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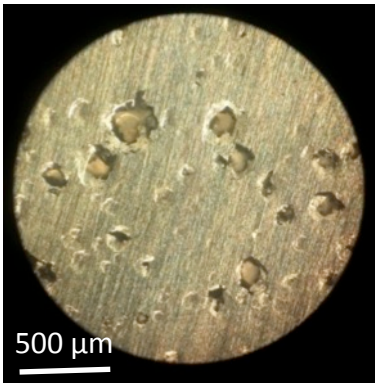
INVESTIGATION OF A SINGLE PIT GENERATED WITH A FLOW MICROCELL

Stéphane Heurtault, Raphaël Robin, Fabien Rouillard, Vincent Vivier

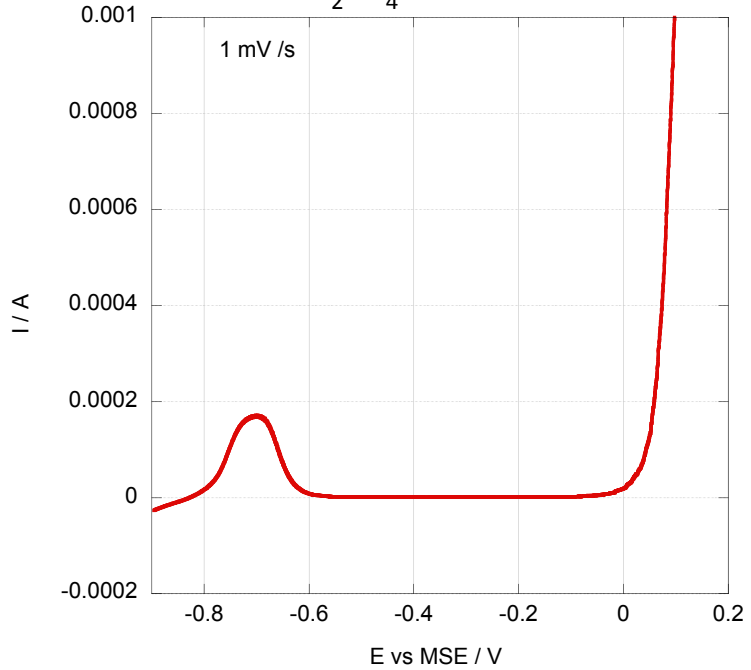
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Stainless steel in a chloride environment



316L stainless steel
0.5 M H₂SO₄ + 0.6 M NaCl



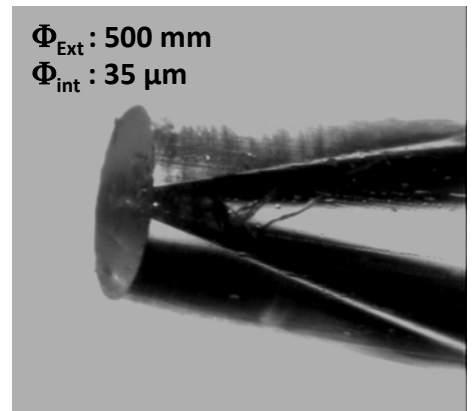
How can we generate a single pit ?

- Lead-in-pencil technique
E.D. Parsons and al., *J. Phys. Chem.* **45** (1941) 1339

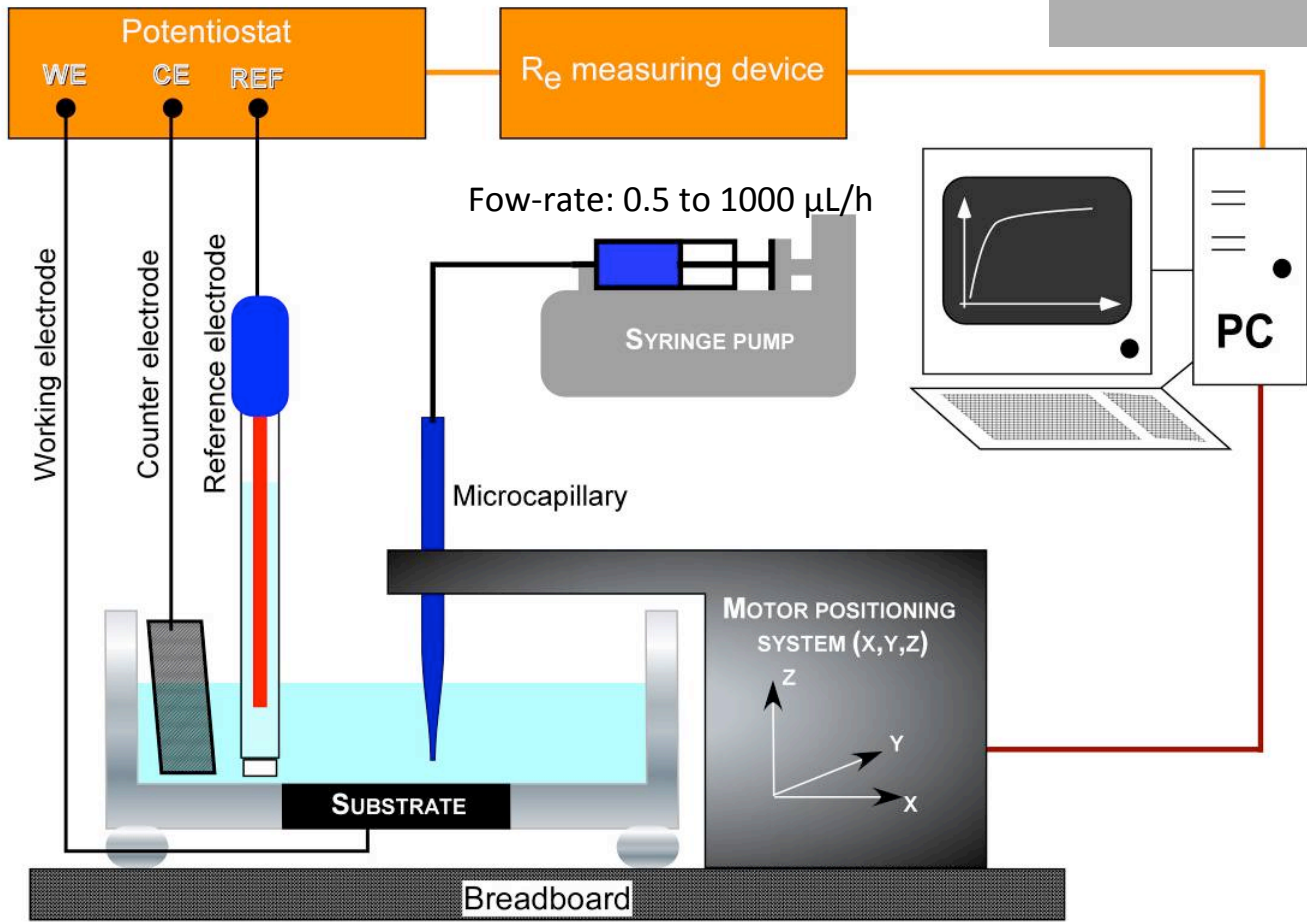
- Single pit with SECM-like techniques
 - Wipf et al. (SECM – trichloroacetate reduction)
 - Fushimi and Seo (Ion gun – Ag/AgCl)
 - Portail et al. (Ion gun – Ag/AgCl + EQCM)

- Pit propagation for long time
 - Lead-in pencil technique
 - Flow microcell

Flow microcell description

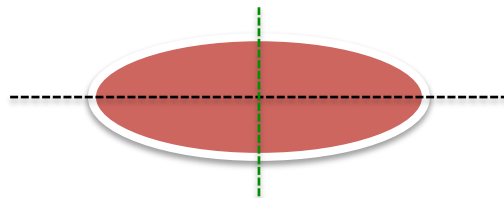
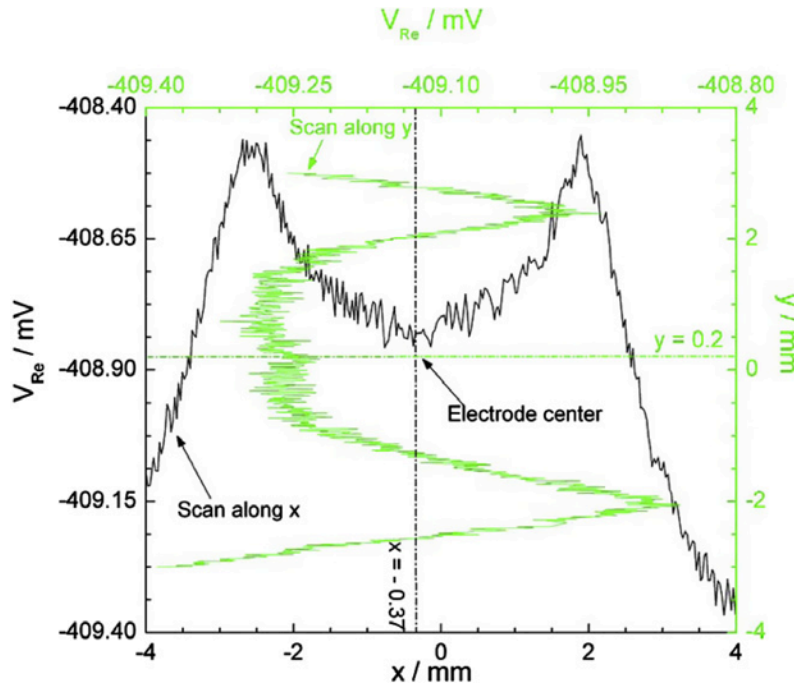


Experimental setup



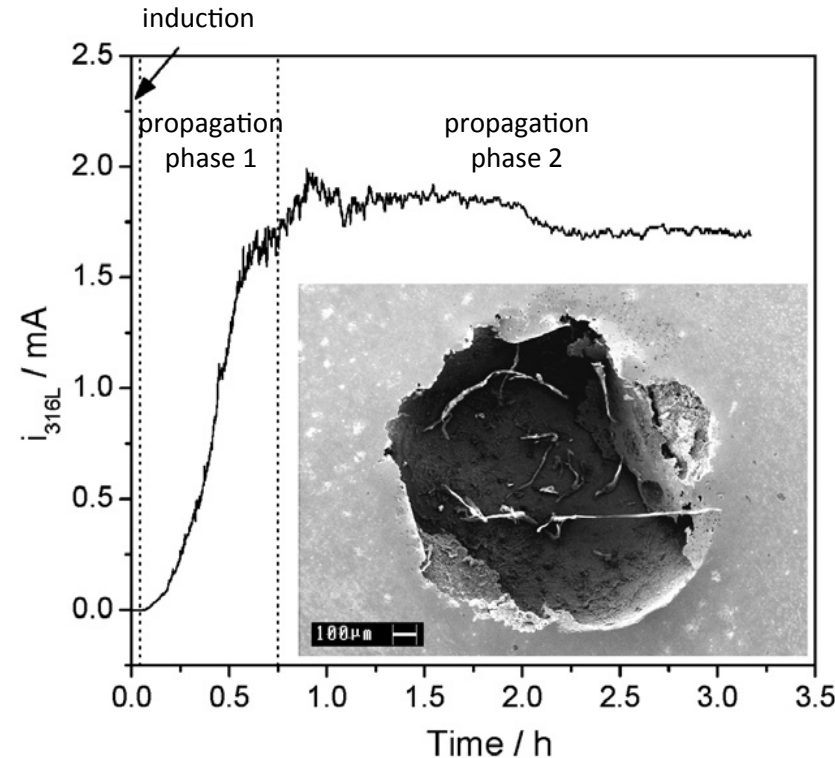
Capillary positioning

Measure of the electrolyte resistance variation due to the presence of the capillary in the close vicinity of the stainless steel electrode



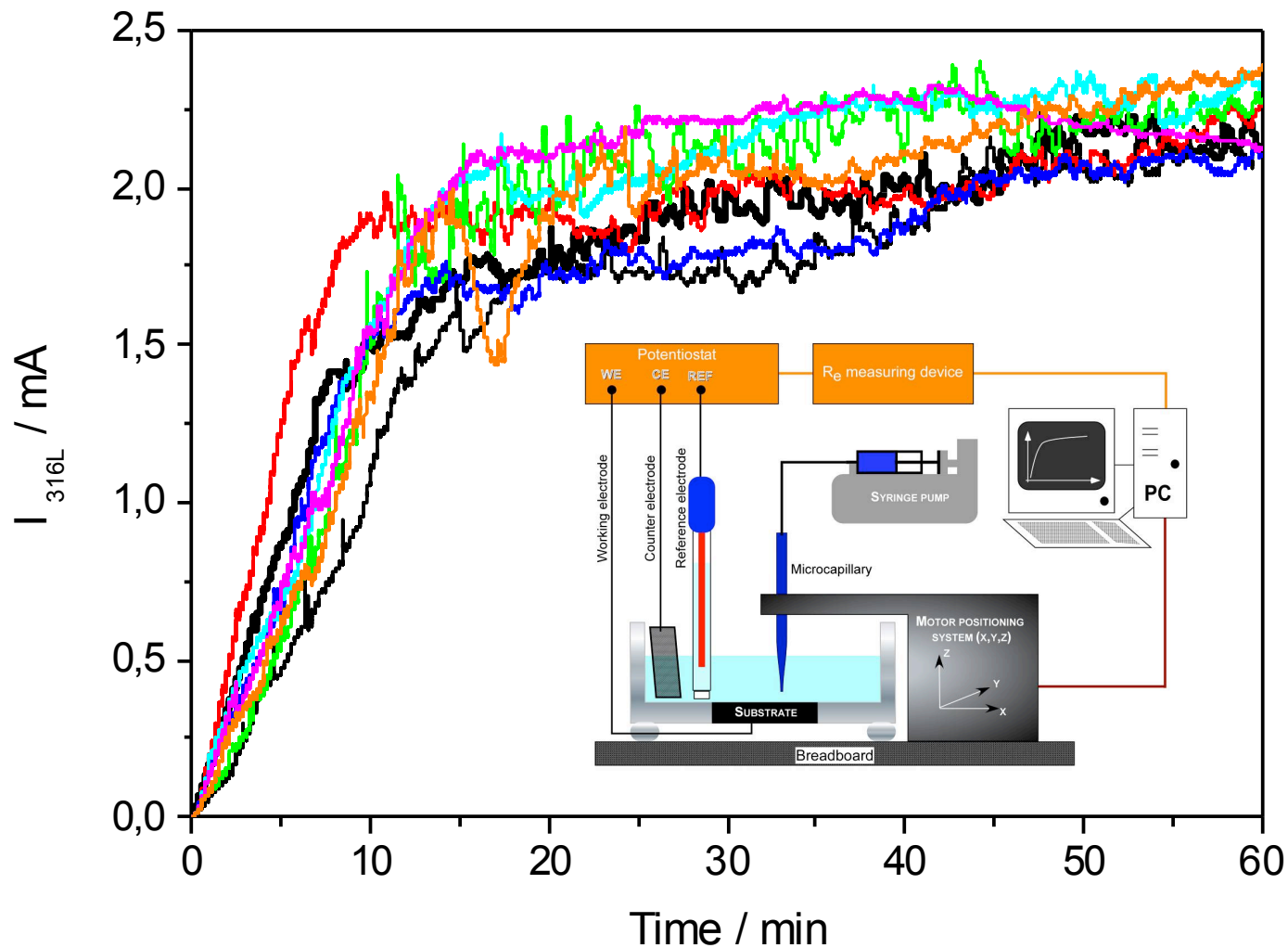
Pit initiation and propagation

Release of chloride ion with a capillary (controlled flow rate) – measure of current (or potential) as a function of time

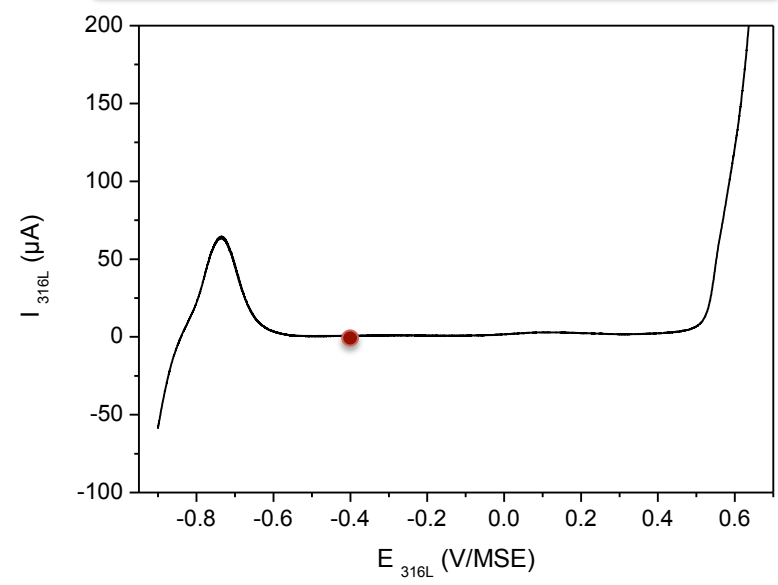


7 identical experiments performed in 0.5 mol/L H_2SO_4 at 20°C
 Flow rate : 5.4 $\mu\text{L}/\text{h}$
 $[\text{Cl}^-] = 3 \text{ mol}/\text{L}$
 $E_{316\text{L}} = 0 \text{ V}/\text{MSE}$

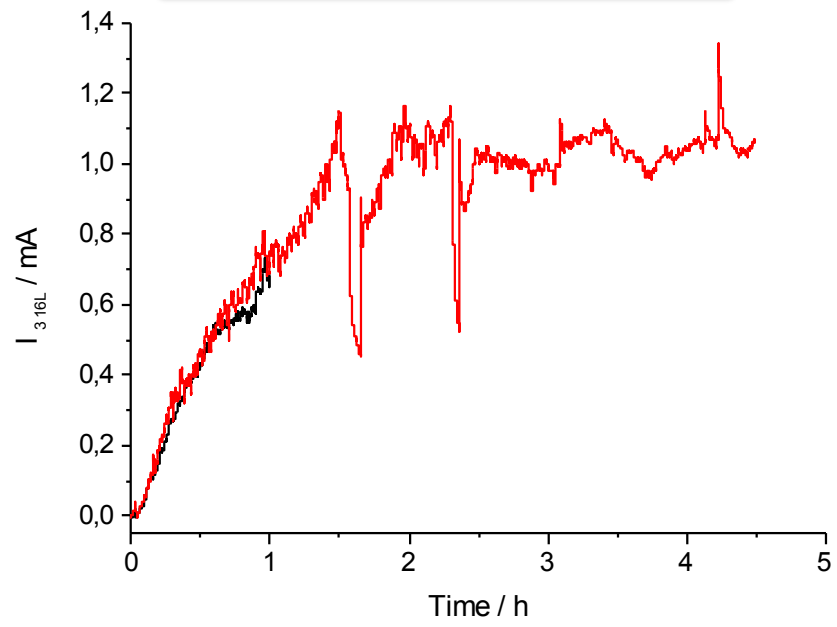
Reproducibility



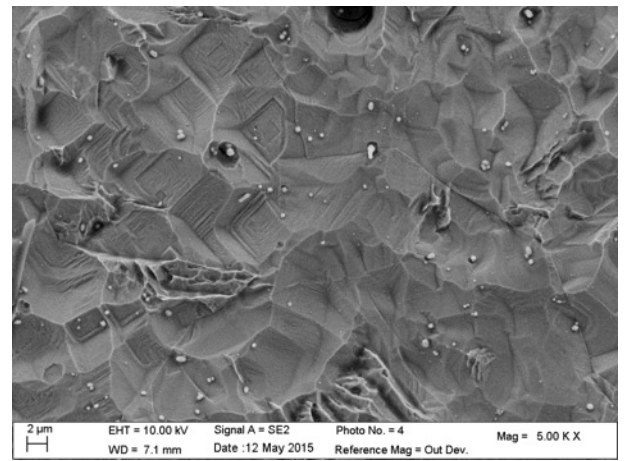
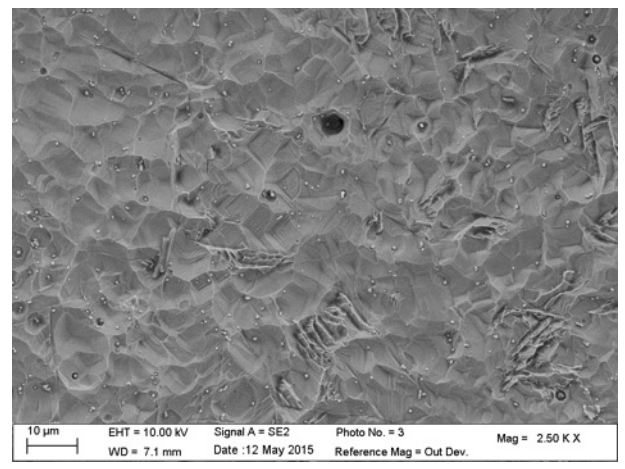
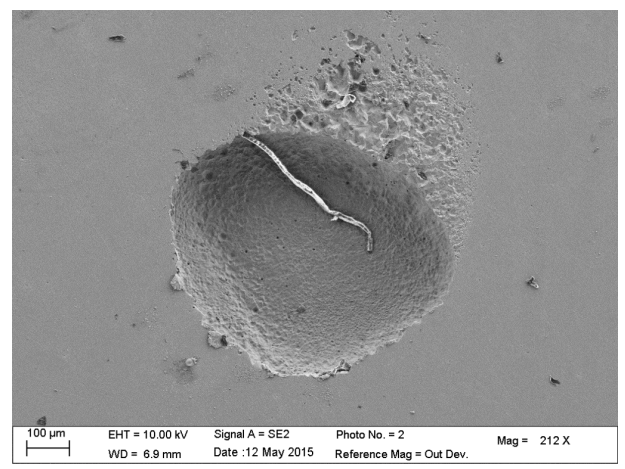
E/I curve in 0.5 mol/L H₂SO₄ solution



Pit generation at - 0.4 V / MSE

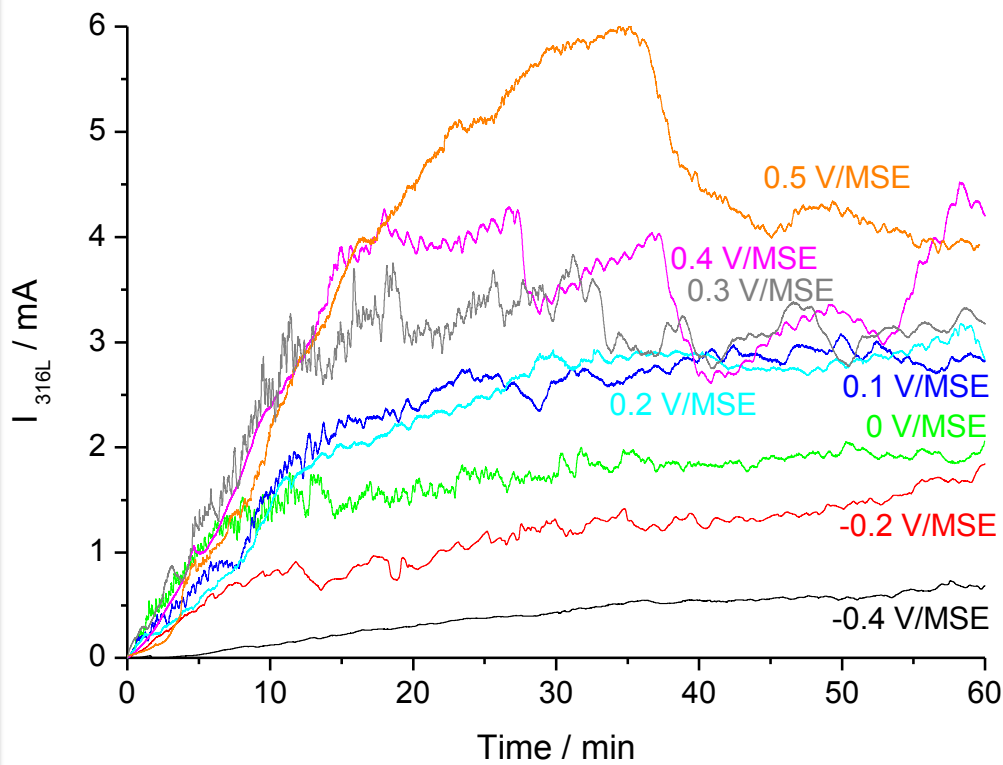


SEM observations after 1 hour

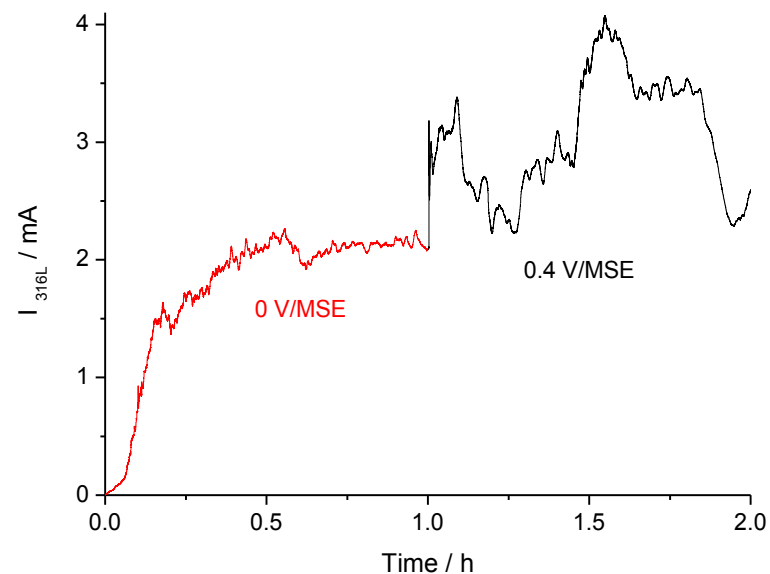
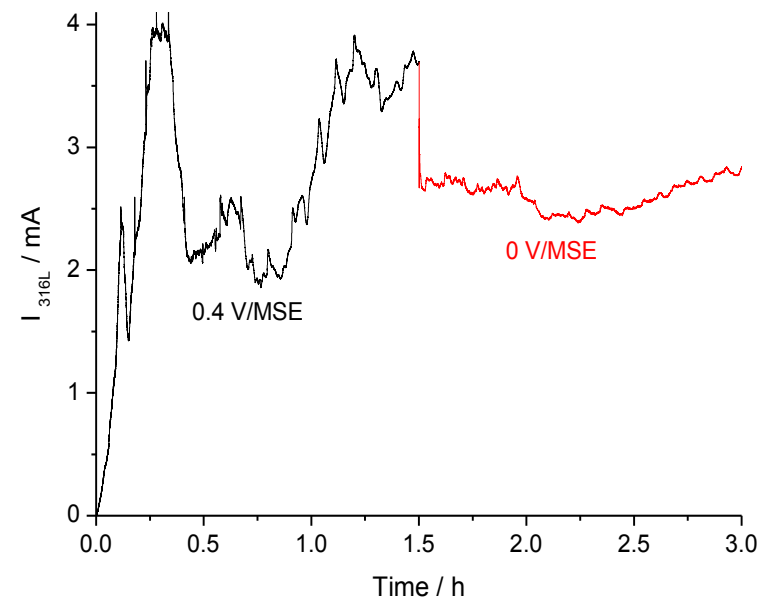


Experiments performed in 0.5 M H_2SO_4 at 20°C
 Flow rate : 5.4 $\mu\text{L}/\text{h}$
 $[\text{Cl}^-] = 3 \text{ M}$

Influence of the electrode potential

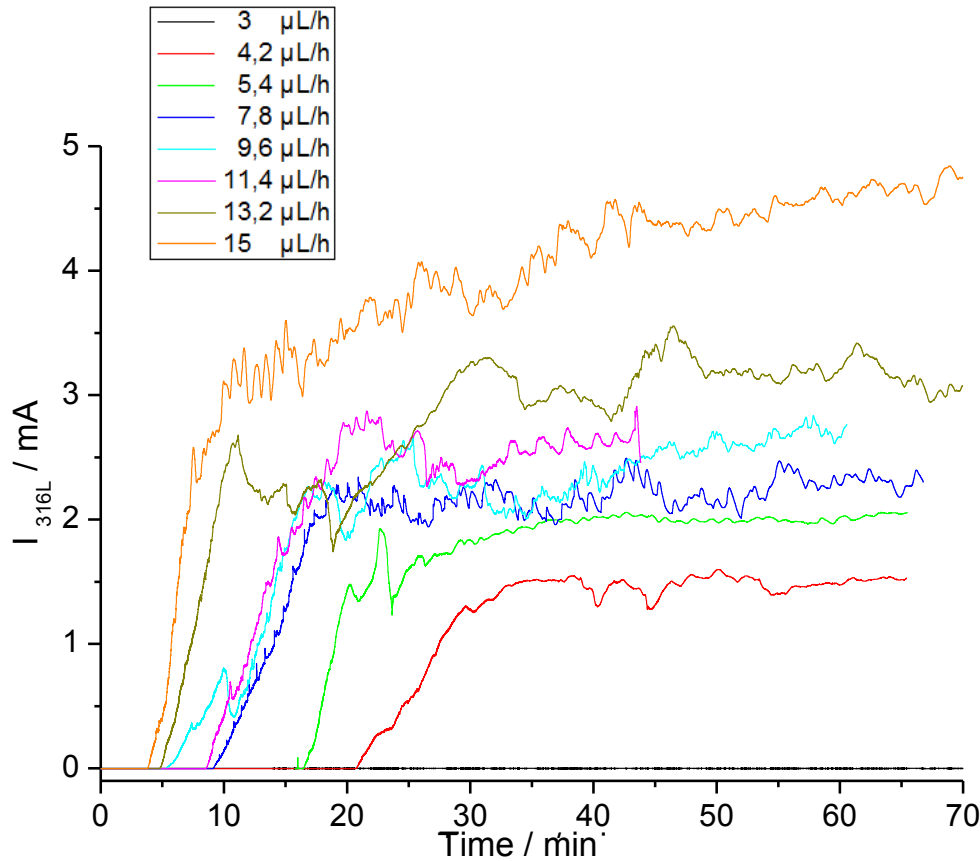


- The current increases with potential
- Current fluctuations increase with potential

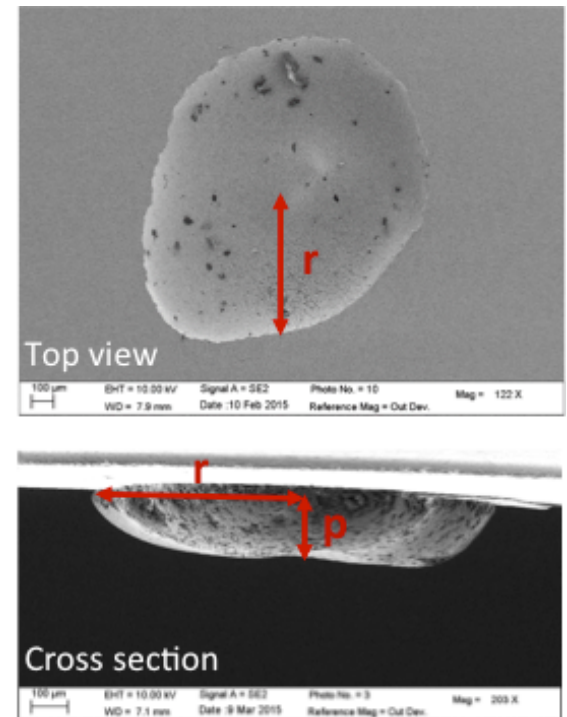


Experiments performed in 0.5 M H₂SO₄ at 20°C
[Cl⁻] = 3 M

Influence of the flow rate

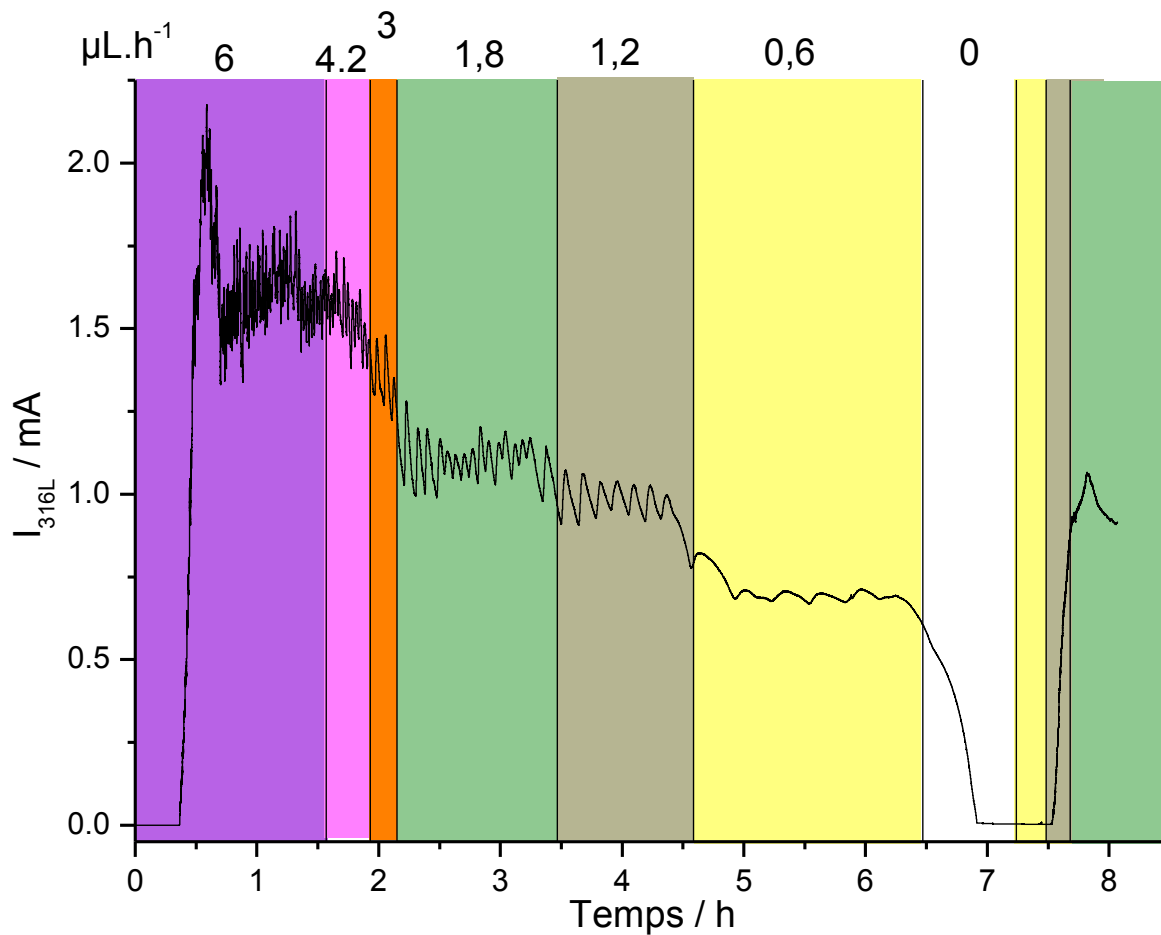


SEM observations of a single pit generated on 316L steel after 1 hour of propagation



- The “steady-state” current increases with the flow rate
- The induction time decreases with the flow rate
- Same evolution when varying the Cl⁻ concentration

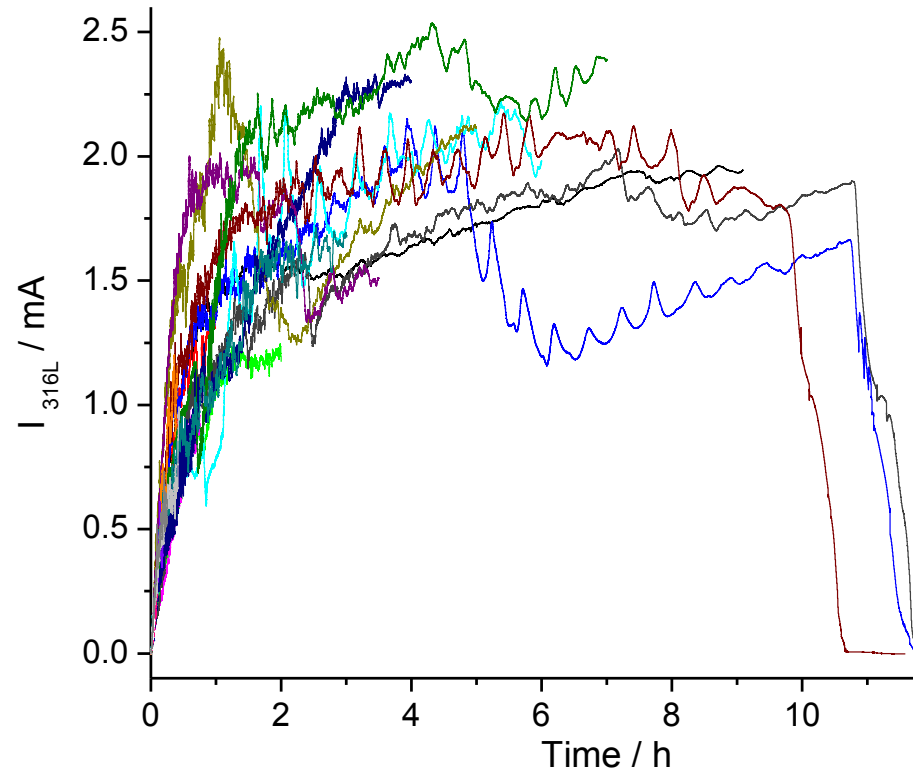
Experiments performed in 0.5 M H₂SO₄ at 20°C
 [Cl⁻] = 3 M



- It's possible to control the rate of the pitting by changing the flow rate
- it's a way to see the influence of the amount of chloride concentration variation on the pitting evolution
- pit can restart after passivation

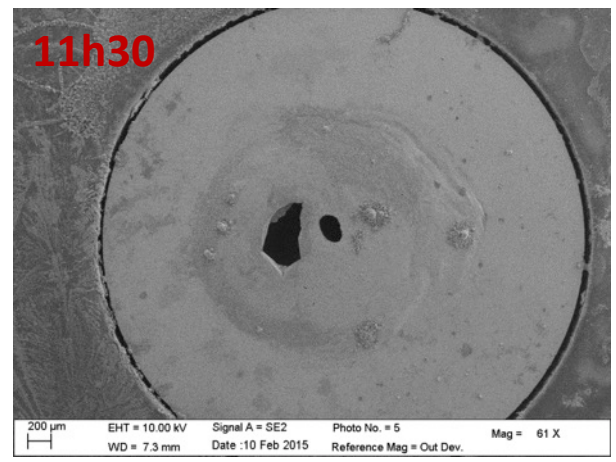
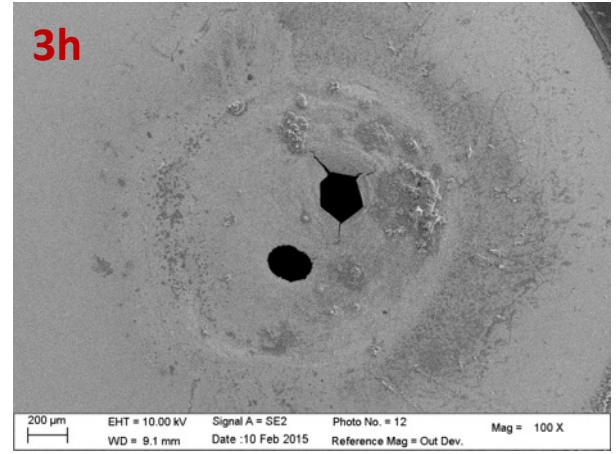
Experiments performed in 0.5 M H₂SO₄ at 20°C
 [Cl⁻] = 1.2 M

Influence of the chloride concentration



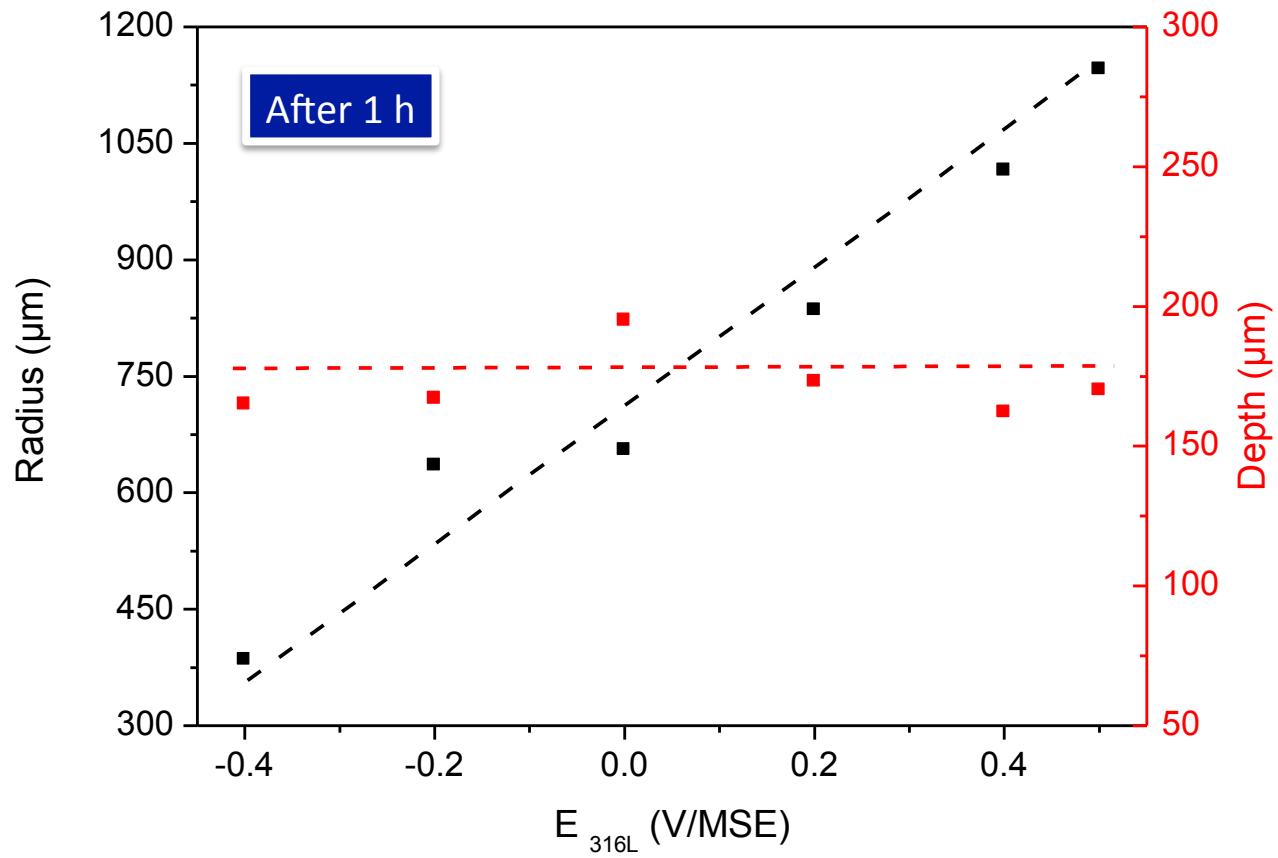
For lower chloride concentration (<1.5 mol/L) formation of a pit with a cover whereas for higher concentration, an open pit was always obtained

20 identical experiments performed as a function of time



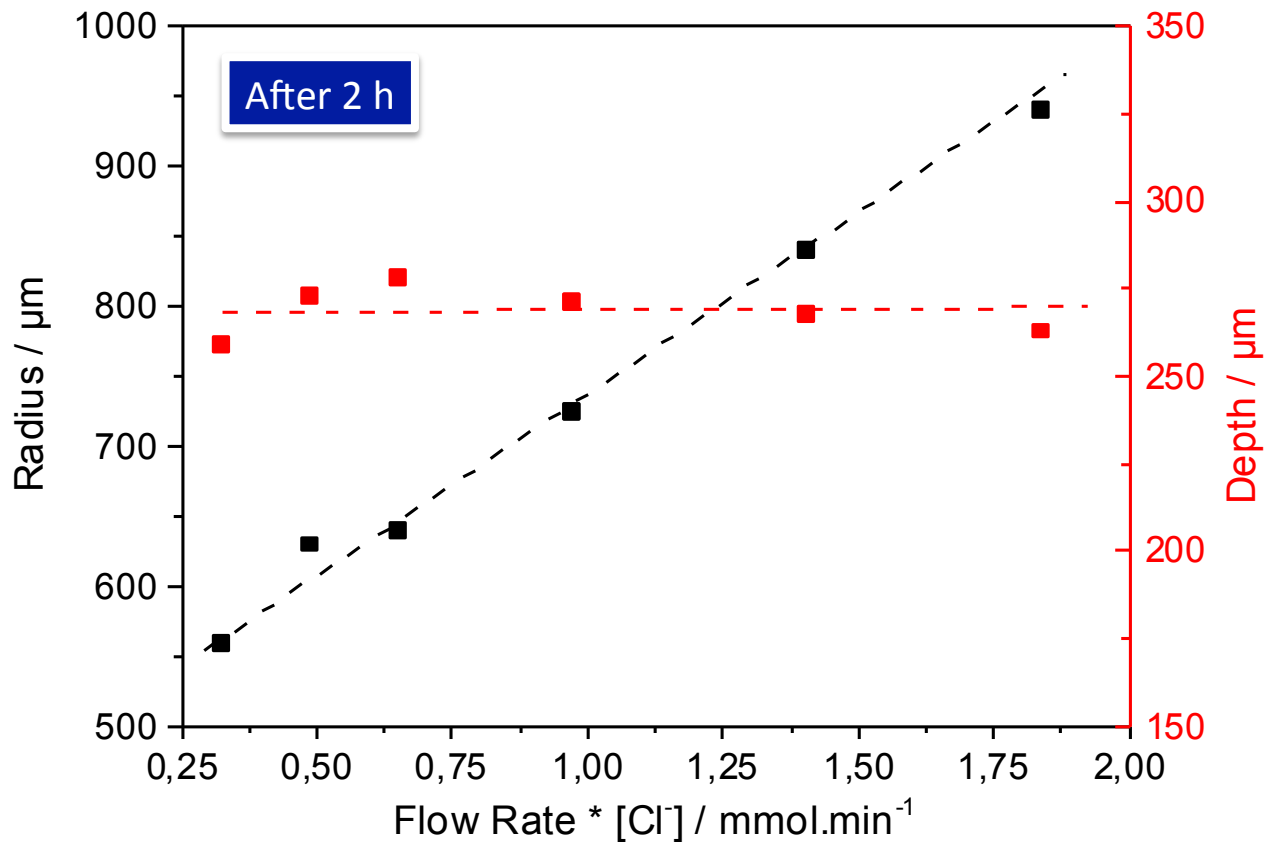
Experiments performed in 0.5 M H₂SO₄ at 20°C with [Cl⁻] = 3 M

Evolution of the pit dimension



Depth and diameter were obtained from optical observations: after 1 h, the mean radius increases with potential whereas the depth remains constant (about 180 μm)

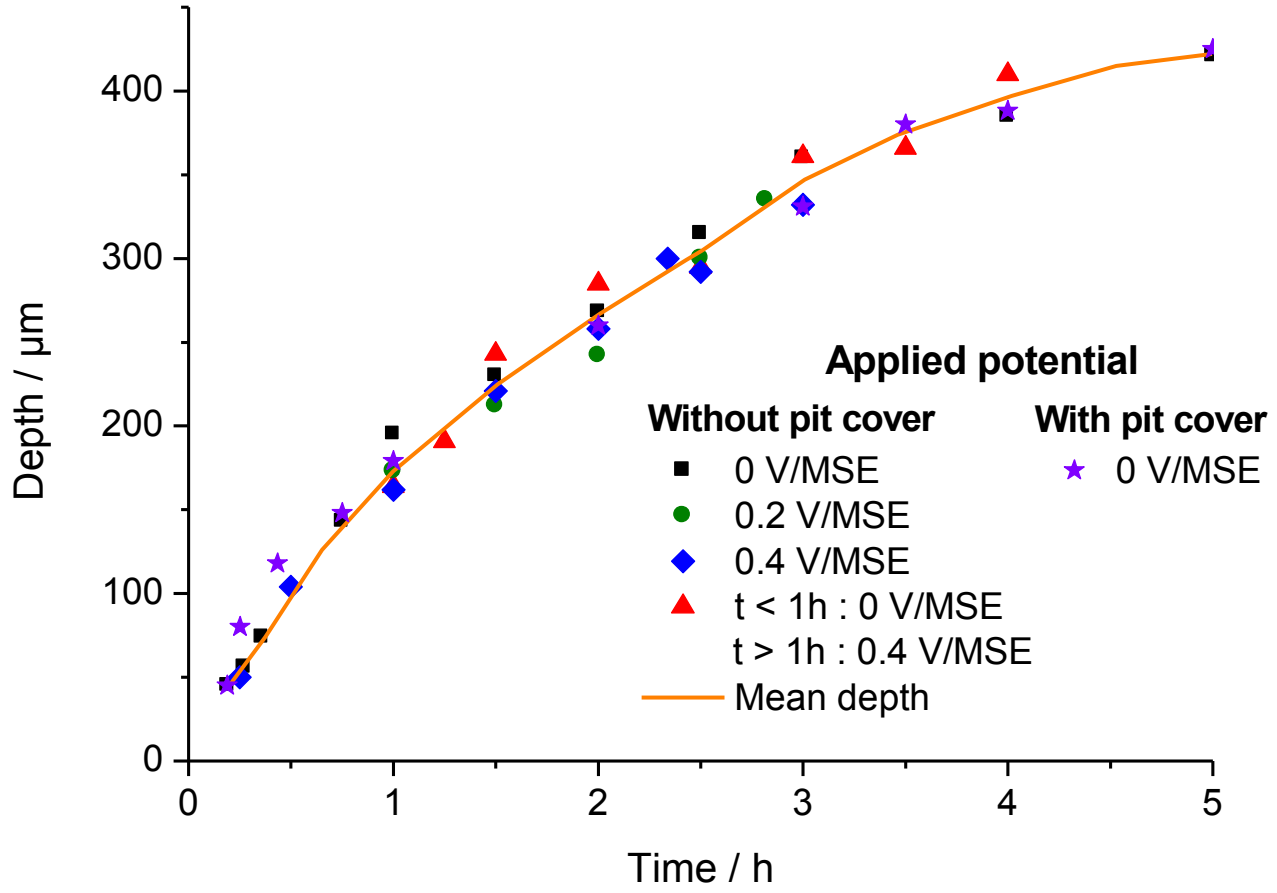
Flow rate and concentration play the same role on pit propagation



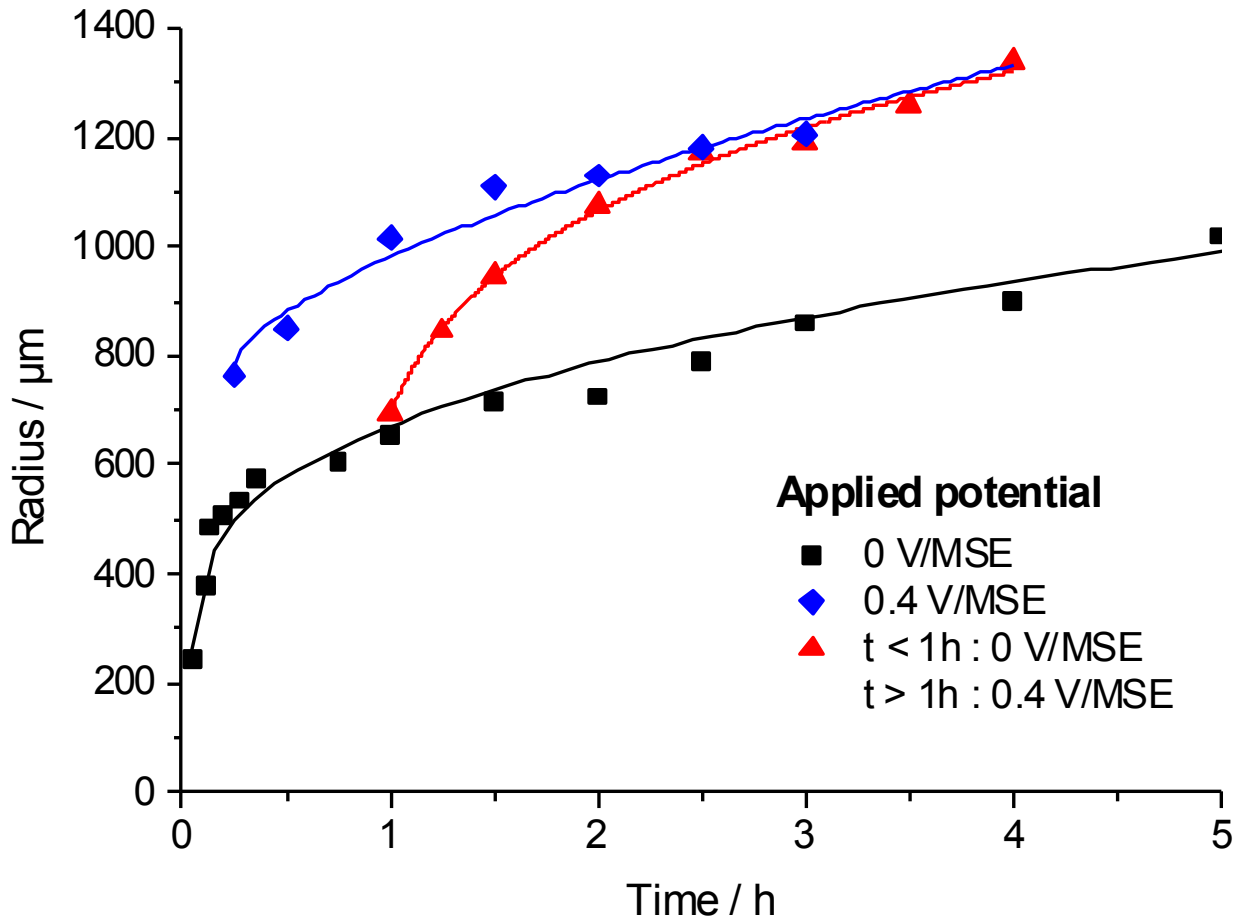
Depth and diameter were obtained from optical observations: after 2 h, the mean radius increases with potential whereas the depth remains constant (about 270 μm)

Influence of both the duration and potential: each point corresponds to one experiment

Evolution of the pit dimension

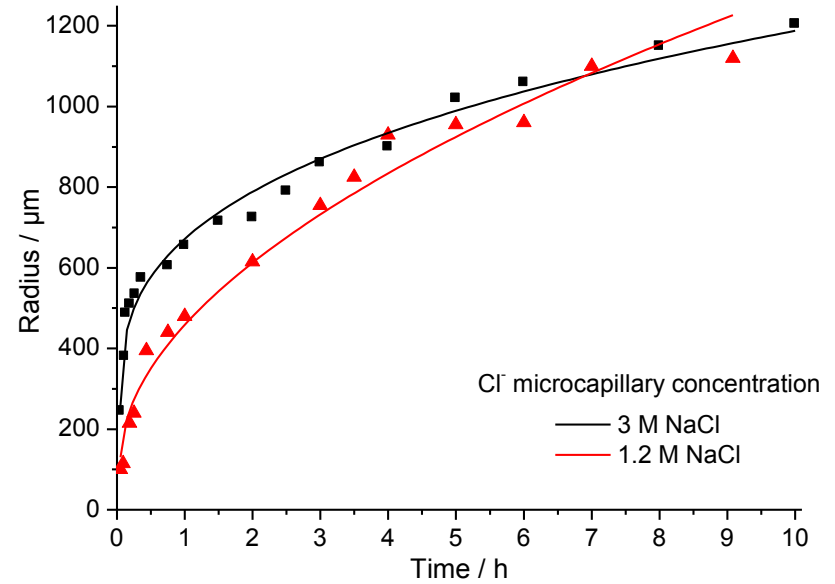
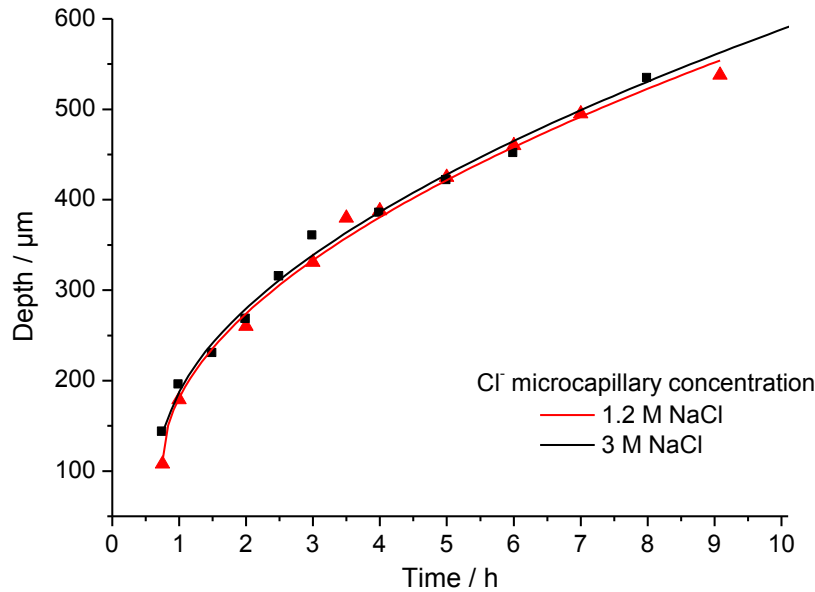


Influence of both the duration and potential: each point corresponds to one experiment



Change in potential modify the pit radius

Fitting of the experimental results



For 3 M NaCl solution

$$p = 126 + 1.57 \cdot |t - 2700|^{0.54} \quad \text{for } t > 45 \text{ min}$$

$$r = 250 + 26.36 \cdot |t - 180|^{0.34} \quad \text{for } t > 3 \text{ min}$$

For 1.2 M NaCl solution

$$p = 111 + 1.93 \cdot |t - 2700|^{0.53} \quad \text{for } t > 45 \text{ min}$$

$$r = 130 + 4.20 \cdot |t - 180|^{0.53} \quad \text{for } t > 3 \text{ min}$$

Analysis of the radius and depth evolutions


Optical measurement of pit parameters

fit




Law $p=f(t)$

Time derivative



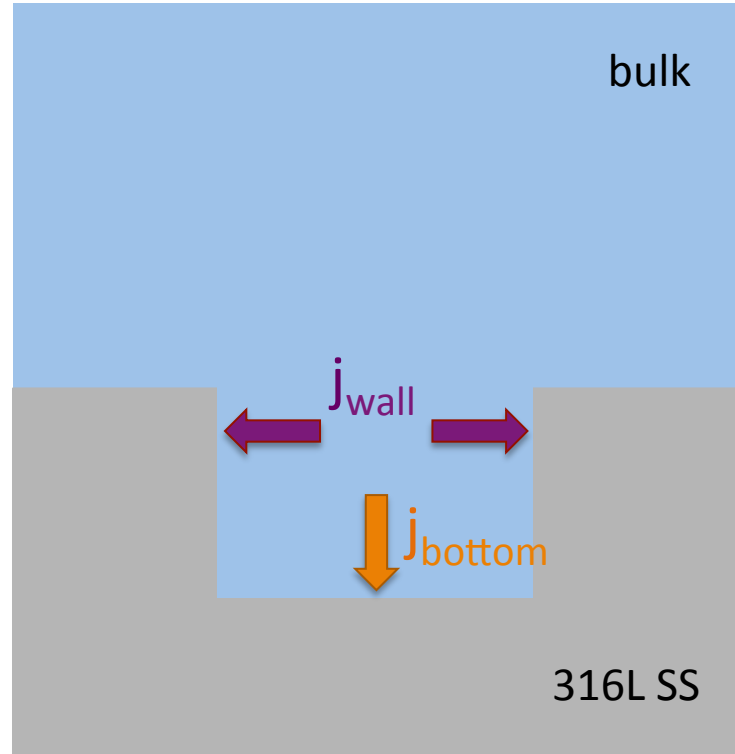
Law $dp/dt=g(t)$

current

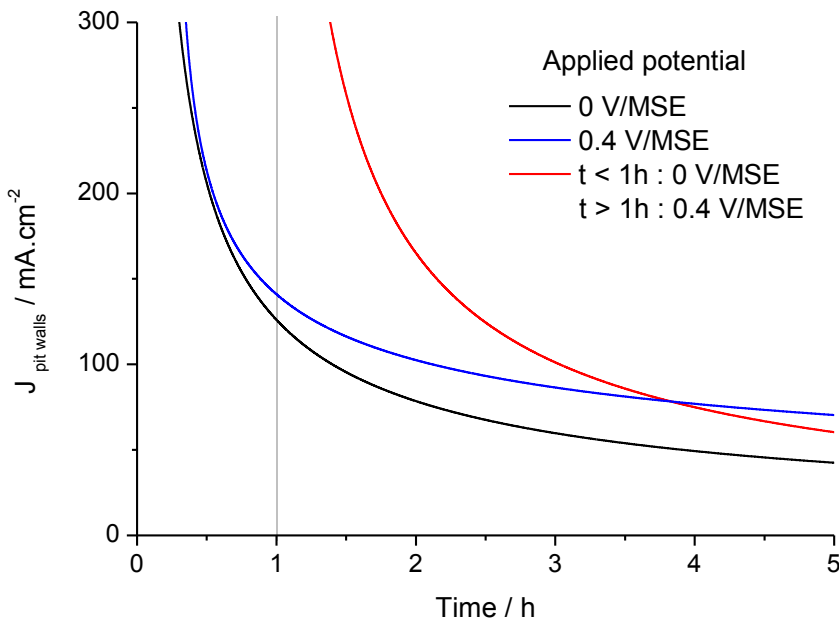


$J = pnF/M dp/dt$

We can distinguish two contribution for the current density



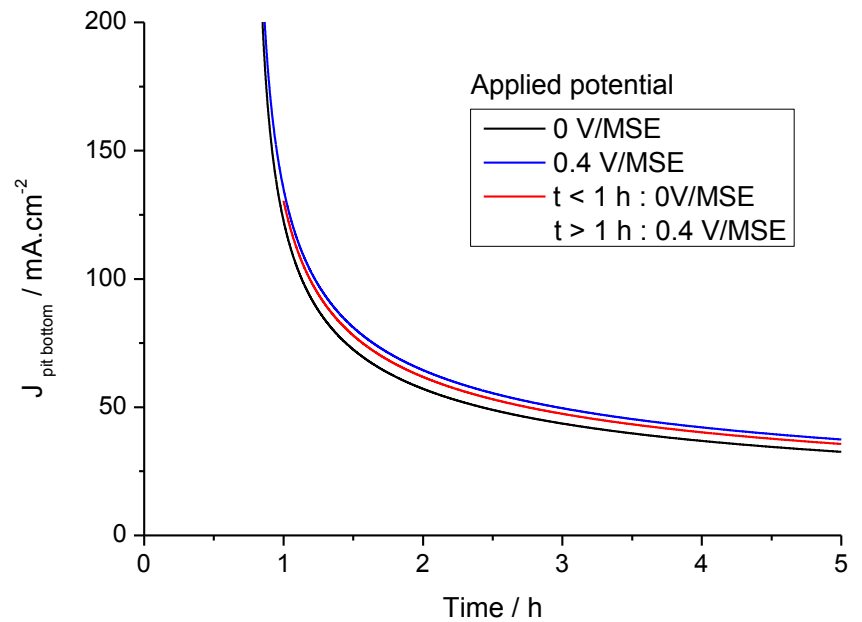
pit wall



Change in potential (1h) modifies the current density on the pit wall

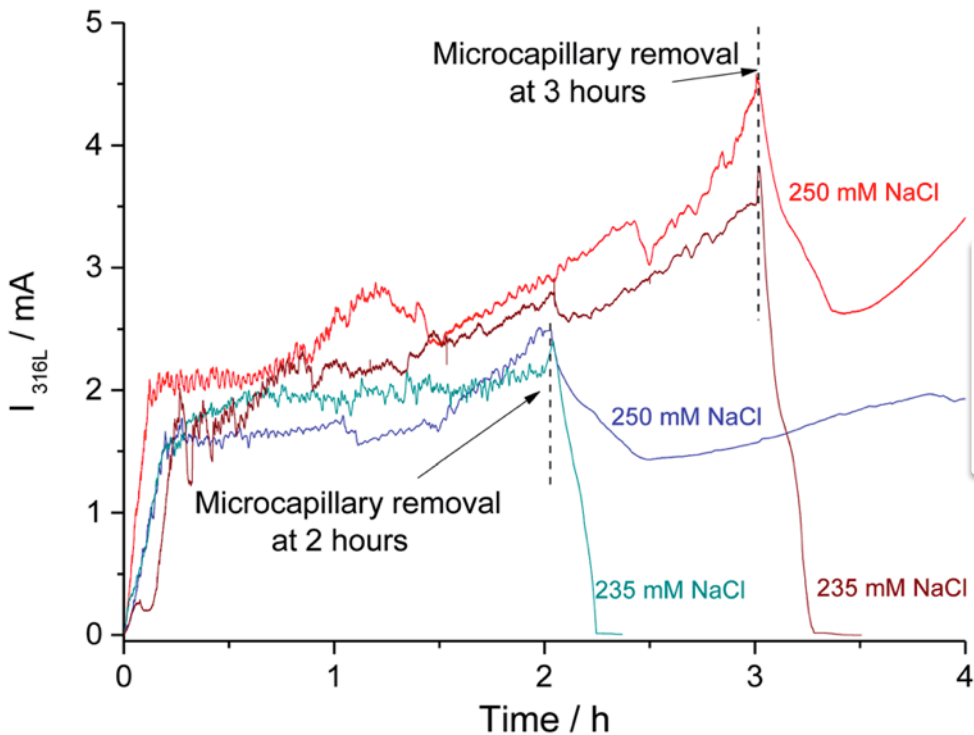
 → Ohmic control of the pit propagation along the radial direction

pit bottom



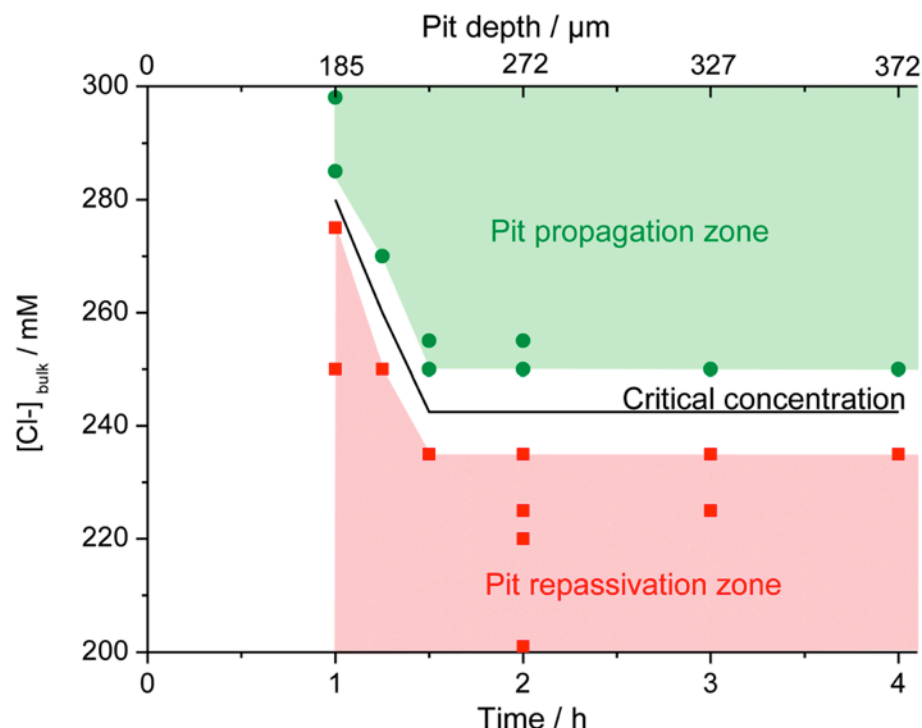
Change in potential (1h) does not modifies the current density on the pit bottom
 Evolution of the pit depth as \sqrt{t}

 → Diffusion control of pit propagation along the z-direction



Chronoamperometry experiments: the microcapillary was removed after 2 hours or 3 hours and the solution bulk was changed.

Zone diagram of a pit evolution



- POSSIBILITY TO GENERATE A SINGLE PIT AT A GIVEN LOCATION AND TO SUSTAIN ITS PROPAGATION FOR LONG TIME
- EVOLUTION OF THE PIT DIMENSIONS AS A FUNCTION OF DIFFERENT PARAMETERS (CHLORIDE CONCENTRATION, ELECTRODE POTENTIAL, TIME...)
- 2 DIFFERENT RATES OF PIT PROPAGATION WERE EVIDENCED: 1 FOR PIT BOTTOM AND 1 FOR PIT WALL
- ZONE DIAGRAM FOR PIT PROPAGATION (ACCOUNTING FOR BULK CONCENTRATION IN CHLORIDE)



Thank you for your attention

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