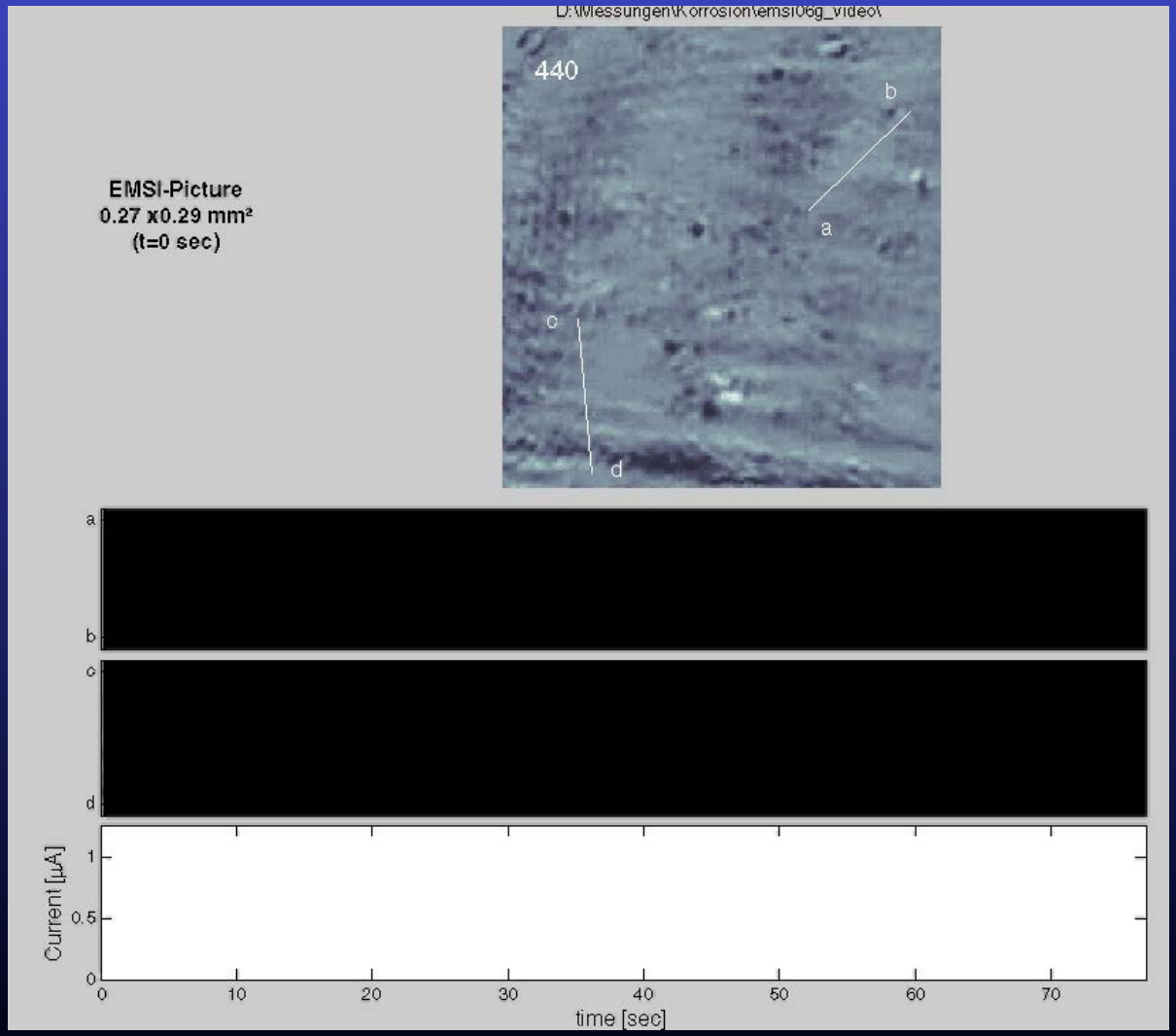
Ellipso-Microscopy (EMSI)



Potential increased from 711 mV (NHE) at 1mV/s

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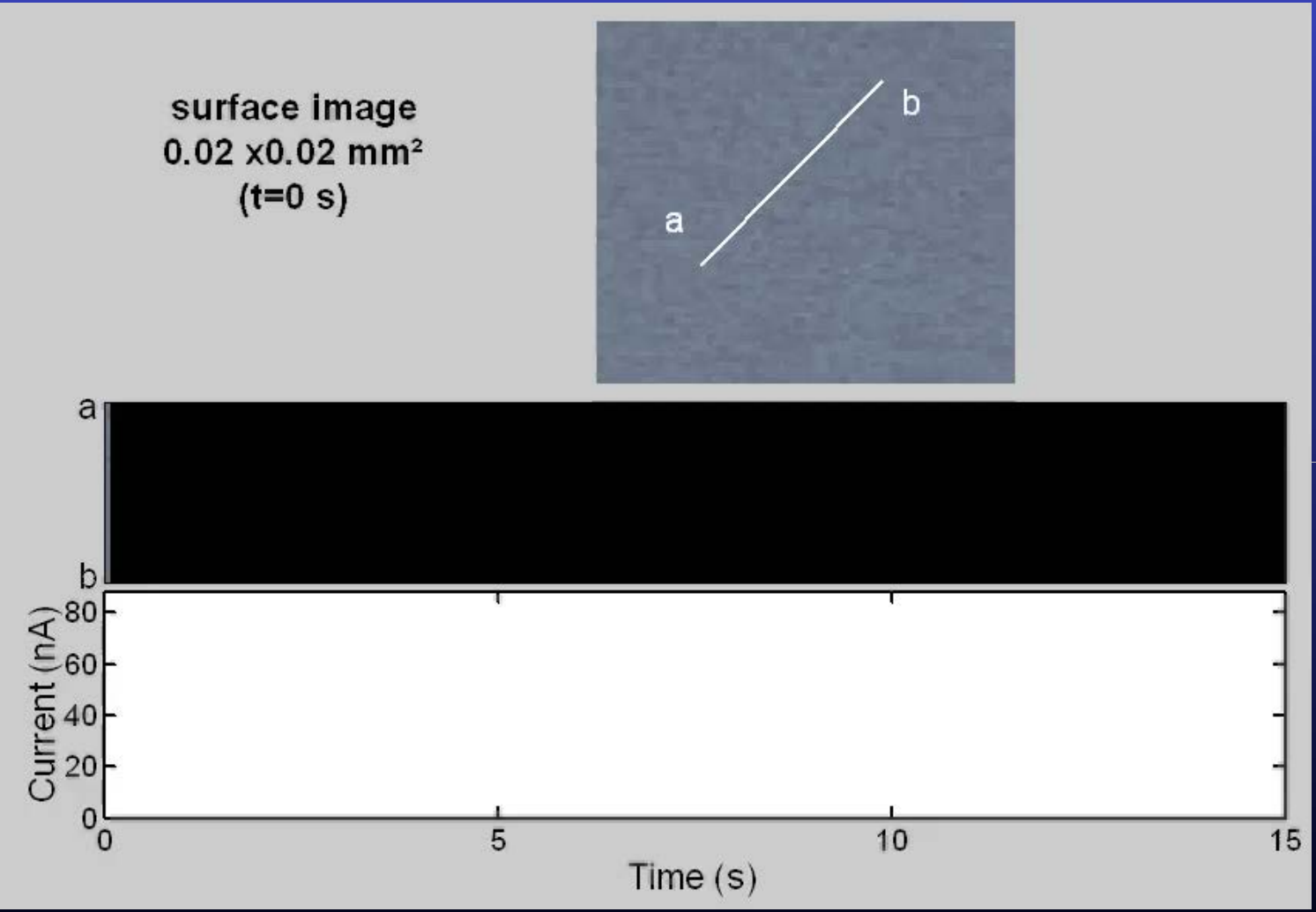
Contrast Enhanced Microscopy



Potential increased from 542 mV (NHE) at 1mV/s

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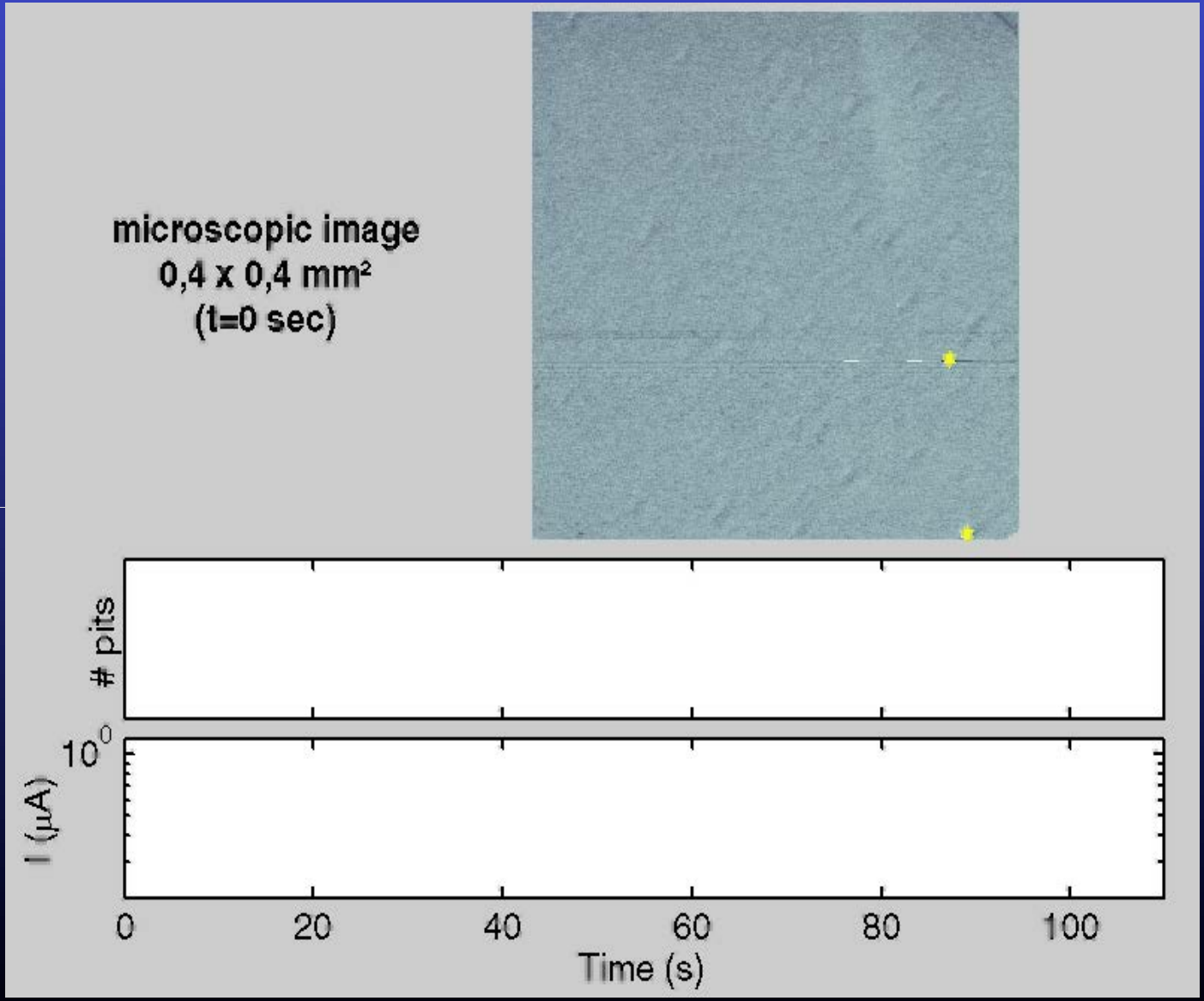
Contrast Enhanced Microscopy

New pit

Highly active pit

Number of pits

current



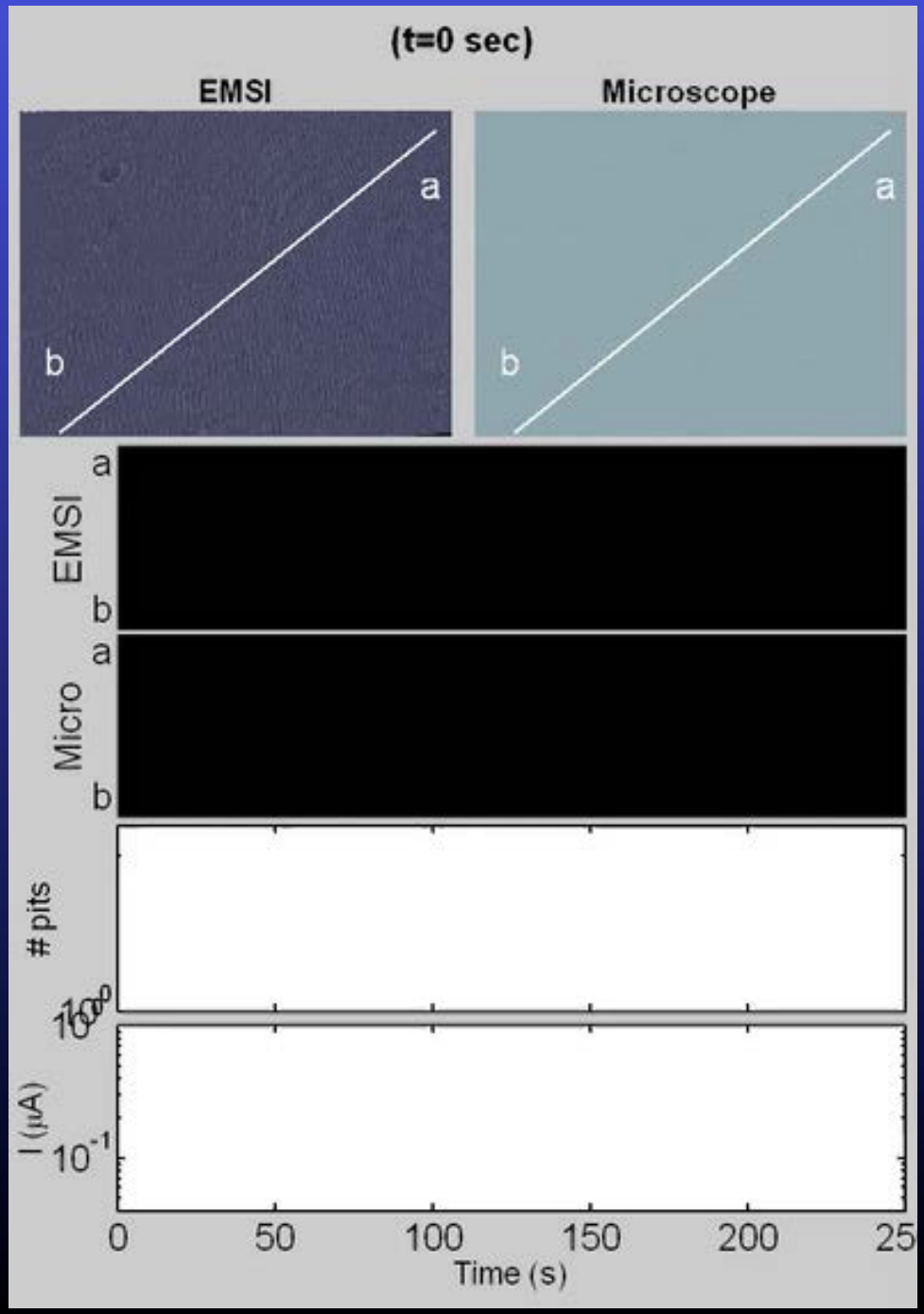
Potential increased from 693 mV (NHE) at 1mV/s

Simultaneous EMSI and Microscopy

Sample was in the electrolyte for 1.5 h , then the potential is switched on to - 400 mV v. Ag/AgCl for 100 s.

After this initiation period the potential is scanned with 20 mV/s to reach 330 mV v. Ag/ AgCl, where it remains.

The first pits appear after 15 min. The temperature is kept at 21.9°C.



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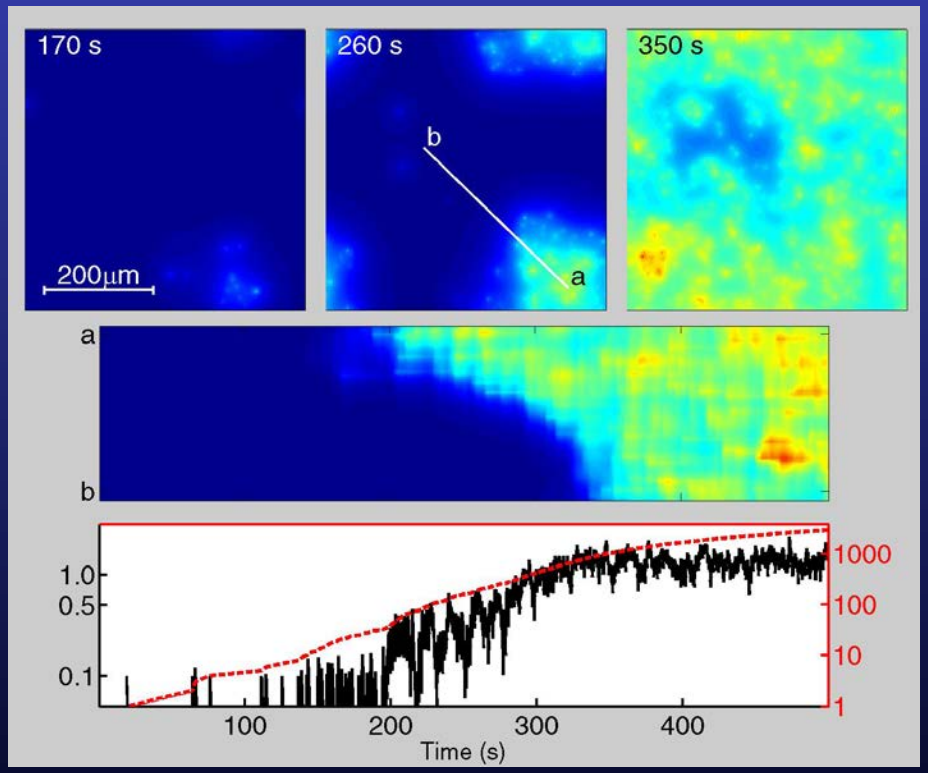
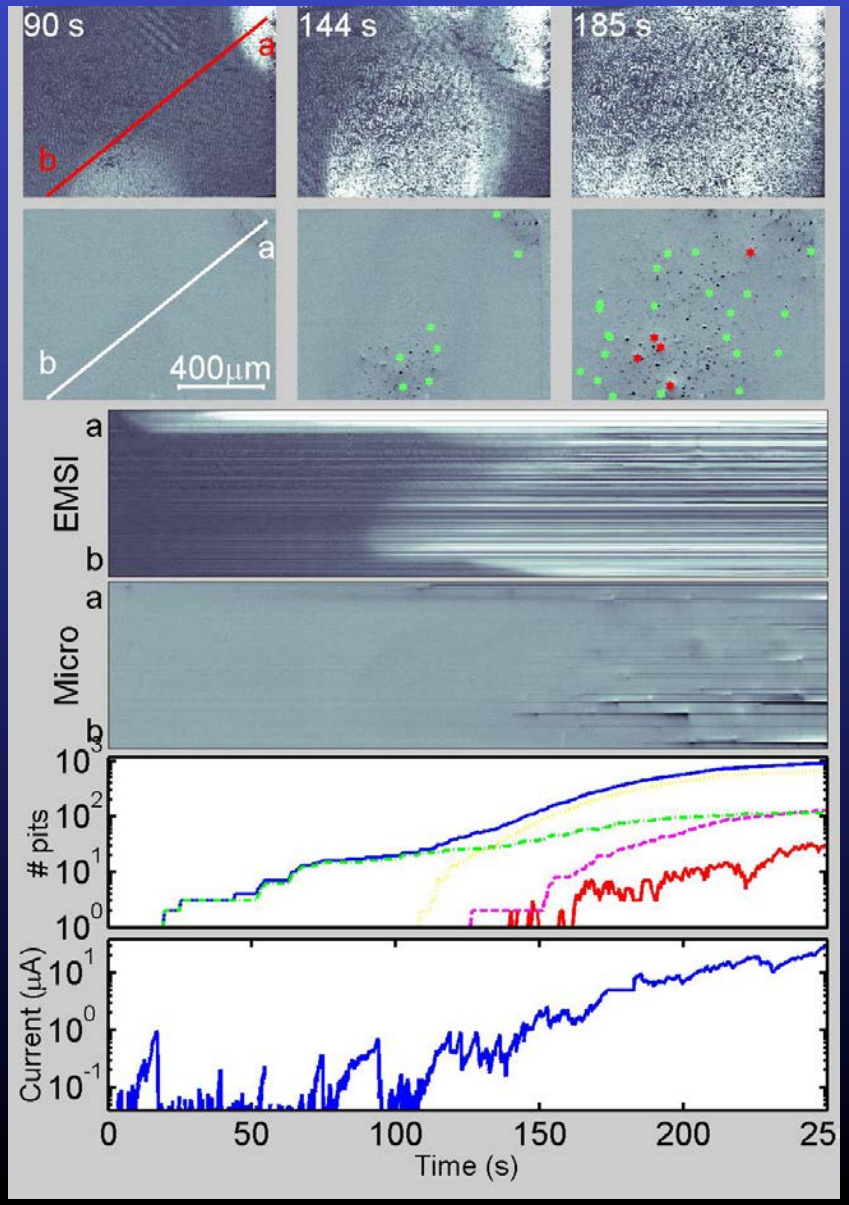
Simulations:

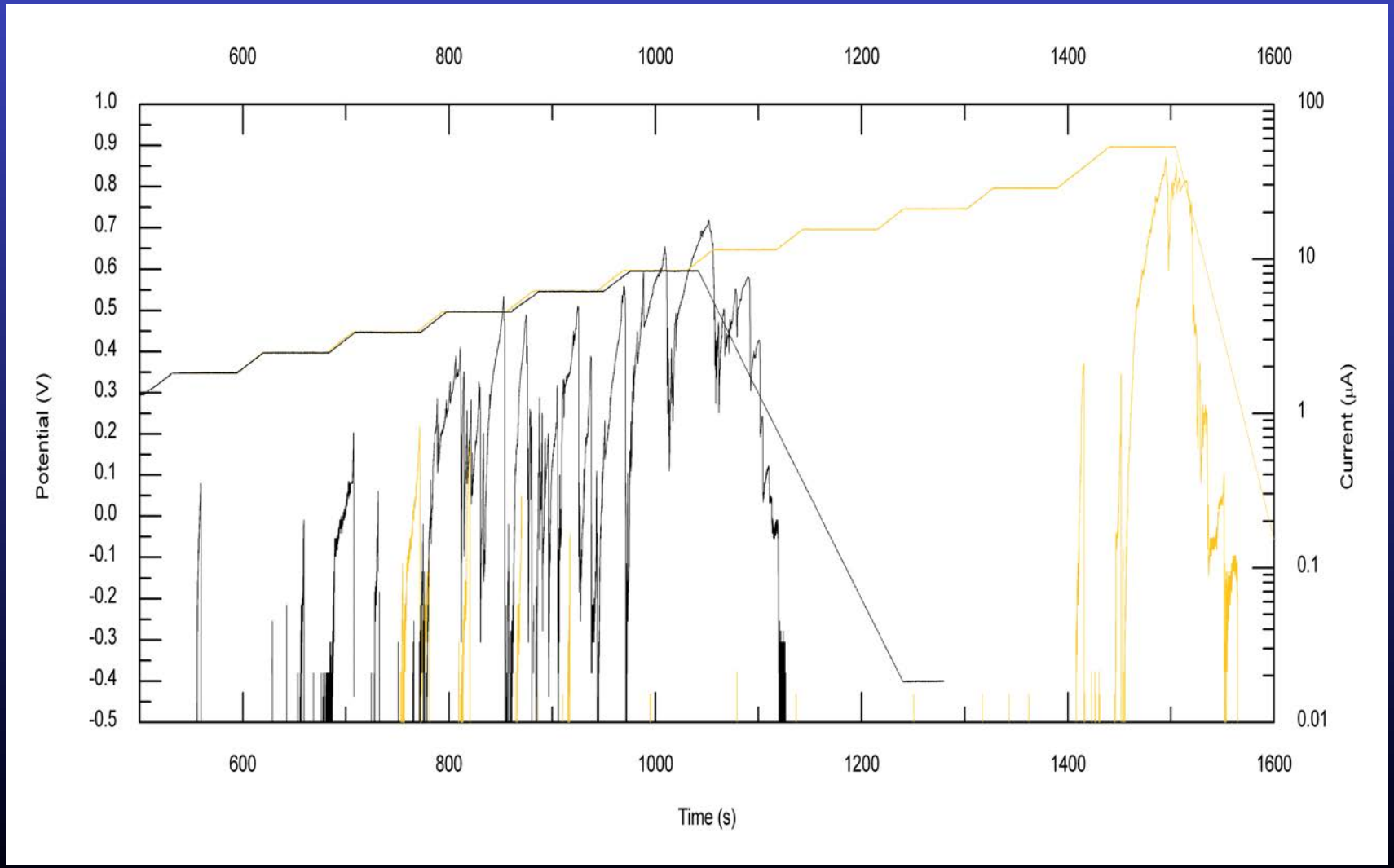


Experiments:



M. Dornhege et al.,
J. Electrochem. Soc. 154, C 24 - C 27 (2007)

Enhancing resistance to pitting corrosion in mechanically polished stainless steel 316 LVM by water treatment



P.E. Klages, Z. Bai, M. Lobban, M.K. Rotermund, HHR, Electrochemistry Communications 15, 54–58 (2012)

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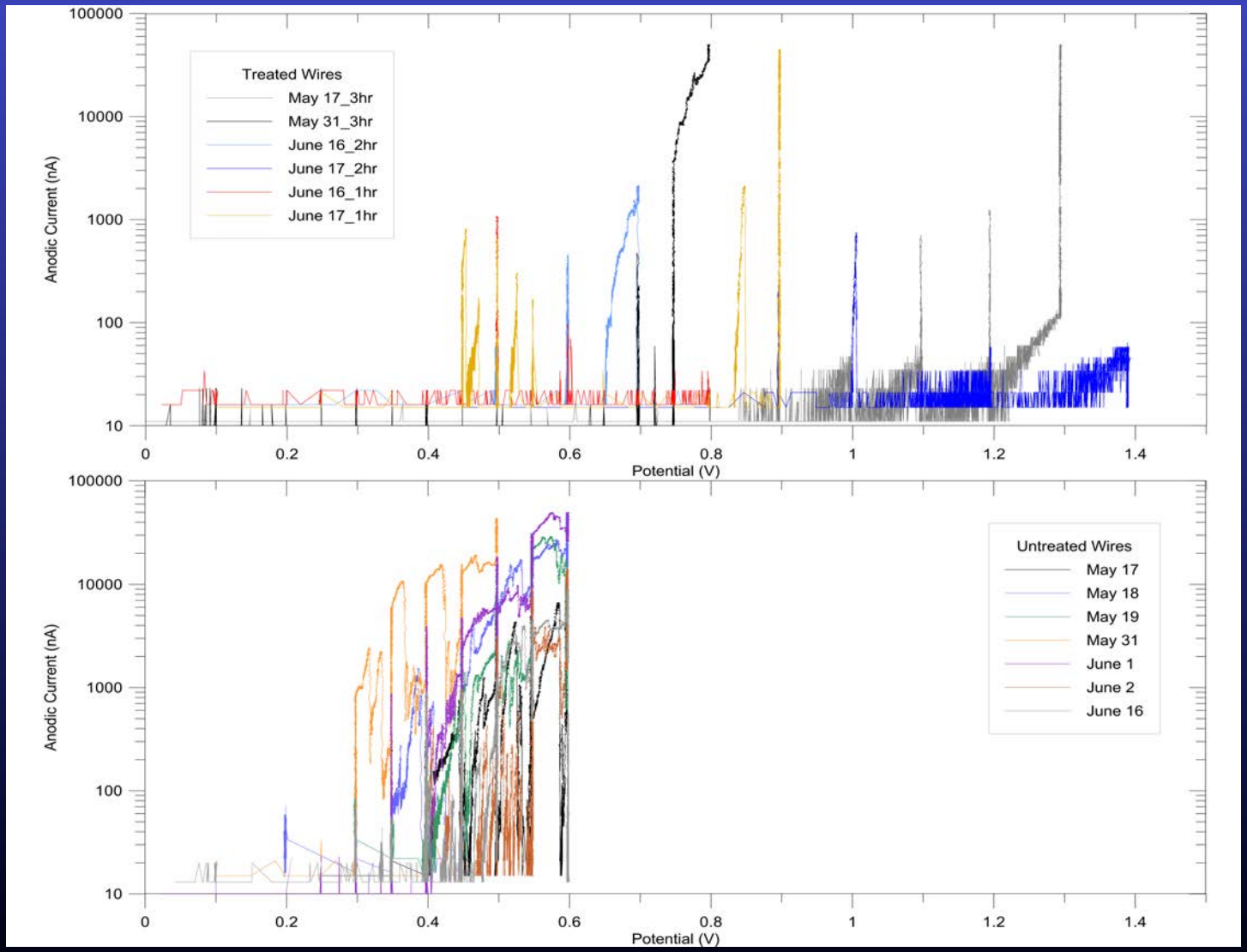
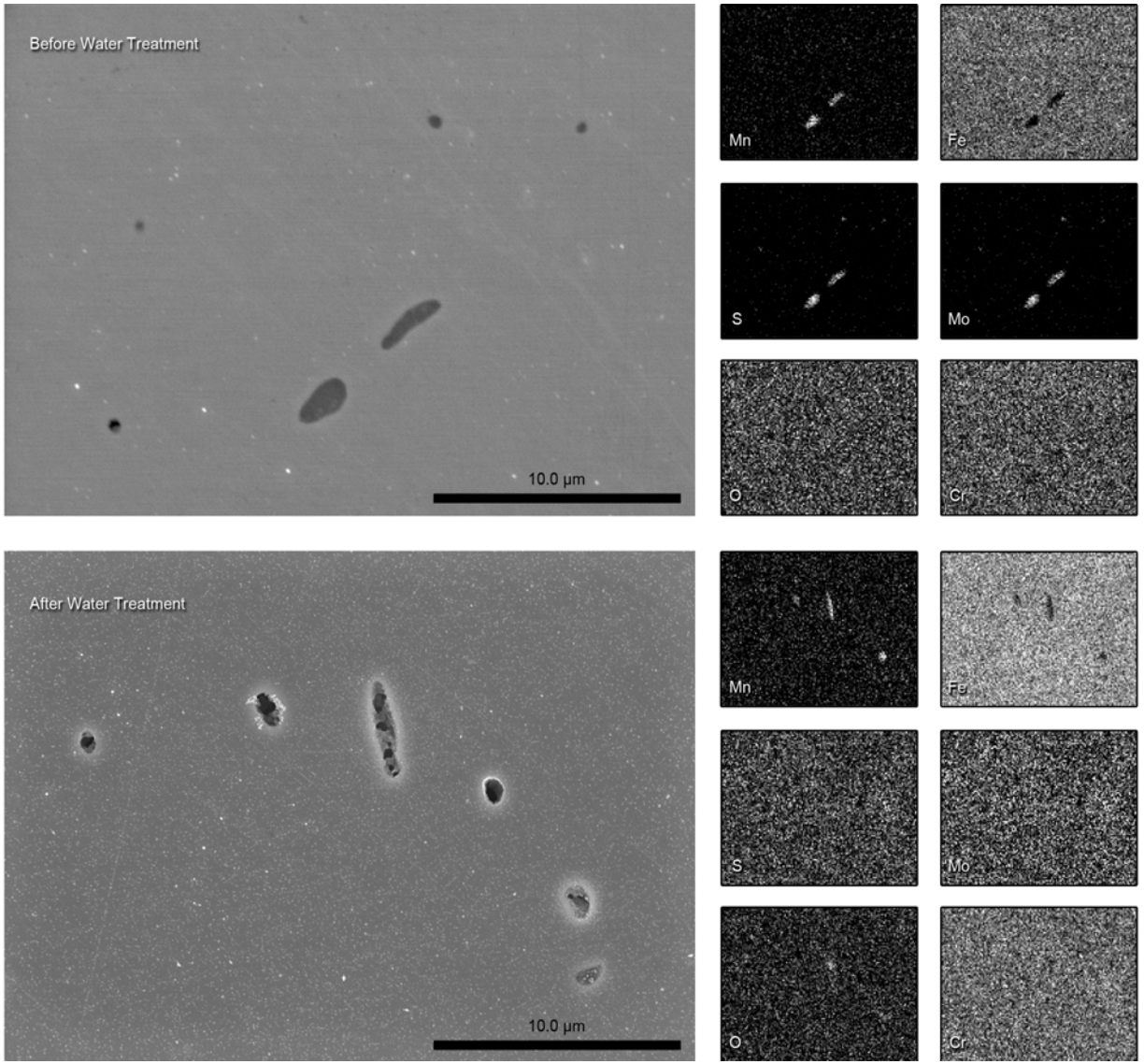


P.E. Klages, Z. Bai, M. Lobban, M.K. Rotermund, HHR, Electrochemistry Communications 15, 54–58 (2012)

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS)



SEM, left, and EDS, right for a SS sample. Each composition map is normalized to its largest signal which is shown as white. Upper half: Untreated sample. The dark grey regions, as seen with the SEM, show enhanced Mn and S (Mo) concentrations in the composition maps. Lower half: After 3 h water treatment. The crevices show no enhancement for S (or Mo) though there is still some Mn for the larger crevices, as well as some O, which was not present at inclusions before treatments.

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Summary and outlook

Predictions:

- Weakening of the passive film in the vicinity of active pits. √
- Exponential growth of **pit** number. √
- Propagation of reaction fronts. √

→ Onset of corrosion = autocatalytic process √
→ Pit propagation caused by interaction among pits √
→ Control and prevention of corrosion onset?! √