DURABOND - Durable composite-to-metal bonded joints for heavily loaded structures at extreme environmental conditions

Physicochemical bonding and degradation phenomena at the adhesive-adherend interface

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Noordwijkerhout, December 11th 2018

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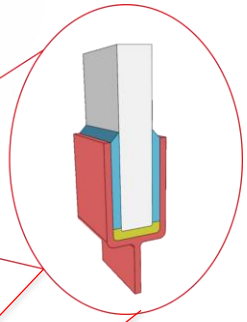
Outline

- Introduction
  - DURABOND
- Physicochemical
  - Scope
  - Approach
    - Diffusion mechanism and degradation
    - Adhesion
- Summary
- Conclude talk

Introduction - DURABOND

Need:

- Weight reduction in structures such as vessels, offshore construction and bridges



Solution:

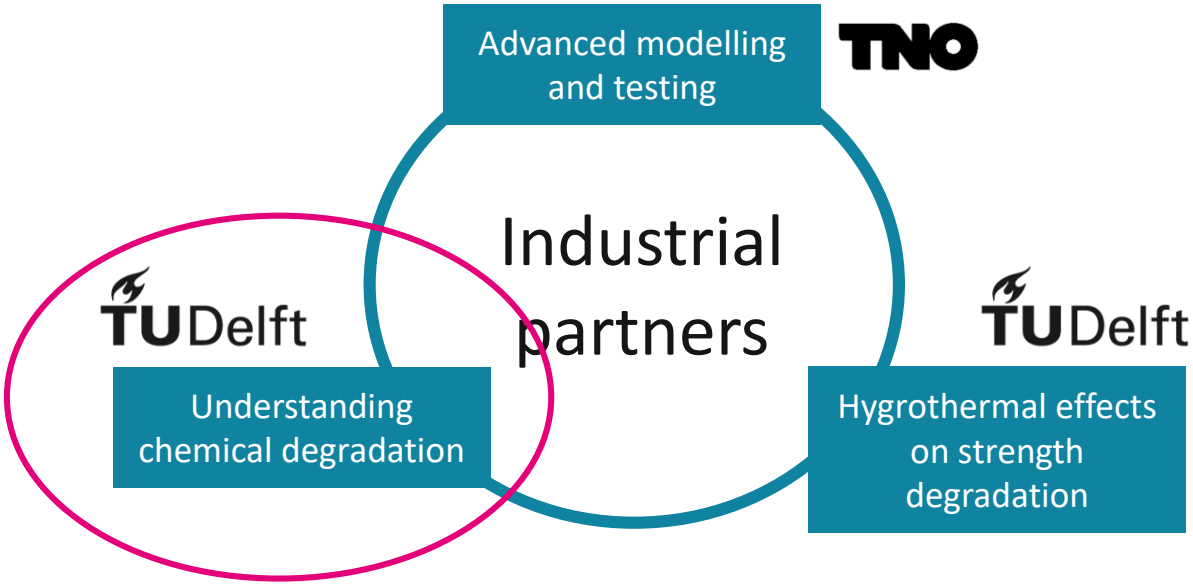
- Adhesive bonding is the prominent technique for these hybrid composite-to-metal joints

Problem:

- (Loss of) interfacial adhesion not well understood

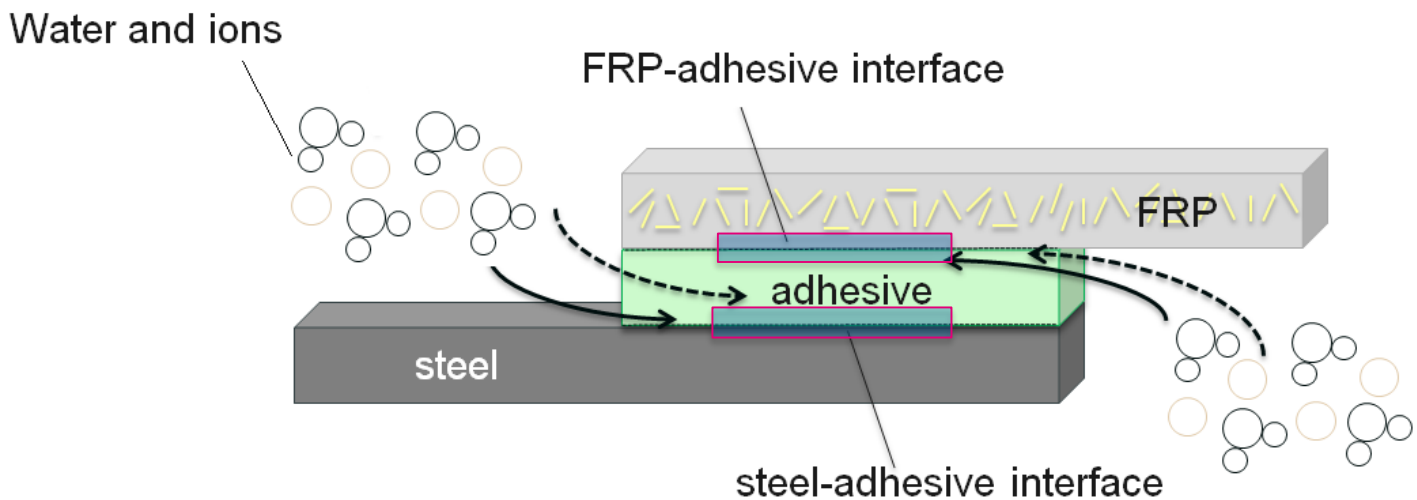
Introduction - DURABOND

To understand, improve and predict the **strength and durability** of **bonded connections** for large, thick, heavily loaded composite or composite metal structures.

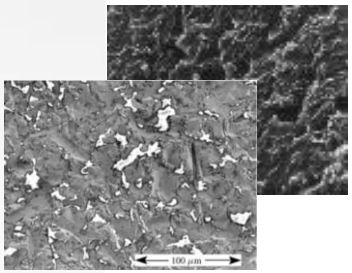


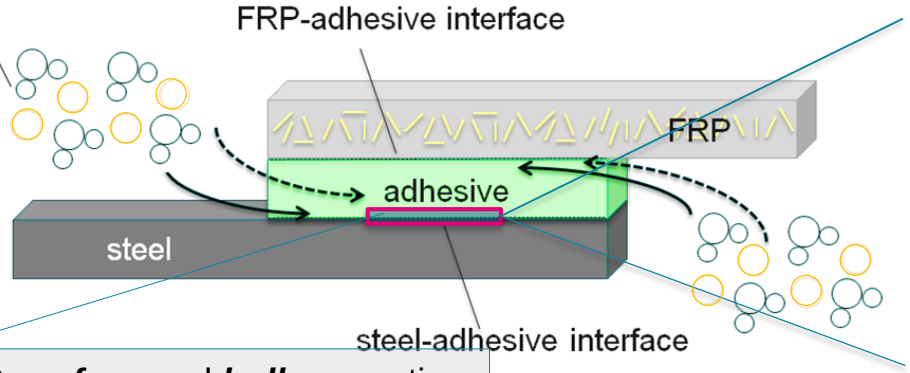
WP 1 - Scope

Study the physicochemical variables of the adherends' surfaces that affect the physicochemical bonding and degradation phenomena.

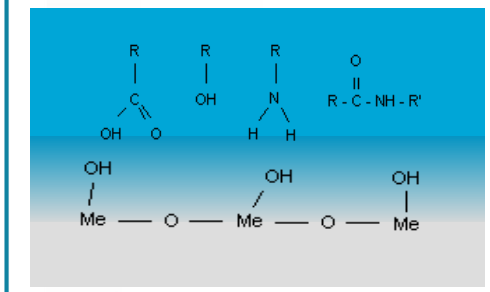


WP 1 - Scope





Interfacial bonding



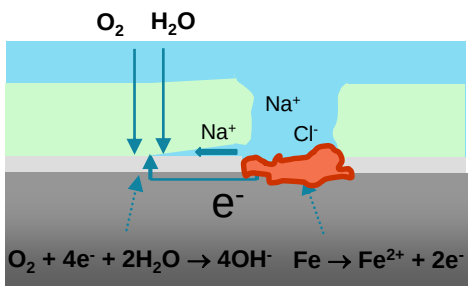
Metal(oxide) Adhesive

Interface: (oxide) ***surface*** and ***bulk*** properties

- acid-base properties
- hydroxyl fraction
- surface energy
- stability
- IEP

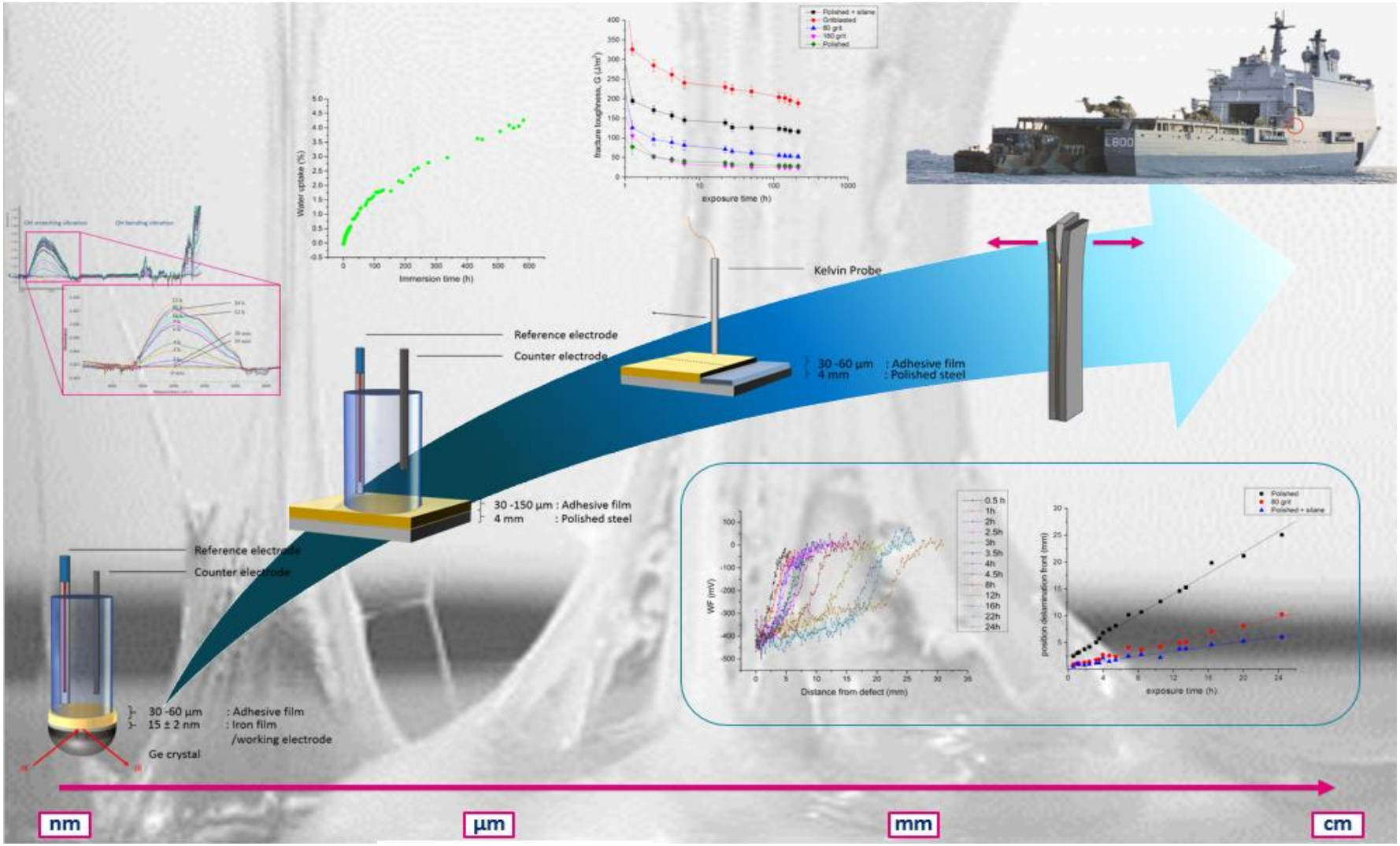
- composition
- morphology
- stability
- electronic properties

Delamination: *local electrochemical activity*



Cathodic delamination

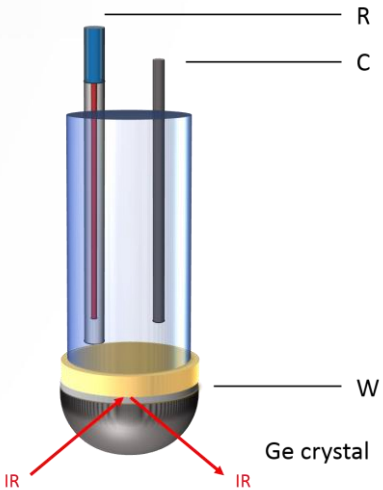
Approach


Water uptake (%)
Immersion time (h)
fracture toughness, G (J/m²)
exposure time (h)
Polished + silane
Gritblasted
80 grit
180 grit
Polished
Kelvin Probe
Reference electrode
Counter electrode
30 -60 µm : Adhesive film
4 mm : Polished steel
30 -150 µm : Adhesive film
4 mm : Polished steel
Reference electrode
Counter electrode
30 -60 µm : Adhesive film
15 ± 2 nm : Iron film
/working electrode
Ge crystal
WF (mV)
Distance from defect (mm)
0.5 h
1h
2h
2.5h
3h
3.5h
4h
4.5h
8h
12h
16h
22h
24h
position delamination front (mm)
exposure time (h)
Polished
80 grit
Polished + silane
nm
µm
mm
cm

Diffusion and degradation mechanism

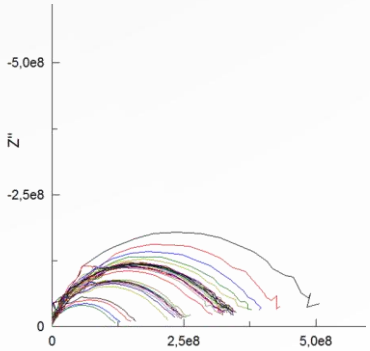
In-*situ* ATR-FTIR (Attenuated Total Reflectance - IR spectroscopy)

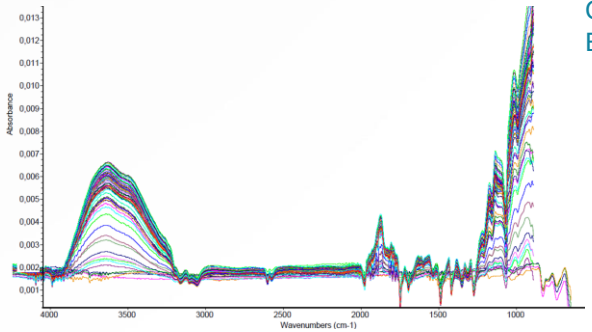
Simultaneous in-*situ* FTIR and electrochemical measurements



Study of:

- Chemical info during exposure
- Perpendicularly resolved interfacial water transport
- Electrochemical/dielectric behavior of the system

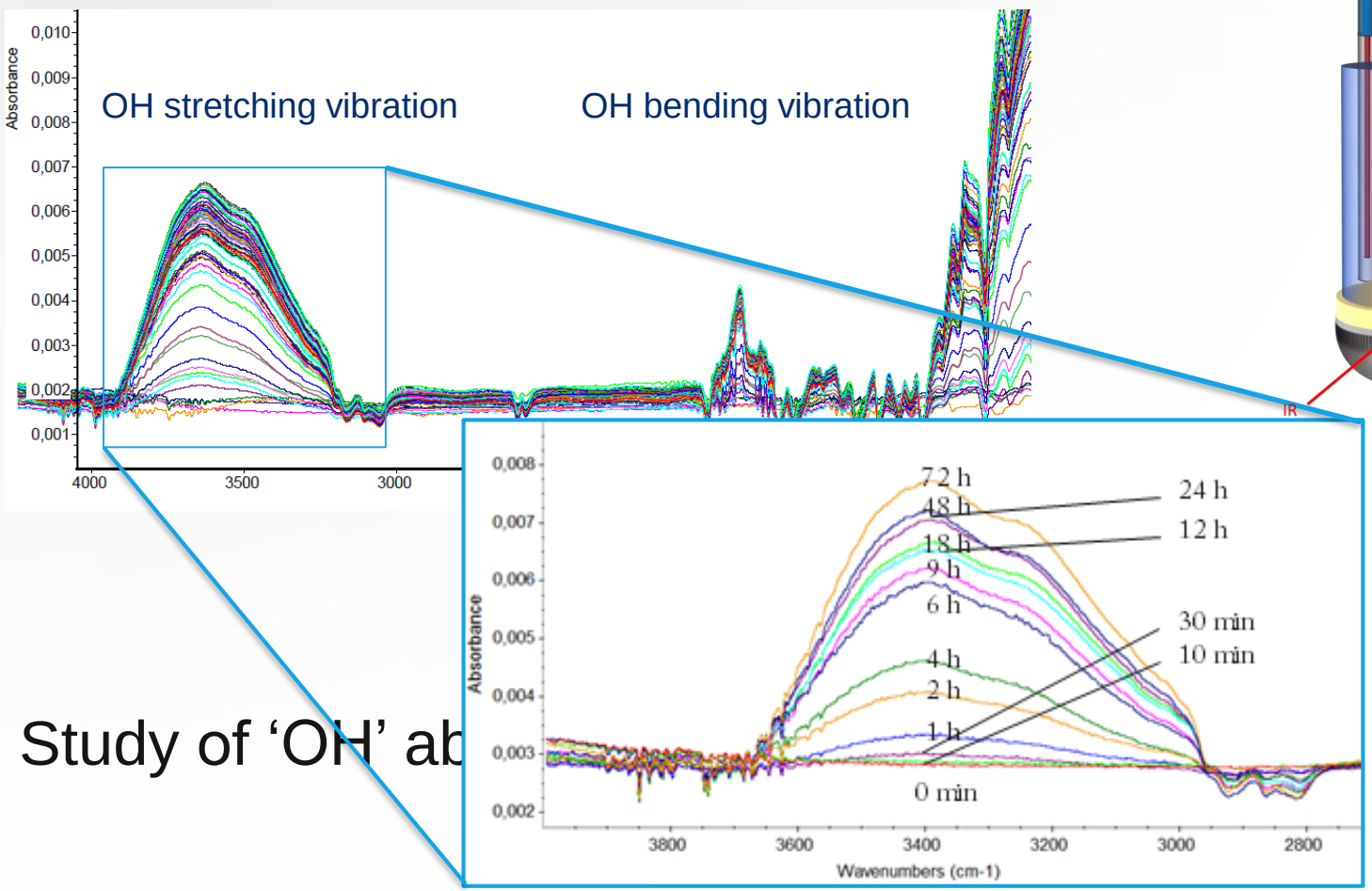


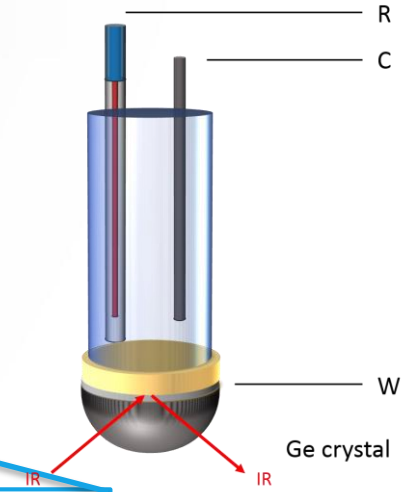


Öhman and Persson **(2007)** Electrochim. Acta, 52, 5159.

Diffusion and degradation mechanism

IR spectroscopy

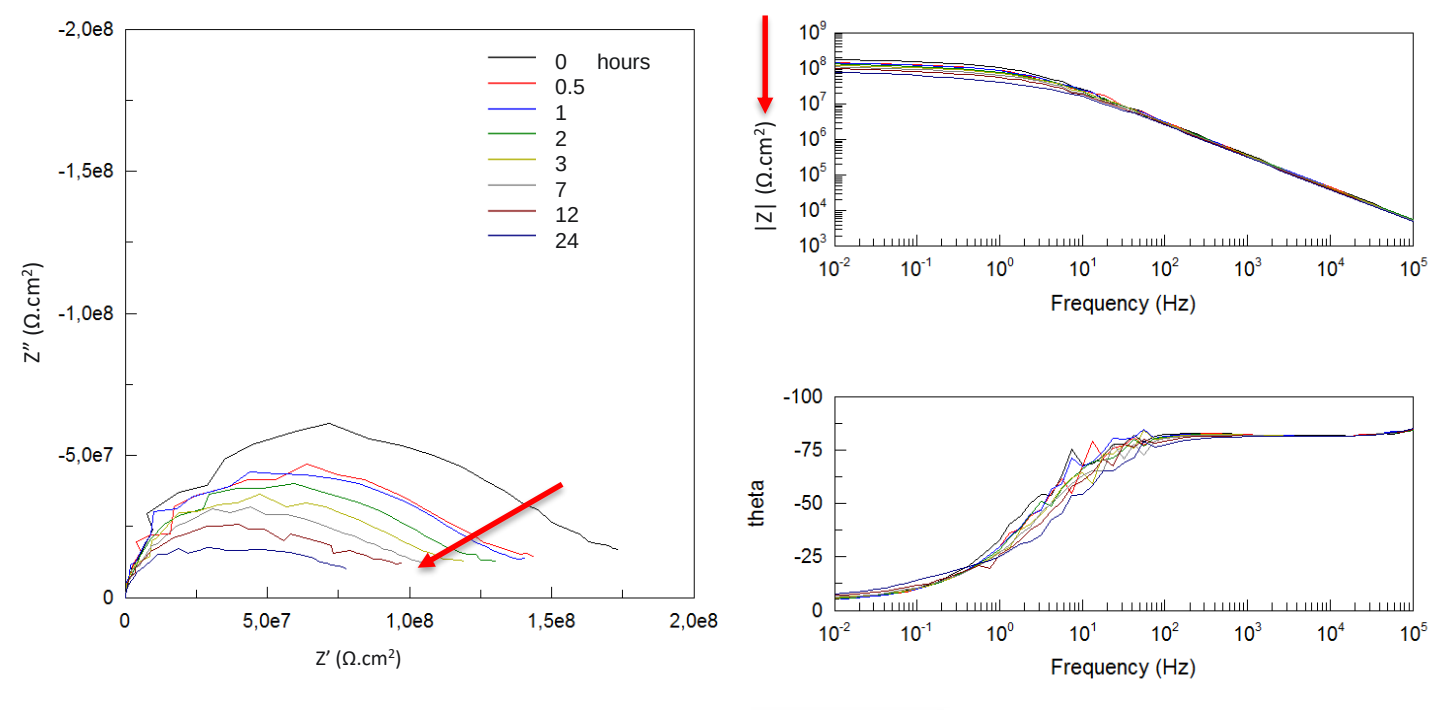




Study of ‘OH’ ab

Diffusion and degradation mechanism

Electrochemical Impedance Spectroscopy



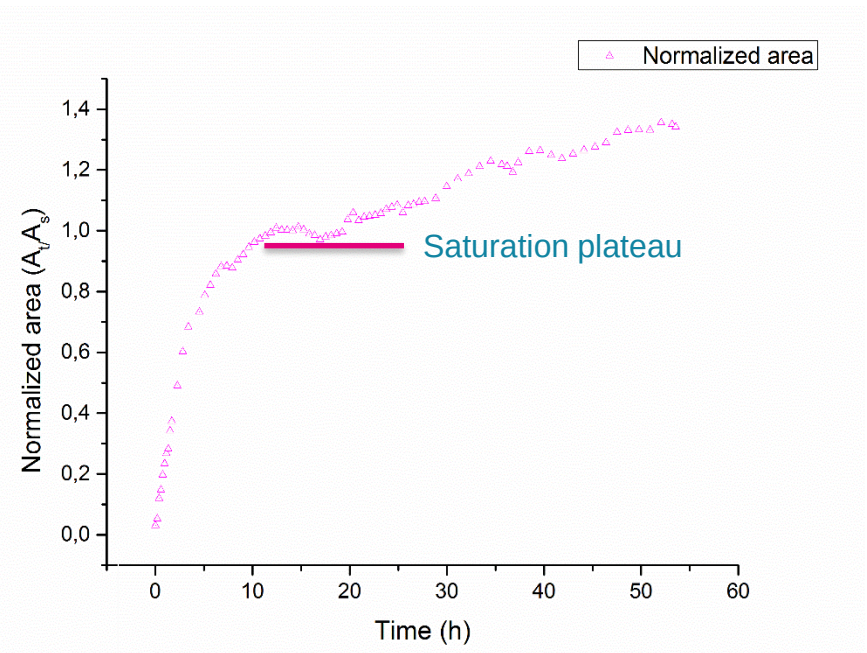
- Decrease in resistive behaviour over time
- Increase in capacitance due to water absorption

Diffusion and degradation mechanism

Normalized peak IR peak-area

Fast fickian diffusion

- Saturation plateau
- Gradual increase of water-concentration



$$\frac{A_t}{A_\infty} = 1 - \frac{8\gamma}{\pi[1-\exp(-2\gamma L)]} \times \sum_{n=0}^{\infty}\left[\frac{\exp(-D(2n+1)^2\pi^2 t/4L^2)\times\left\{(2n+1)\pi/2L\exp(-2\gamma L)+(-1)^n(2\gamma)\right\}}{(2n+1)(4\gamma^2+(2n+1)^2\pi/4L^2)}\right]$$

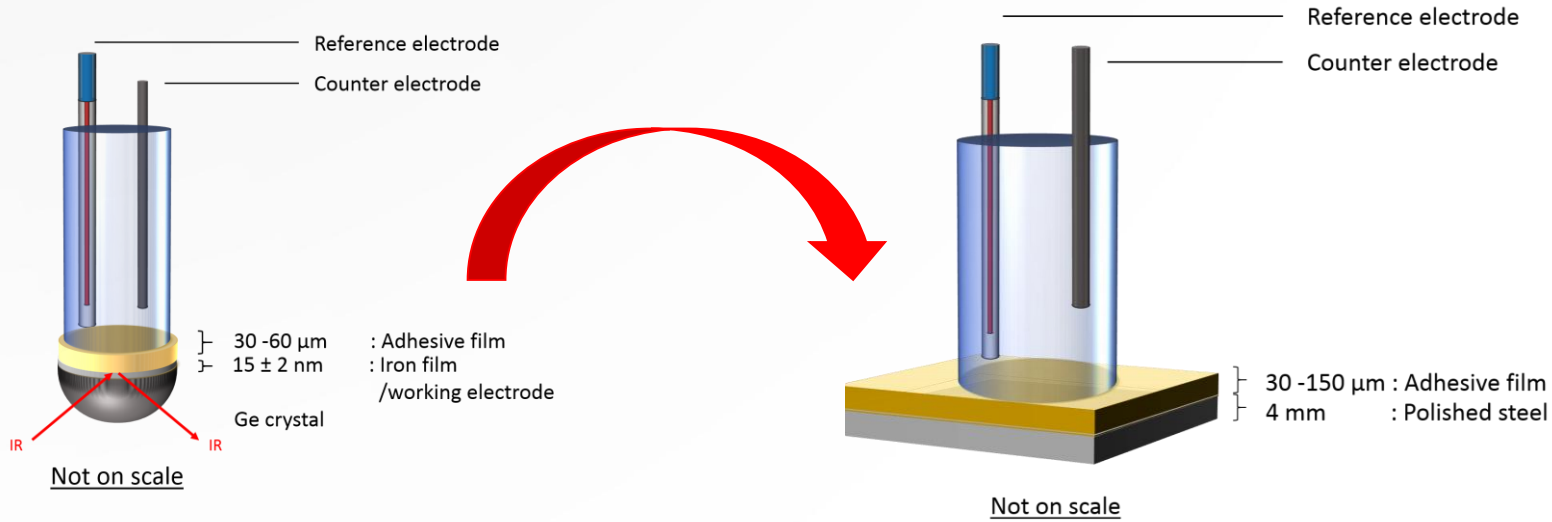
Fieldson & Barbari (1992) and Lindfjors (2011)

Diffusion and degradation mechanism

Upscale

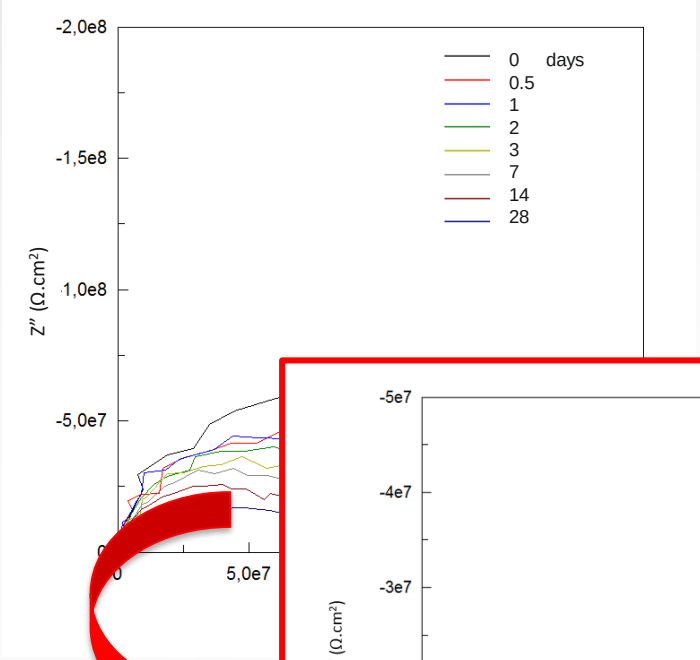
Materials

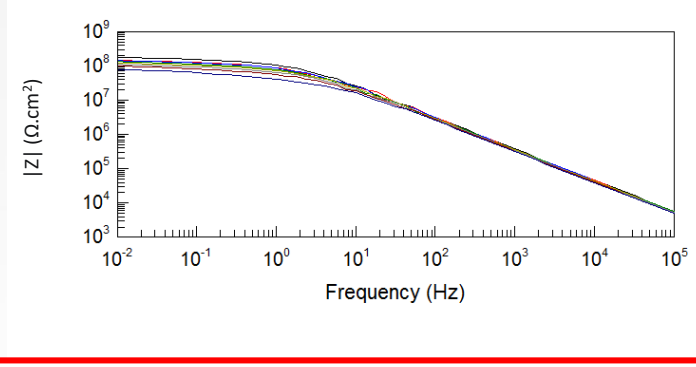
- Steel: S690 QL
- Adhesive: Araldite 2015 2k Epoxy

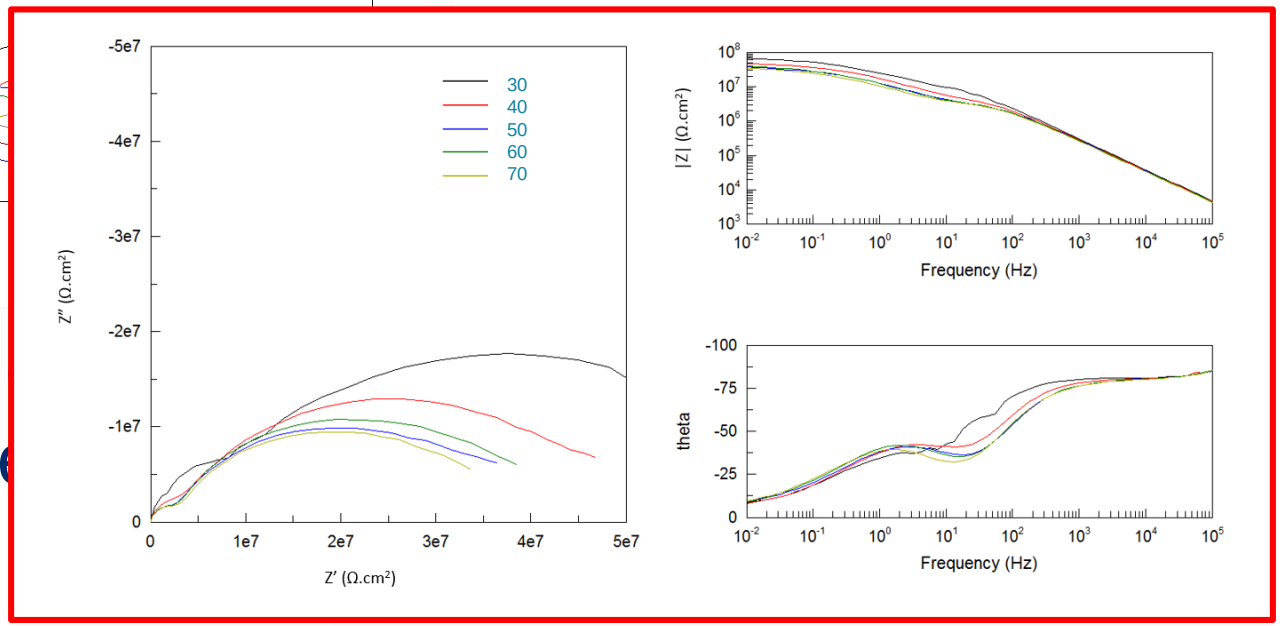


Öhman and Persson **(2007),** Electrochim. Acta, 52, 5159.

Diffusion and degradation mechanism







- Singl
- Decre

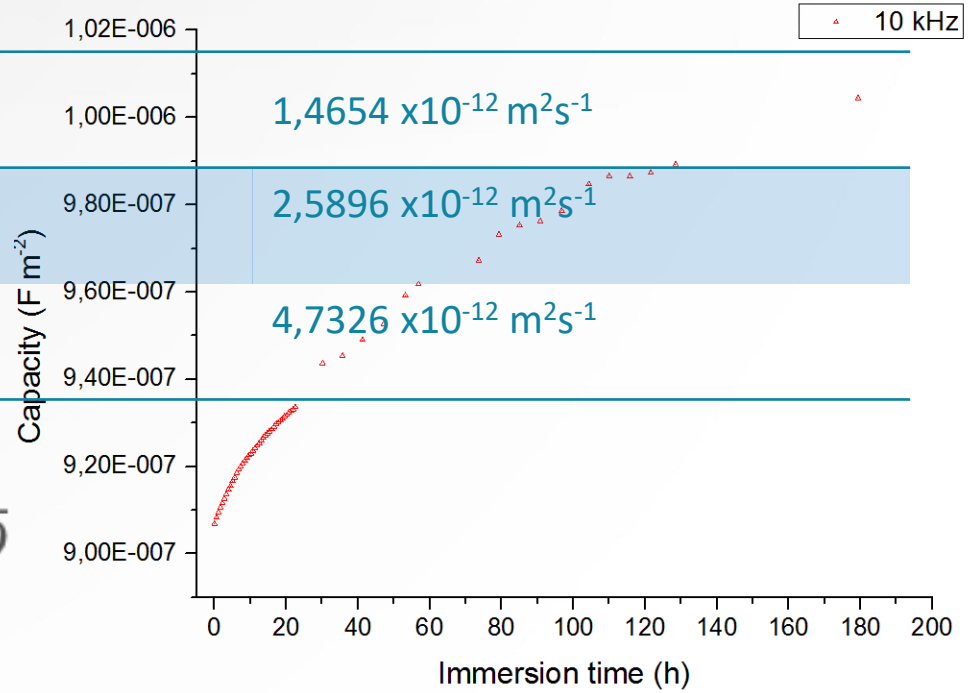
Diffusion and degradation mechanism

High-f impedance to calculate diffusion coeff.

$$C_p = \frac{1}{2\pi f Z_i}$$

$$\frac{\log C_{pt} - \log C_{p_0}}{\log C_{p\infty} - \log C_{p_0}} = \frac{2\sqrt{t}}{L\sqrt{\pi}}\sqrt{D}$$

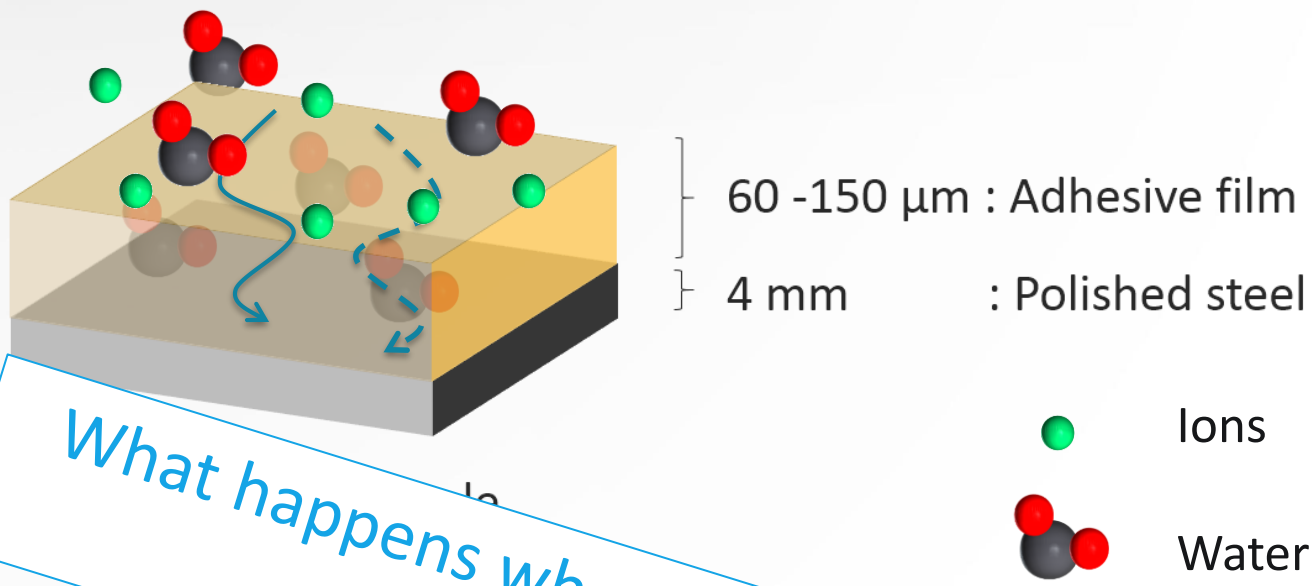
Impedance (NaCl)	1,4654 x10^{-12} m^{2}s^{-1}
ATR-FTIR (NaCl)	2,5896 x10^{-12} m^{2}s^{-1}
ATR-FTIR (DI-H_2O)	4,7326 x10^{-12} m^{2}s^{-1}



Capacitance determined in capacitive region (high f)

J.M. Hu, J.Q. Zhang, C.N. Cao, Prog. Org. Coat., 46 (2003), pp. 273-279
J.M. Hu, J.T. Zhang, J.Q. Zhang, C.N. Cao, J. Mater. Sci., 39 (2004), pp. 4475-4479

Diffusion and degradation mechanism



What happens when ions/water reach the interface?

Adhesion

Adsorption

Mechanical

Intermolecular bonds

Acid-base interactions

(incl. H-bonding)

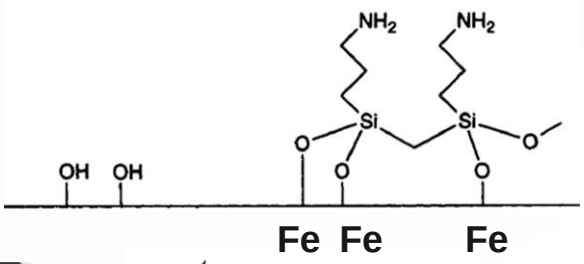
10 - 40 kJ/mol

Interatomic bonds

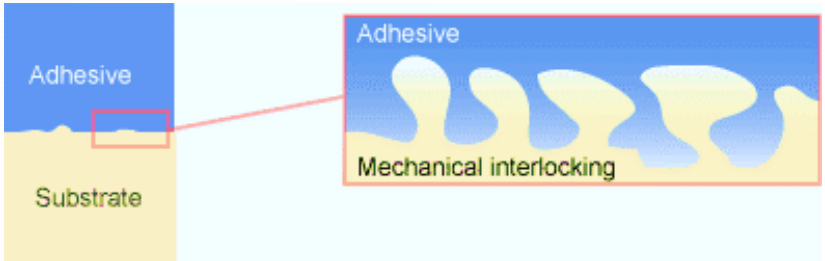
Covalent bonding

Silanes (Fe-O-Si)

60 -700 kJ/mol

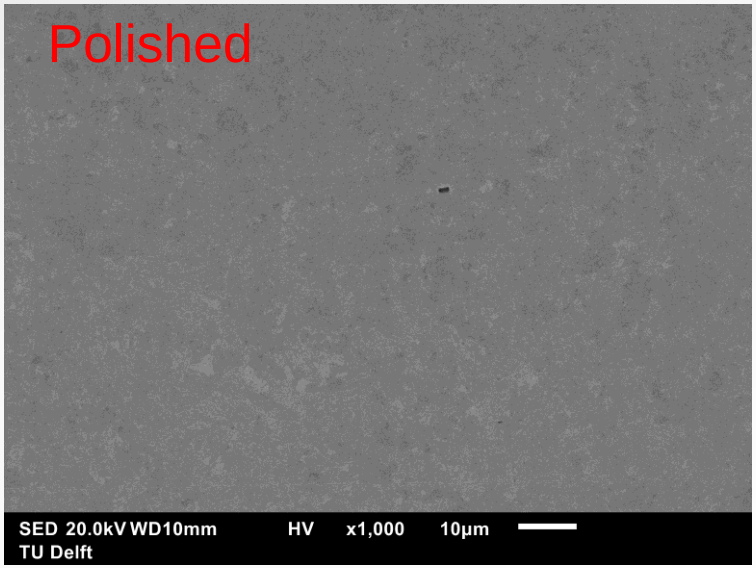


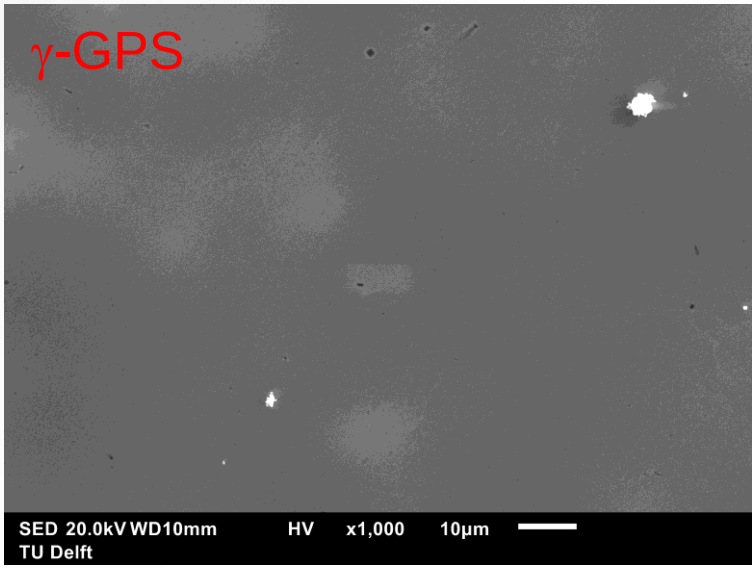
Mechanical interlocking

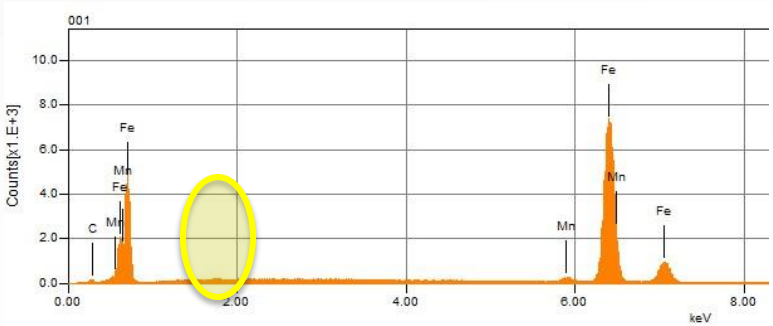


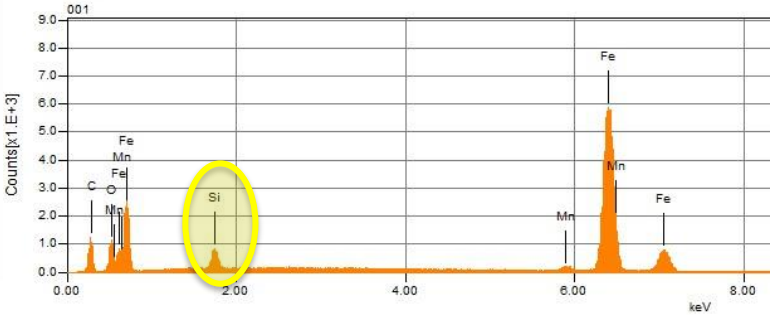
Adhesion

Surface morphology and chemistry by SEM-EDX

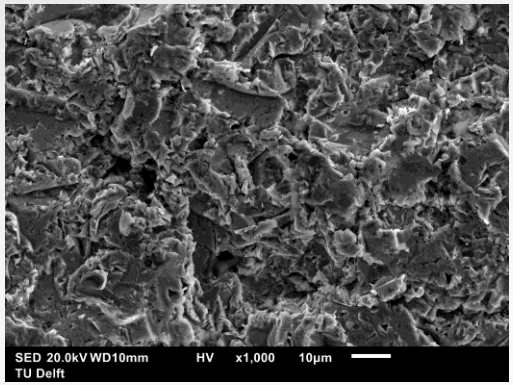




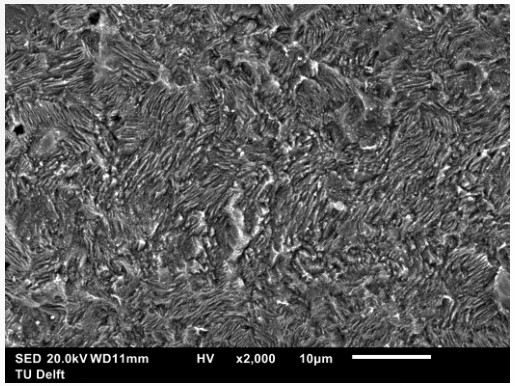




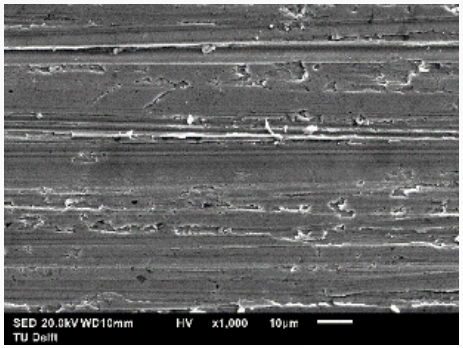
Adhesion



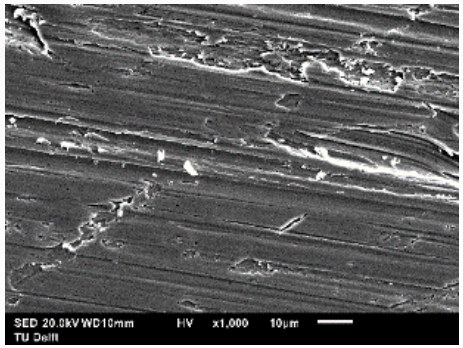
Gritblasted



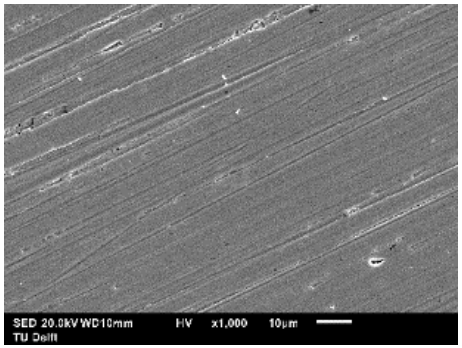
NP-etching



Sand #180
Ø ~ 82 µm



Sand #320
Ø ~ 48 µm



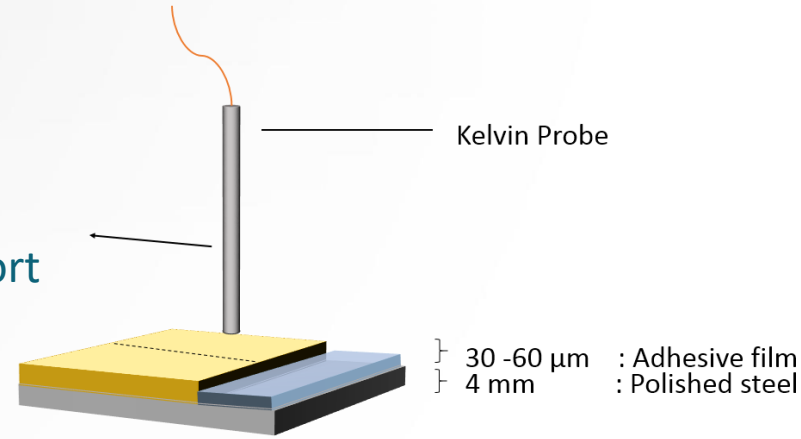
Sand 800
Ø ~ 24 µm

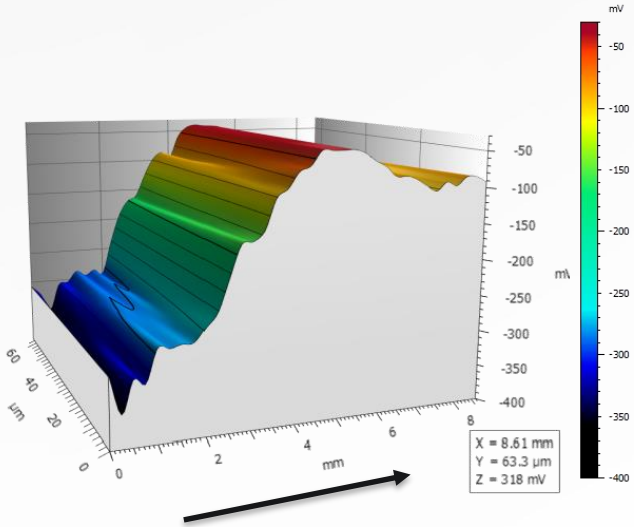
Adhesion

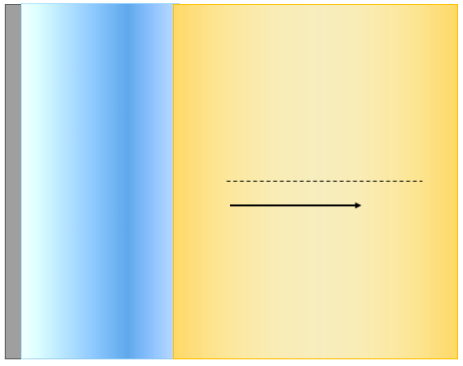
Exposed interface

Scanning Kelvin Probe (SKP)

- Artificial electrolyte reservoir
- Laterally resolved interfacial water transport
- Environment ~ 93% RH



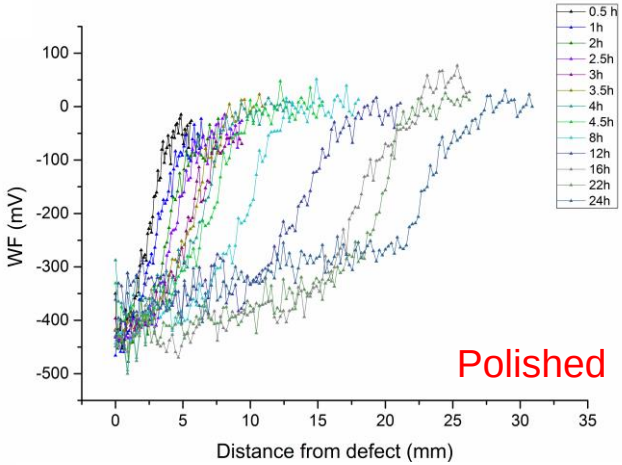


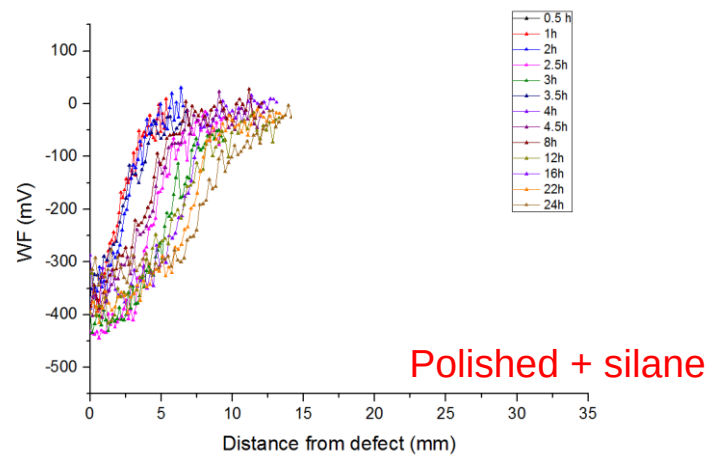


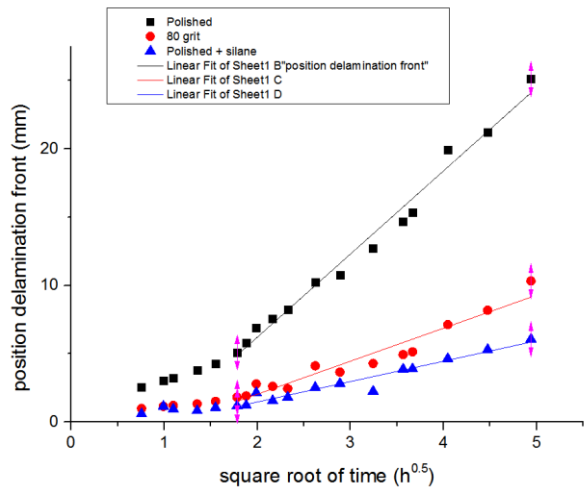
Artificial defect with electrolyte

Adhesion

Interfacial stability - SKP







RH = 93%; 3.5 wt% NaCl

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	7.60795	5.17053	1.80033
Pearson's r	0.99213	0.96736	0.97002
Adj. R-Square	0.9829	0.92994	0.93558
		Value	Standard Error
position delamination front	Intercept	-5.94996	0.74172
	Slope	6.08637	0.23157
C	Intercept	-2.78983	0.61147
	Slope	2.41686	0.1909
D	Intercept	-1.50782	0.36081
	Slope	1.49138	0.11265

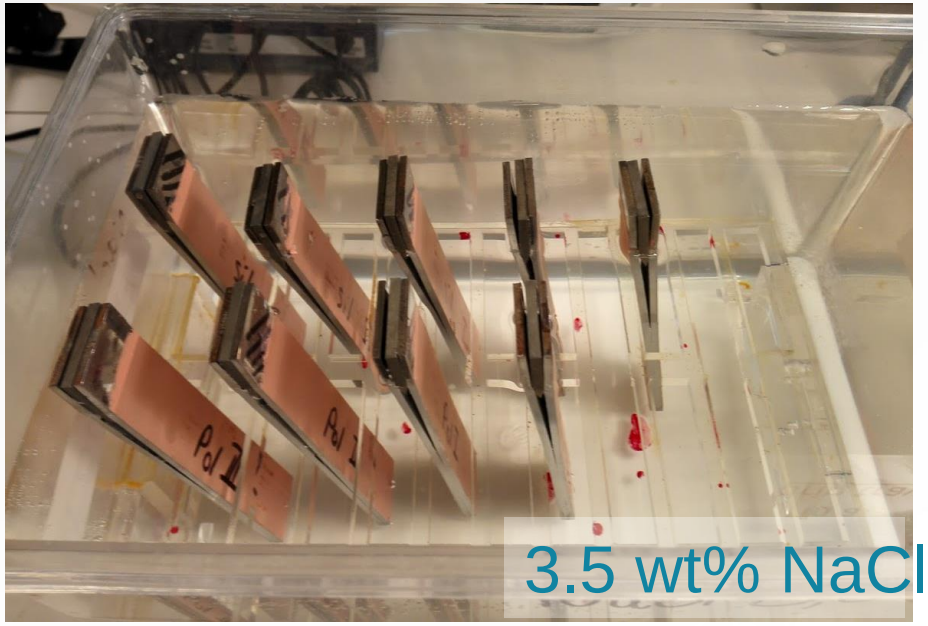
- 60.3%

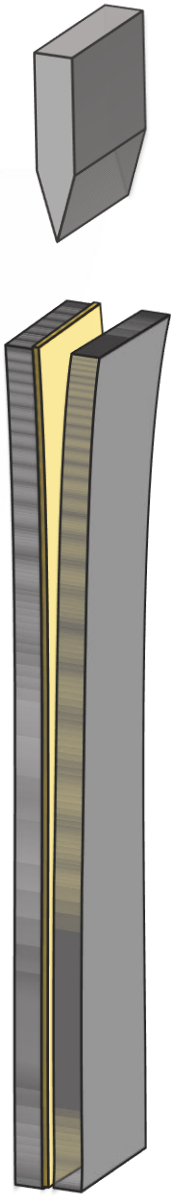
- 75.5%

Adhesion

Static Wedge test

- Moisture and corrosive durability of interface
- Opening mode load
- Crack length and fracture energy over time



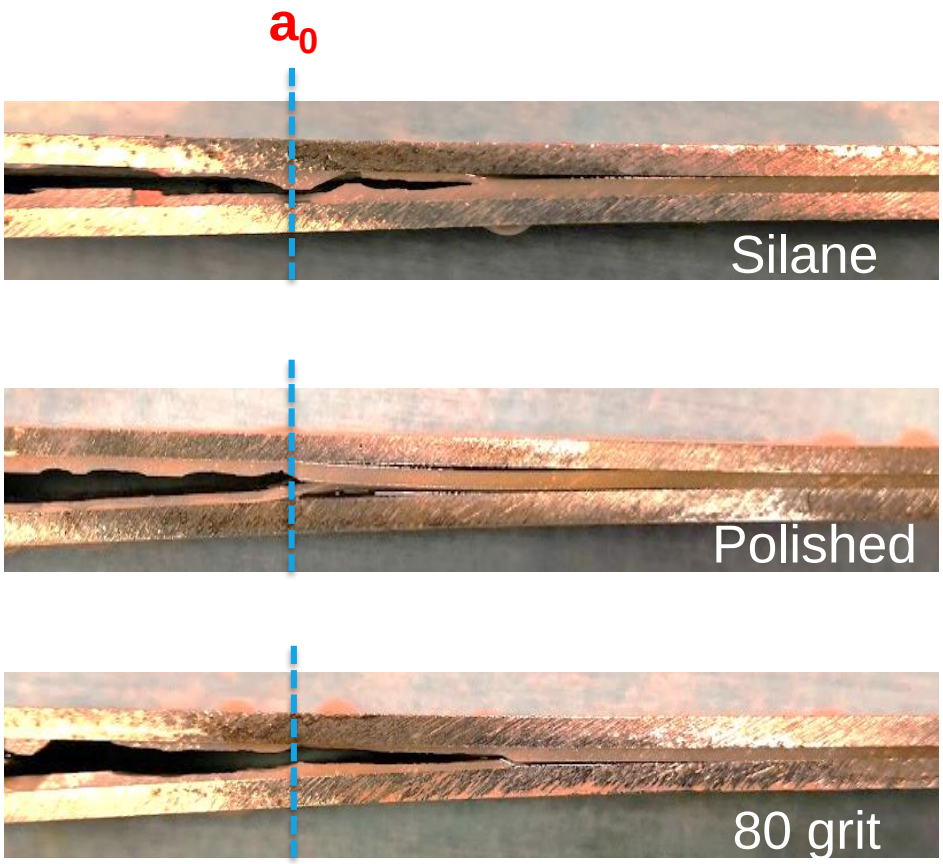


Adhesion

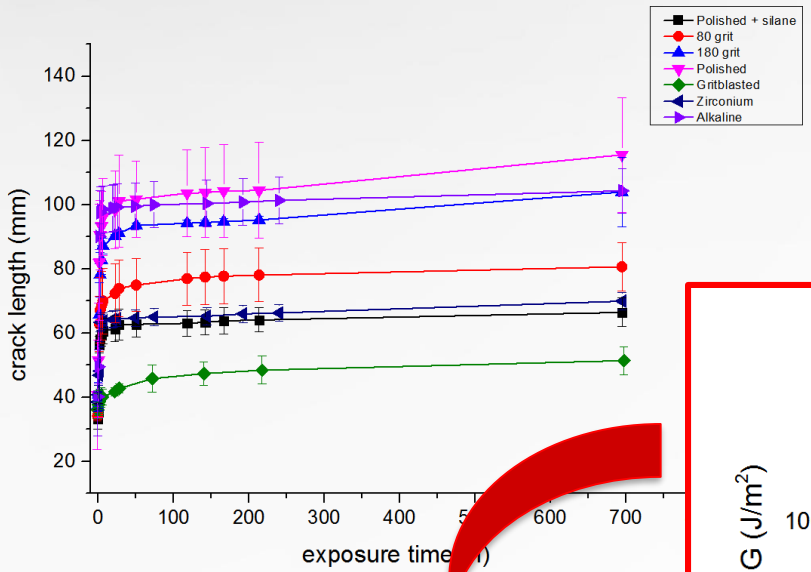
Static Wedge test

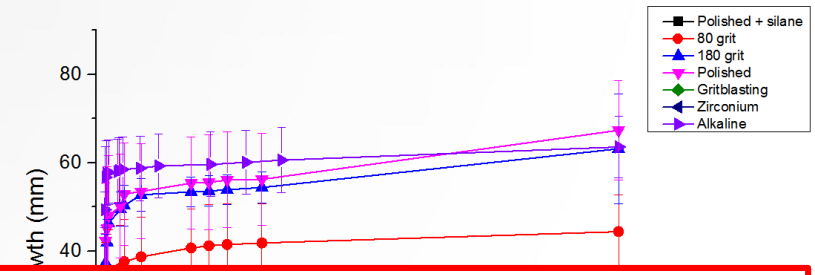
Crack propagation paths

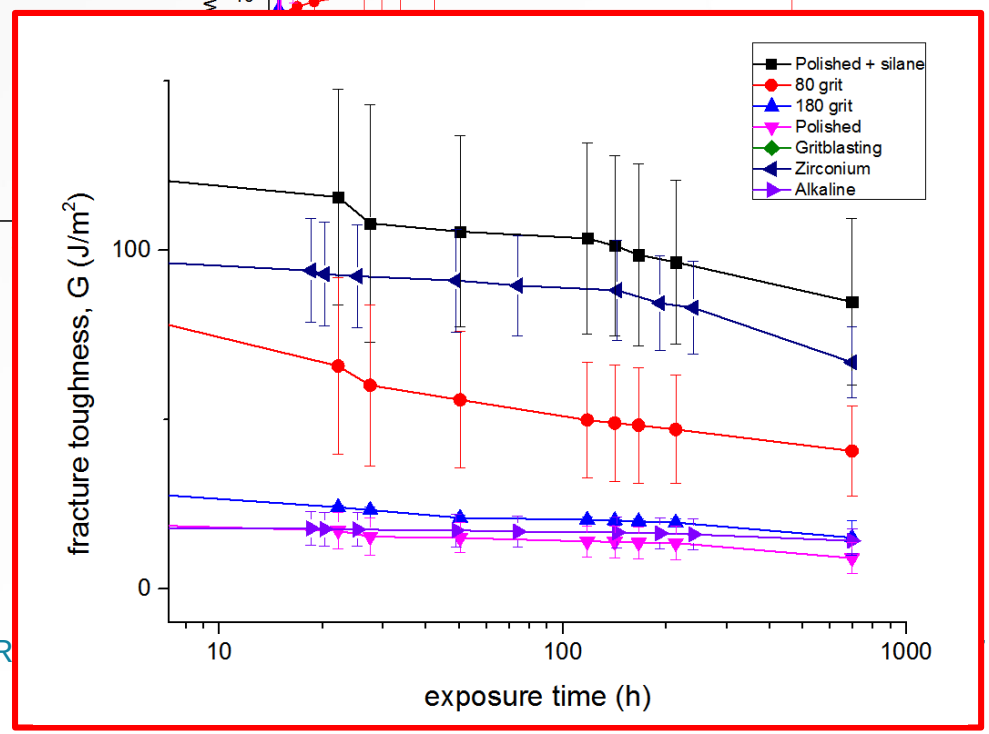
- Initial cohesive failure in all 3 cases
- Crack jumps to interface or remains in adhesive
- In the end (near-) interfacial failure dominates



Adhesion







$$G_I = \frac{Y^2 \times E \times h^3[3((a+0.6h)^2 - h^2)]}{16[(a+0.6h)^3 + a \times h^2]}$$

Y = crack opening displacement
h = adherend thickness
E = Young's Modulus
a = crack length

N. Brack, A.N. R

Conclusion

Kretschmann geometry enables us to assess diffusion towards interface

- Fast diffusion of water, followed by ions
- Buried interface is stable

Combination of SKP and SWT proof importance of stable interface

Promoting interatomic/intermolecular bonding shows large improvement of durability of adhesion

Behaviour of loaded and unloaded systems directly related to eachother

Approach provides tools to translate information from small- to large scale

Acknowledgement

This research is carried out under the ***Durabond*** project in the framework of the research program of the Materials innovation institute M2i (www.m2i.nl)

Thank you

materials innovation institute

NWO Toegepaste en Technische Wetenschappen

TU Delft