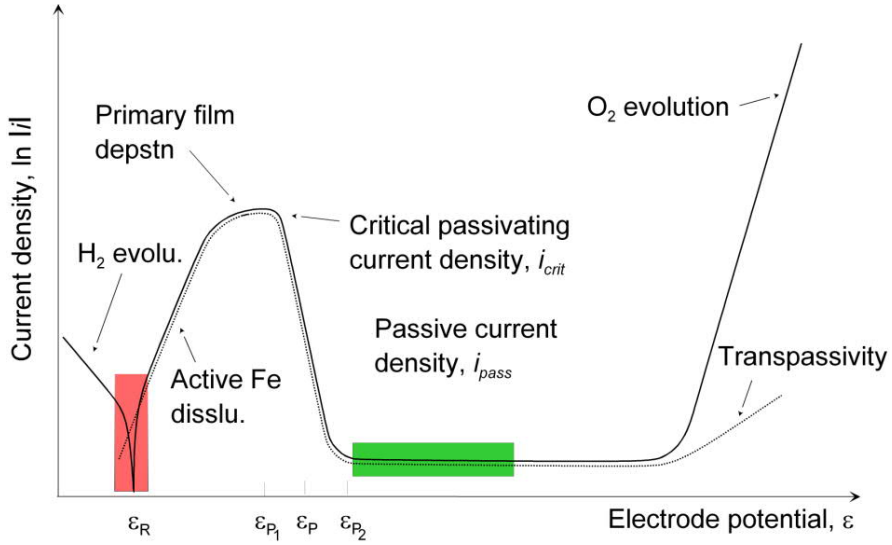
MAX-PLANCK-INSTITUT
FÜR EISENFORSCHUNG GmbH

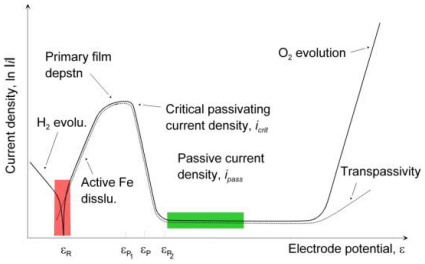
Fundamental Aspects of Coating Delamination: Old Beliefs and New Insights

Michael Rohwerder

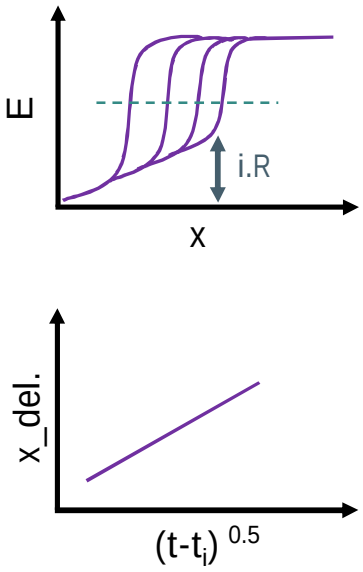
Beschichtungsprüfung heute für den Korrosionsschutz von morgen- GfKorr

SKP AND DELAMINATION



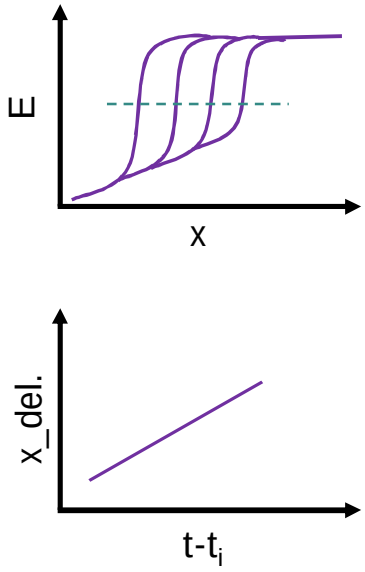


BACKGROUND



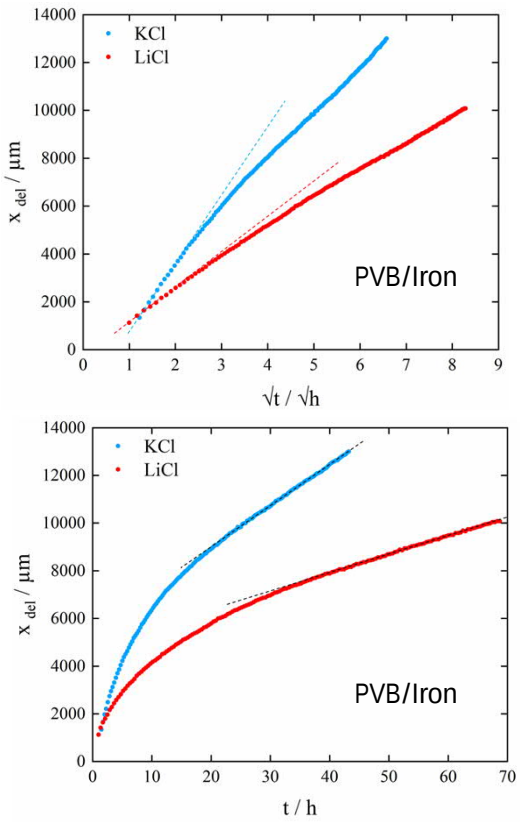
$x(t) = k(t-t_i)^{0.5}$

Cation migration controls delamination kinetics



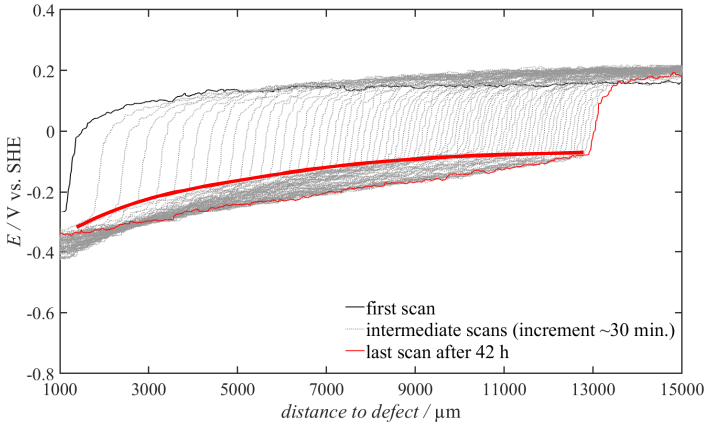
$x(t) = k(t-t_i)^{1}$

Oxygen Reduction Reaction (ORR) controls kinetics

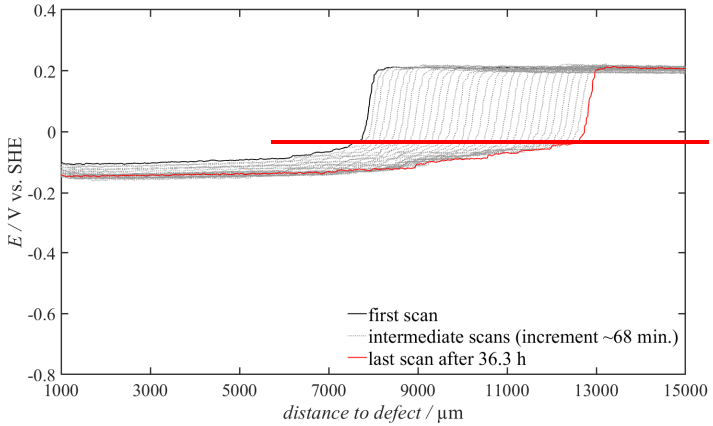


SKP AND DELAMINATION

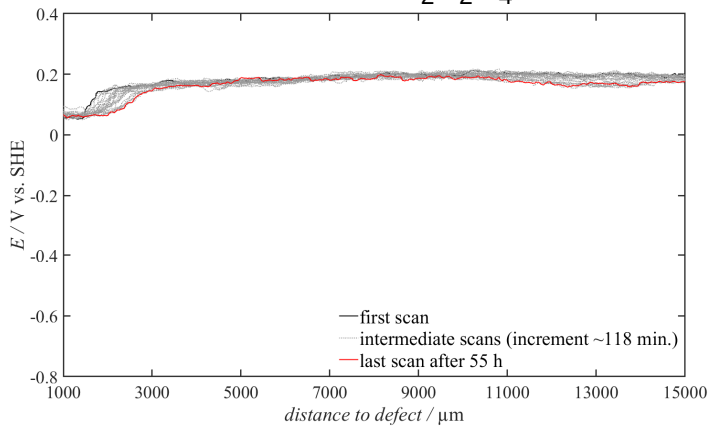
PVB- 1 M KCl



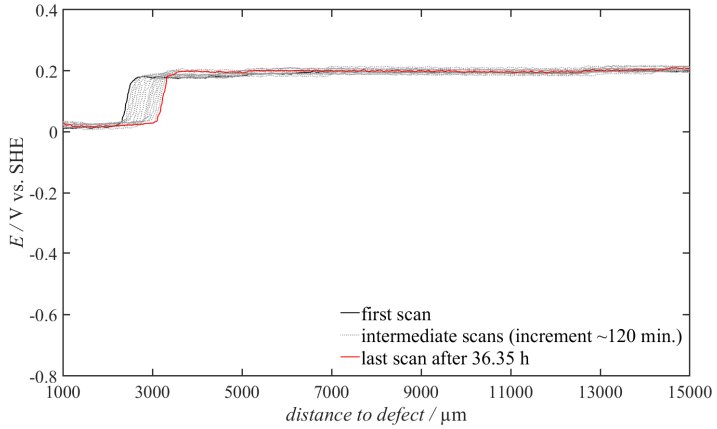
PVB- 0.05 M KCl

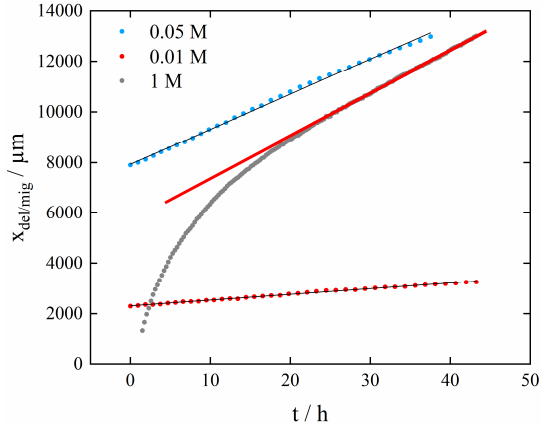


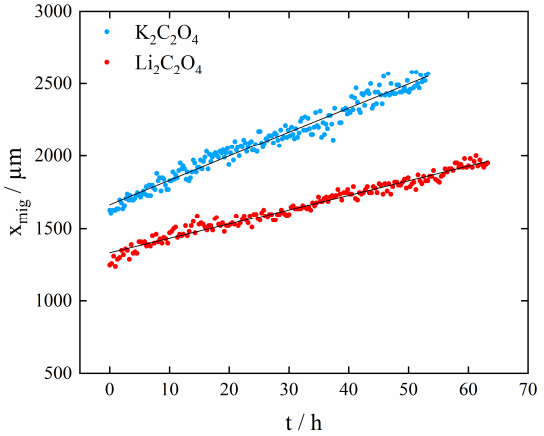
PVB- 0.5 M $K_2C_2O_4$



PVB- 0.01 M KCl



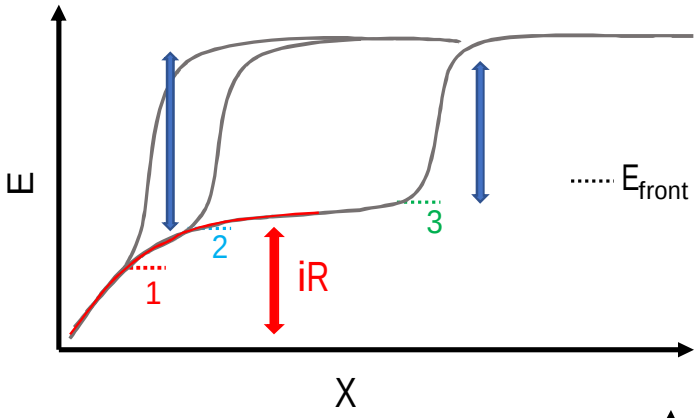




N. Khayatan, M. Rohwerder, A new insight into the rate determining step of cathodic delamination, Corrosion Science 202 (2022) 110311.

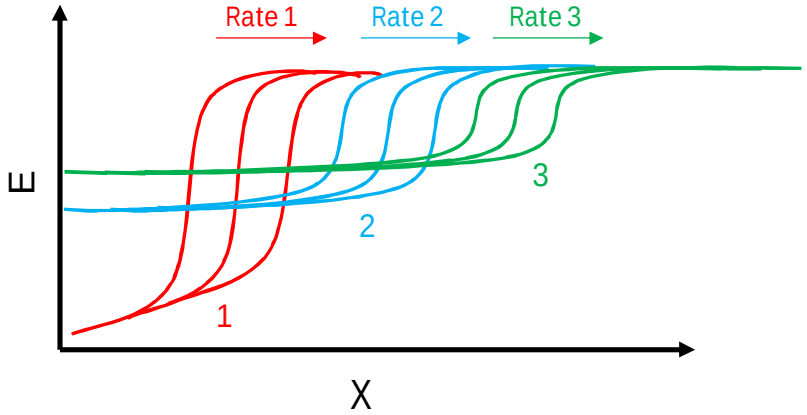
CORRELATION BETWEEN DEL. RATE AND DEL. FRONT POTENTIAL

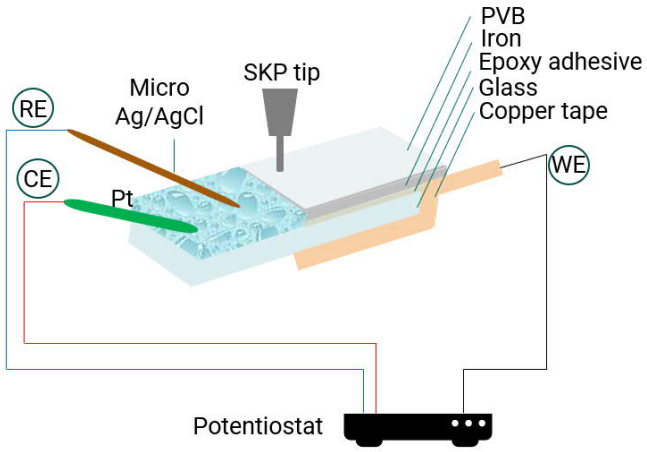
Conventional delamination experiment:

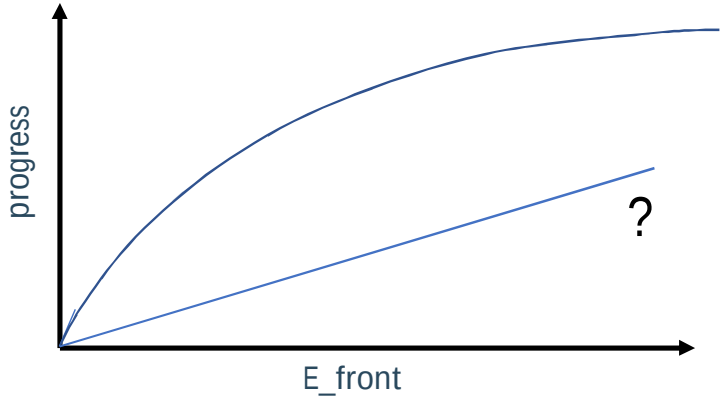


Potential controlled experiment:

go to higher potentials ➔ inhibit ORR







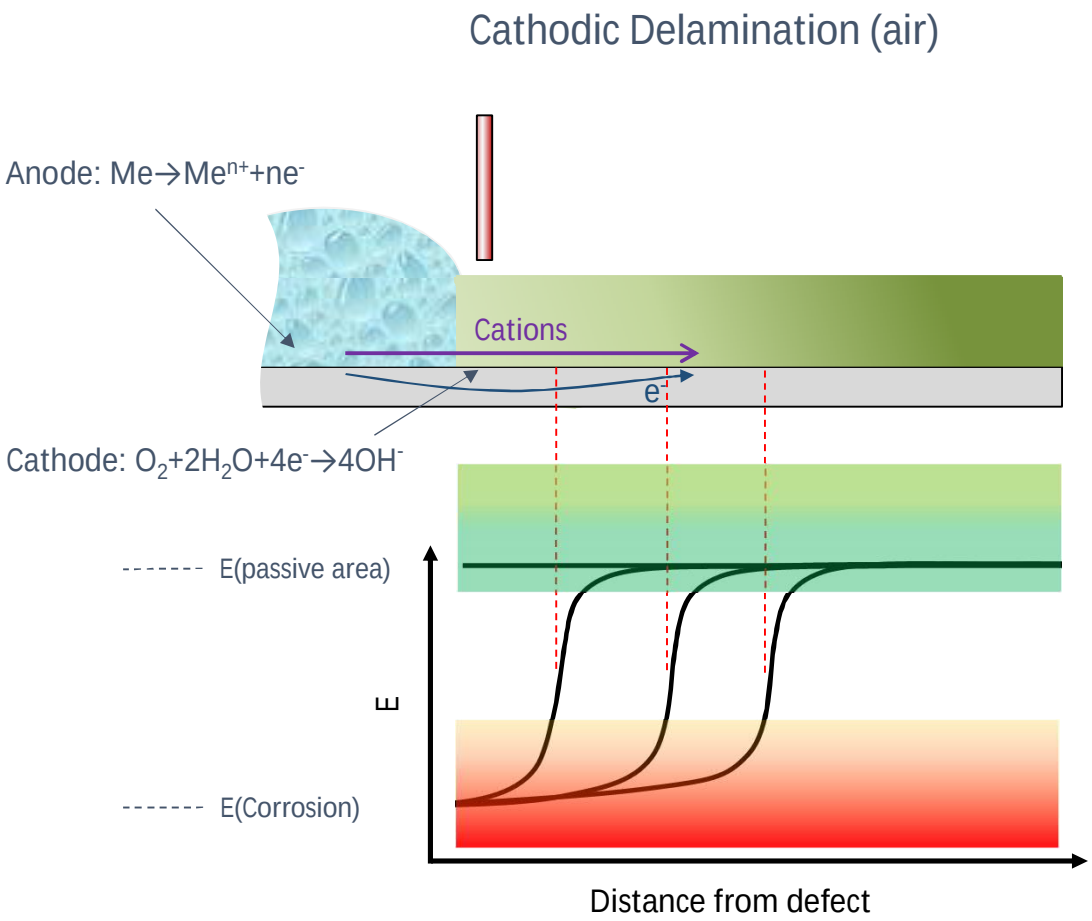
State of the art:

sqrt(t) : cation migration is rds

linear: ORR or degradation kinetics rds

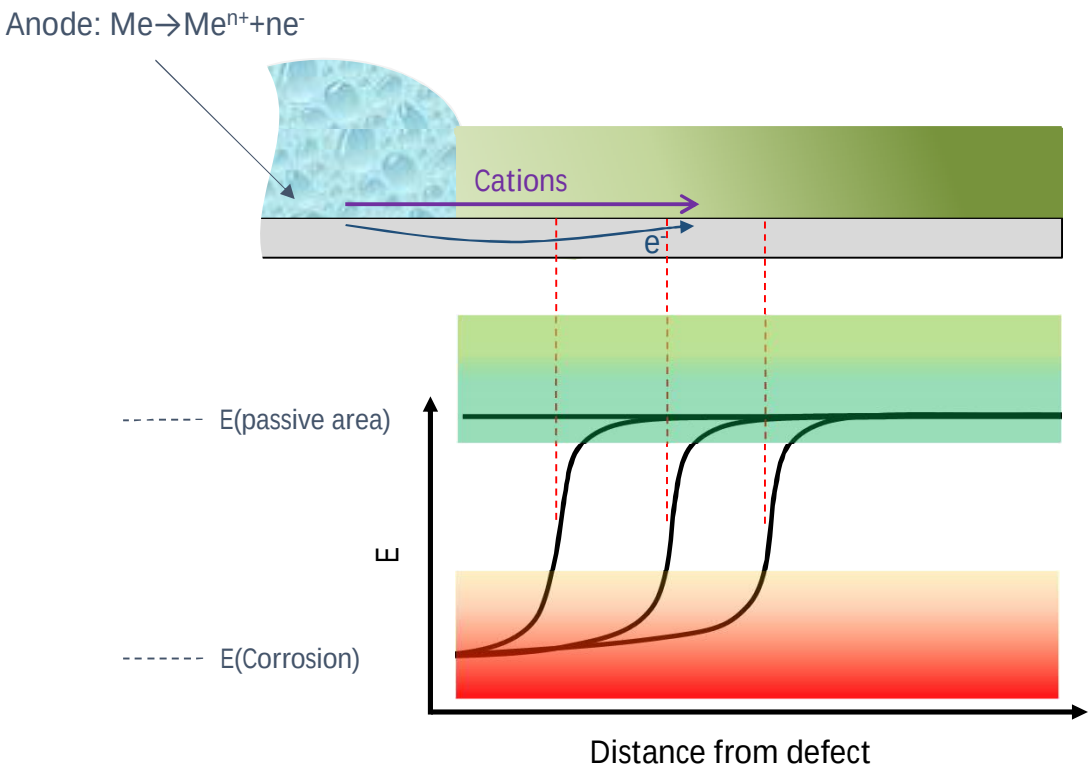
N. Khayatan

SKP AND DELAMINATION

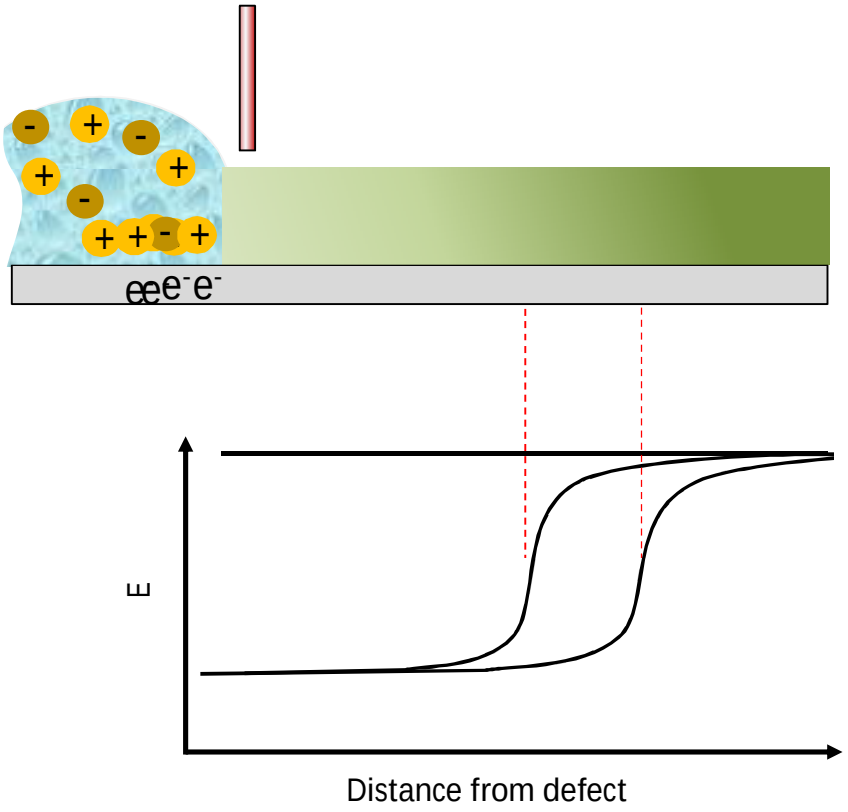


SKP AND DELAMINATION

Cathodic Delamination (air)

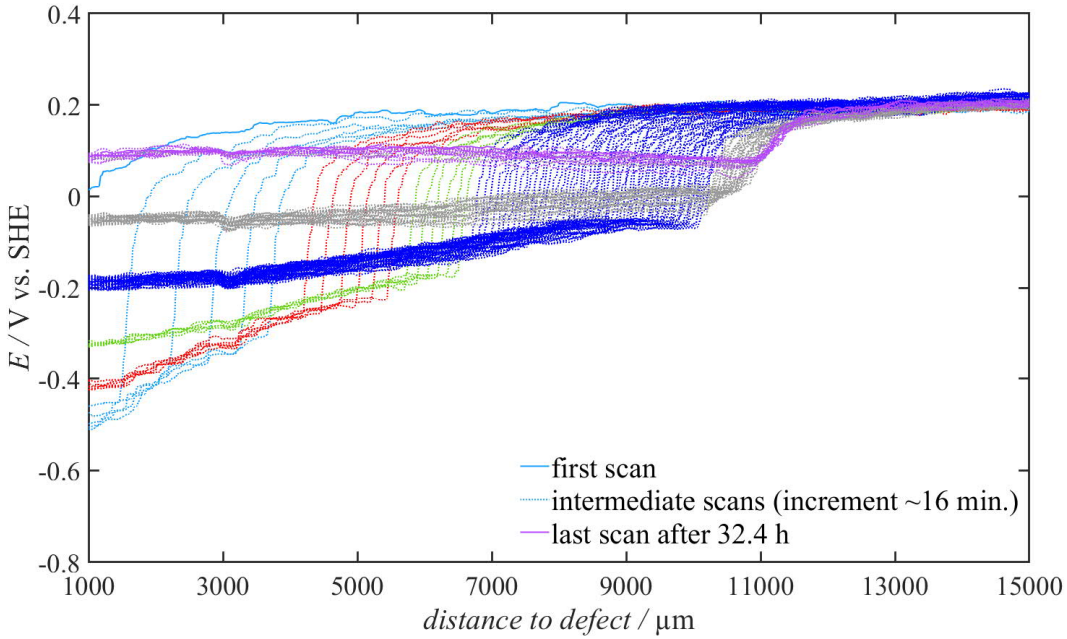


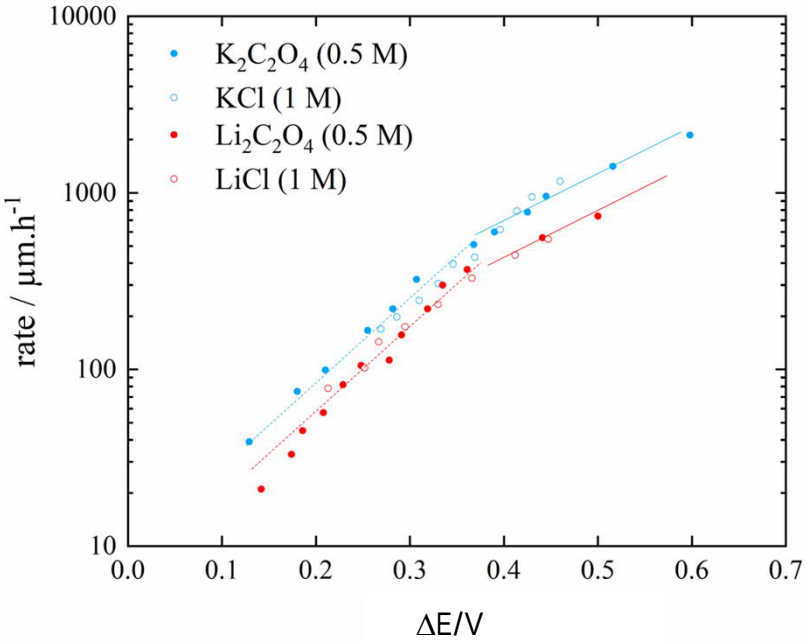
Cation Migration (nitrogen)



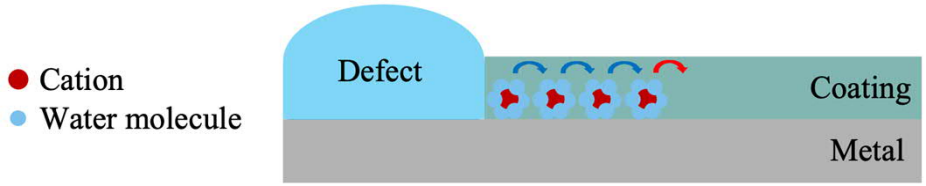
for coated steel: no case of delamination caused by free corrosion
known where migration occured without direct delamination

CORRELATION BETWEEN DEL. RATE AND DEL. FRONT POTENTIAL





Khayatan et al., submitted



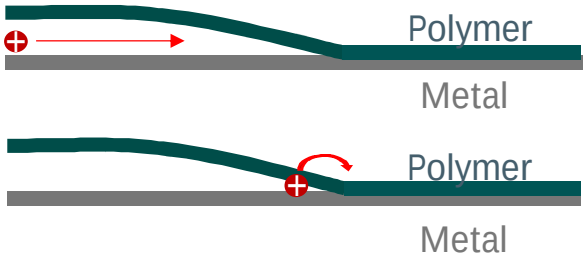
cation insertion rate determining, changes the mobility at the interface/on the surface

N. Khayatan

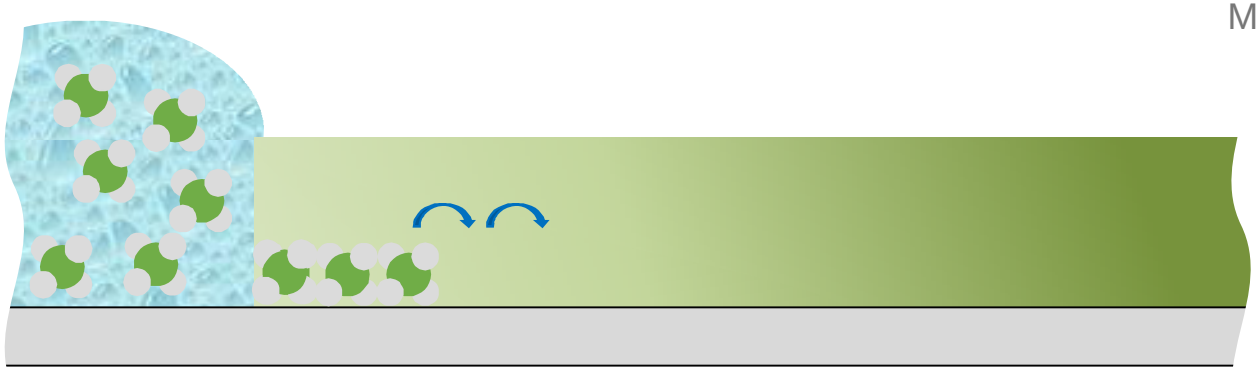
Results & Discussion

Old theory: Cation migration from the defect to the delamination front is rate determining

New hypothesis: Insertion of cation at the front is rate determining

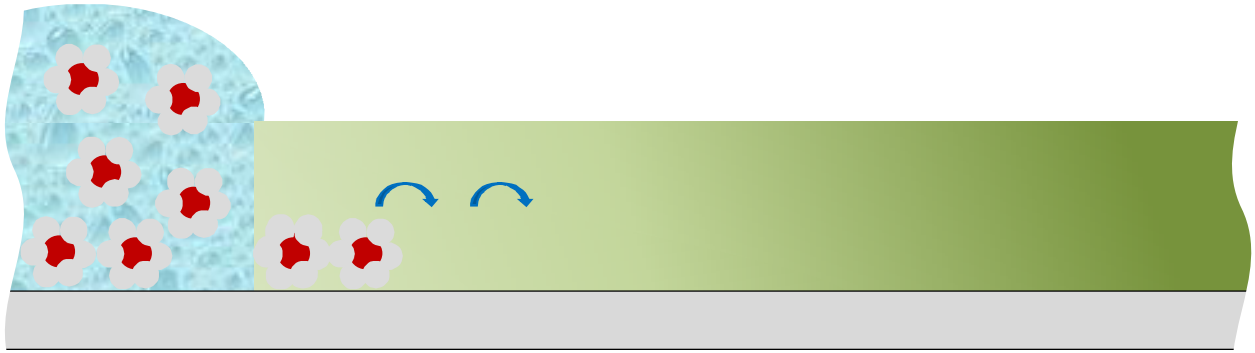


Cation
Cation
Water



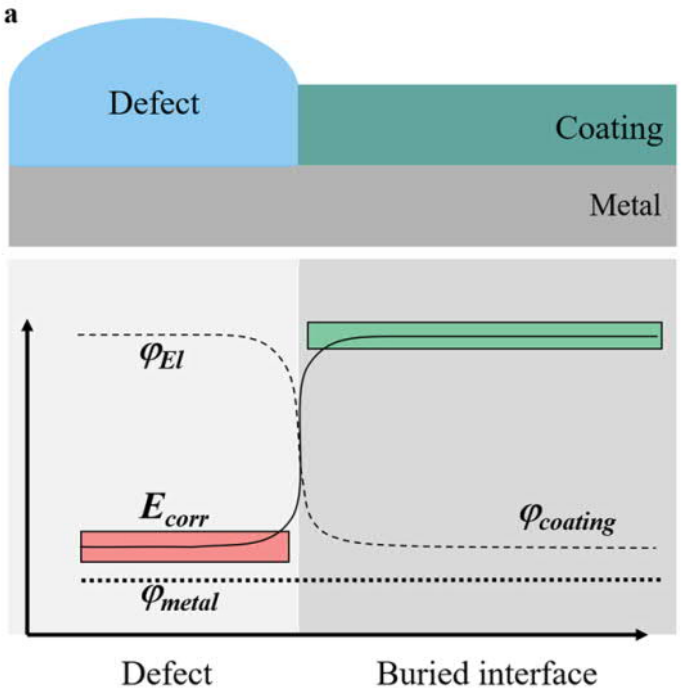
Bigger hydrated cation

Slower insertion



CORRELATION BETWEEN DEL. RATE AND DEL. FRONT POTENTIAL

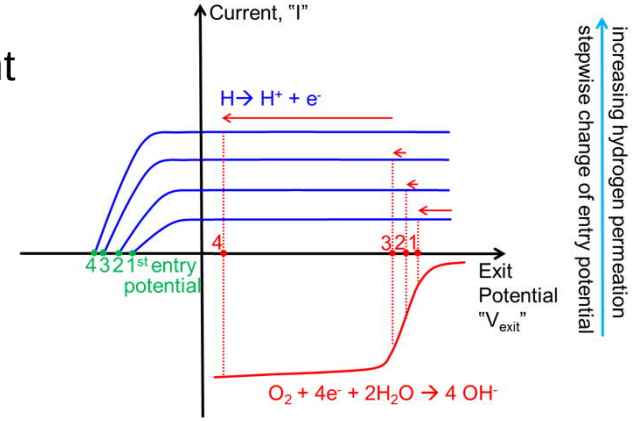
N. Khayatan, M. Rohwerder, A new insight into the rate determining step of cathodic delamination, Corrosion Science 202 (2022) 110311.

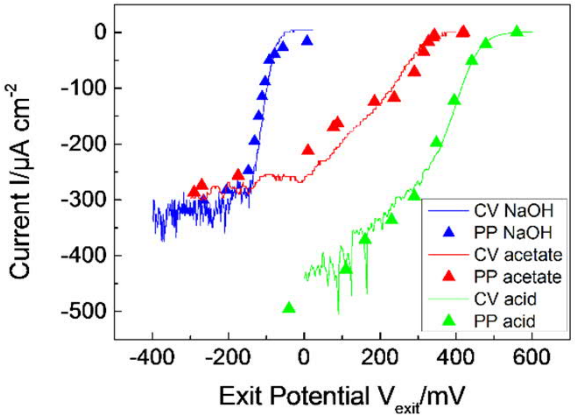


role of ORR?

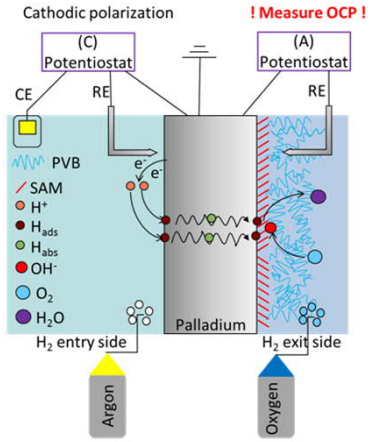
MEASURING ORR AT THE BURIED COATING/METAL INTERFACE

- At equilibrium, hydrogen entry side permeation current is equal to ORR current
- Dynamic electrochemical equilibrium potential established at exit side between ORR and hydrogen oxidation



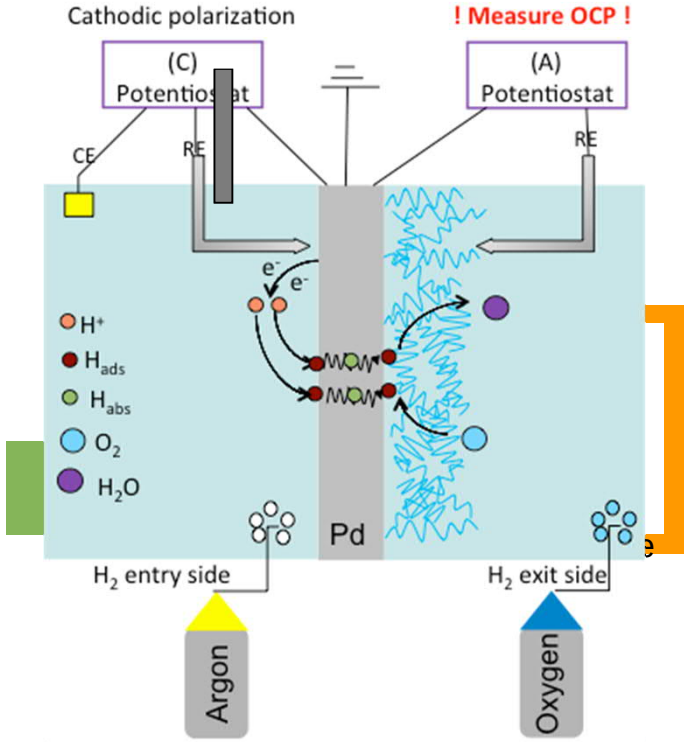


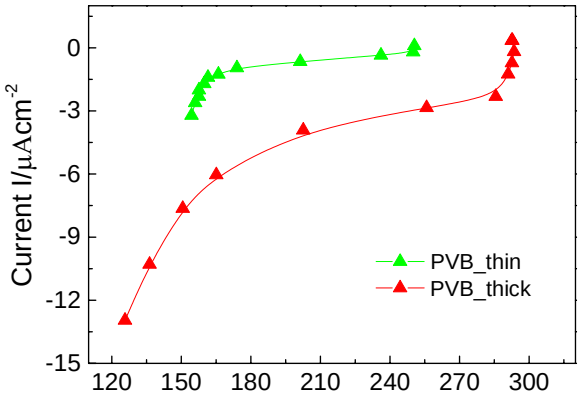
- Sound match between I(U) curve from permeation based potentiometry (pp) and cyclic voltammetry for bare Pd



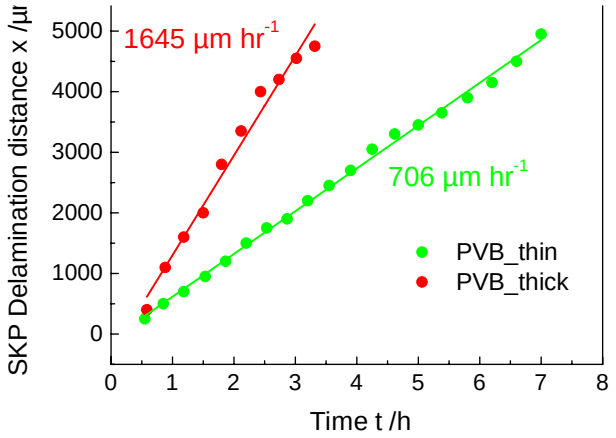
Vijayshankar et al., Electrochim. Acta 189 (2016) 111-117

CORRELATING DELAMINATION KINETICS AND ELECTROCHEMICAL ACTIVITY AT TAILORED INTERFACES





no exception found so far for any coating on steel

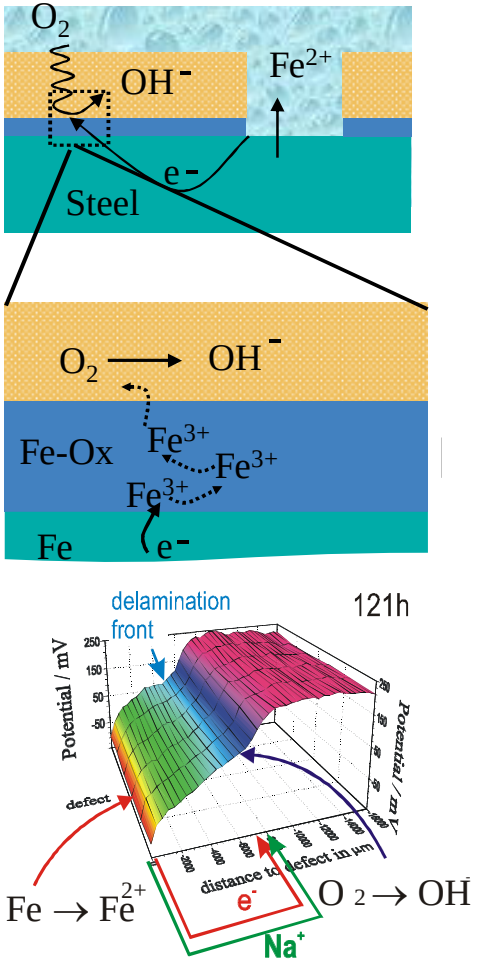


- Earlier onset of ORR for PVB_thick
- Corresponding higher delamination rate with the SKP
- i.e. slower delamination correlates with lower ORR rates; however, now we know: not rds

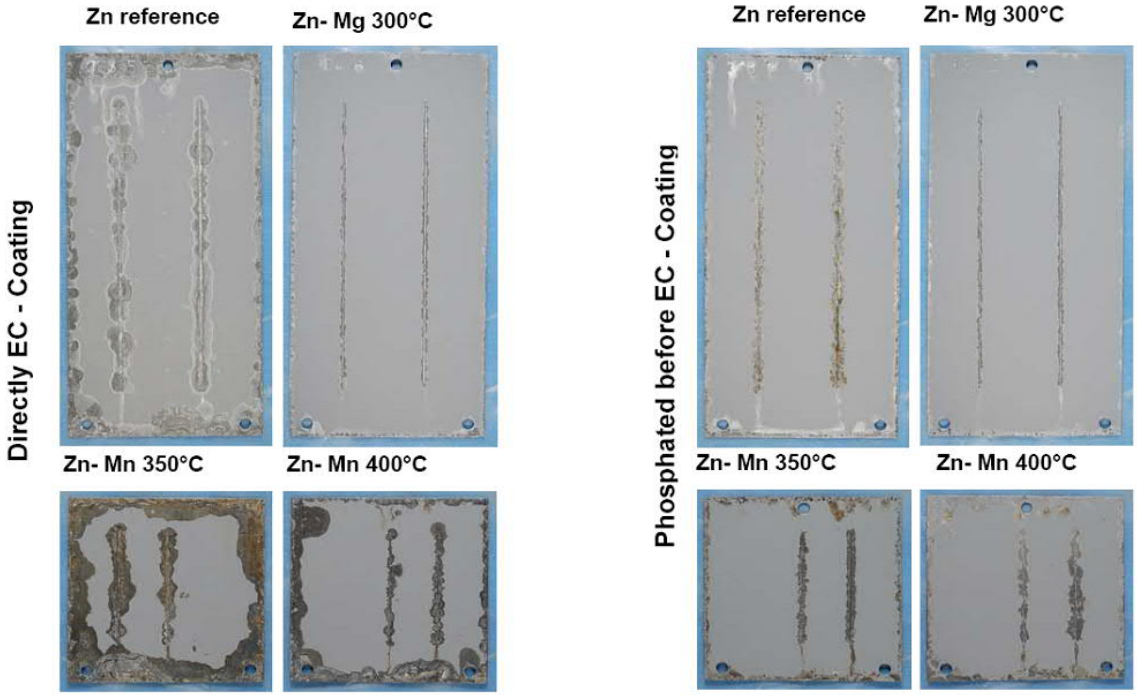
Vijayshankar et al., JES 163 (2016) C778-C783

INFLUENCE OF MATERIAL ON DELAMINATION MECHANISM

Steel

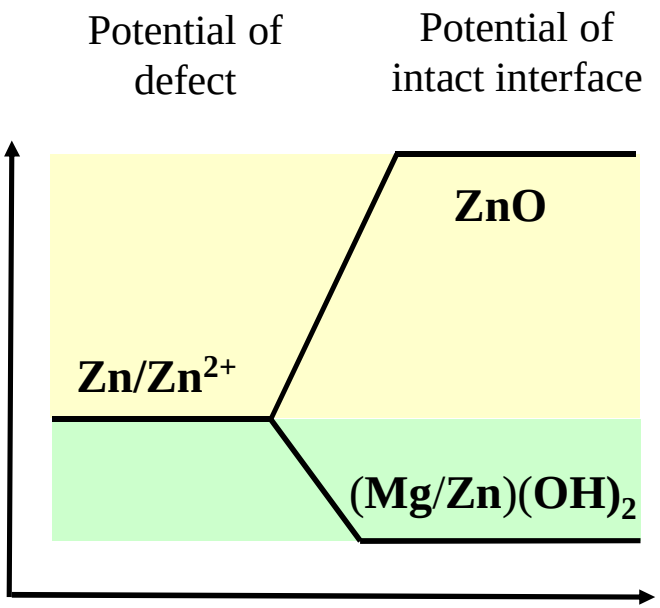


Industrial tests: delamination from scribe

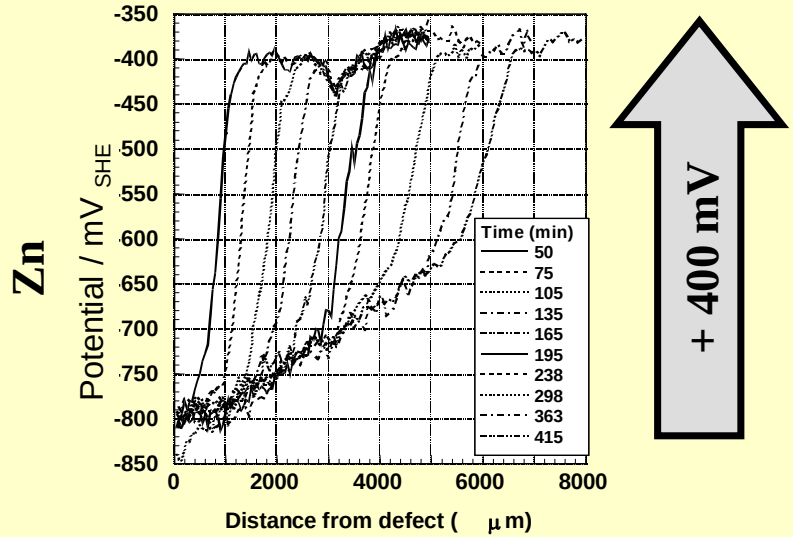


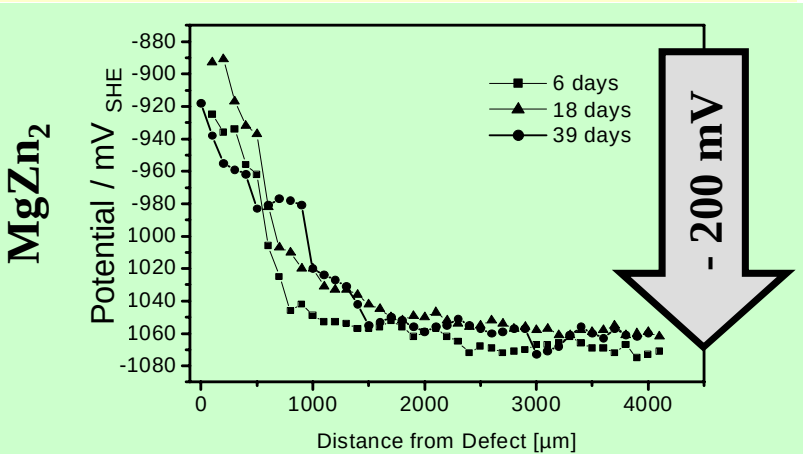
Photos after 10 cyclic VDA 621-415 (CCT) of Zn-Mn (0,5µm PVD Mn on 7.5 µm EG diffusion annealed at 350 and 400°C) and Zn-Mg (0.5µm PVD Mg on 7.5 µm EG diffusion annealed at 300°C) diffusion alloy coating material

Potential differences as driving forces



Formation of local cathode at the delamination front impeded due to unusual potential difference

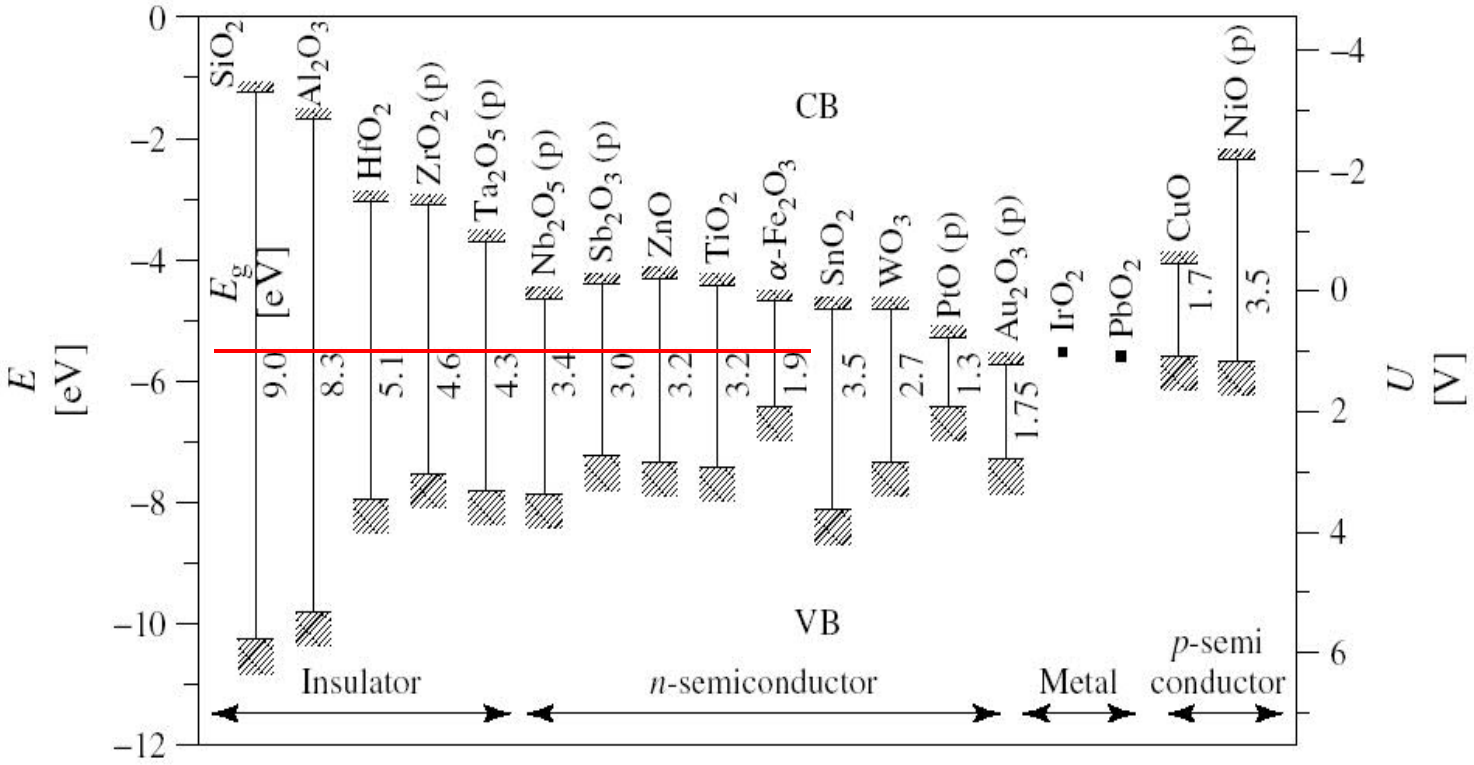




Electrode Potentials and Delamination:

Hausbrand et al.,J. Electrochem. Soc., **155** *(2008)* C369 , M. Hausbrand et al., Corros. Sci. **51**(9) (2009) 2107

BAND GAP AND POTENTIAL

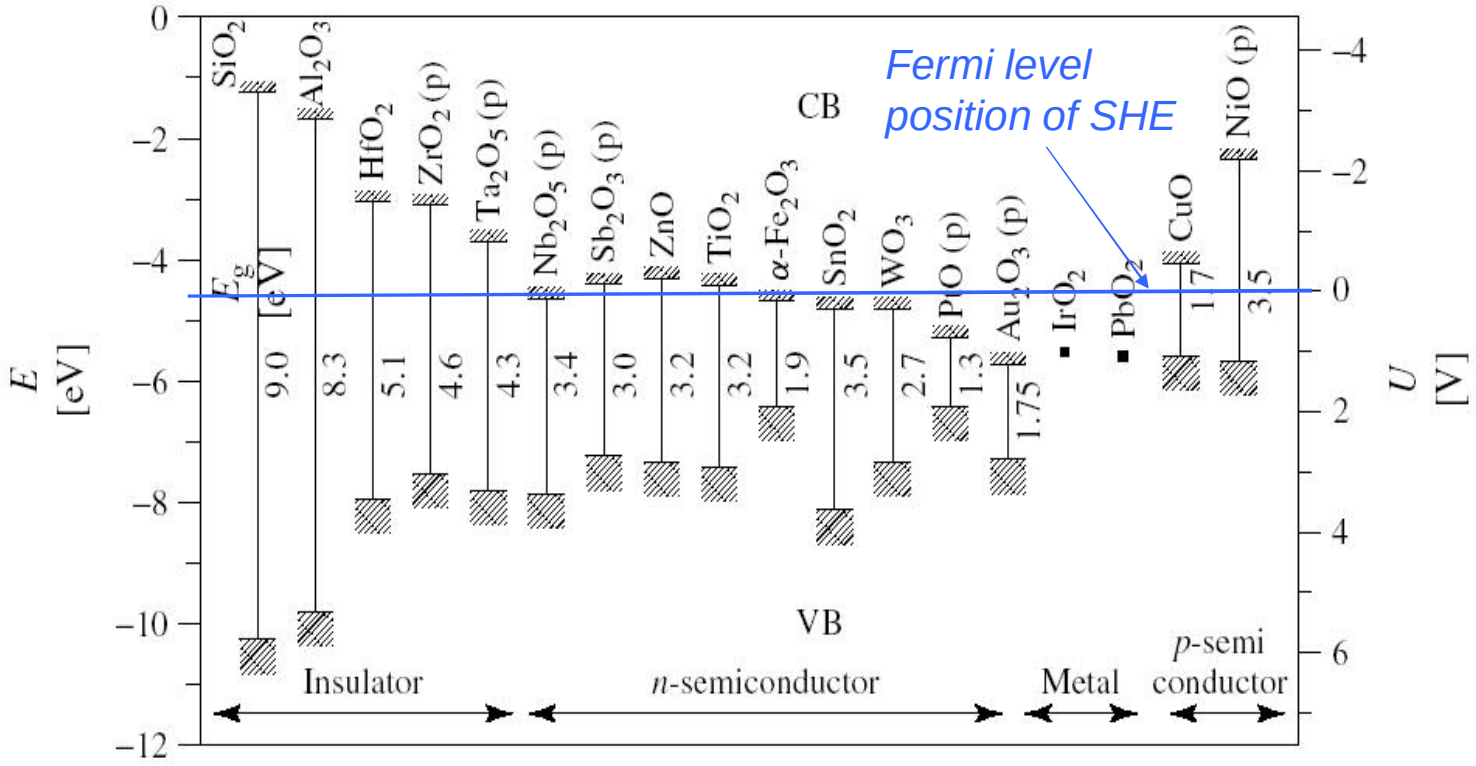


From: Schultze, Hassel, in: Encyclopedia of Electrochemistry, vol.4 (Frankel, Stratmann, eds.), p. 234

Band gap increases with decreasing nobility

Position of valence and conduction band for different oxides

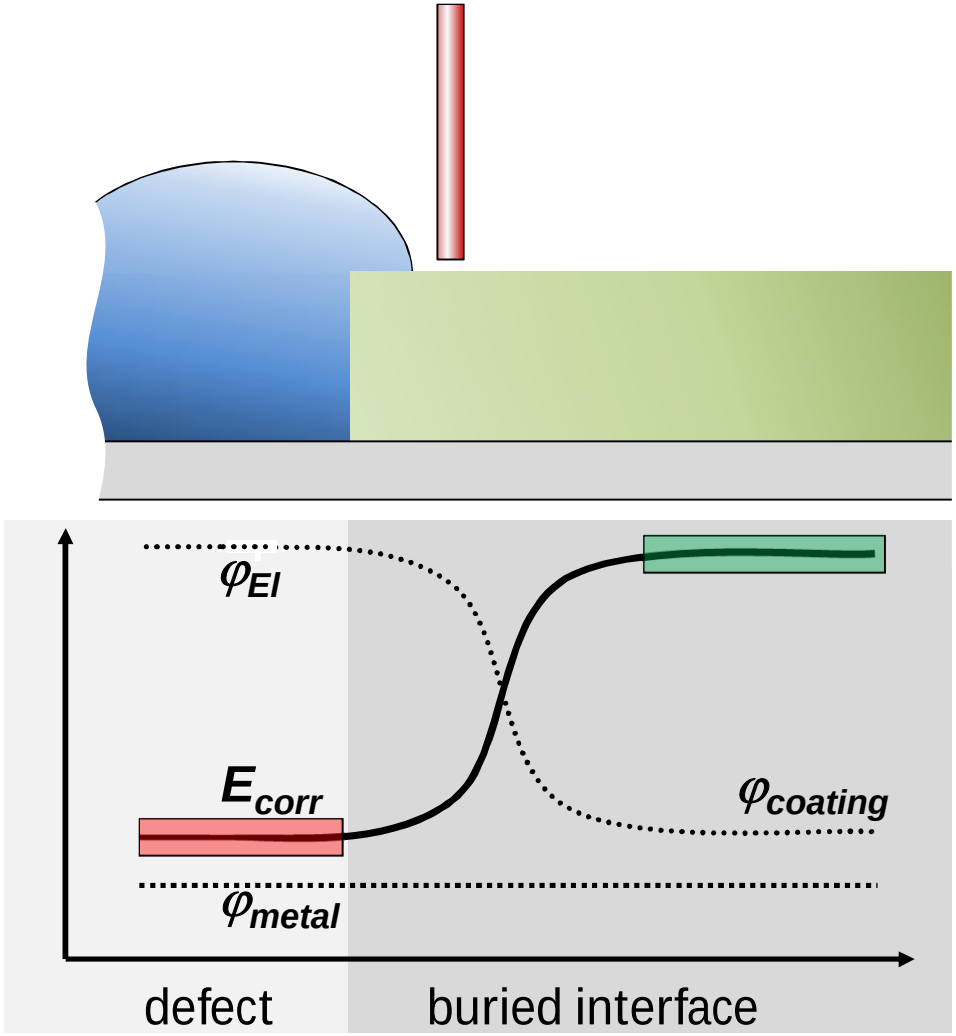
BAND GAP AND POTENTIAL



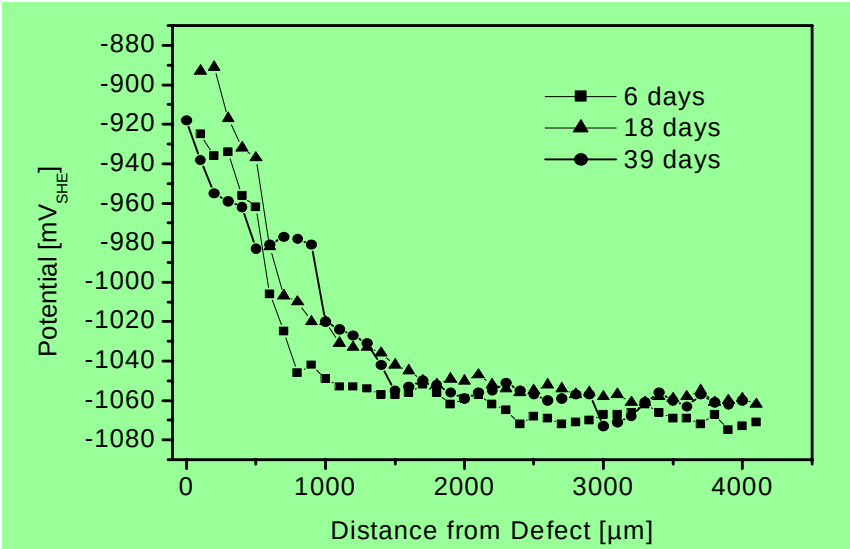
From: Schultze, Hassel, in: Encyclopedia of Electrochemistry, vol.4 (Frankel, Stratmann, eds.), p. 234

Band gap increases with decreasing nobility and conduction band shifts upwards

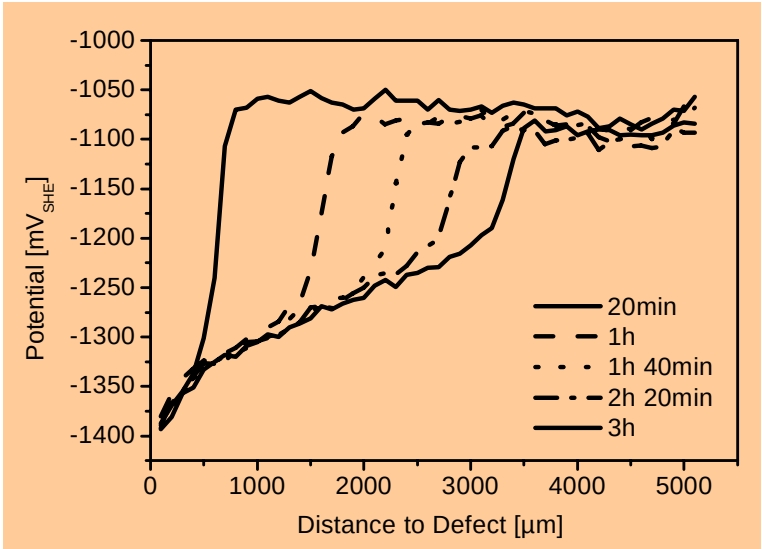
Position of valence and conduction band for different oxides


φEl
Ecorr
φcoating
φmetal
defect
buried interface

Delamination of coating from $MgZn_2$

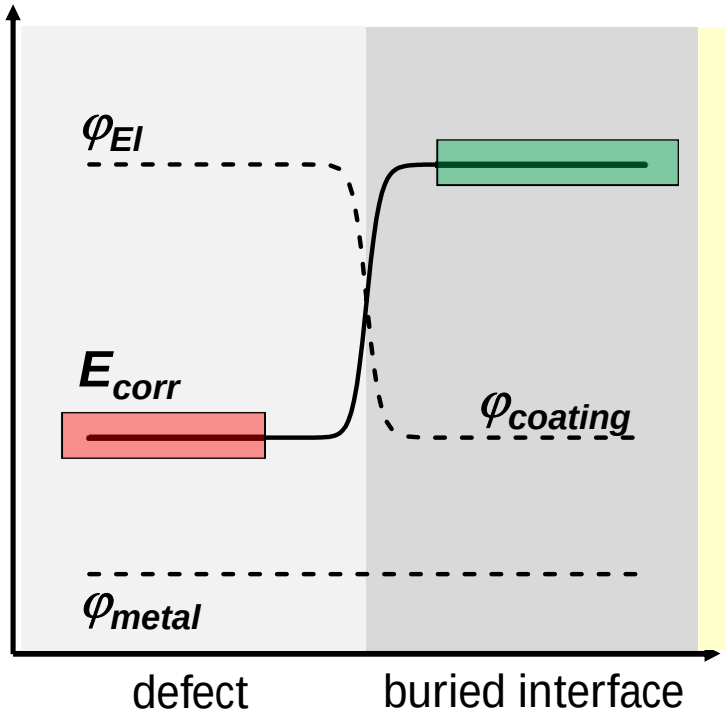


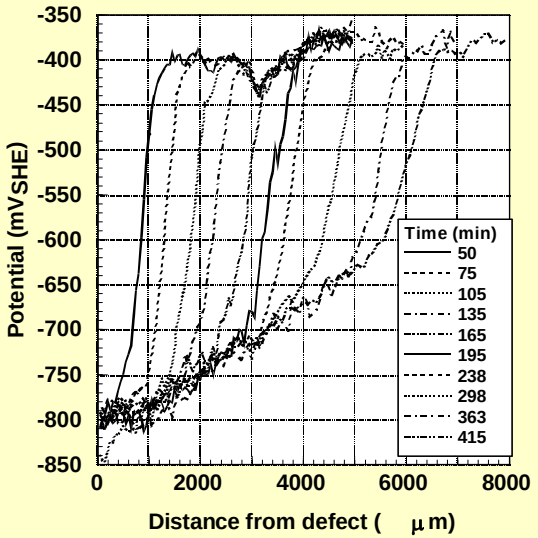
Delamination with Mg in the defect

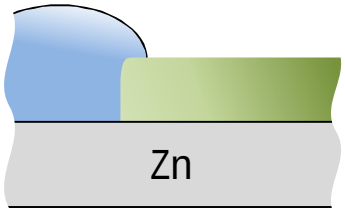


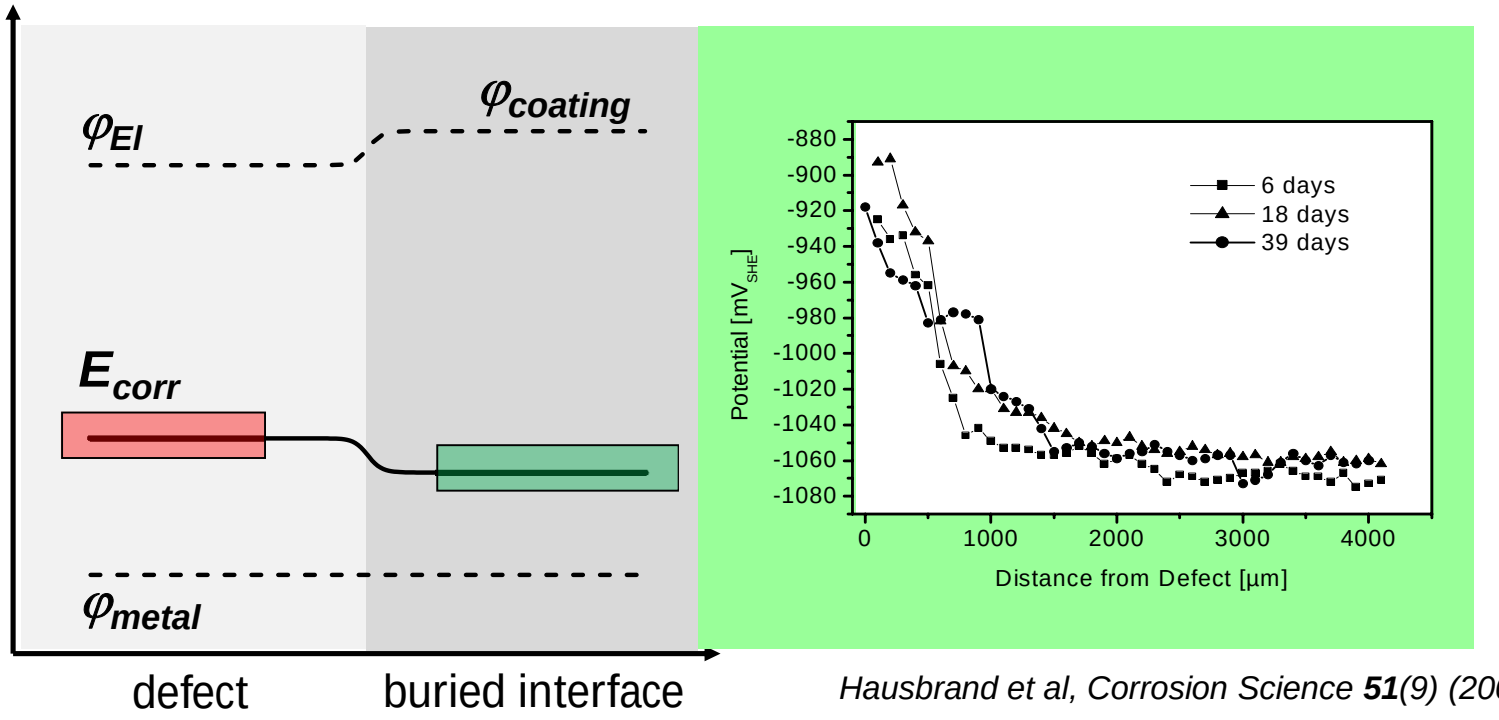
*Hausbrand et al, Corrosion Science **51**(9) (2009) 2107-2114*

Hausbrand et al, J. Electrochem. Soc. 155(7) (2008) C369-C379


φEl
Ecorr
φcoating
φmetal
defect
buried interface


Potential (mVSHE)
-350
-400
-450
-500
-550
-600
-650
-700
-750
-800
-850
0
2000
4000
6000
8000
Distance from defect (µm)
Time (min)
50
75
105
135
165
195
238
298
363
415

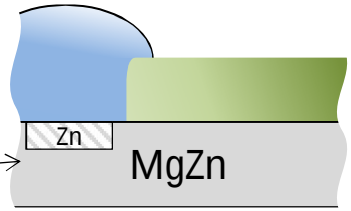

Zn

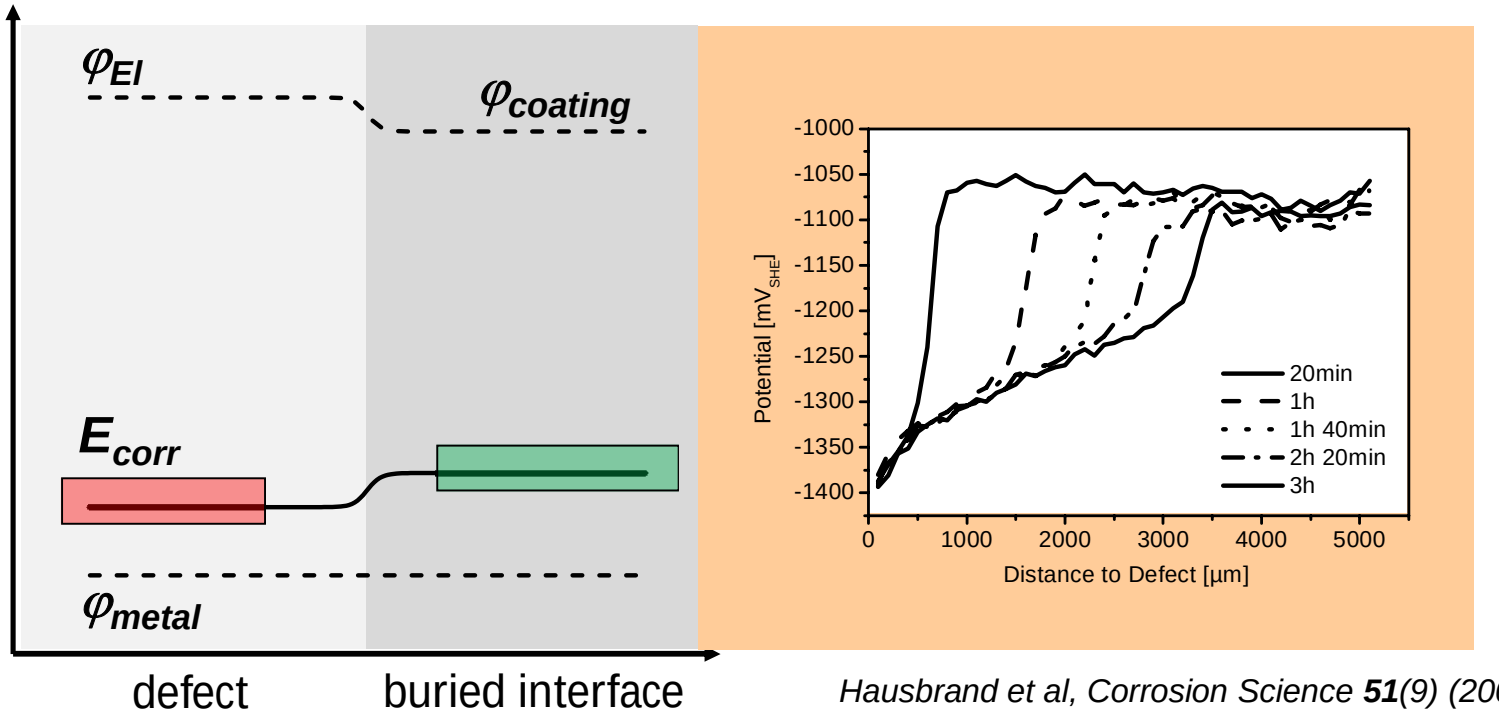


*Hausbrand et al, Corrosion Science **51**(9) (2009) 2107-2114*

Hausbrand et al, J. Electrochem. Soc. 155(7) (2008) C369-C379

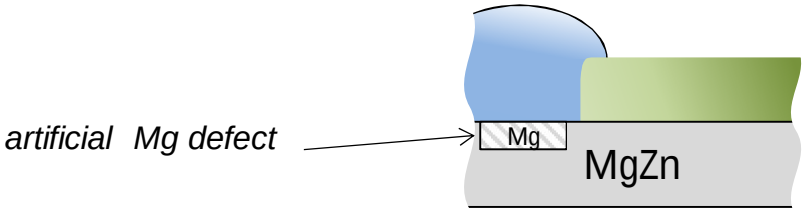
due to de-alloying:
surface is mainly zinc



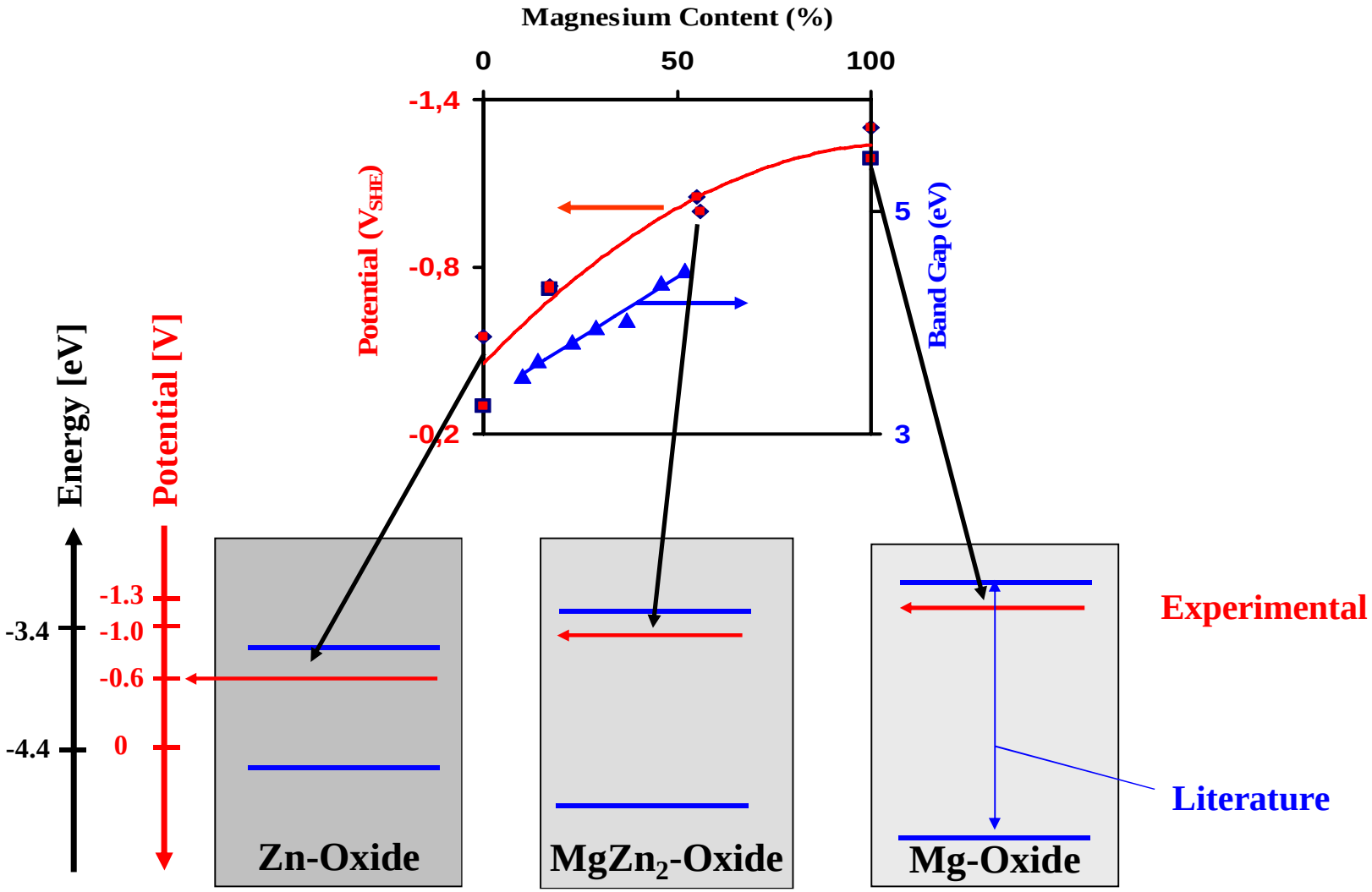


*Hausbrand et al, Corrosion Science **51**(9) (2009) 2107-2114*

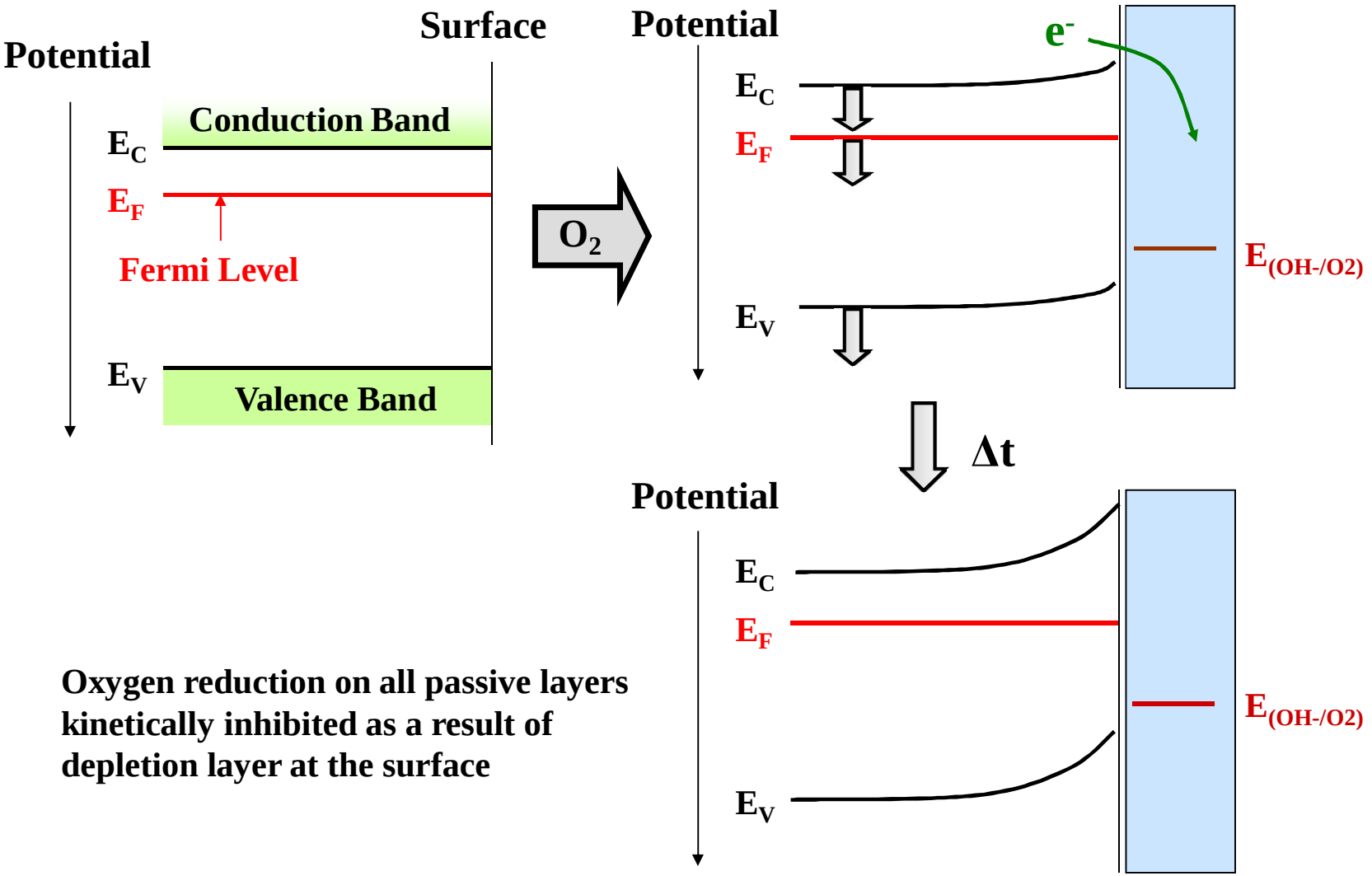
Hausbrand et al, J. Electrochem. Soc. 155(7) (2008) C369-C379



TUNING THE FERMI LEVEL BY ALLOYING

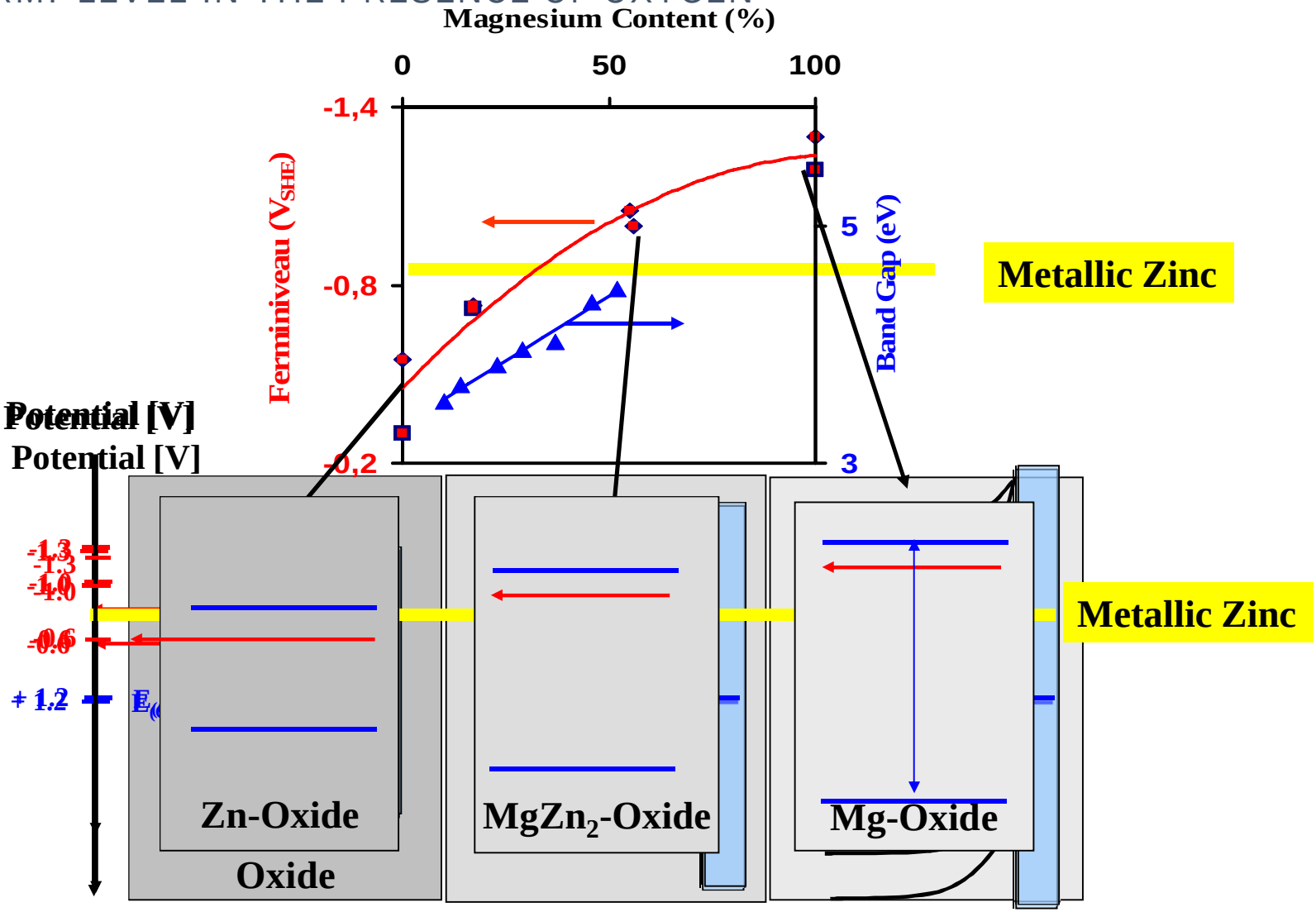


THE FERMI-LEVEL IN THE PRESENCE OF OXYGEN



Oxygen reduction on all passive layers kinetically inhibited as a result of depletion layer at the surface

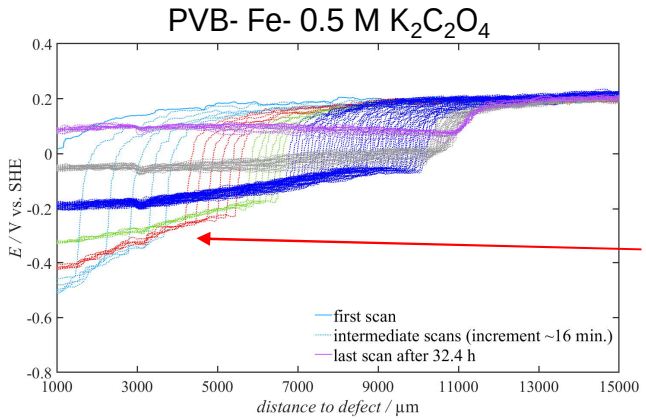
THE FERMI-LEVEL IN THE PRESENCE OF OXYGEN



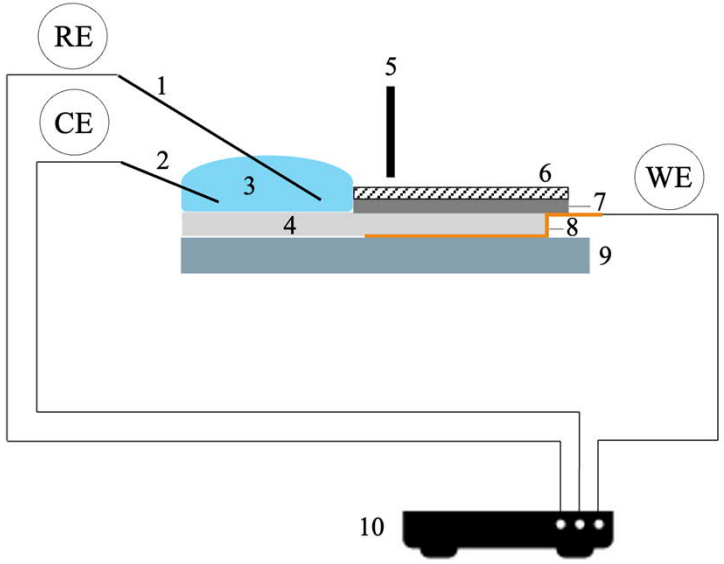
Again, also in this case of oxide side dominated delamination behaviour, both ORR as well progress of cations are likewise affected by the oxide

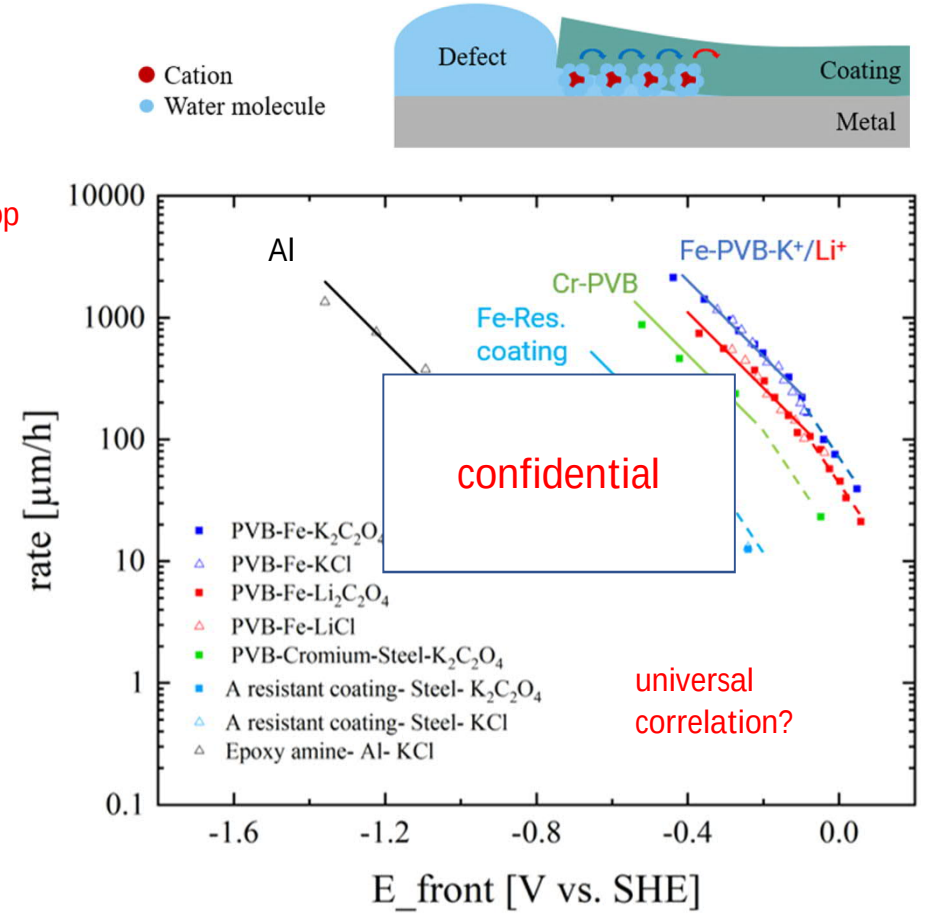
Hence, so far for steel as well as galvanised steel, ORR as well as cation progress are likewise affecetd by either coating or semiconducting properties of the metal oxide

Fundamental Aspects of delamination of organic coatings



just need to simulate iR drop in the confined zome of the delaminated interface

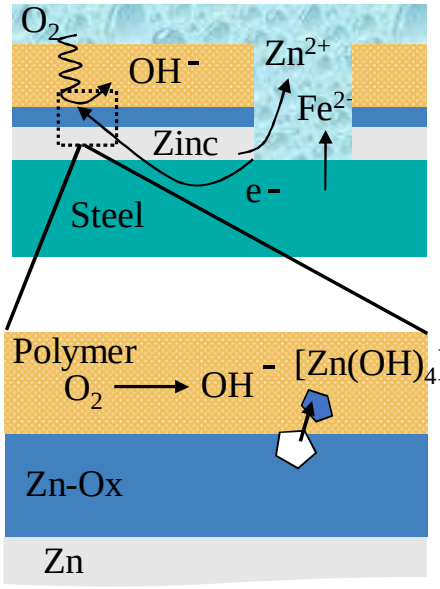




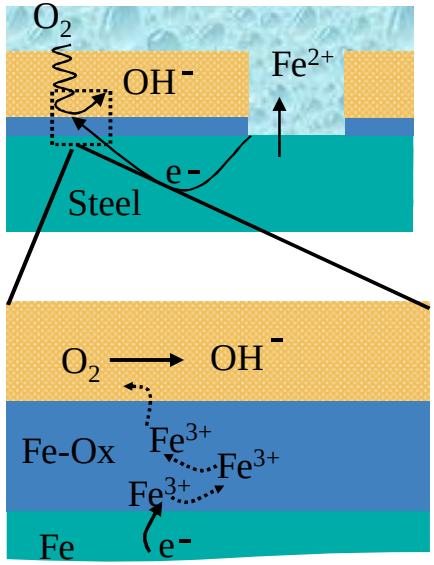
from Khayatan et al, Corrosion Science 202 (2022) 110311 + unpublished results

Influence of material on delamination mechanism

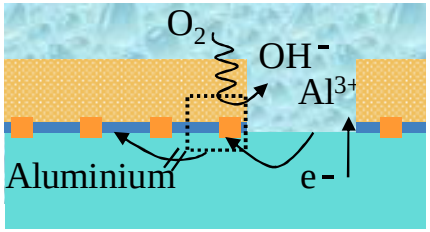
Galvanised Steel

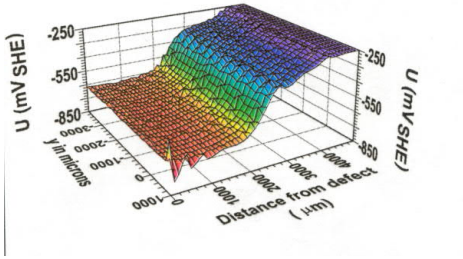


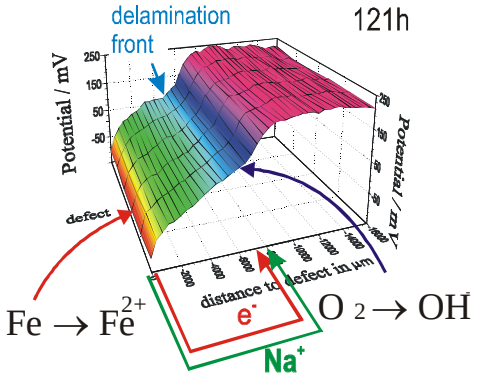
Steel



Al Alloys

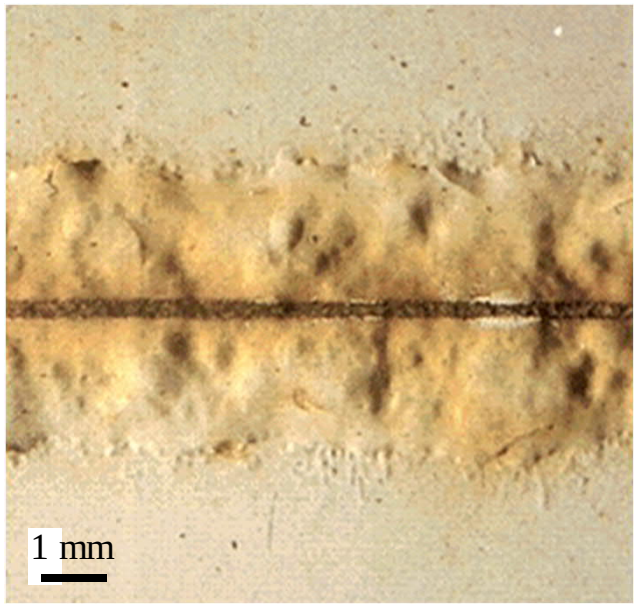




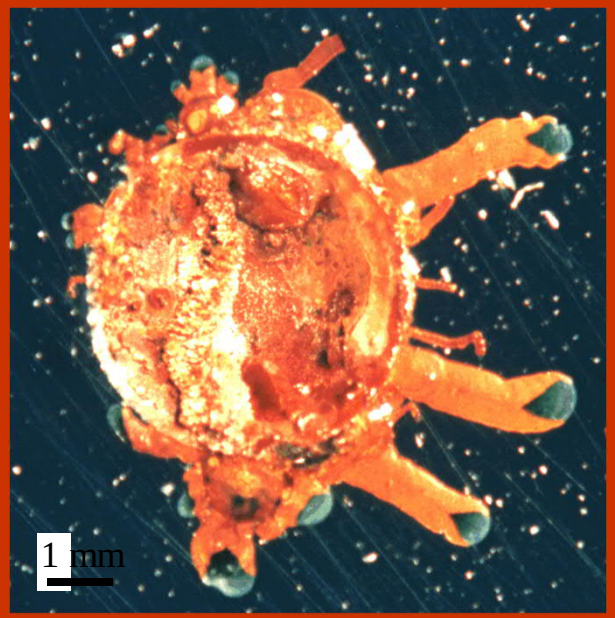


Influence of material on delamination mechanism

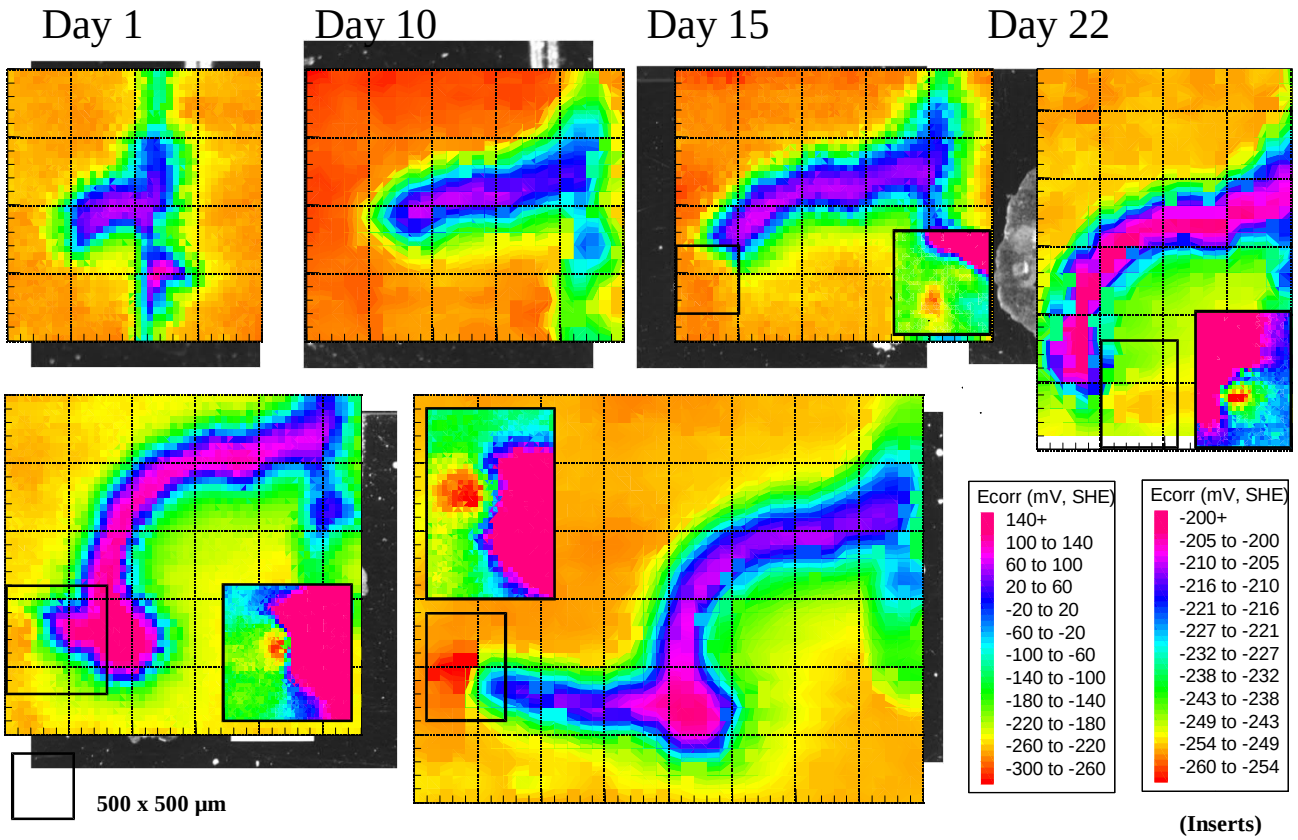
Kathodische Enthaftung auf Stahl



Filiformkorrosion auf Stahl

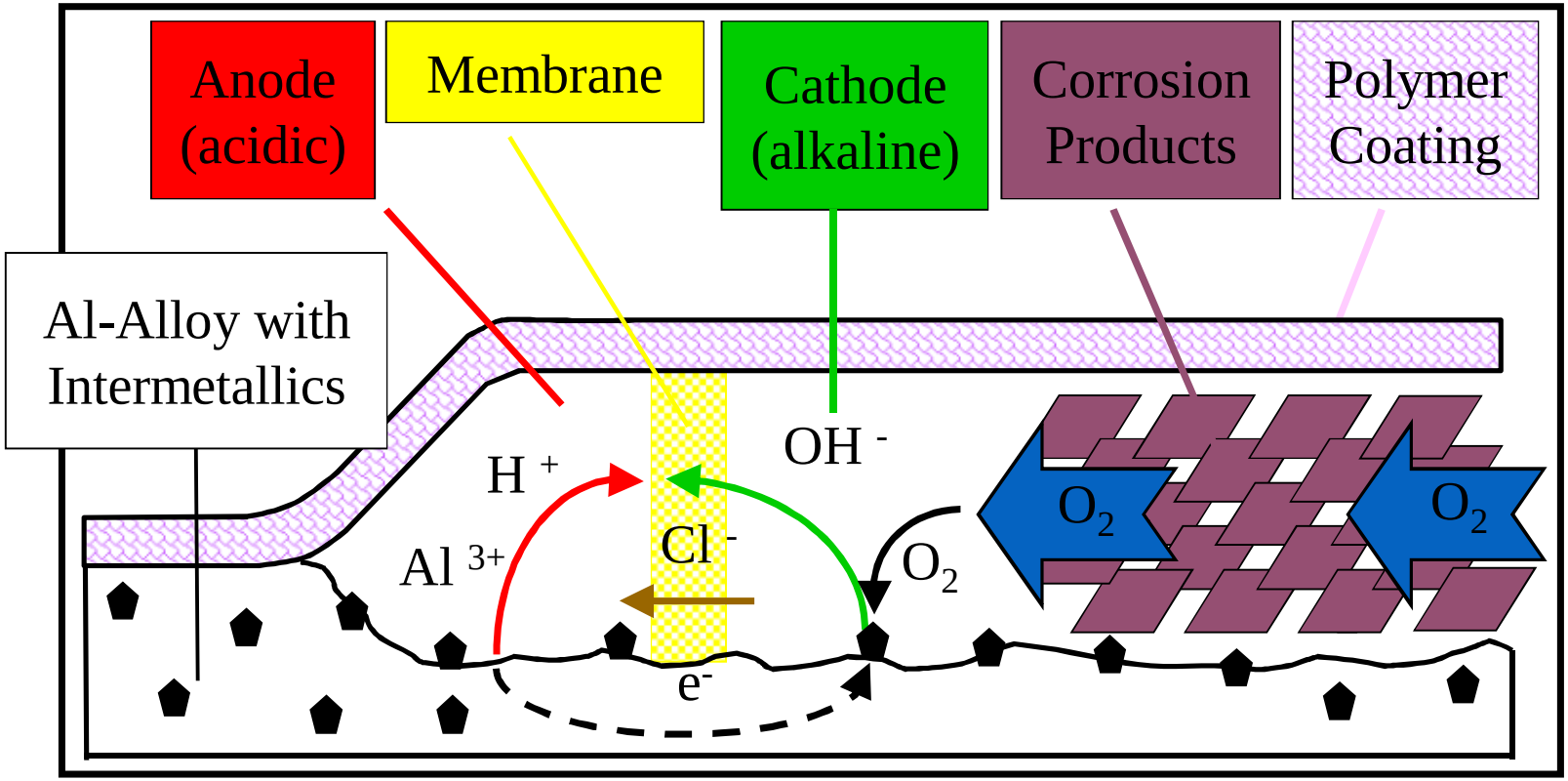


Filiform corrosion on Al: optical microscopy and SKP

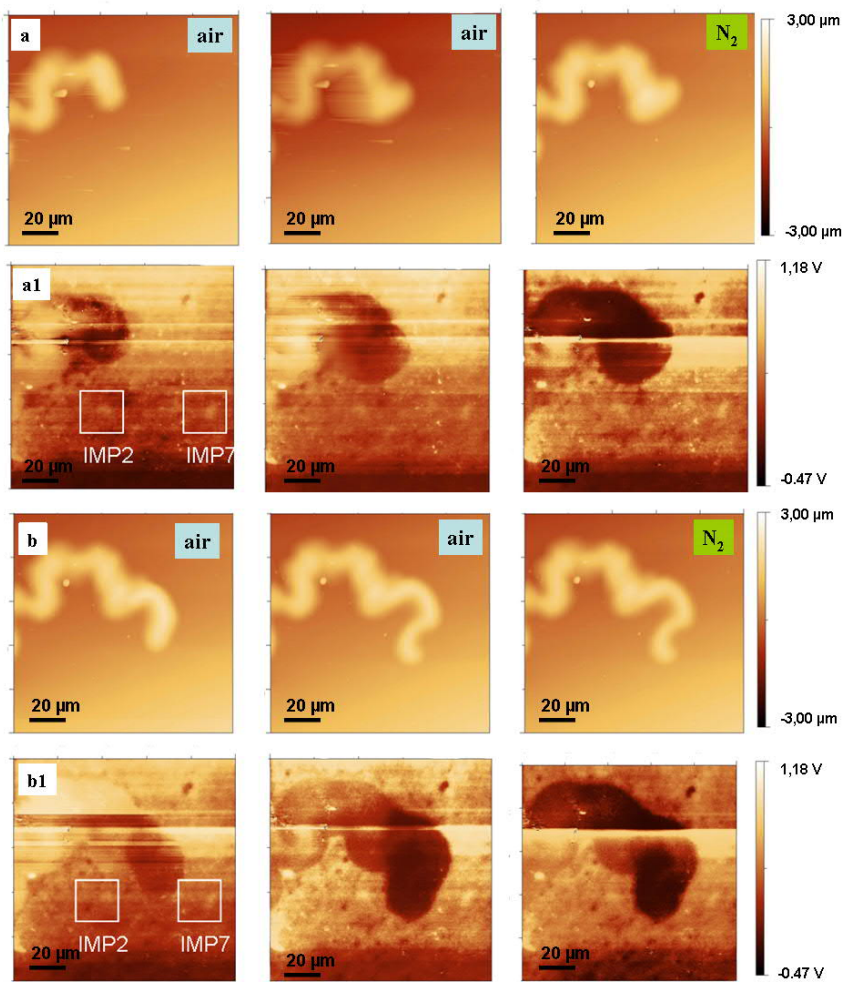


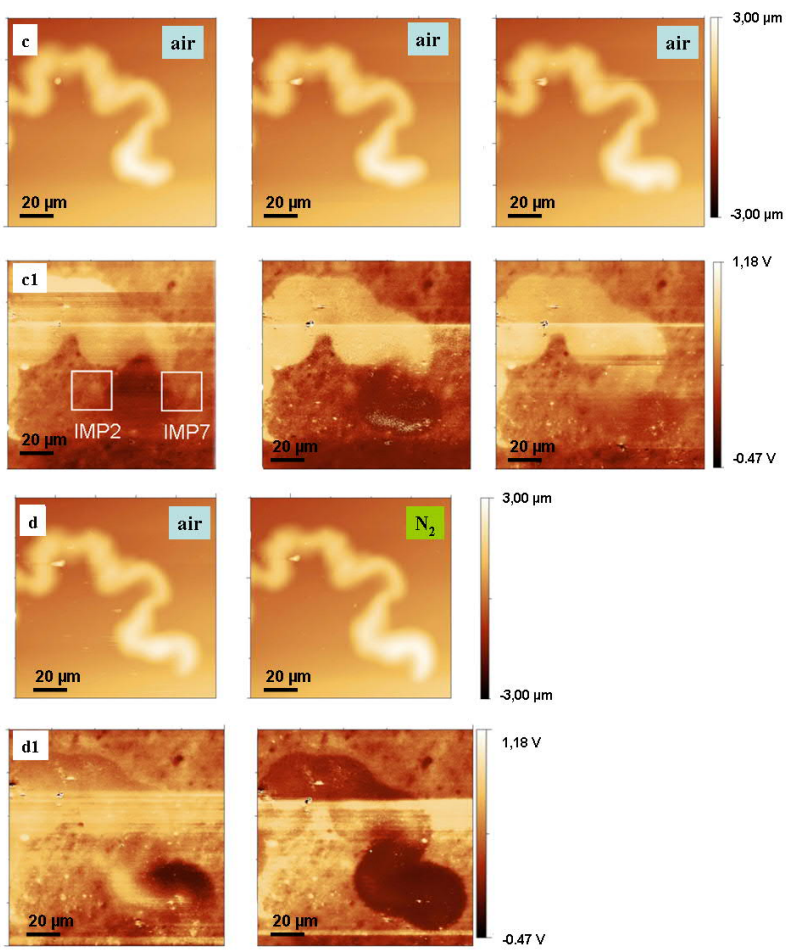
Stored at 86% RH, ambient temperature, initiated with NaCl solution in defect

Mechanism of FFC

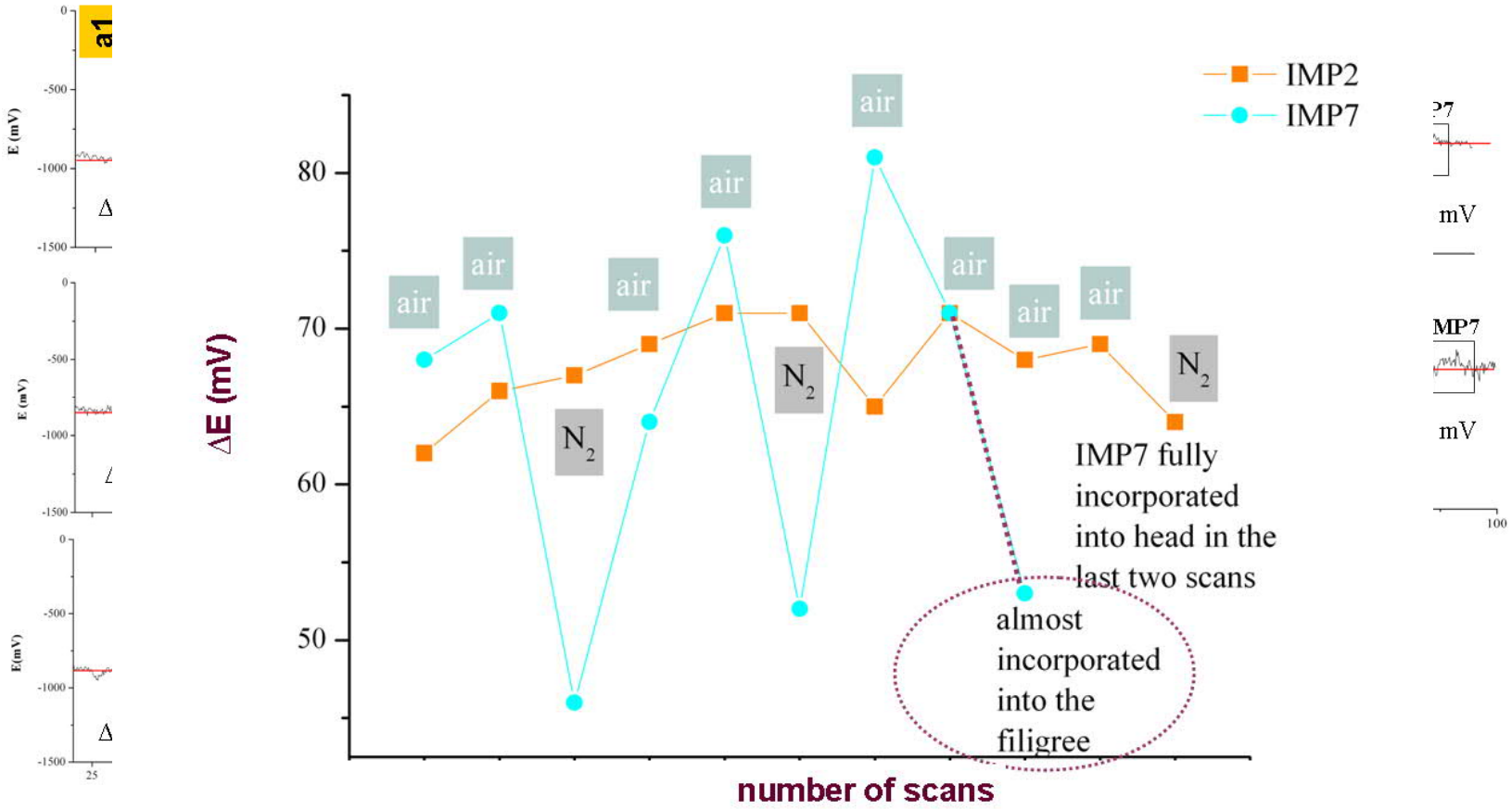


Tracking FFC by in situ skpfm: Al-Cu alloy under cyclic conditions



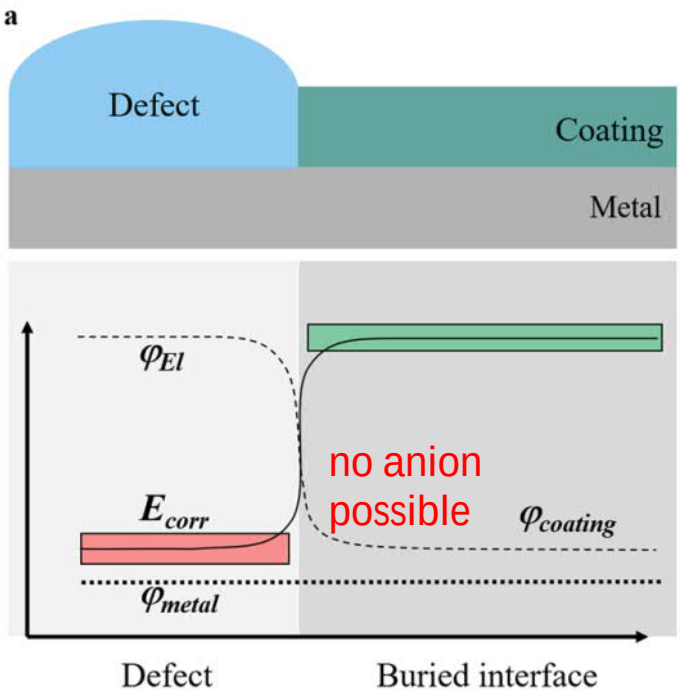


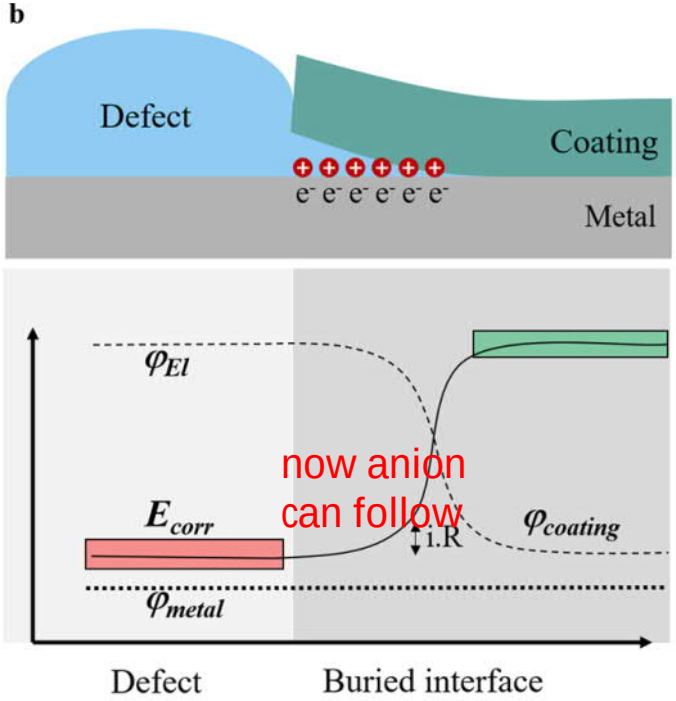
Senöz et al., Corrosion Science **58** (2012) 307-314

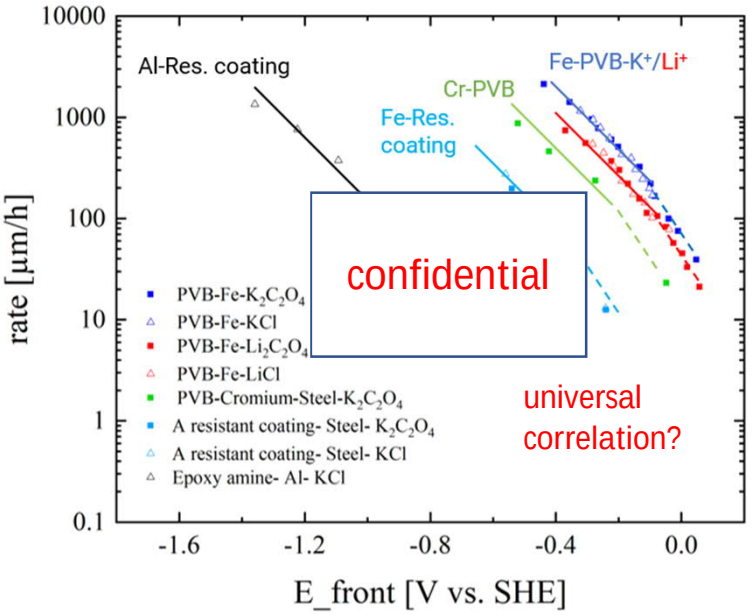


Senöz et al., Corrosion Science **58** (2012) 307-314

CORRELATION BETWEEN DEL. RATE AND DEL. FRONT POTENTIAL







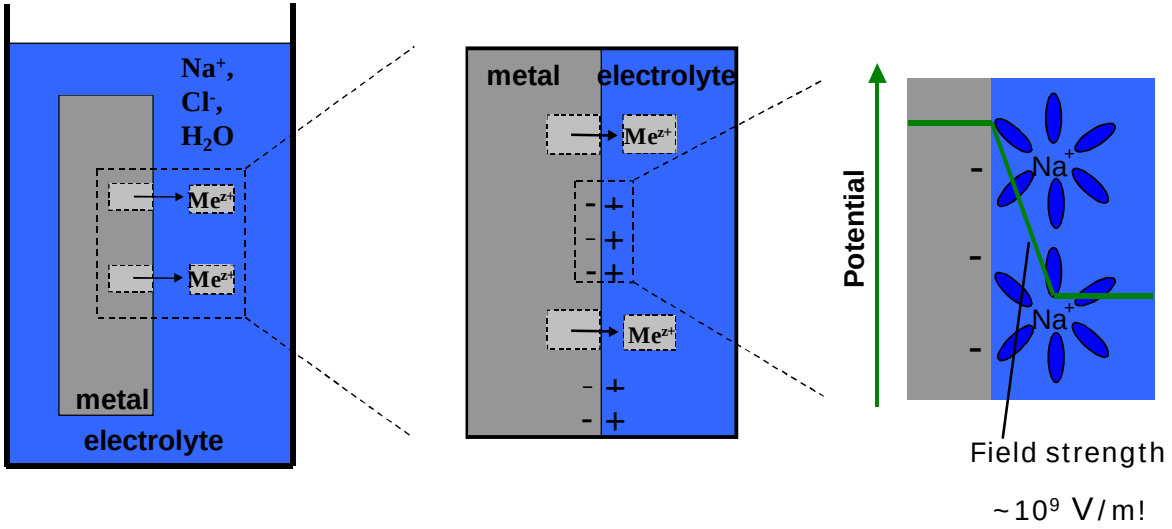
Then homogeneous anodic delamination; but first step can be cathodic delamination on weak spots, as found in FFC

from Khayatan et al, Corrosion Science 202 (2022) 110311 + unpublished results

N. Khayatan, M. Rohwerder, A new insight into the rate determining step of cathodic delamination, Corrosion Science 202 (2022) 110311.

confidential

Structure of the interface metal/electrolyte



- **Formation of an electrochemical double layer at the metal surface**
- **Potential drop between metal and electrolyte correlates with the electrode potential E**

➔ **Coating lowers amount of ions ➔ diffuse double layer ➔ low driving force**

THANK YOU FOR YOUR ATTENTION!