Investigation of a single pit generated with a flow microcell

S. Heurtault, R. Robin, F. Rouillard, V. Vivier

INVESTIGATION OF A SINGLE PIT GENERATED WITH A FLOW MICROCELL

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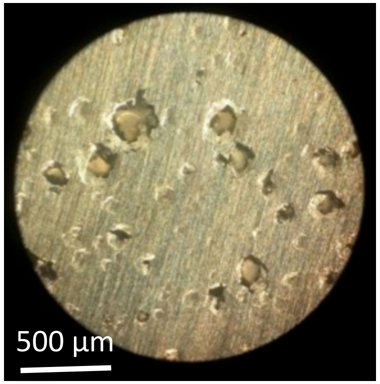
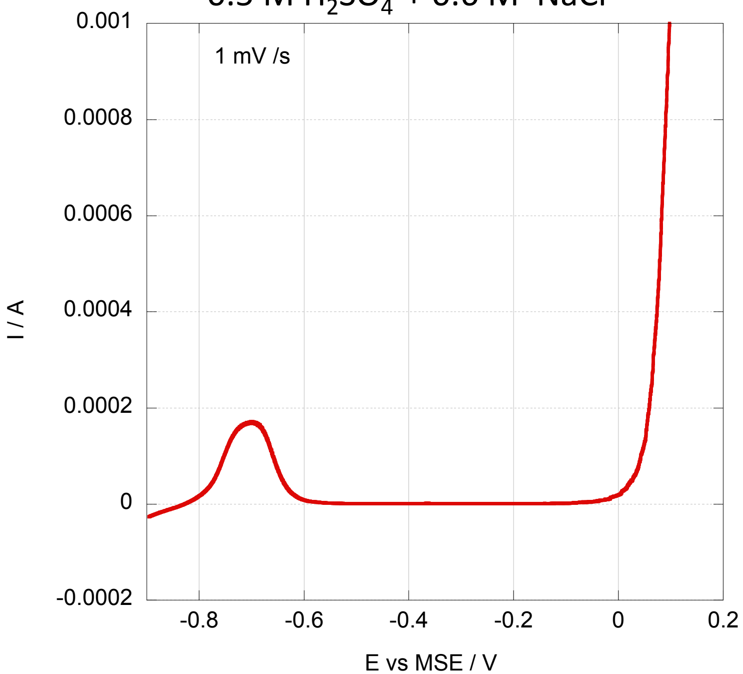
Stainless steel in a chloride environment



316L stainless steel
0.5 M H_2SO_4 + 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

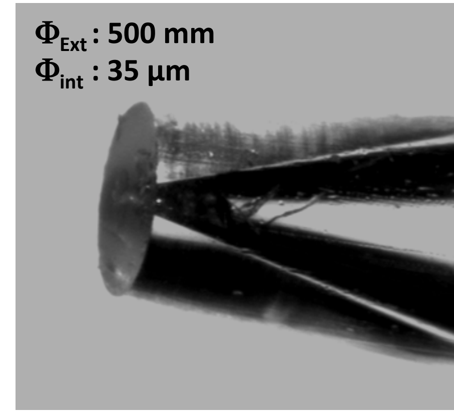
Wipf et al. (SECM – trichloroacetate reduction)
Fushimi and Seo (Ion gun – Ag/AgCl)
Portail et al. (Ion gun – Ag/AgCl + EQCM)

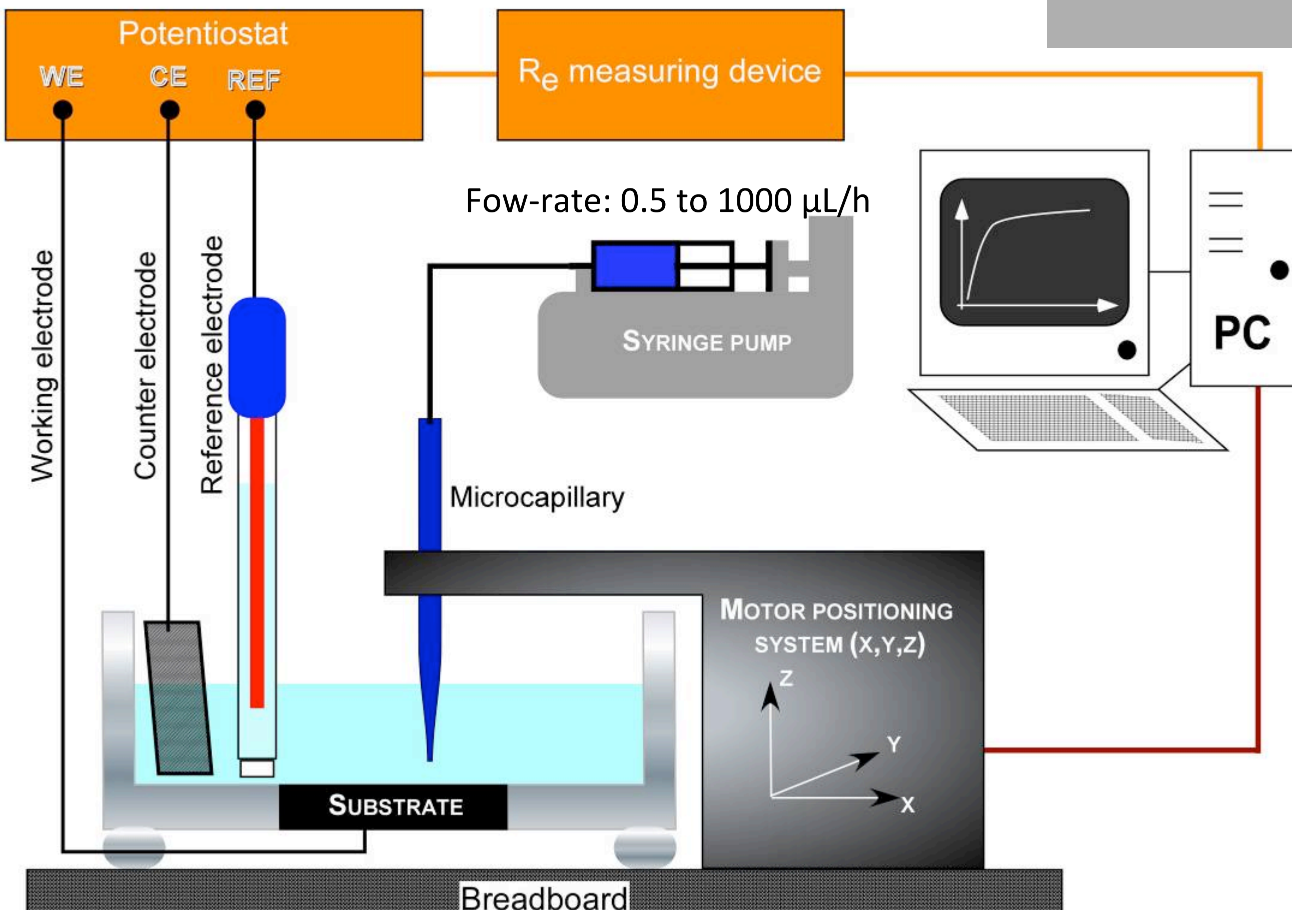
- Pit propagation for long time

Lead-in pencil technique
Flow microcell

Experimental setup

Flow microcell description



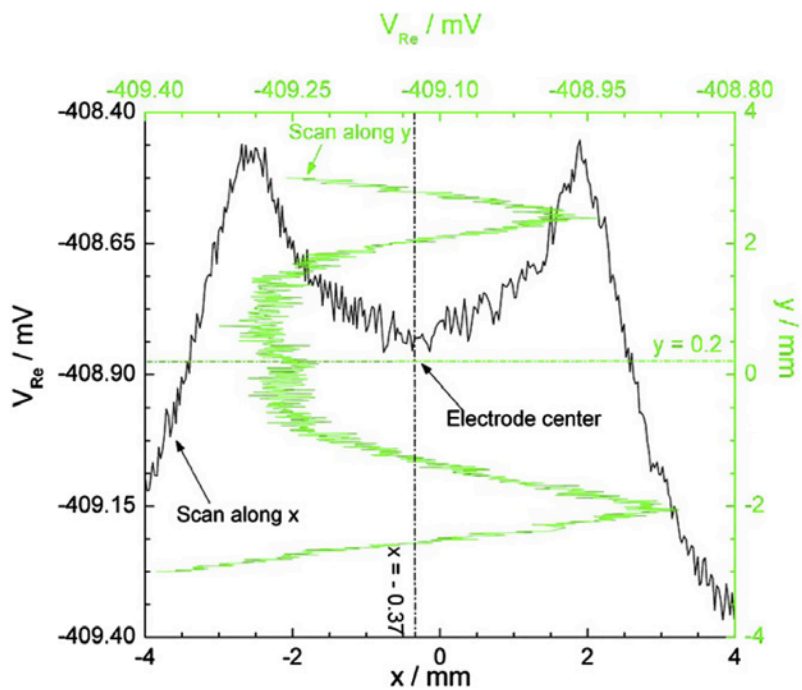


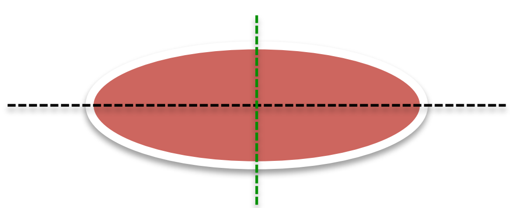
N. Aouina, F. Balbauld-Célérier, F. Huet, S. Joiret, H. Perrot, F. Rouillard, V. Vivier, *Electrochim. Acta,* **104** (2013) 274-281.

Experimental setup

Capillary positioning

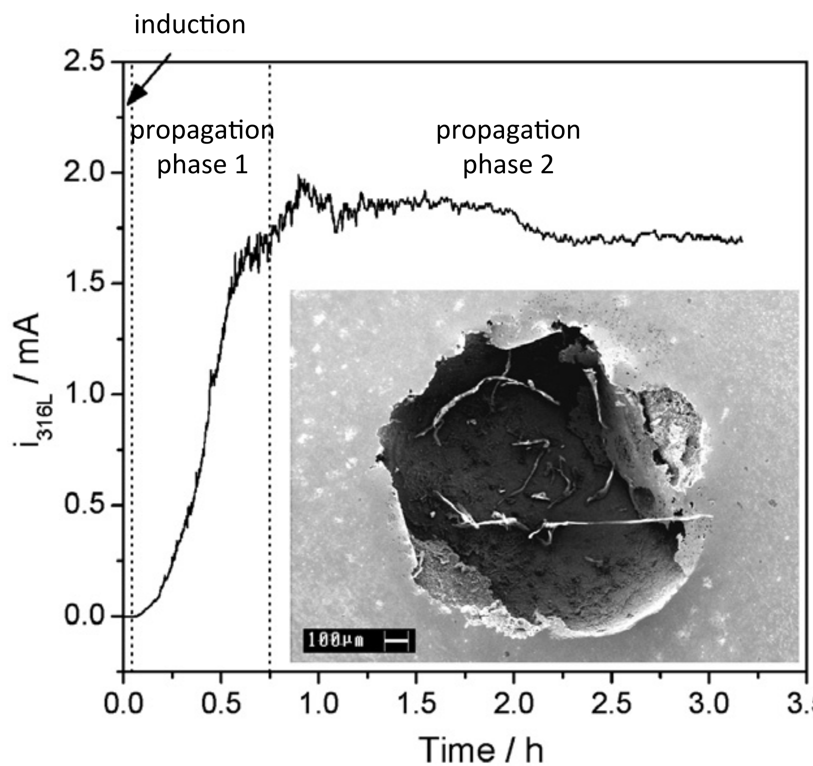
Measure of the electrolyte resistance variation due to the presence of the capillary in the close vicinity of the stainless steel electrode





Pit initiation and propagation

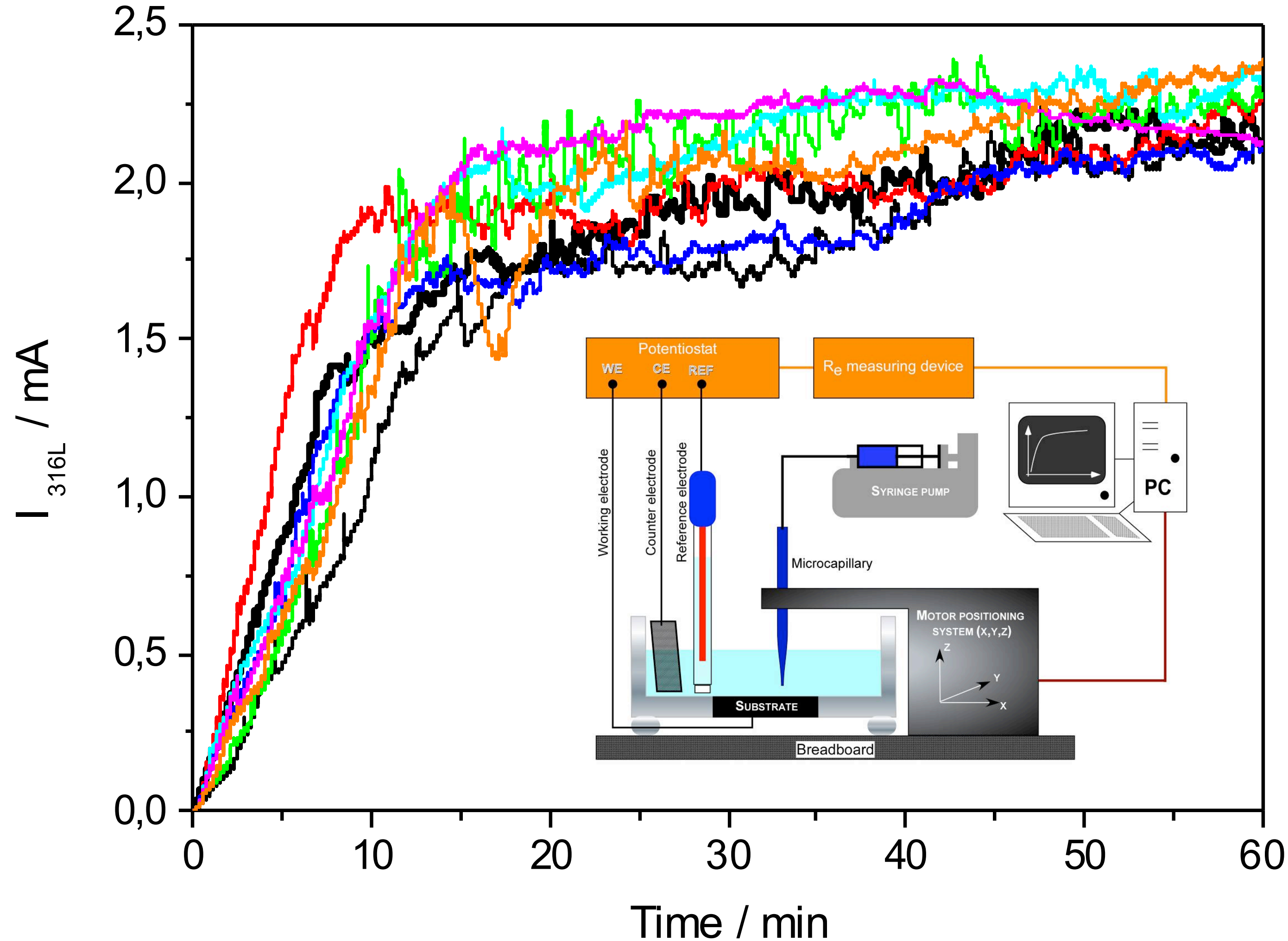
Release of chloride ion with a capillary (controlled flow rate) – measure of current (or potential) as a function of time



N. Aouina, F. Balbauld-Célérier, F. Huet, S. Joiret, H. Perrot, F. Rouillard, V. Vivier, *Corr. Sci.*, **62** (2012) 1-4.

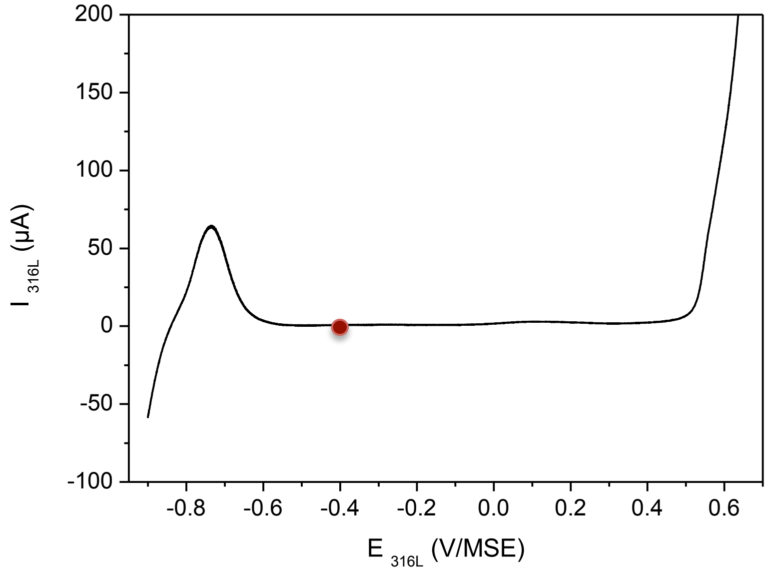
Reproducibility

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

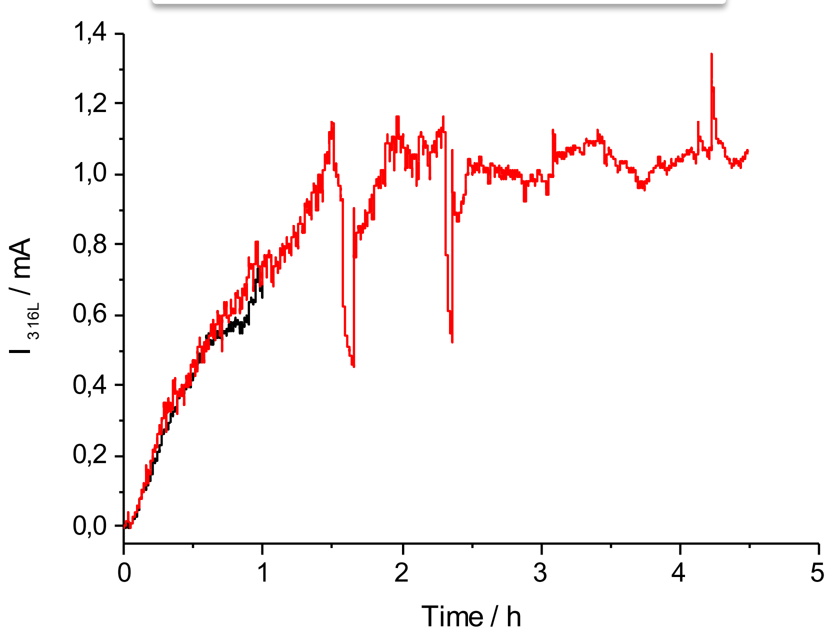


Influence of the electrode potential

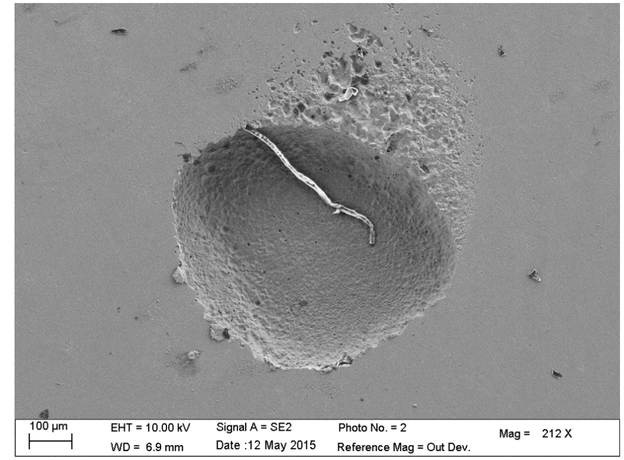
E/I curve in 0.5 mol/L H_2SO_4 solution

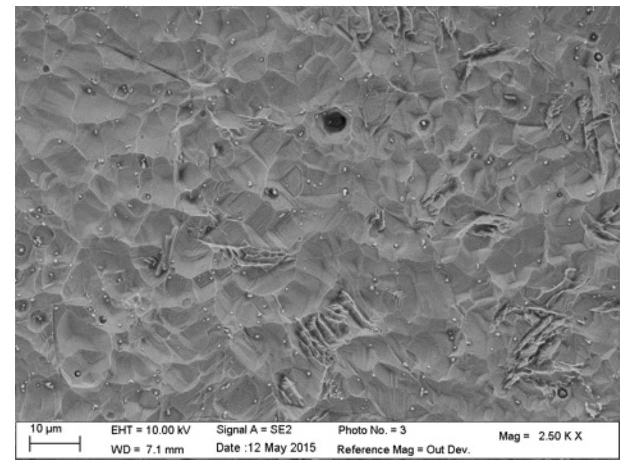


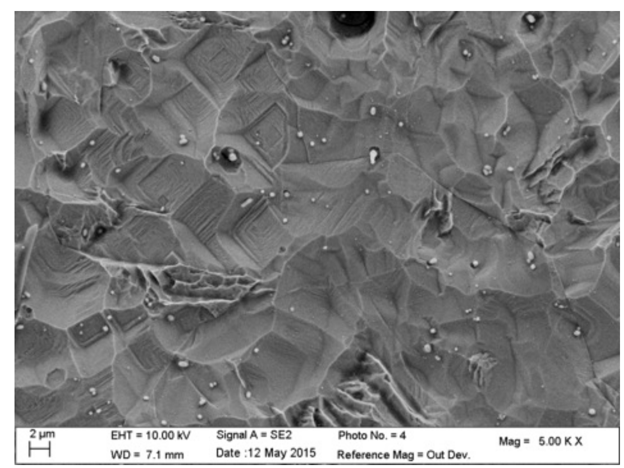
Pit generation at - 0.4 V / MSE



SEM observations after 1 hour

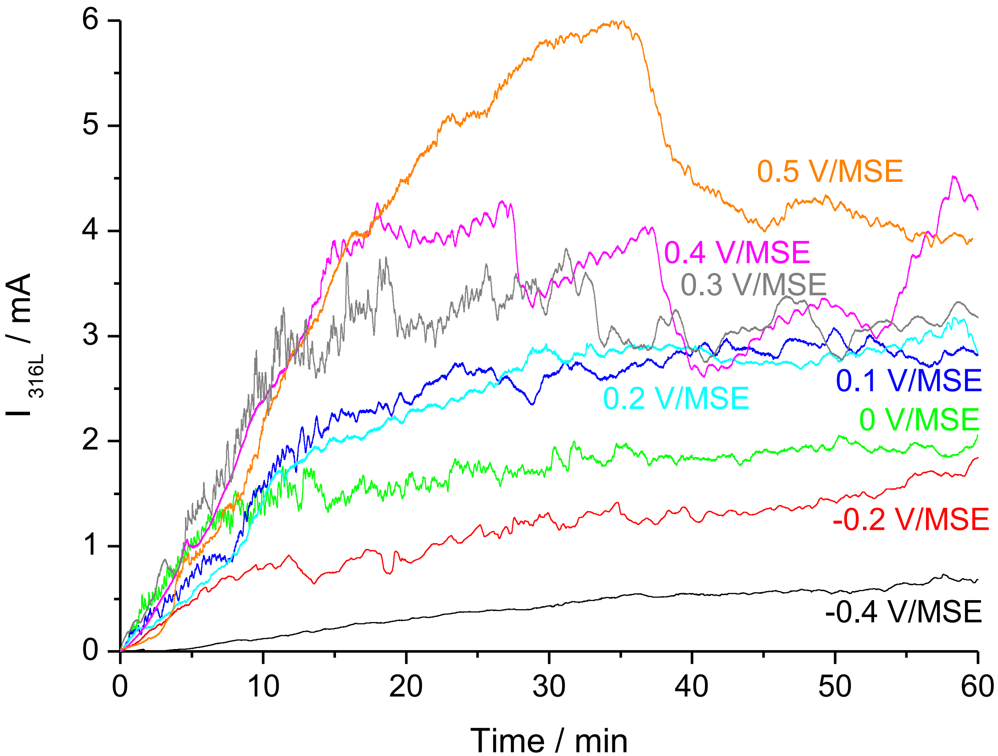


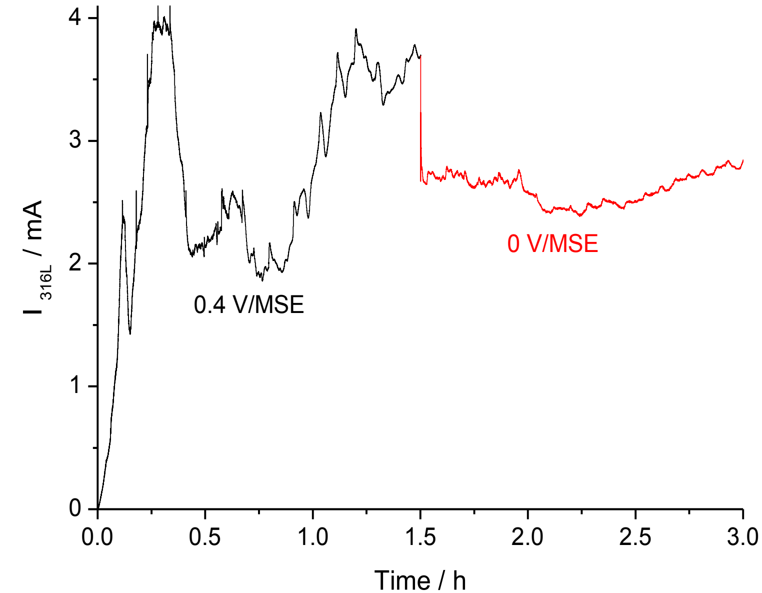


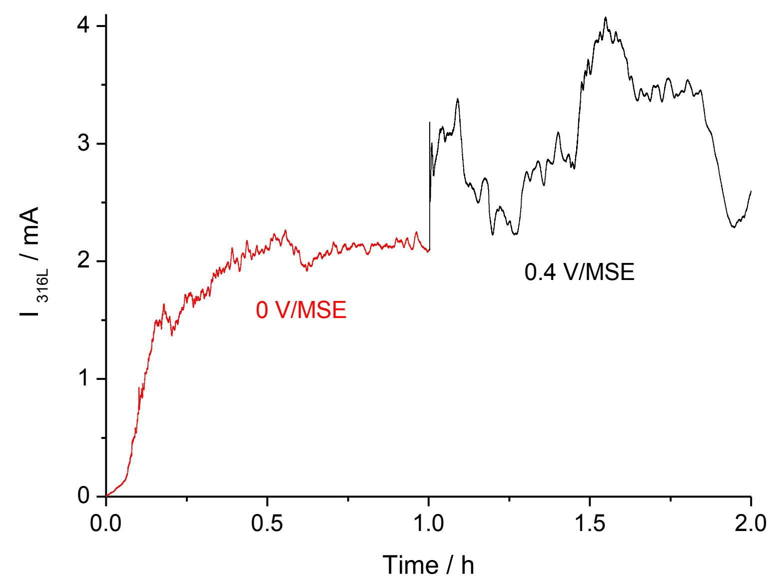


Influence of the electrode potential

Experiments performed in 0.5 M H_2SO_4 at 20°C
Flow rate : 5.4 µL/h
$[Cl^-]$ = 3 M



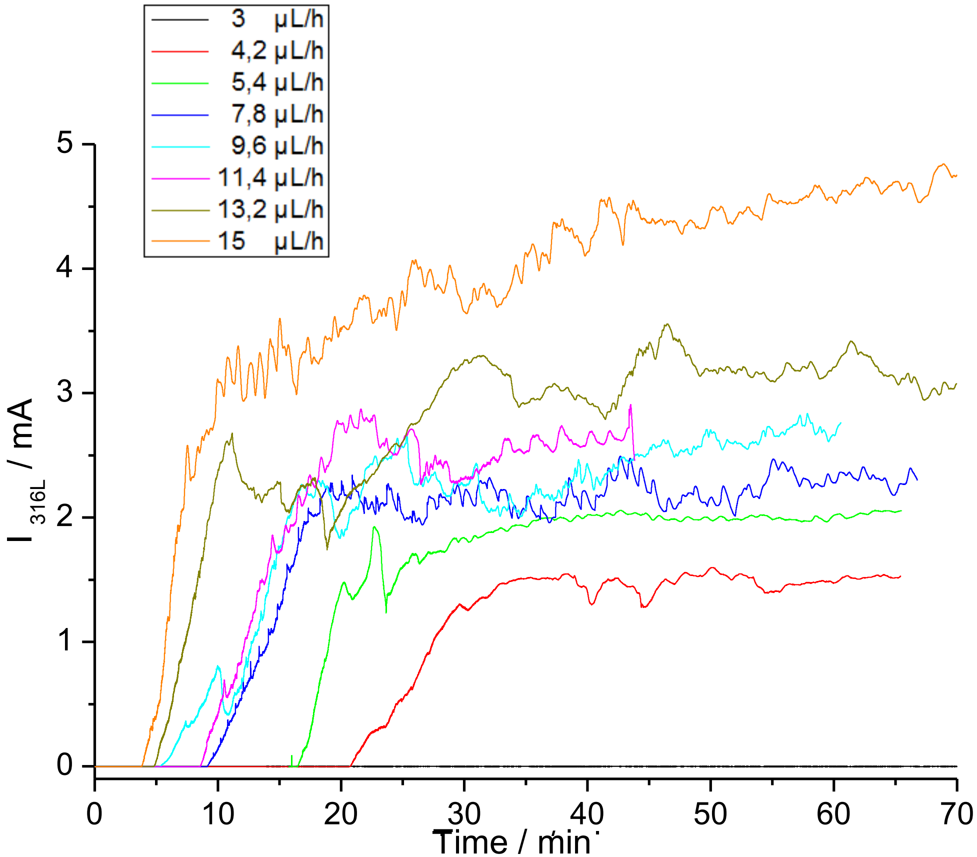




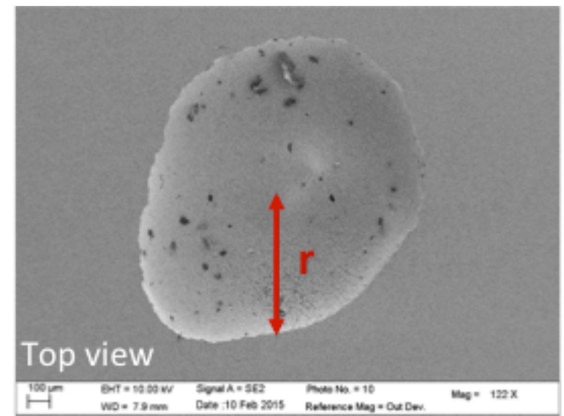
- The current increases with potential
- Current fluctuations increase with potential

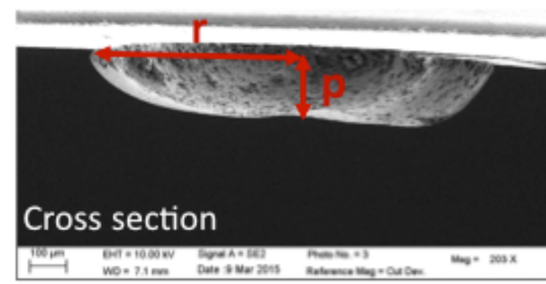
Influence of the flow rate

Experiments performed in 0.5 M H_2SO_4 at 20°C
$[Cl^-]$ = 3 M



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

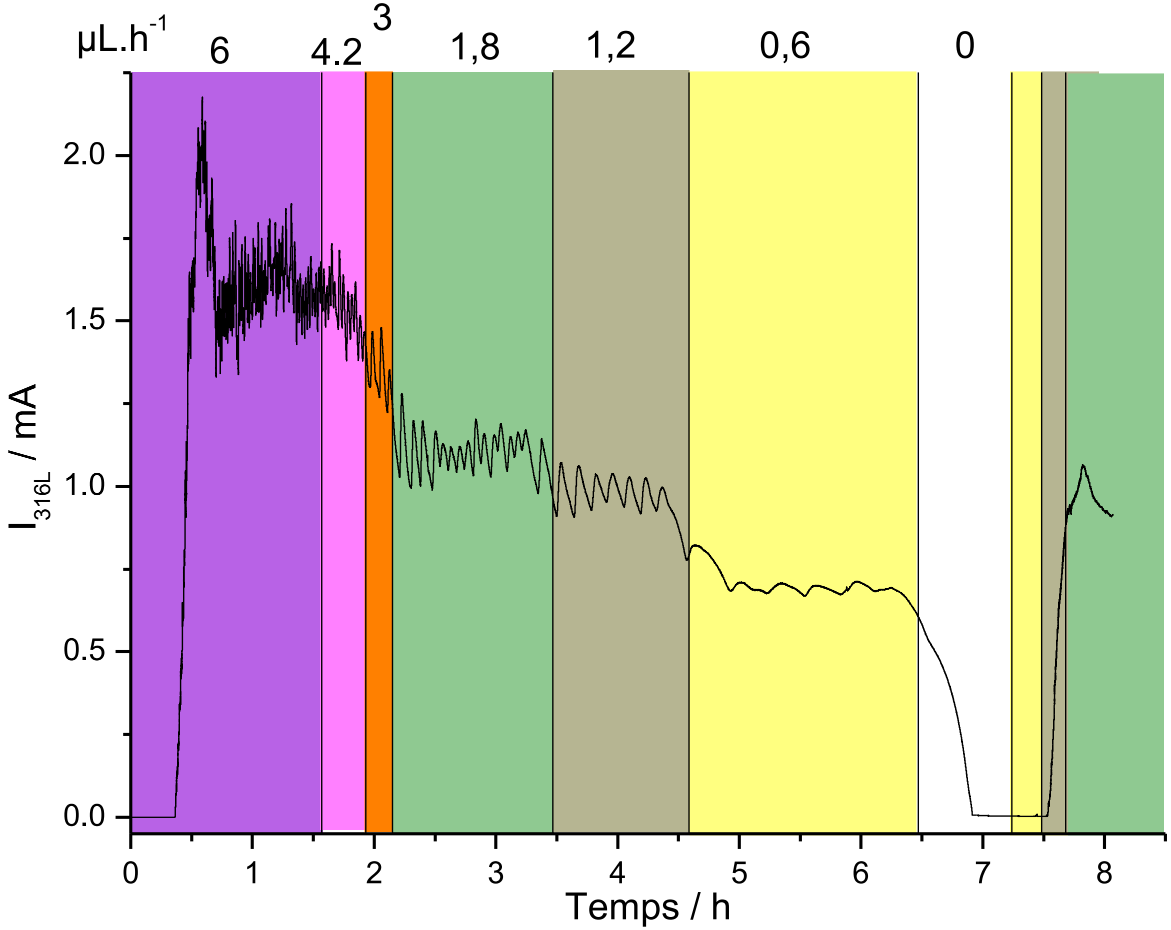




- The "steady-state" current increases with the flow rate
- The induction time decreases with the flow rate
- Same evolution when varying the Cl^- concentration

Experiments performed in 0.5 M H_2SO_4 at 20°C
$[Cl^-]$ = 3 M

Influence of the flow rate



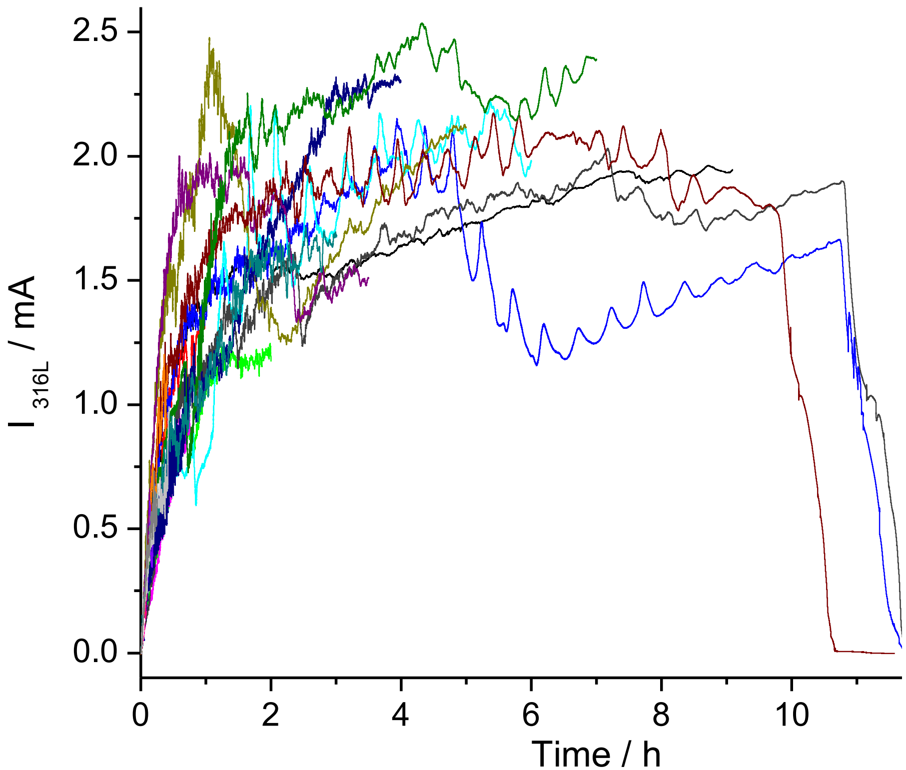
It's possible to control the rate of the pitting by changing the flow rate

→ it's a way to see the influence of the amount of chloride concentration variation on the pitting evolution

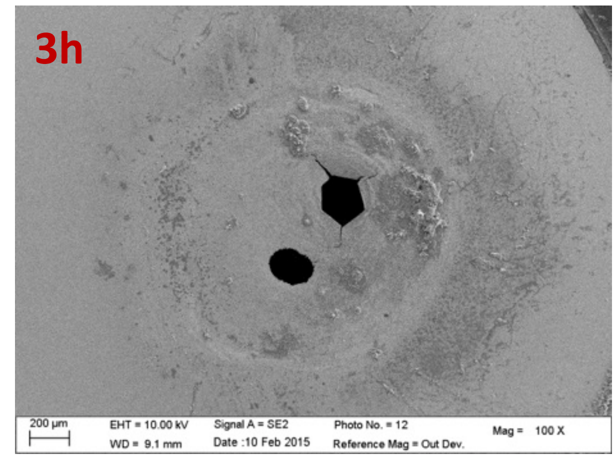
→ pit can restart after passivation

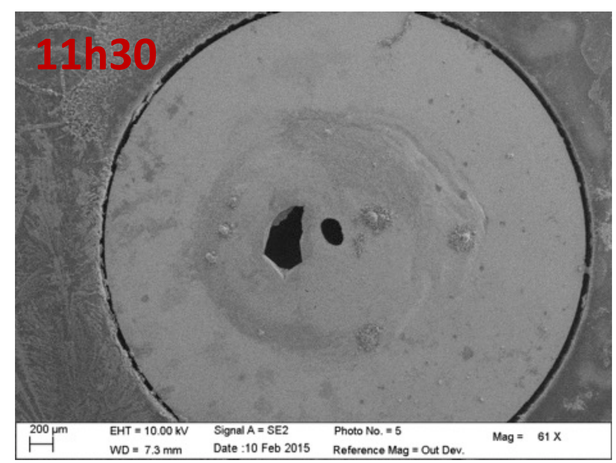
Influence of the chloride concentration

Experiments performed in 0.5 M H_2SO_4 at 20°C
$[Cl^-]$ = 1.2 M



20 identical experiments performed as a function of time

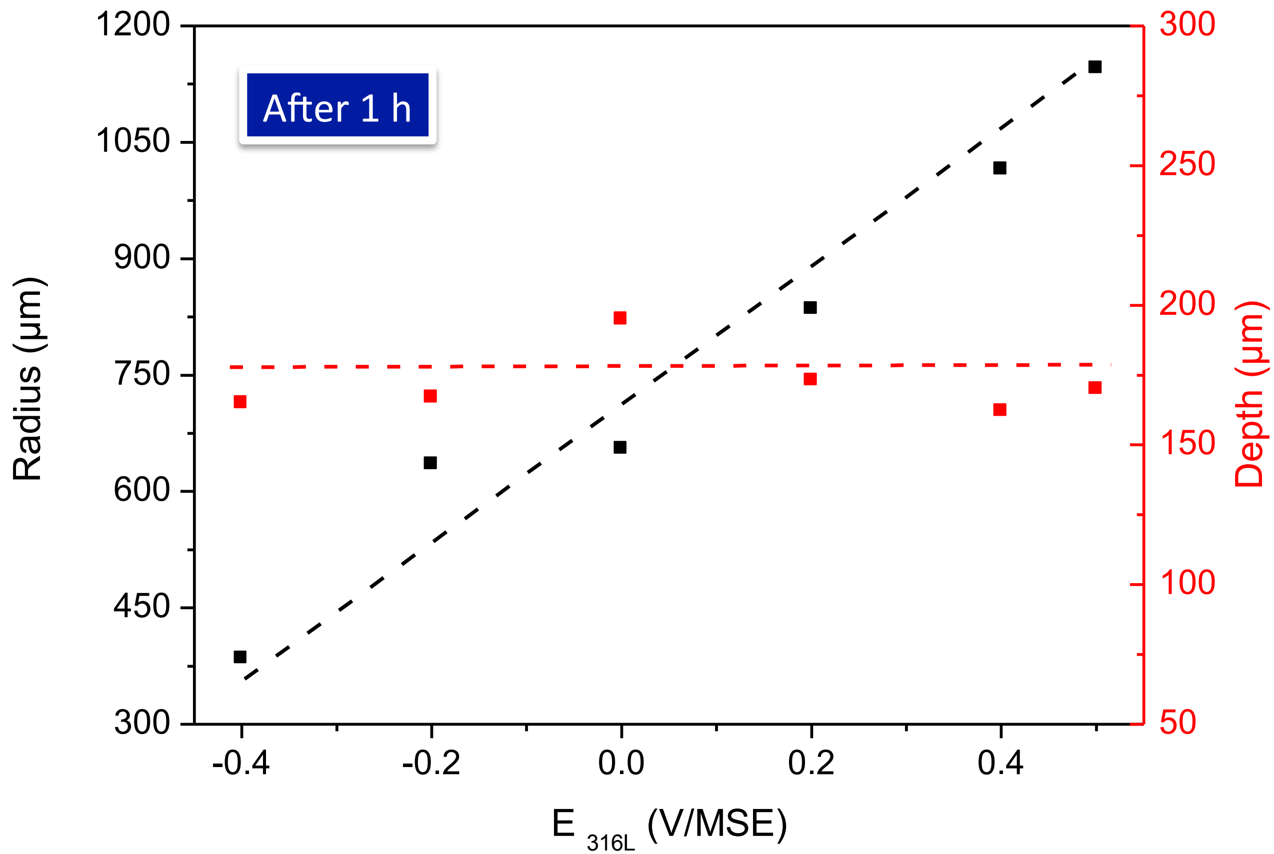




For lower chloride concentration (<1.5 mol/L) formation of a pit with a cover whereas for higher concentration, an open pit was always obtained

Evolution of the pit dimension

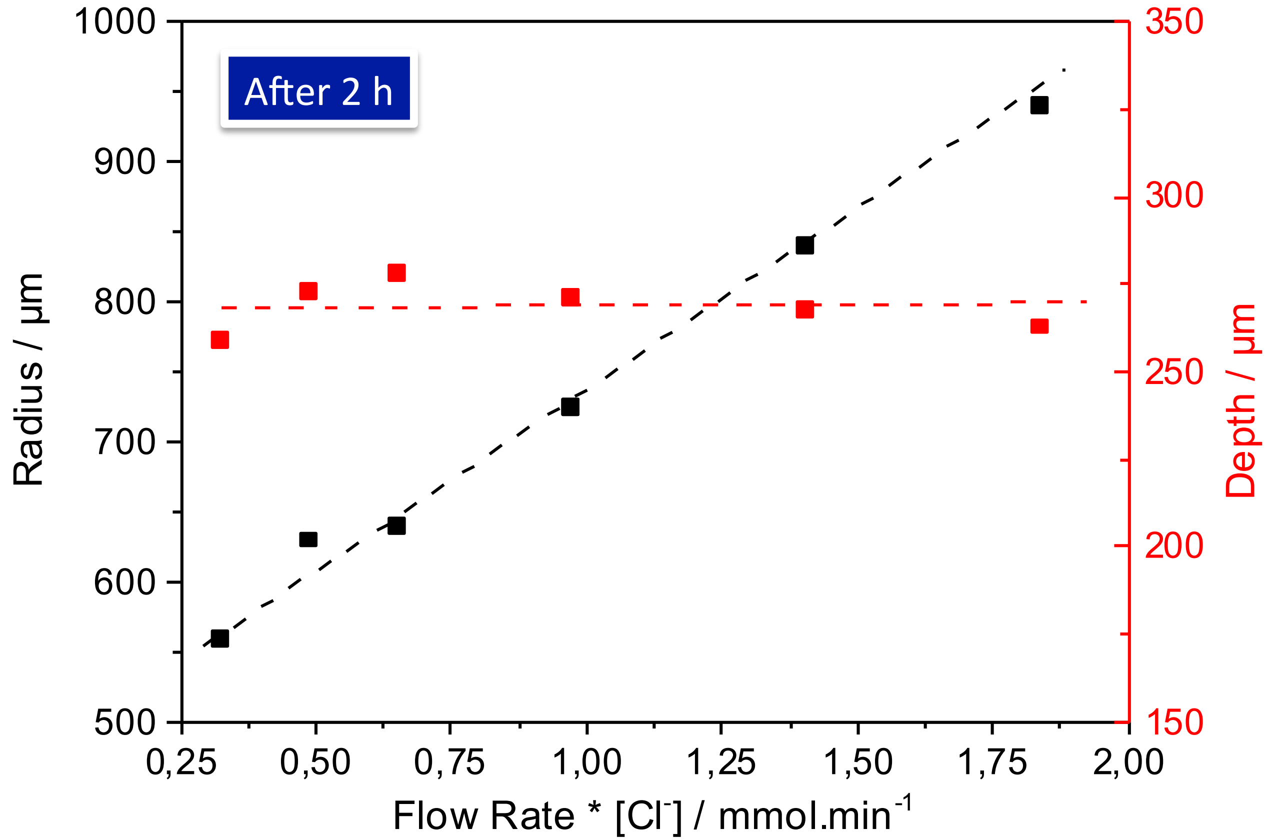
Experiments performed in 0.5 M H_2SO_4 at 20°C with $[Cl^-]$ = 3 M



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)

Evolution of the pit dimension

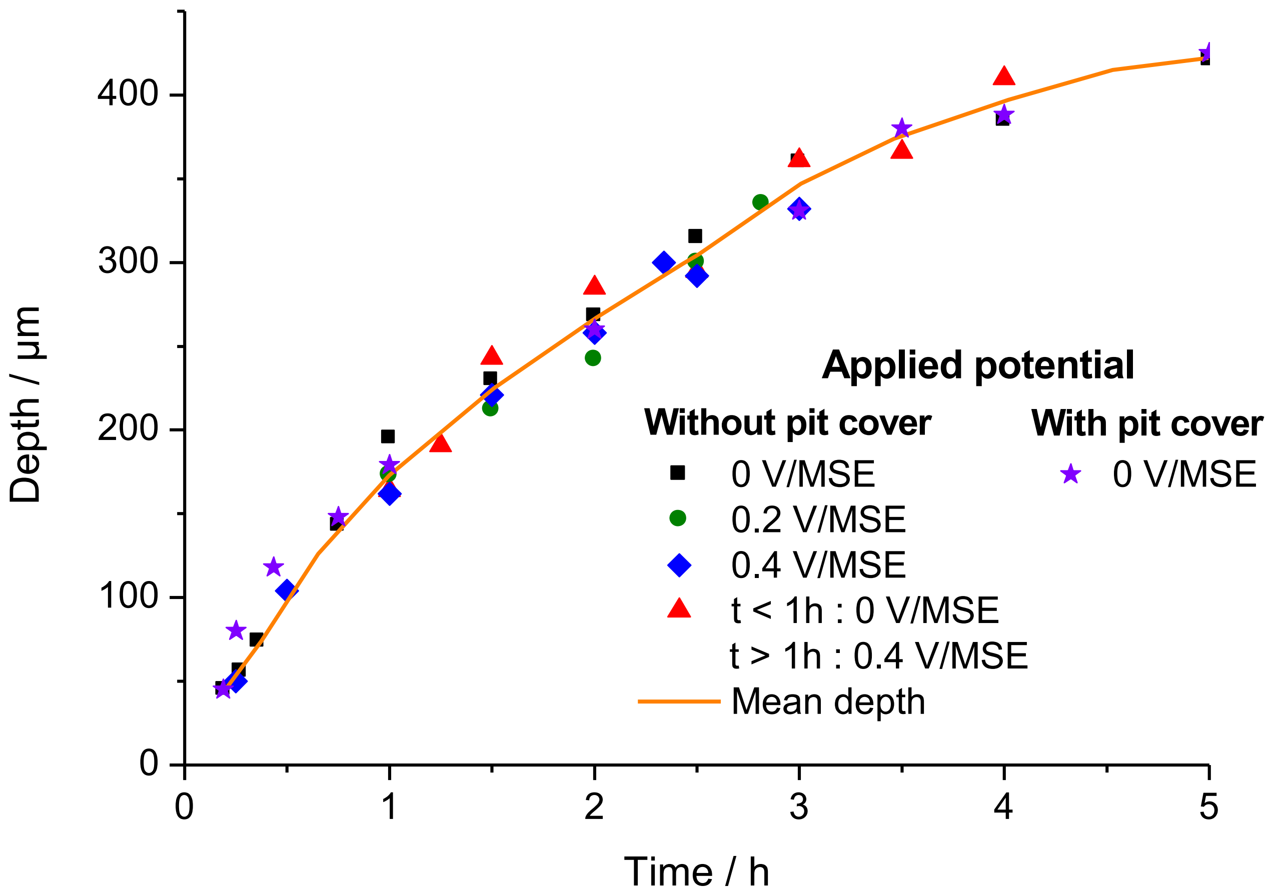
Flow rate and concentration play the same role on pit propagation



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)

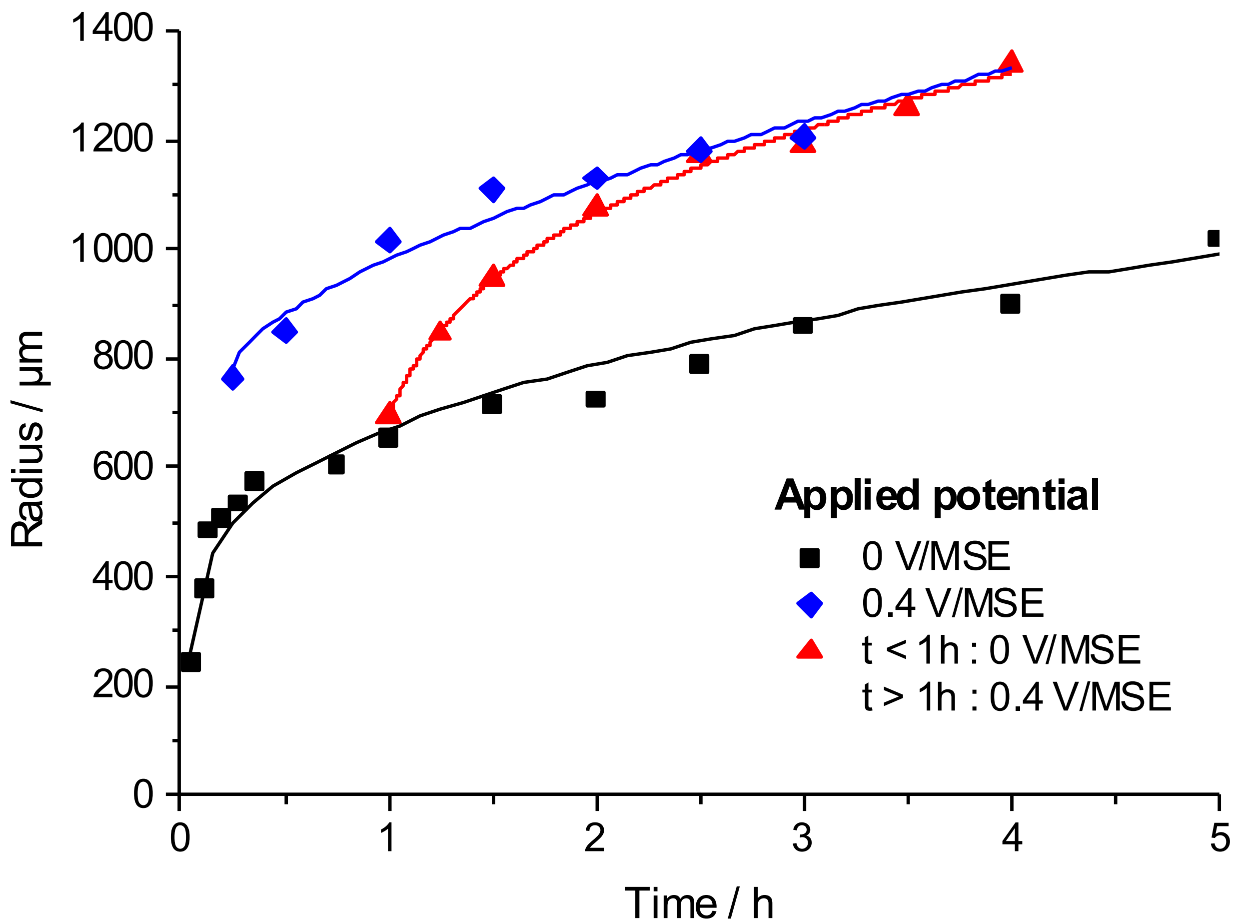
Evolution of the pit dimension

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



Evolution of the pit dimension

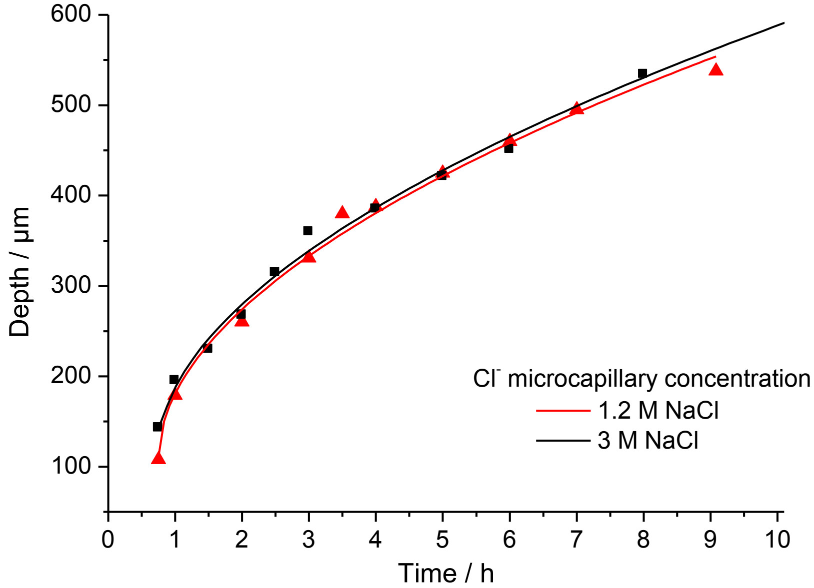
Influence of both the duration and potential: each point corresponds to one experiment

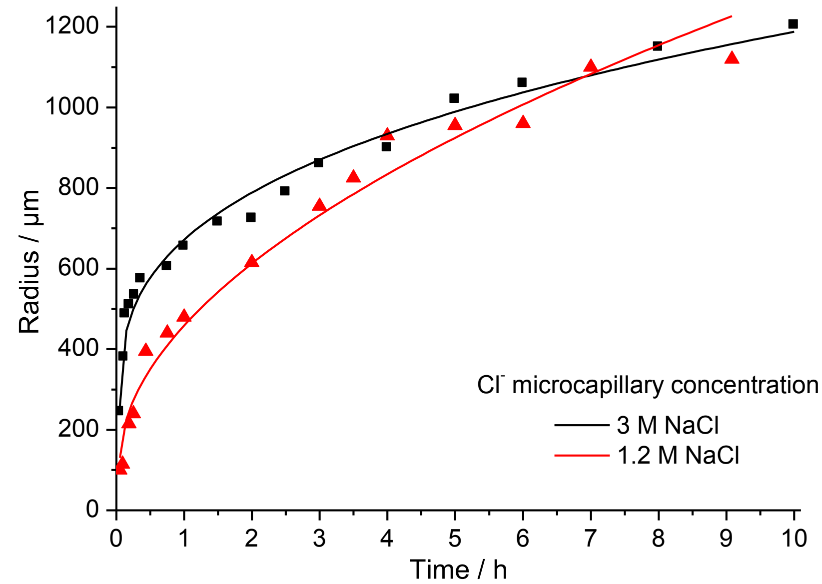


Change in potential modify the pit radius

Evolution of the pit dimension

Fitting of the experimental results





For 3 M NaCl solution

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

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

For 1.2 M NaCl solution

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

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

Analysis of the radius and depth evolutions

Optical measurement of pit parameters

fit ↓

Law p=f(t)

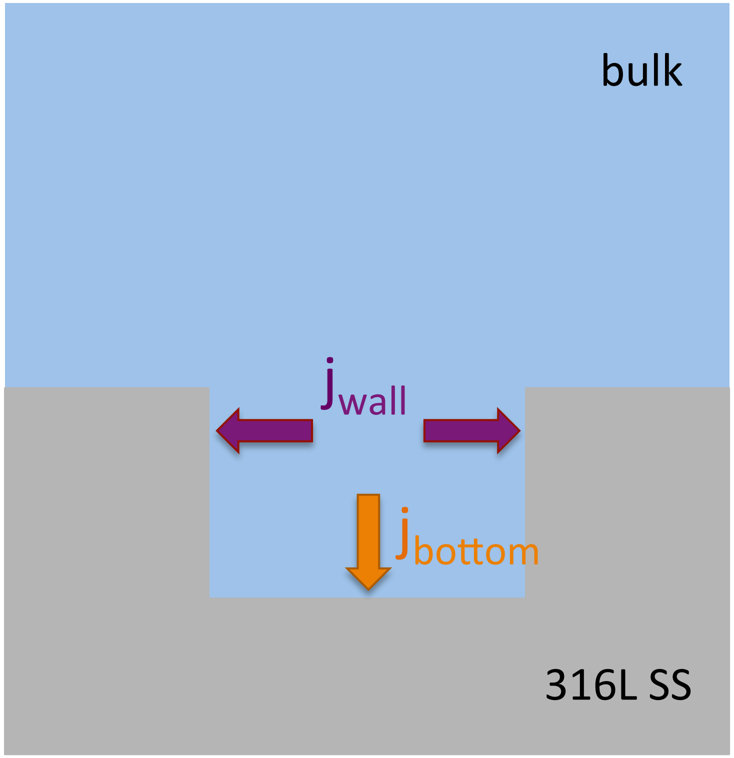
Time derivative ↓

Law dp/dt=g(t)

current ↓

J = ρnF/M dp/dt

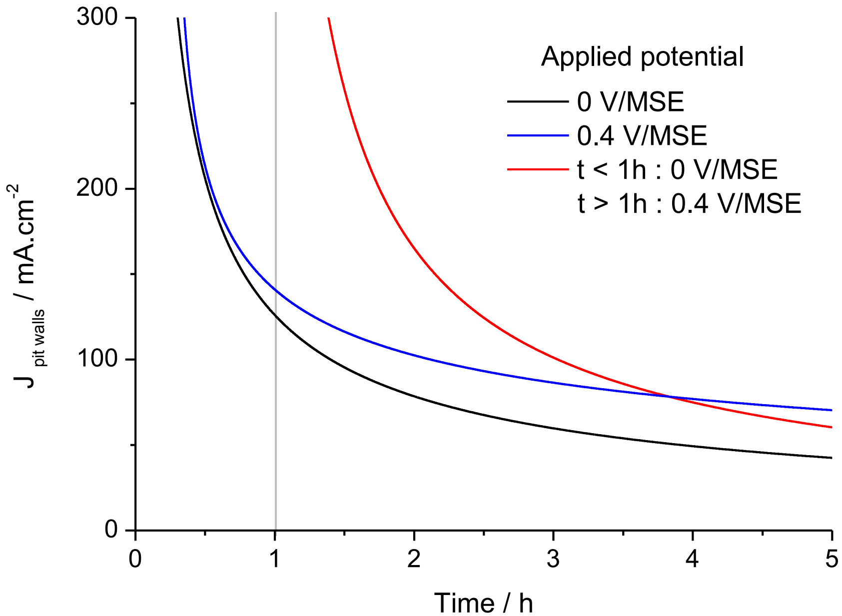
We can distinguish two contribution for the current density



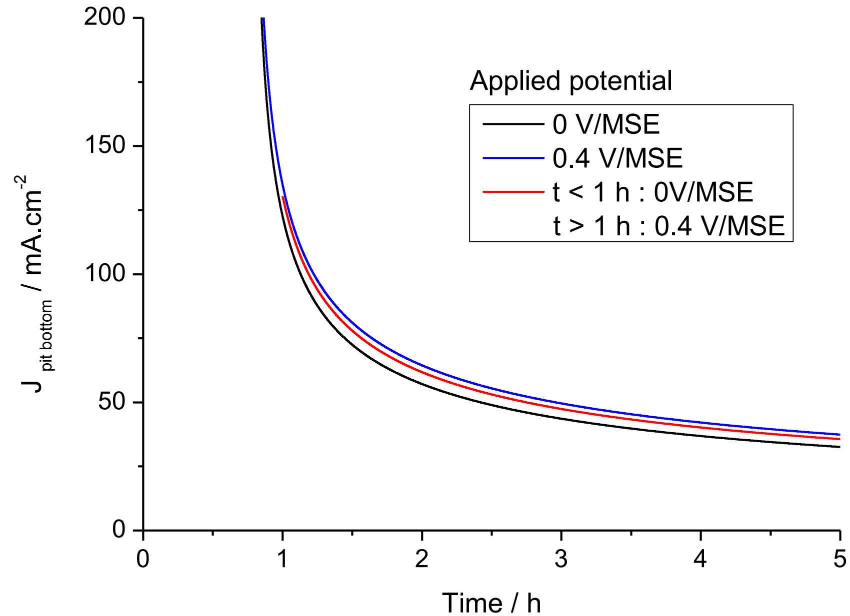
Evolution of the pit dimension

UMR 8235

pit wall



pit bottom



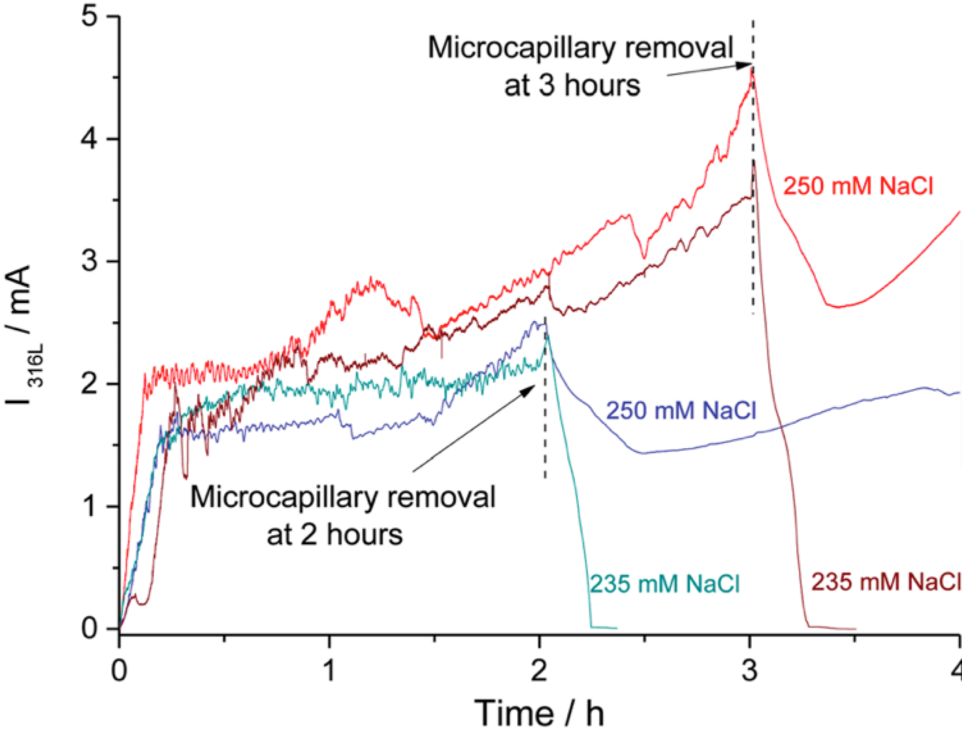
Change in potential (1h) modifies the current density on the pit wall

→ Ohmic control of the pit propagation along the radial direction

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

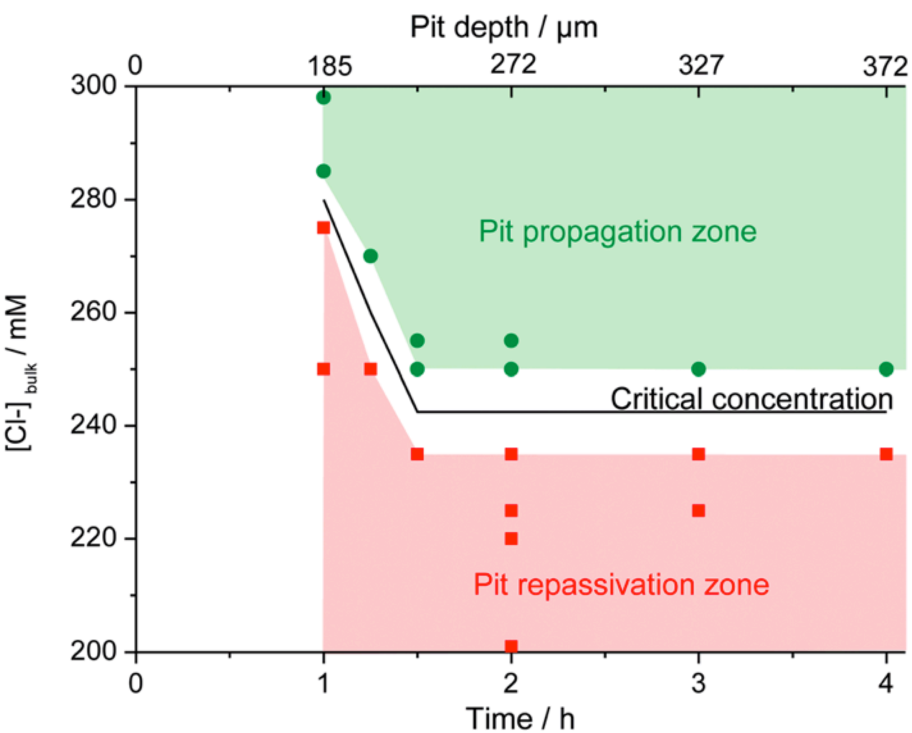
→ Diffusion control of pit propagation along the z-direction

Propagation / repassivation



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

Zone diagram of a pit evolution



Conclusions

- 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)

Acknowledgements

Thank you for your attention

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