An in situ spectro-electrochemical monitoring of aqueous effects on polymer/metal oxide interfaces

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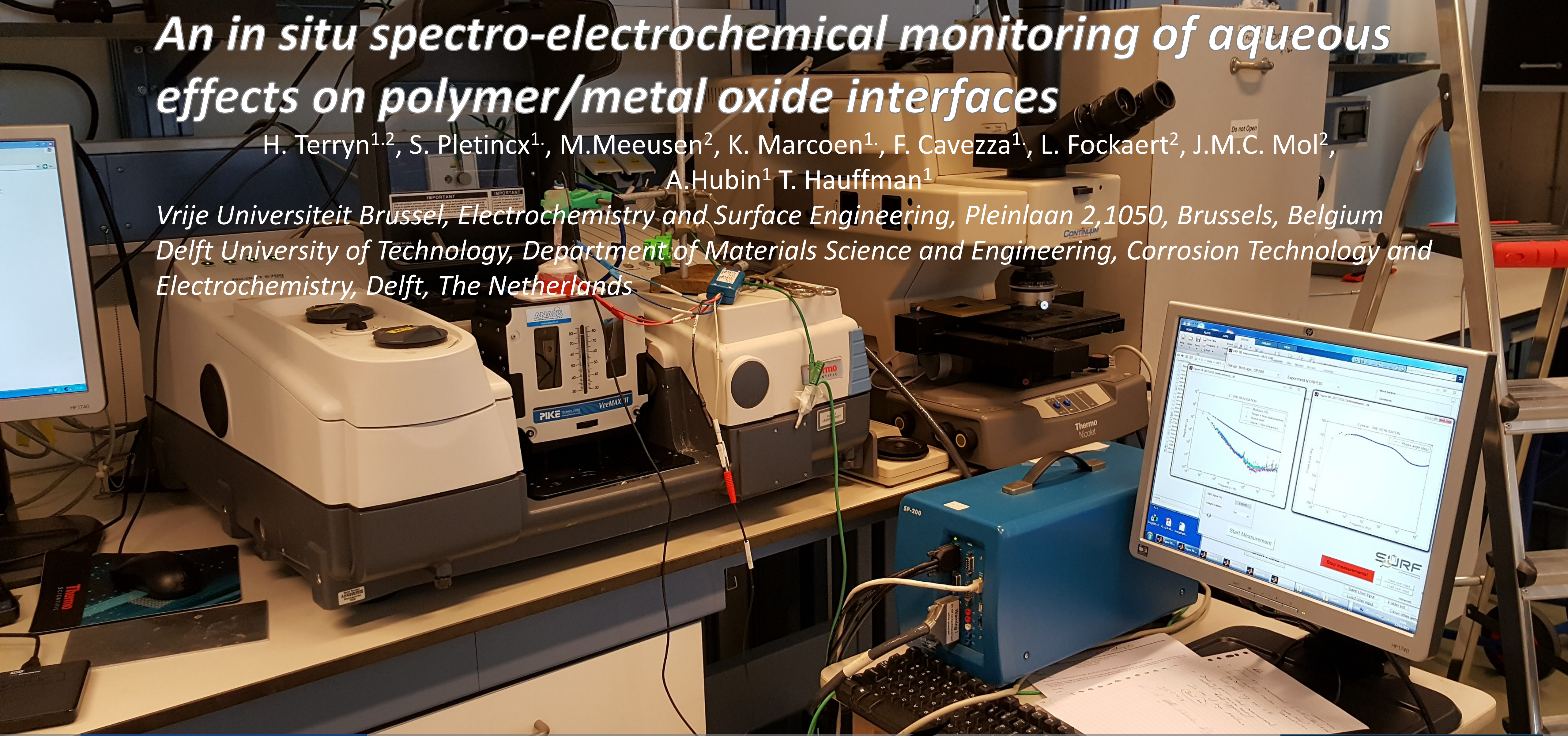
Delft University of Technology, Department of Materials Science and Engineering, Corrosion Technology and Electrochemistry, Delft, The Netherlands



VRIJE UNIVERSITEIT BRUSSEL

Research Group Electrochemical and Surface Engineering

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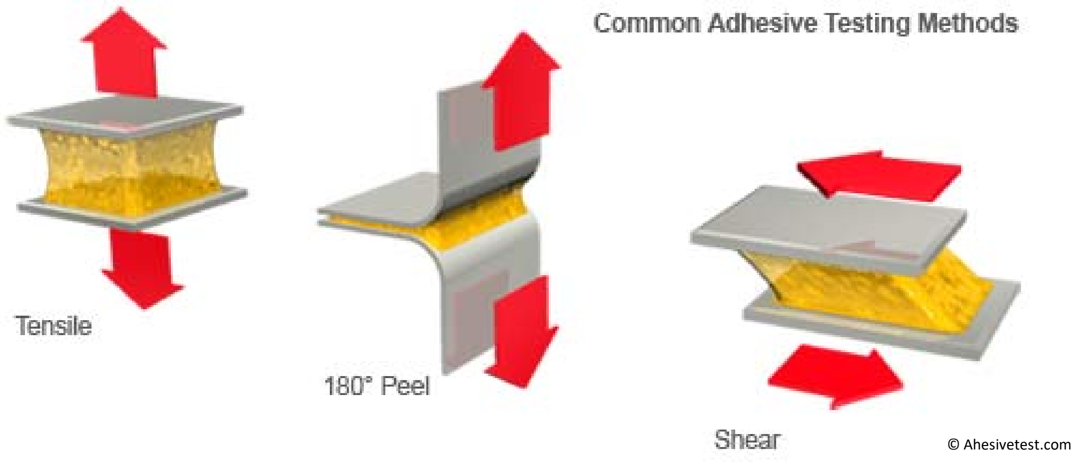
Obtaining information of the solid/solid interface

- **Long-term stability of the polymer/metal interface** in humid or corrosive environments largely determines the performance of the composite system.

- Information on the interfacial adhesion strength mainly comes from **macroscopic tests** (pull and peel tests, salt spray, …)

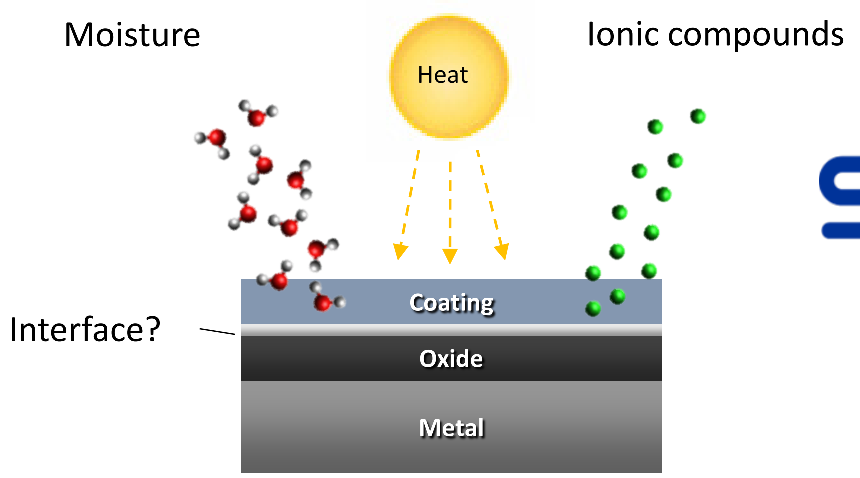


- Several processes occurring **simultaneously** leading to failure.
  → Empirical value of the coating/adhesive durability.

- Reaching the buried interface of a organic/inorganic hybrid structure **without severe alterations** of this region by mechanical sectioning (e.g. sputtering, cross section, …)

Polymer/Metal Oxide systems are widely used

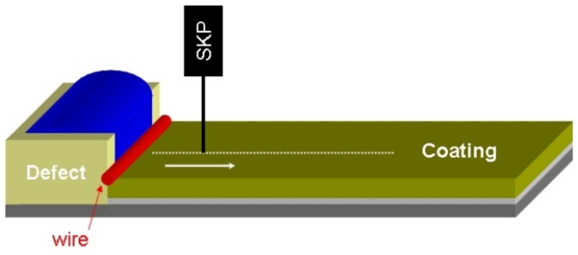
- **Long-term stability of the polymer/metal interface** in humid or corrosive environments largely determines the performance of the composite system.
- For example: interfaces aerospace, automotive,packaging, construction, electronics, litho,
- Real life systems are commonly exposed to a combination of **environmental influences**: moisture, ionic compounds and temperature profiles. Delamination is a big issue for a lot of systems: implementation of new metals, new conversions, new coatings
- How to understand what is happening locally at the hybrid interface and this under technologically relevant conditions?

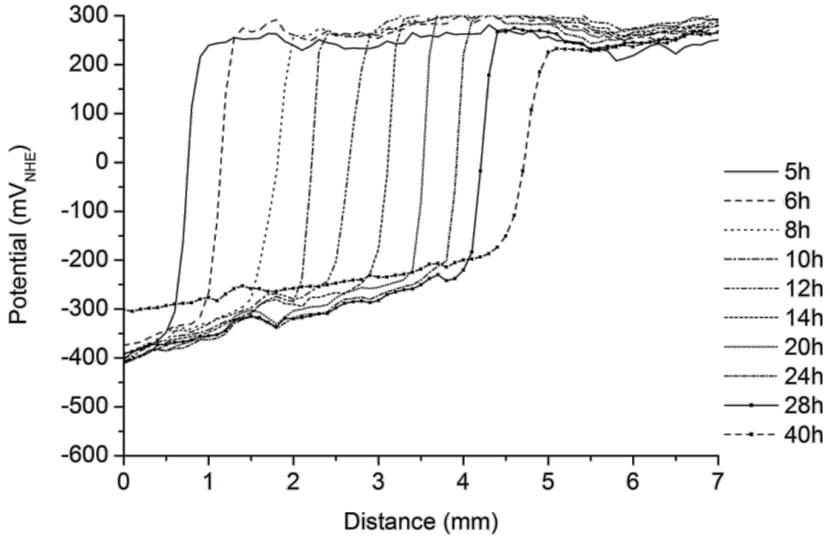


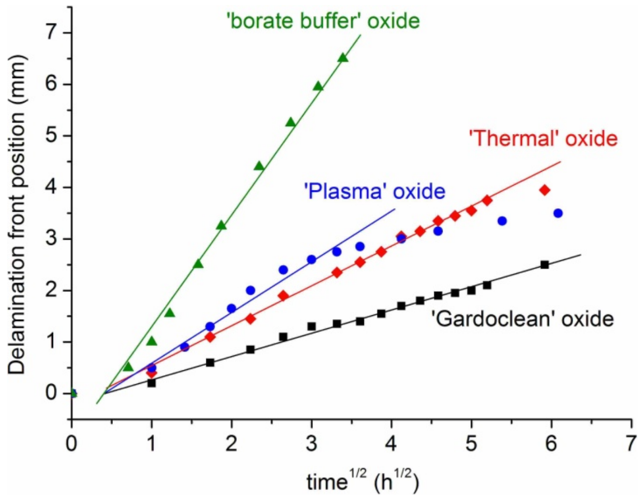
Review paper
Probing the formation and degradation of chemical interactions from model molecule/metal oxide to buried polymer/metal oxide interfaces
Pletincx, S., Fockaert, L. L. I., Mol, J. M. C., Hauffman, T. & Terryn, H., 6 Jun 2019, In : npj Materials Degradation. 3, 23, 12 p.

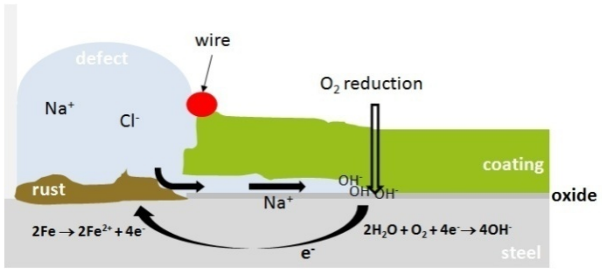
Influence of Interface Design in Delamination collaboration MPIE-Dusseldorf G.Grundmeier, M. Rohwerder

SKP





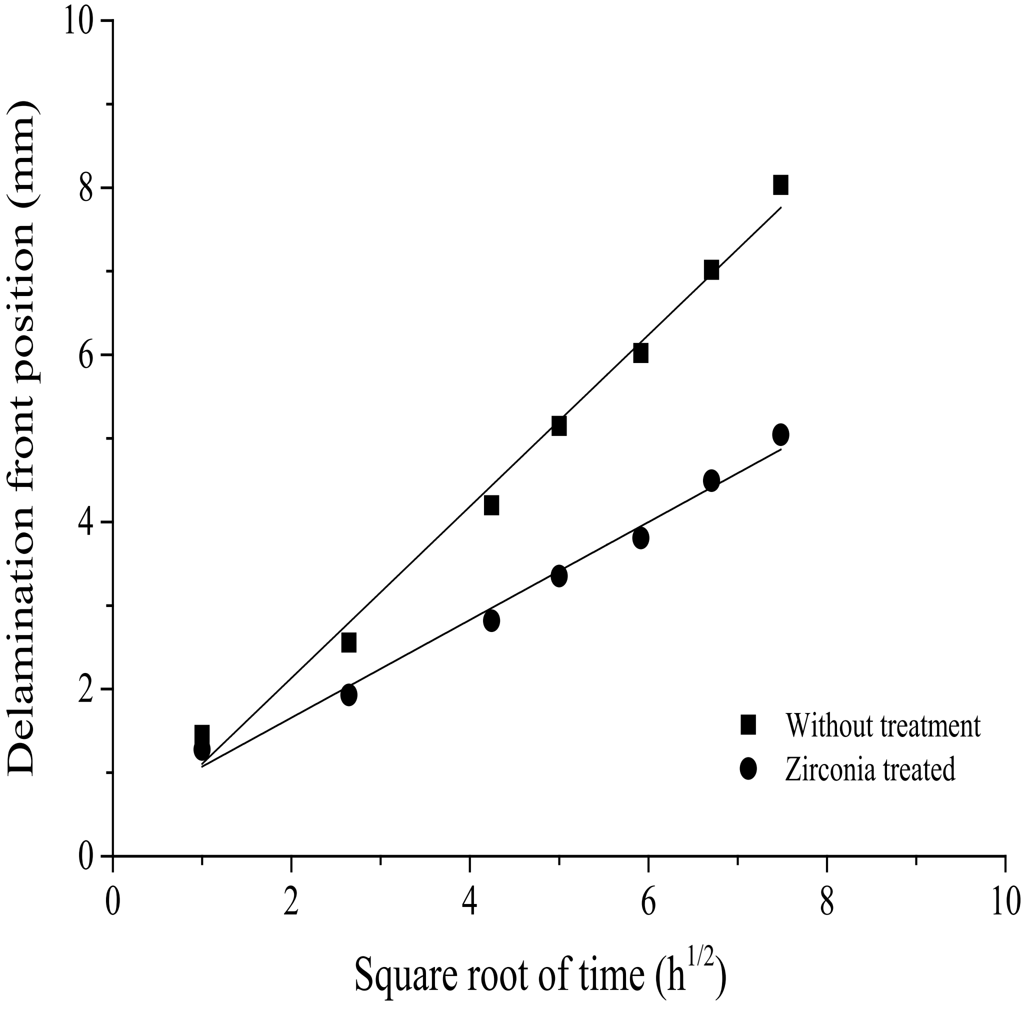


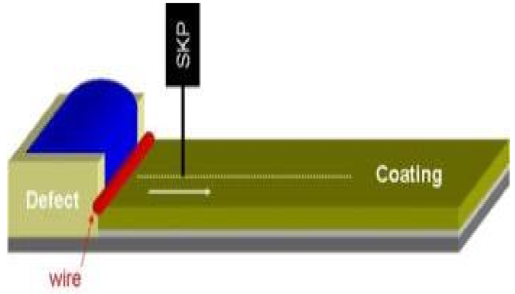


➡ Delamination controlled by cation migration along the oxide/coating interface

Wielant Jan, Posner Ralf, Hausbrand Rene, Grundmeier Guido, Terryn Herman, Cathodic delamination of polyurethane films on oxide covered steel - Combined adhesion and interface electrochemical studies. , Corrosion Science, 51, (2009) 1664 - 1670

Delamination study of epoxy coating from carbon steel
New interface by Zr oxide/fluoride film





Scanning Kelvin Probe (SKP)

- ✓ Delamination is under control of ion mobility at the interface.
- ✓ Zirconia treatment effectively decrease the delamination of epoxy coated carbon steel samples.

The influence of a Zr-based conversion treatment on interfacial bonding strength and stability of epoxy coated carbon steel
Sababi, M., Terryn, H. & Mol, J. M. C., 1 Apr 2017, In : Progress in Organic Coatings. 105, p. 29-36 8 p

Selection of model polymer/metal oxide system

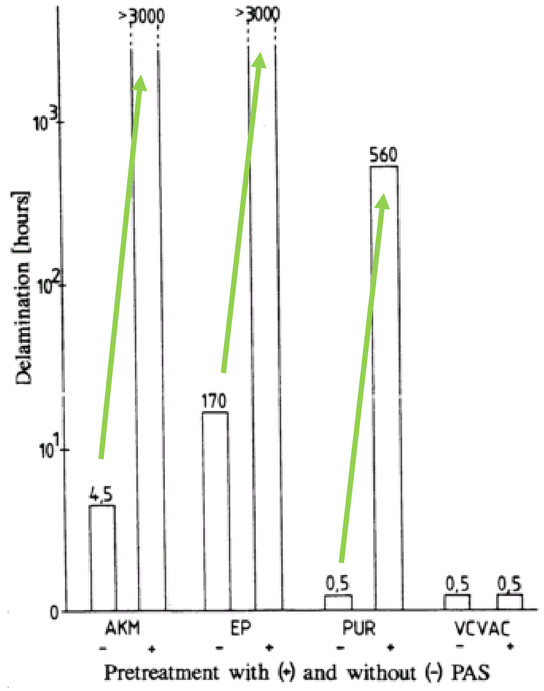
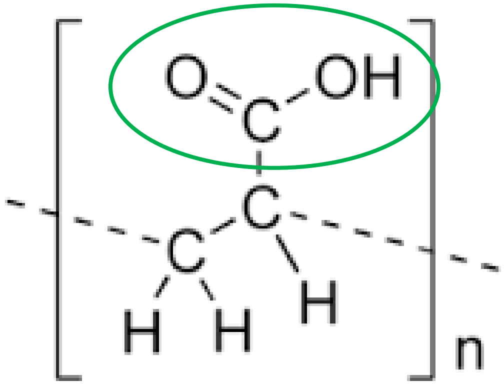


Figure 6. Wet Adhesion of Different Top Layers (40 µm) on a Polyacrylic Acid Adhesion Layer.

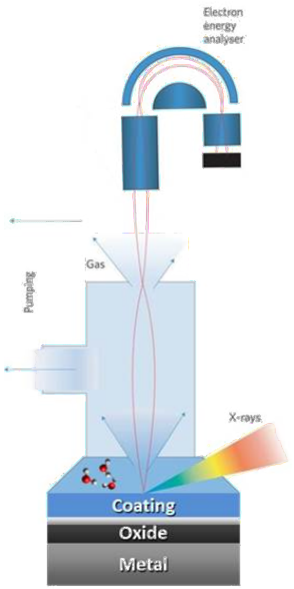
Funke et al. (1996)

Why improvement of wet adhesion for poly (acrylic acid) (PAA)?

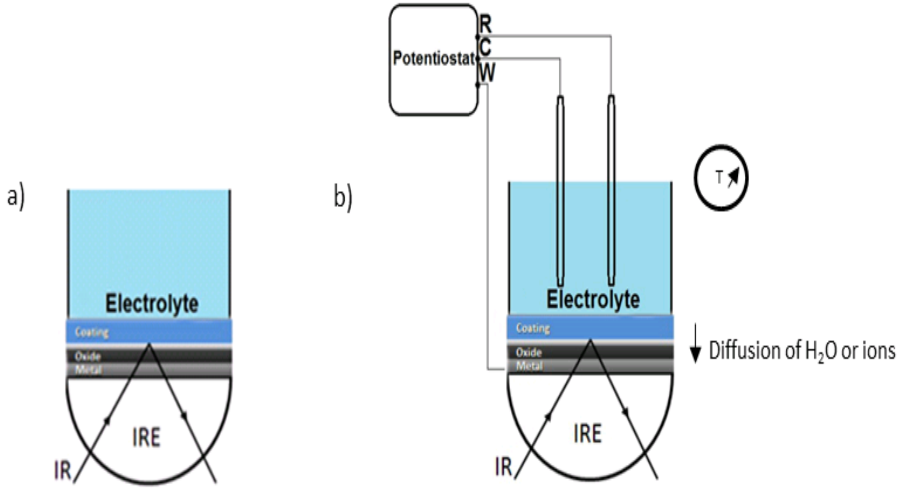
Use a model system to simplify the complex realistic case.



How to reach the interface with surface analysis techniques and add environmental influences?



Complementary

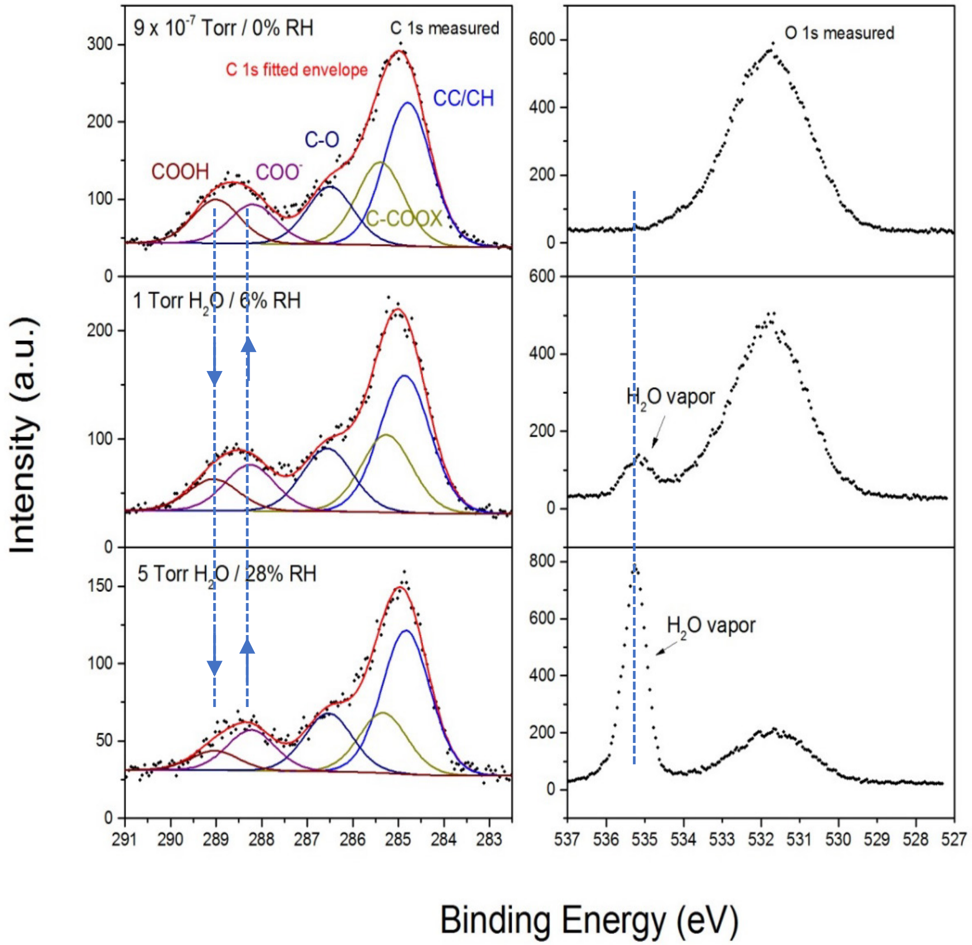


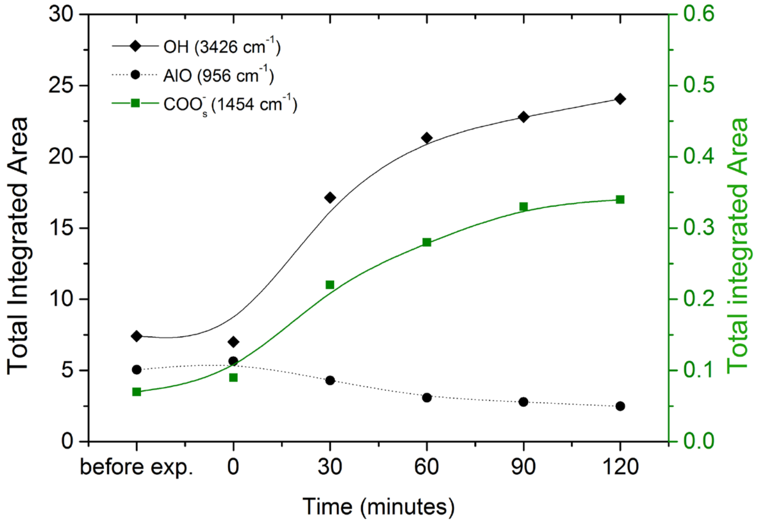
- Near interface molecular information from FTIR
- Information of entire polymer/metal oxide system by EIS

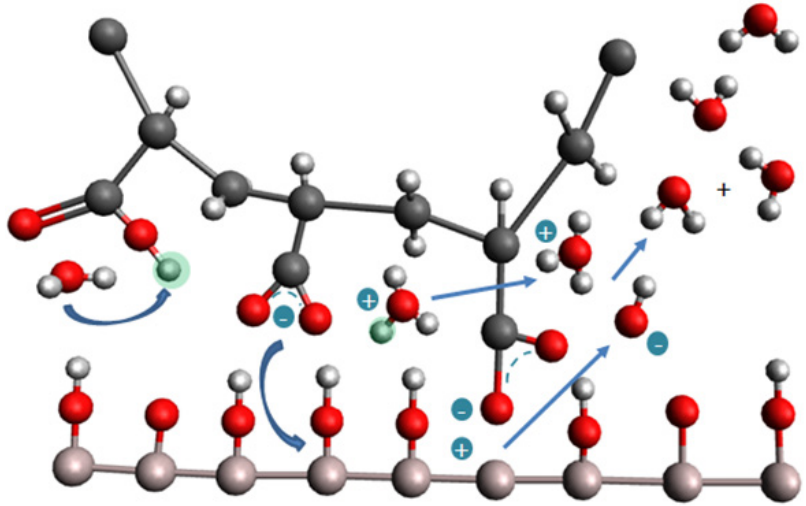
Near Ambient XPS Collaboration H.Bluhm Berkeley

Infrared spectroscopy ATR-FTIR Kretschmann and ORP-EIS

Unravelling the Chemical Influence of Water on the PMMA/Aluminum Oxide Hybrid Interface In Situ
Pletincx, S., Marcoen, K., Trotochaud, L., Fockaert, L-L., Mol, J. M. C., Head, A. R., Karslioğlu, O., Bluhm, H., Terryn, H. & Hauffman, T., 17 Oct 2017, In : Scientific Reports - Nature. 7, 1, p. 13341 13341







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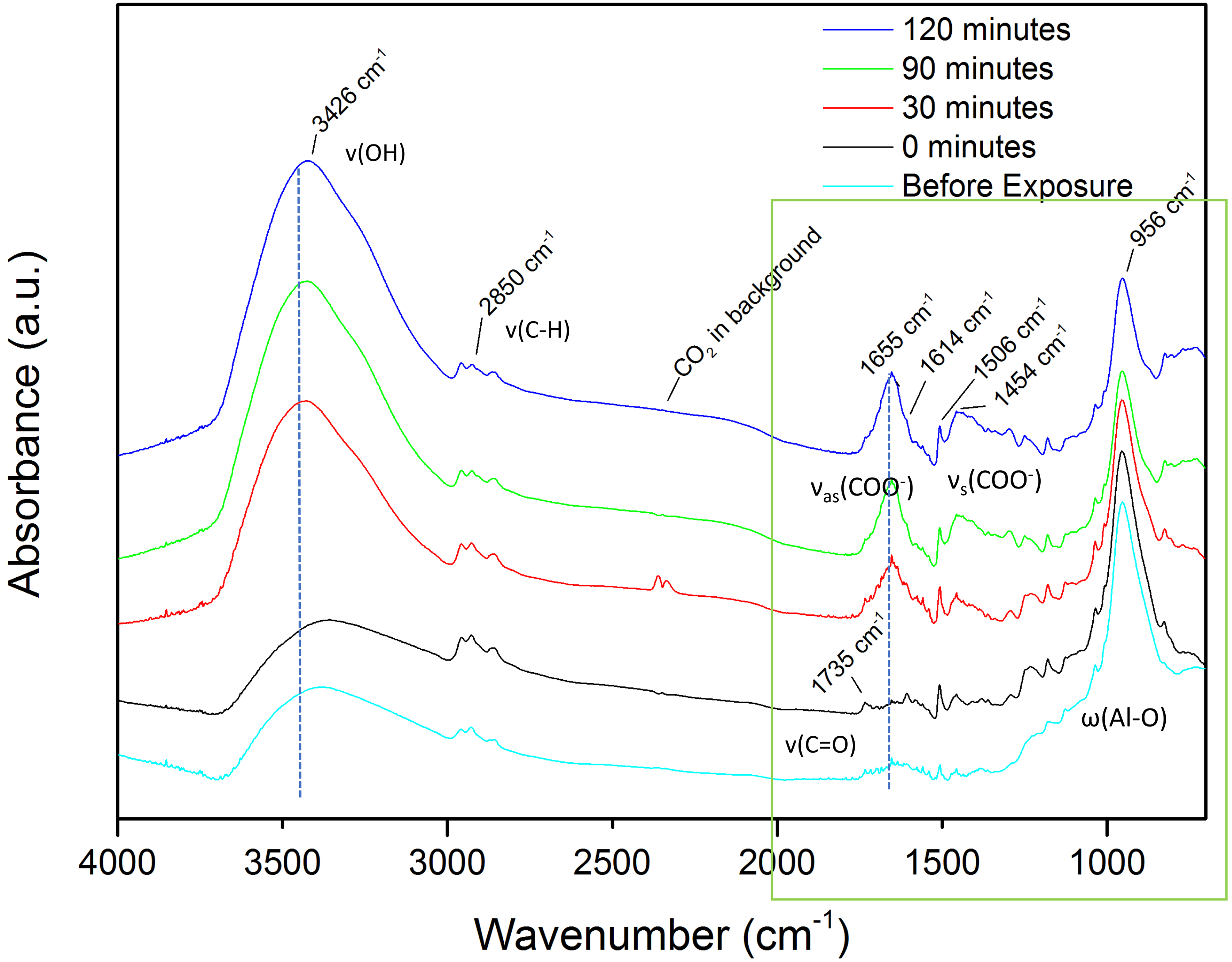
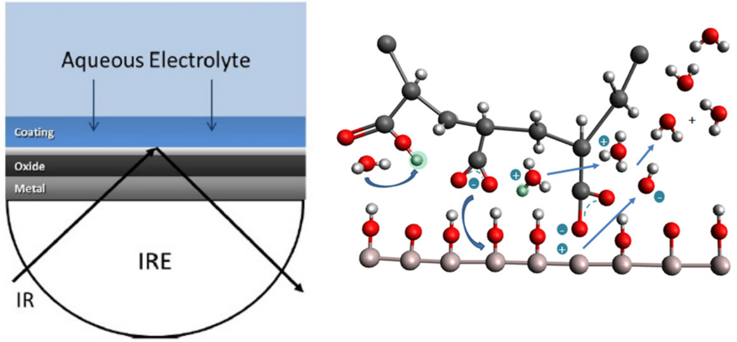
- Water **deprotonates** the carboxylic acid functional group of PAA.
- Carboxylate **anion is formed** and attacks a hydroxyl group on the surface.
- Carboxylate **ionic bond is formed** with the aluminum hydroxide.

In-situ monitoring of **electrolyte diffusion** at PAA/aluminum oxide interface. (Background Al – Air)



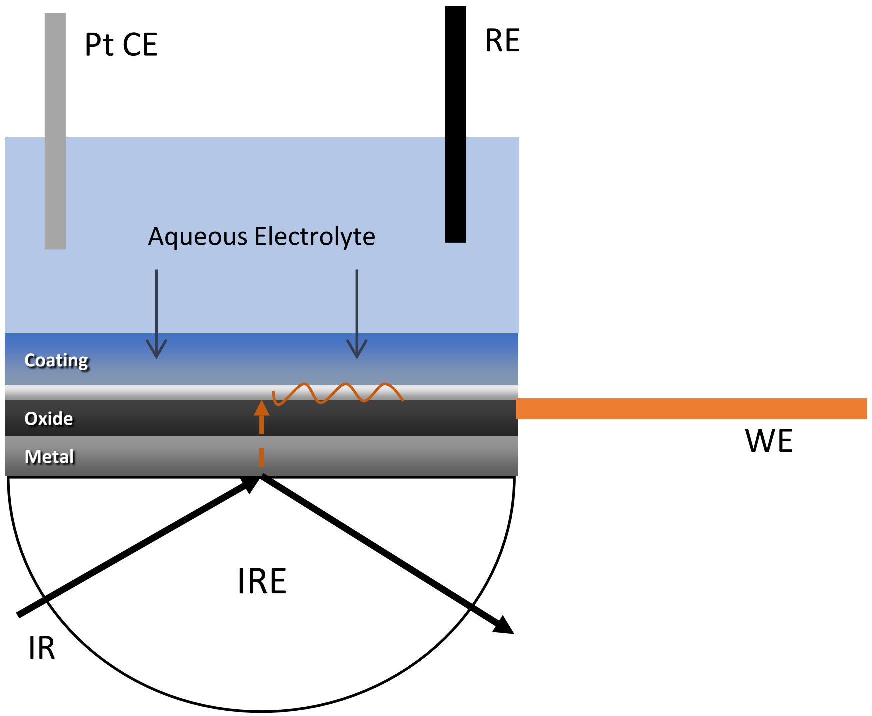


- Increasing OH peaks at 3446 cm^{-1} and 1655 cm^{-1} show **water build-up at the interface**.
- Carboxylate symmetric and asymmetric (1614 cm^{-1}) increase in time when water is present at the interface. **Same trend observed with APXPS**.
- Al-OH peak (956 cm^{-1}) is **decreasing in exposure time**.

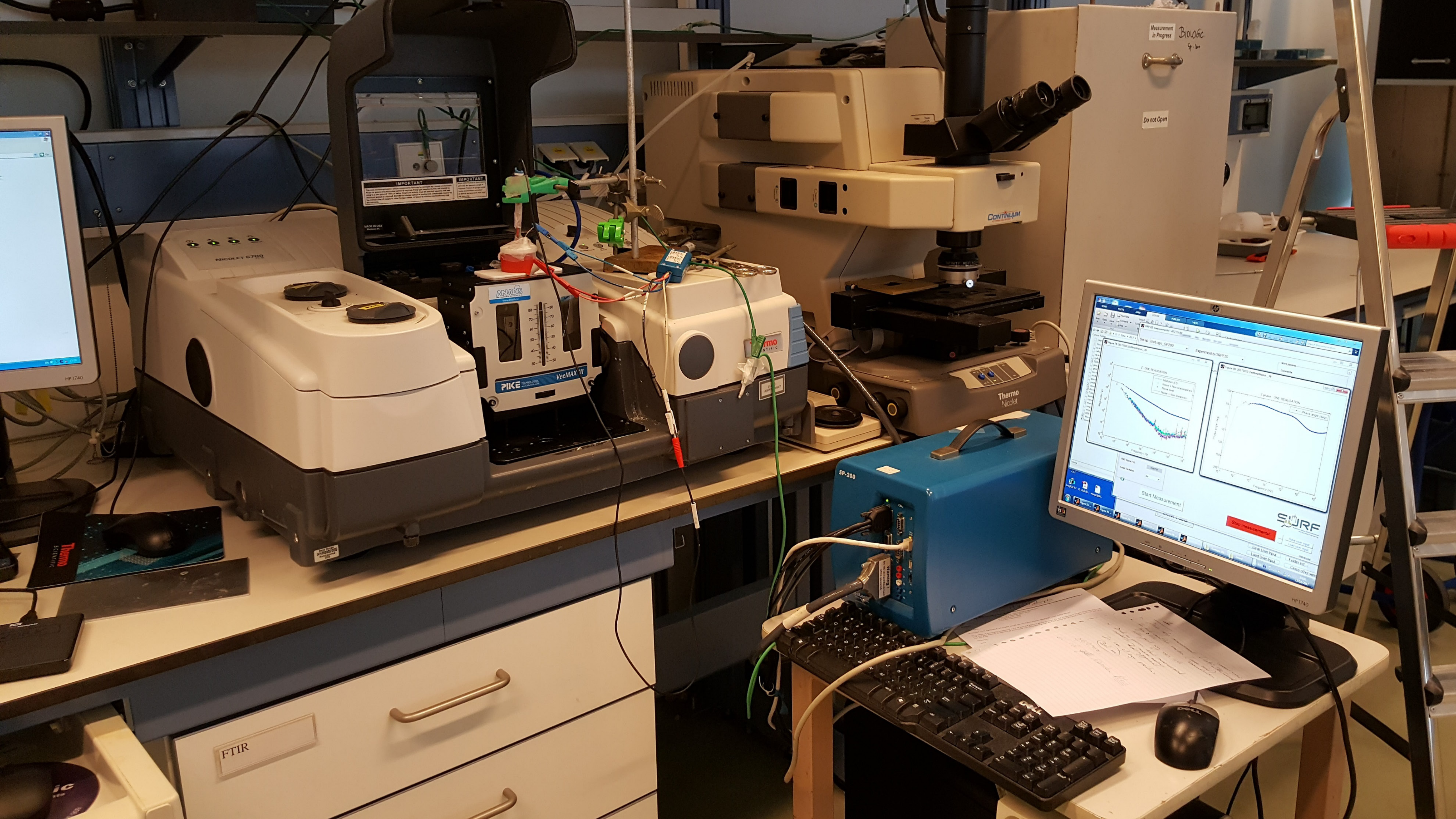
Pletincx et al. Sci. Rep. **7** (2017) doi:10.1038/srep45123

Obtaining an interface spectrum and information on the whole hybrid system **simultaneously**

Thin PAA coating



- A **borate buffer** is used to keep the bulk solution at pH 8 and acts as a supporting electrolyte.
  - → No corrosive de-adhesion, only effect of electrolyte is monitored.


NICOLET 6700
ANADIS
PIKE TECHNOLOGIES
VeeMAX III
CONTINUUM
Thermo Nicolet
Measurement in Progress
BioLogic
Do not Open
SP-200
Start Measurement
SURF
HP 1740
DELL
FTIR

Application of ORP-EIS vs EIS

- Necessities for a reliable EIS measurement:
  - ❖ Causality
  - ❖ Linearity
  - ❖ Stationarity

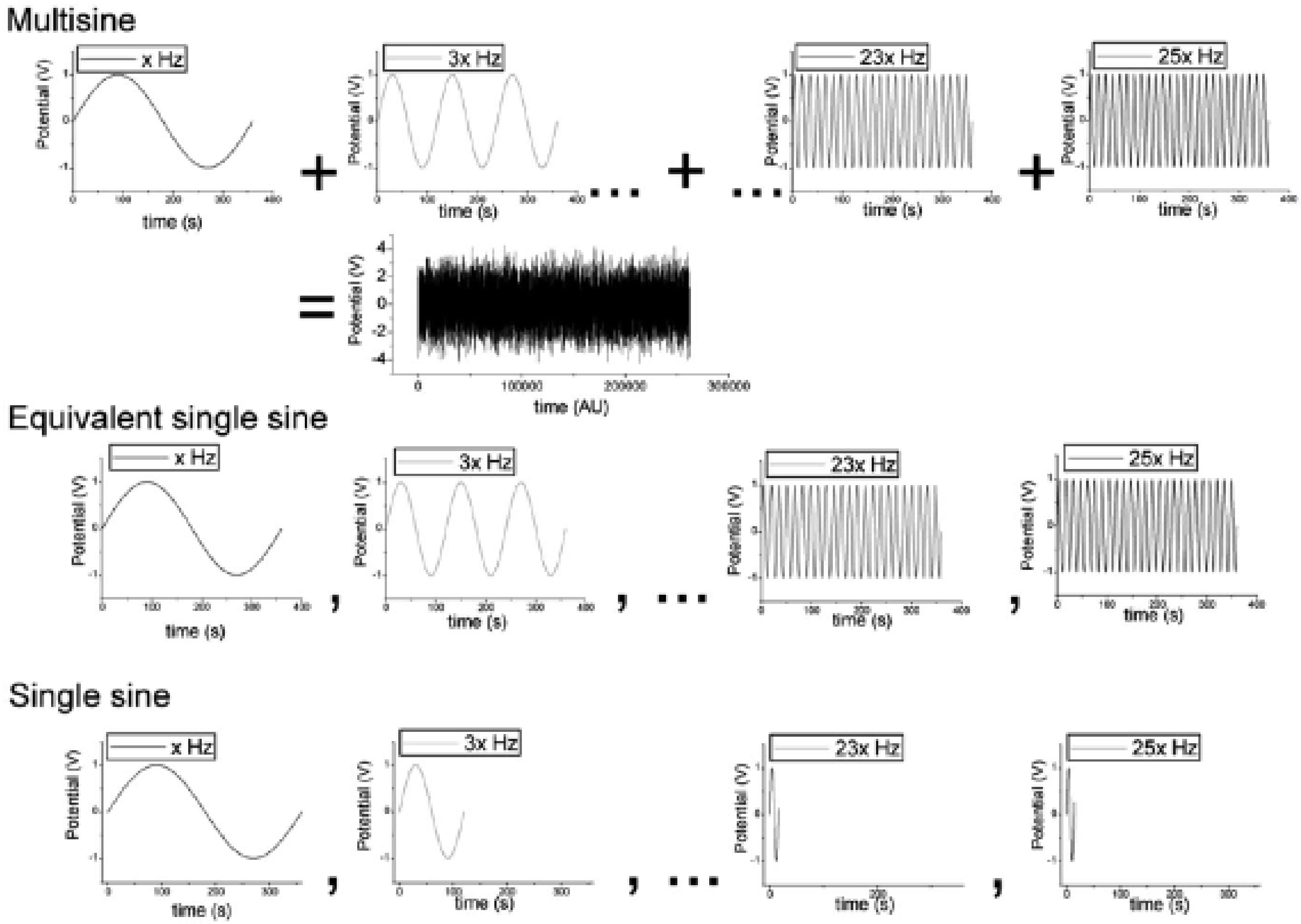
- Solution: apply a small perturbation Va in the stationary regime of the process

- Problems:
  - ❖ poor S/N ratio
  - ❖ initial, rapidly evolving stages of processes are not described

➡ Odd-Random-Phase EIS

Van Ingelgem, Y., Tourwé, E., Blajiev, O., Pintelon, R., & Hubin, A. *Electroanalysis 21* (2009) 730.
Breugelmans, T, Van Ingelgem, Y, A. Hubbin. Electrochemistry communications 12 (2010) 5.

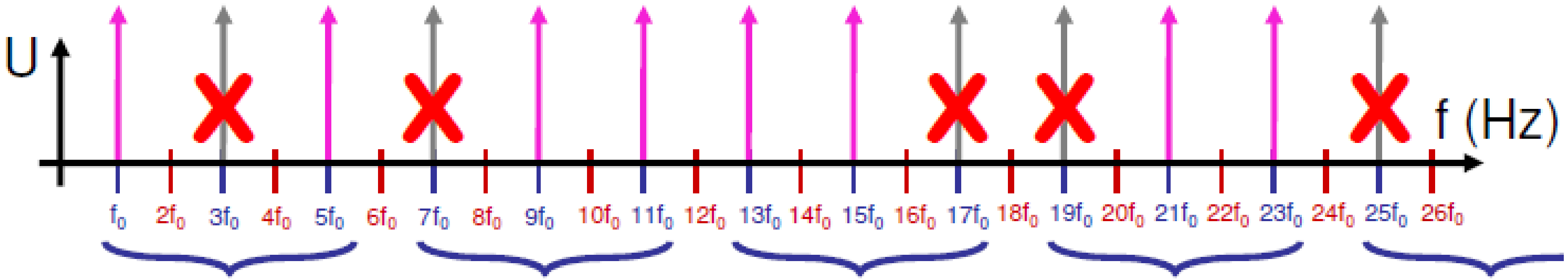
Application of ORP-EIS vs EIS



- Advantages:
  - High frequencies are excited many times more
  - Measurement time decreases

Van Ingelgem, Y., Tourwé, E., Blajiev, O., Pintelon, R., & Hubin, A. *Electroanalysis 21* (2009) 730.
Breugelmans, T, Van Ingelgem, Y, A. Hubbin. Electrochemistry communications 12 (2010) 5.

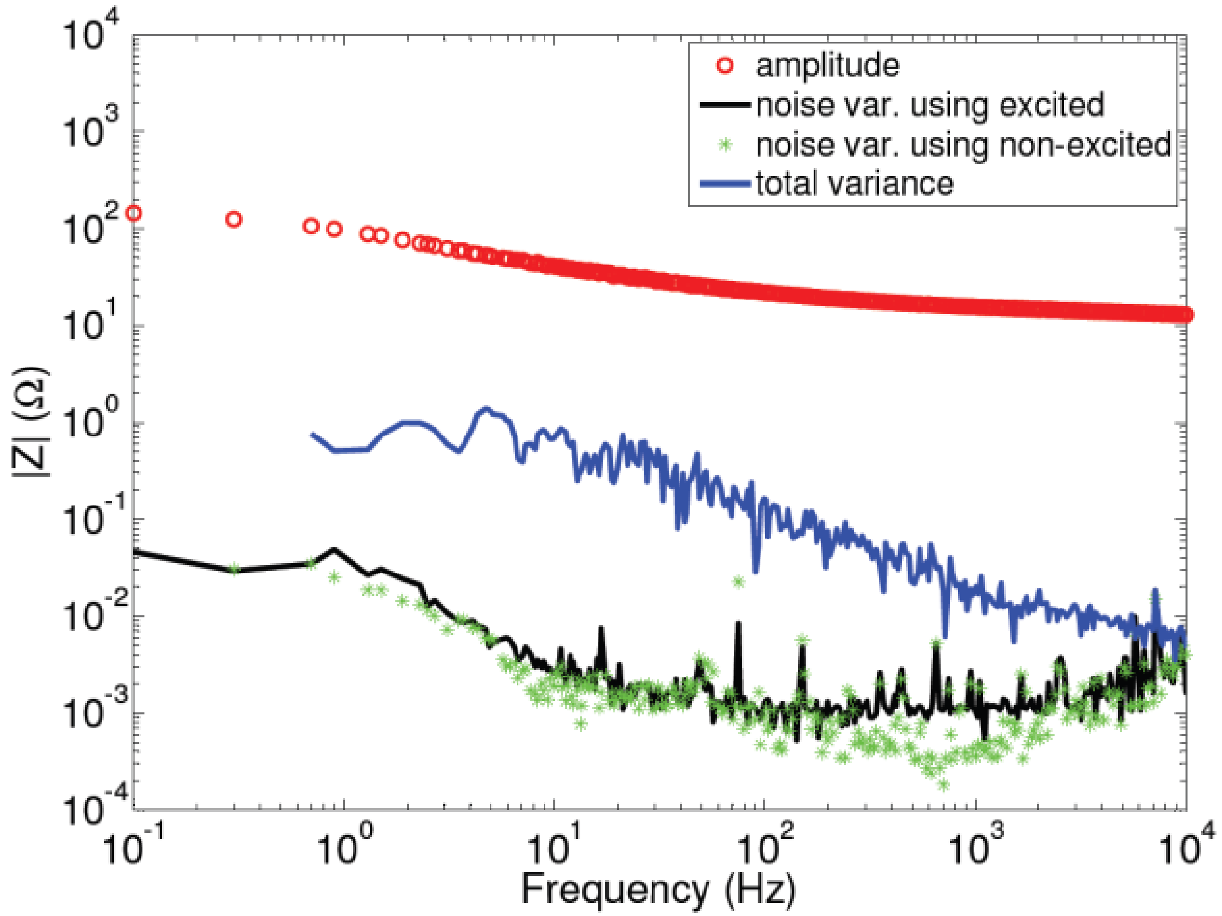
Application of ORP-EIS vs EIS



- Advantages:
  - Data analysis:
    - ❖ 5 periods measured
    - ❖ Last 4 used to calculate the standard deviation at the excited and non-excited frequencies
  - Extra information
    - ❖ Noise
    - ❖ Non-linearities
    - ❖ Non-stationarities

Van Ingelgem, Y., Tourwé, E., Blajiev, O., Pintelon, R., & Hubin, A. *Electroanalysis 21* (2009) 730.
Breugelmans, T, Van Ingelgem, Y, A. Hubbin. Electrochemistry communications 12 (2010) 5.

Application of ORP-EIS vs EIS



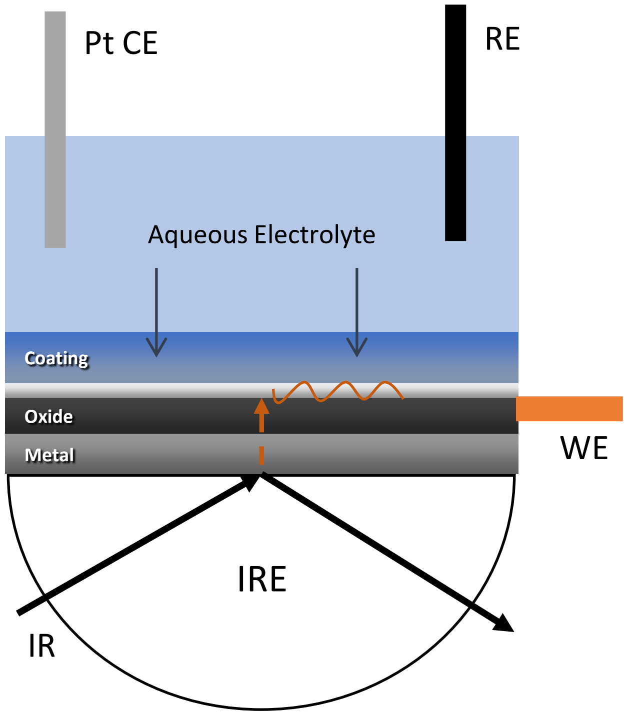
- impedance value
- noise level
- non-stationary behaviour
- non-linear behaviour (total variance)

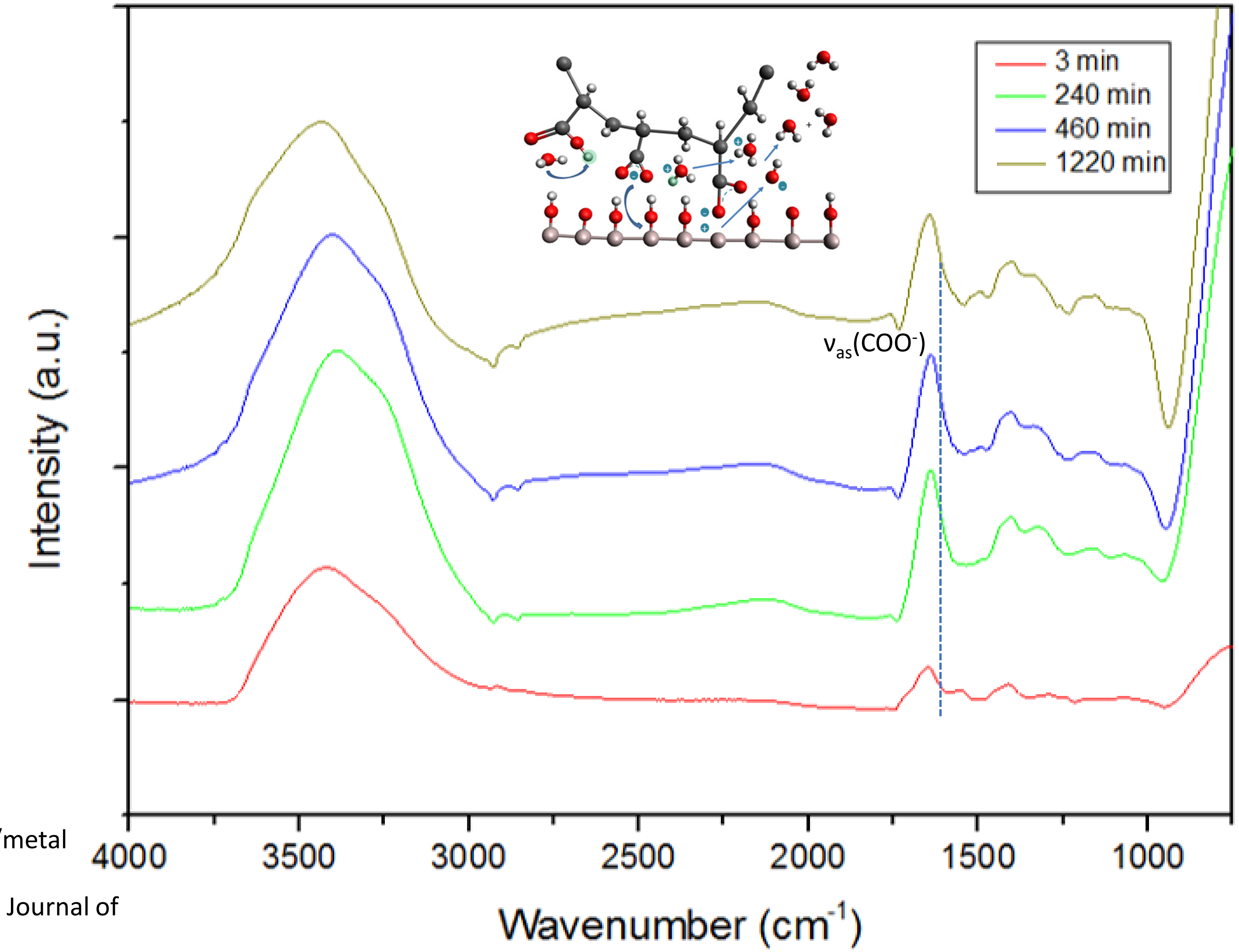
Linear : σ_{tot} overlaps $\sigma_Z(\omega_{ne})$

Stationary : $\sigma_Z(\omega_e)$ overlaps $\sigma_Z(\omega_{ne})$

- Advantages:
  - Fitting ORP-EIS data to EEC:
    - ❖ Weight with std noise/non-linearities/non-stationarities
    - ❖ Evaluation residual vs noise curve

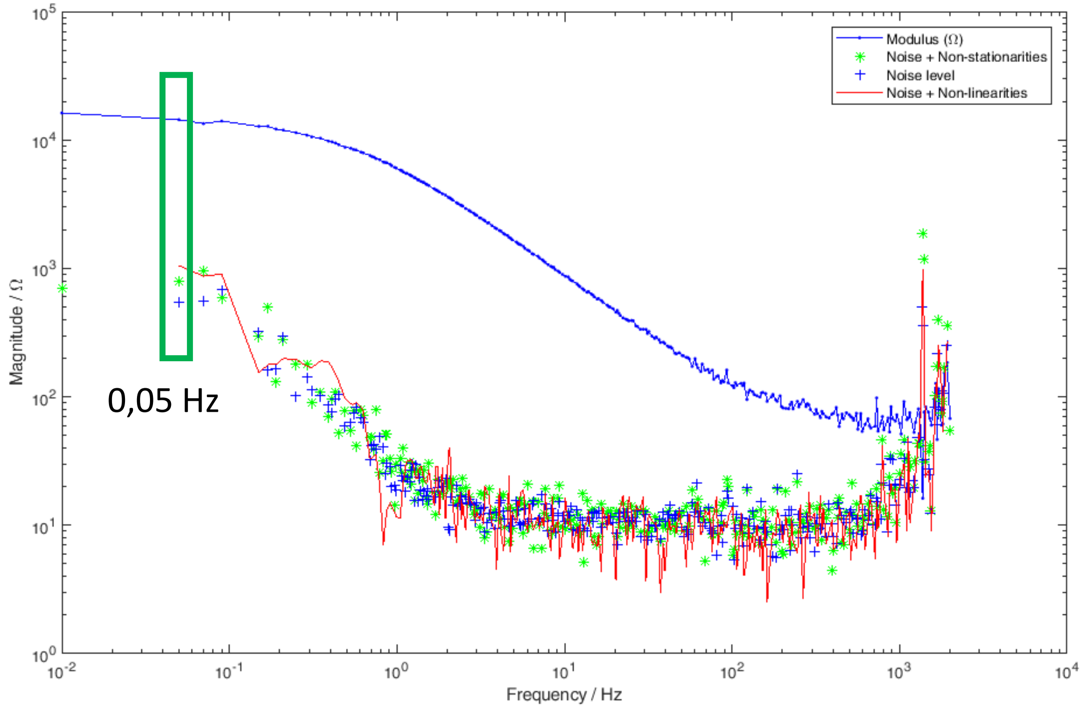
In-situ monitoring of **electrolyte diffusion** at PAA/aluminum oxide interface. (Background Al – PAA coating before immersion)

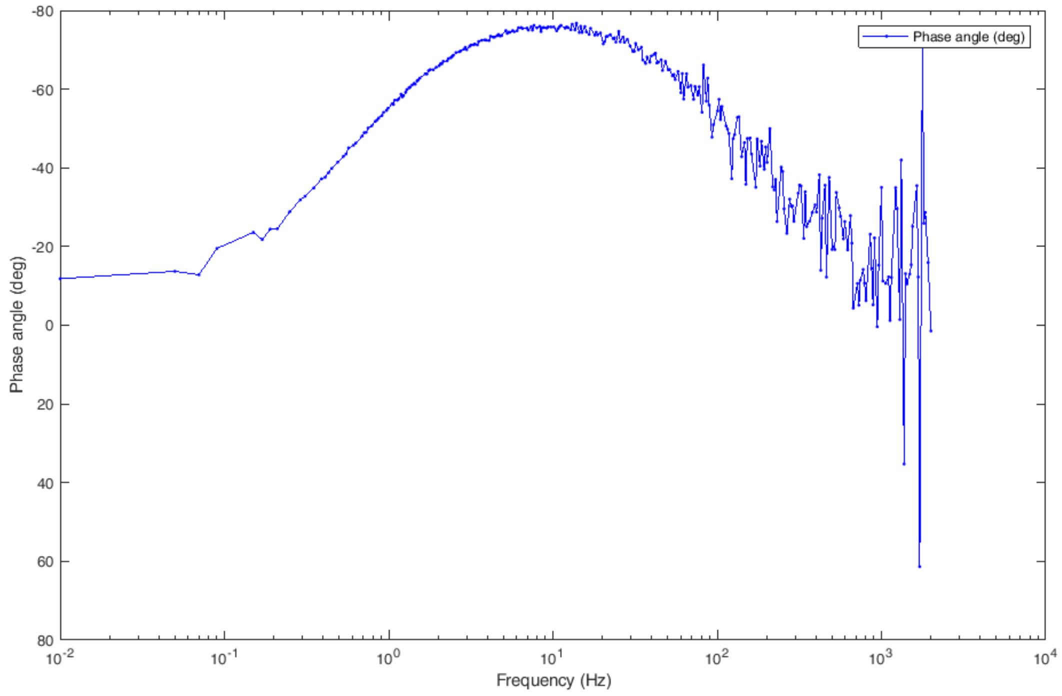




An in situ spectro-electrochemical monitoring of aqueous effects on polymer/metal oxide interfaces
Pletincx, S., Mol, J. M. C., Terryn, H., Hubin, A. & Hauffman, T., 1 Sep 2019, In : Journal of Electroanalytical Chemistry. 848, 113311.

Odd Random Phase Multisine Electrochemical Impedance Spectroscopy

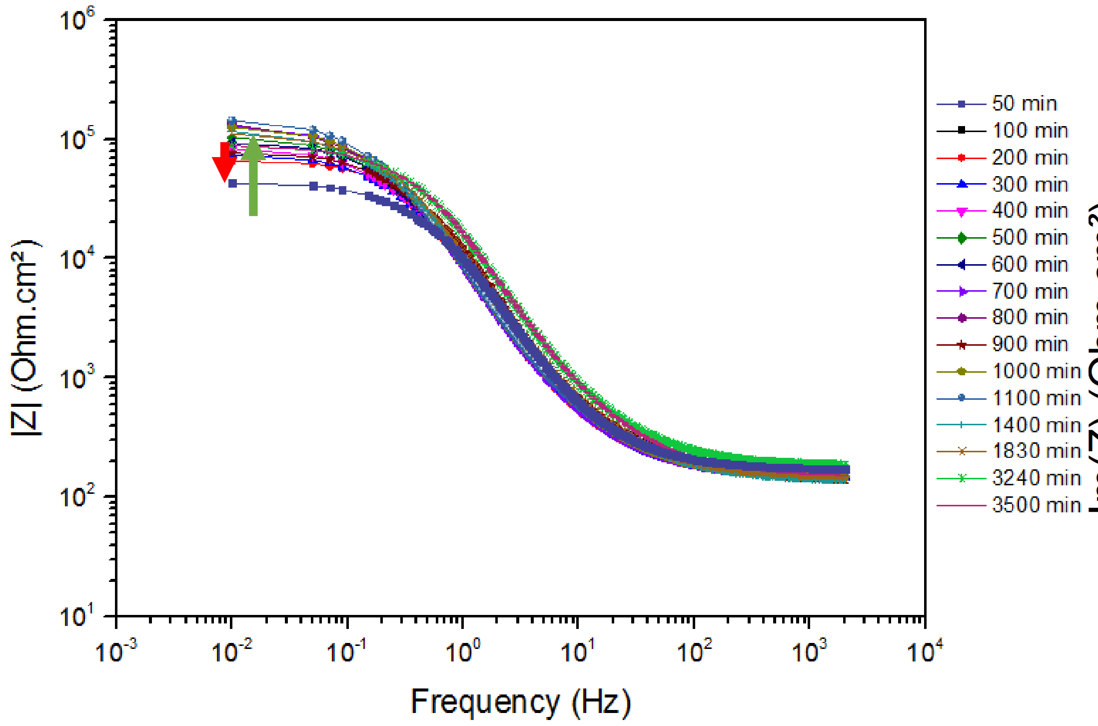


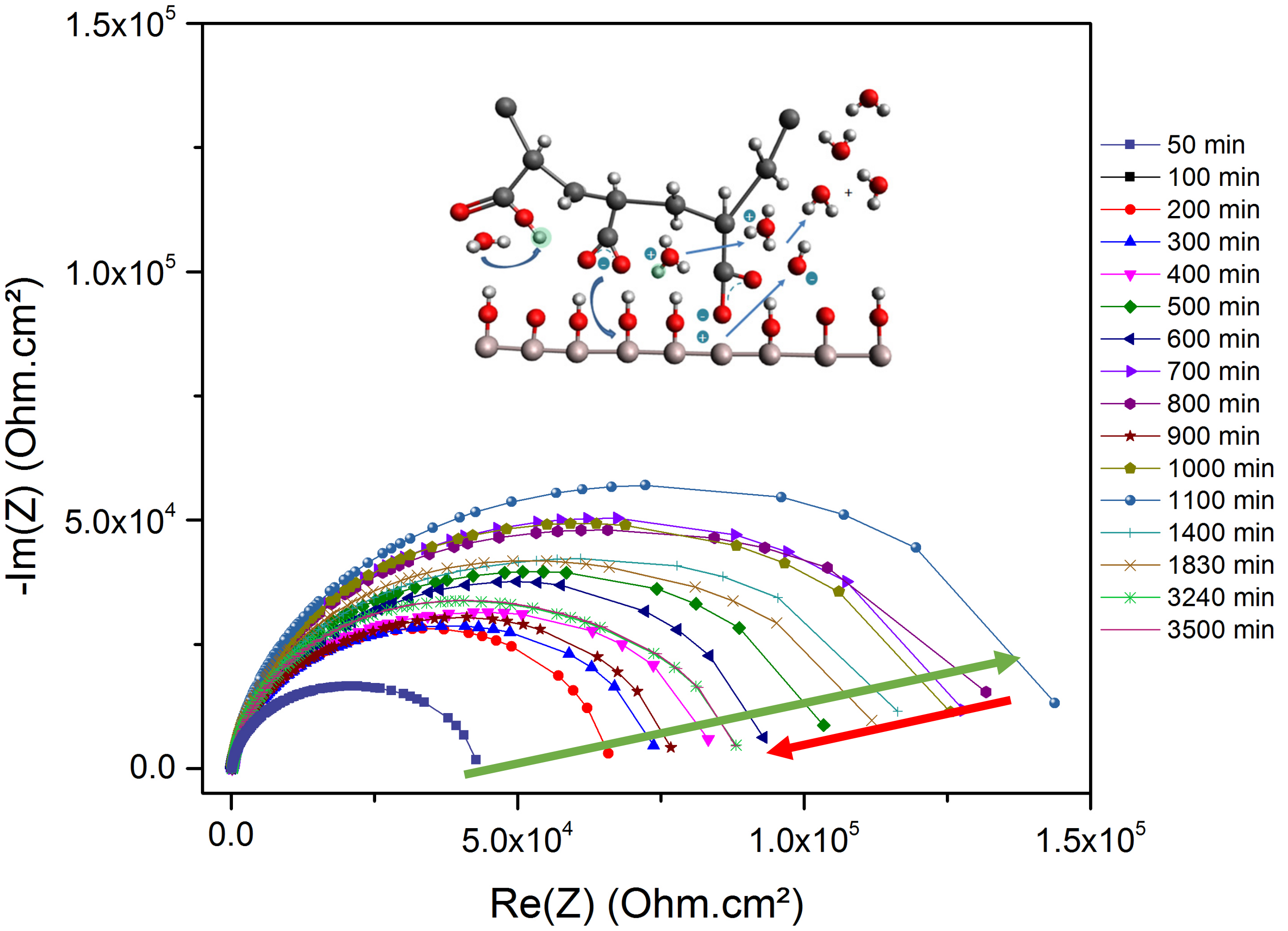


Stationary and Linear

An in situ spectro-electrochemical monitoring of aqueous effects on polymer/metal oxide interfaces
Pletincx, S., Mol, J. M. C., Terryn, H., Hubin, A. & Hauffman, T., 1 Sep 2019, In : Journal of Electroanalytical Chemistry. 848, 113311.

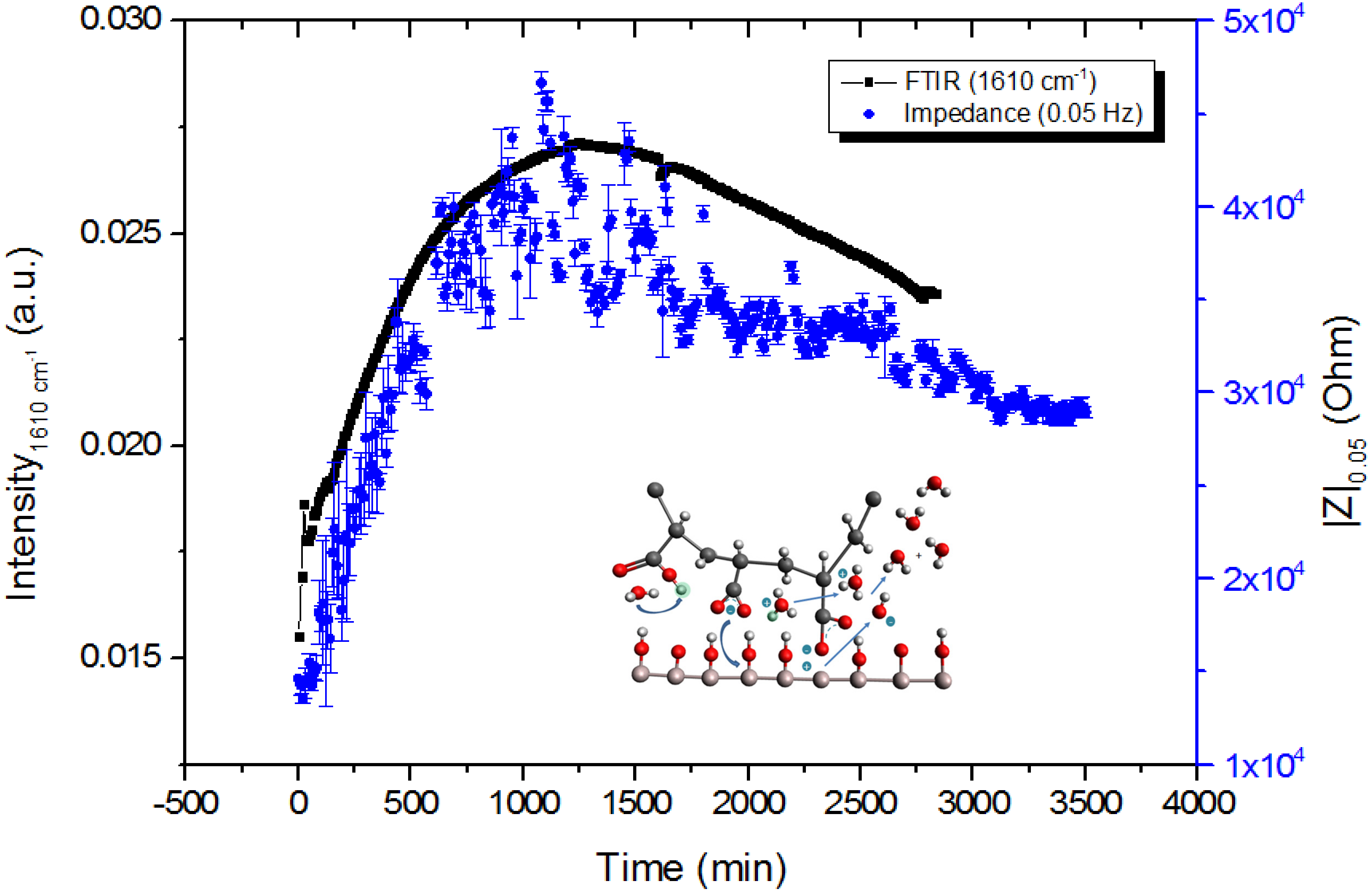
Impedance spectroscopy: 10 mV excitation around OCP





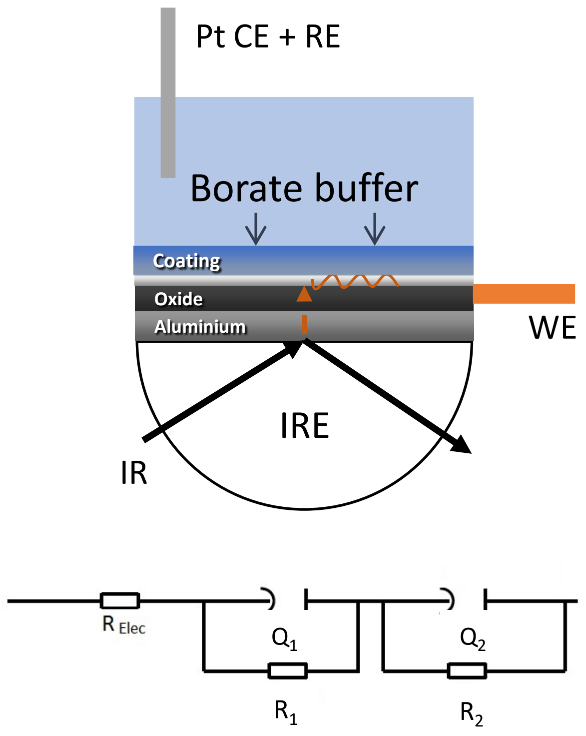
0,01 wt% PAA – Aluminum Oxide exposed to 0,1 M Borate Buffer.

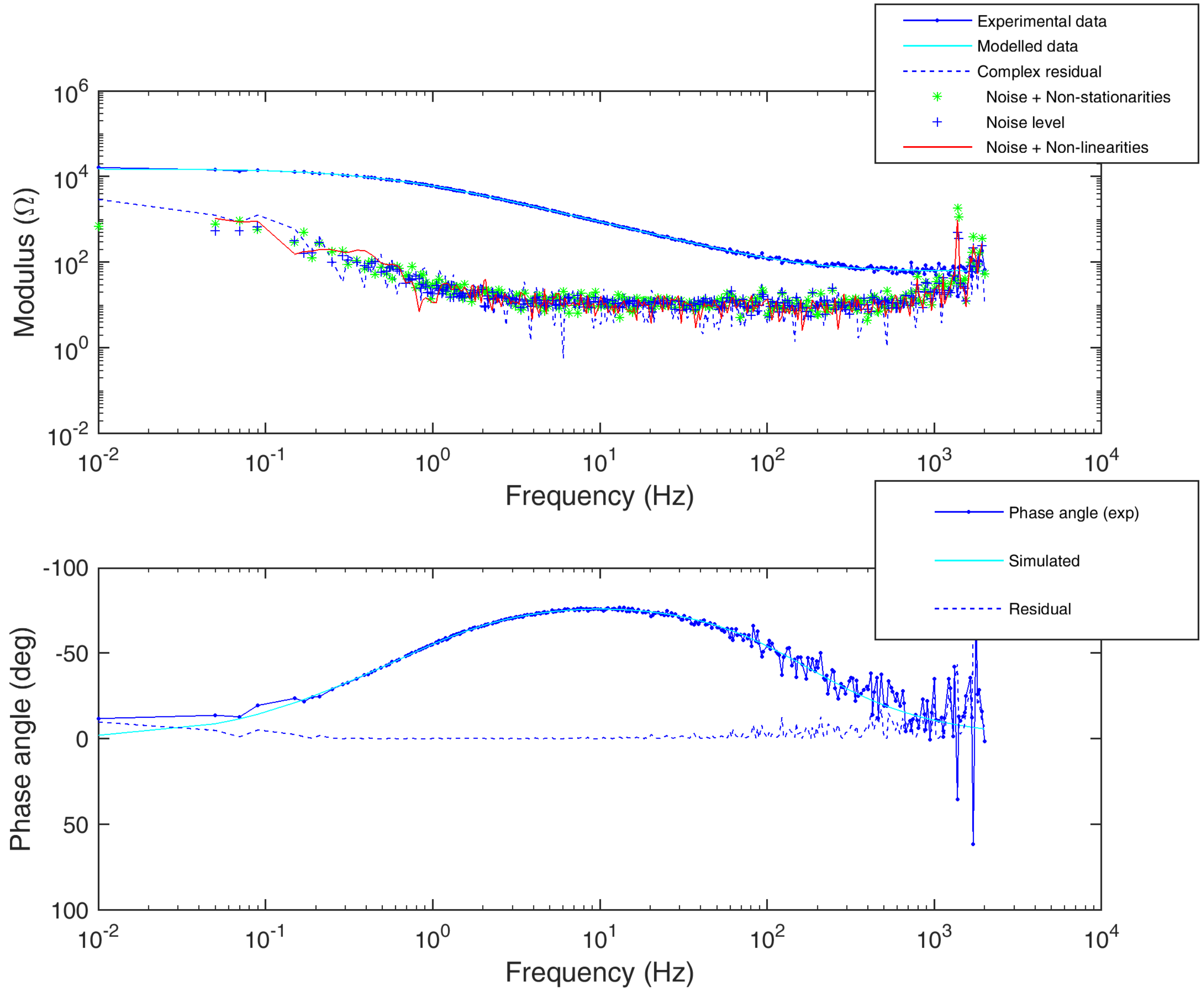
An in situ spectro-electrochemical monitoring of aqueous effects on polymer/metal oxide interfaces Pletincx, S., Mol, J. M. C., Terryn, H., Hubin, A. & Hauffman, T., 1 Sep 2019, In : Journal of Electroanalytical Chemistry. 848, 113311.



An in situ spectro-electrochemical monitoring of aqueous effects on polymer/metal oxide interfaces Pletincx, S., Mol, J. M. C., Terryn, H., Hubin, A. & Hauffman, T., 1 Sep 2019, In : Journal of Electroanalytical Chemistry. 848, 113311.

In-situ monitoring of **Poly(acrylic acid)**/aluminum oxide interface.





Noise levels show linear and stationary behavior after 10 mV multisine perturbation

Complex residual near real noise values → indication that model is valid.

Large contribution of noise at high frequency → only solution resistance.

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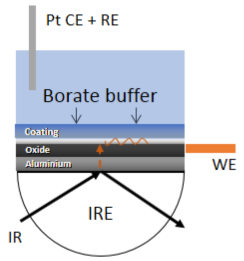
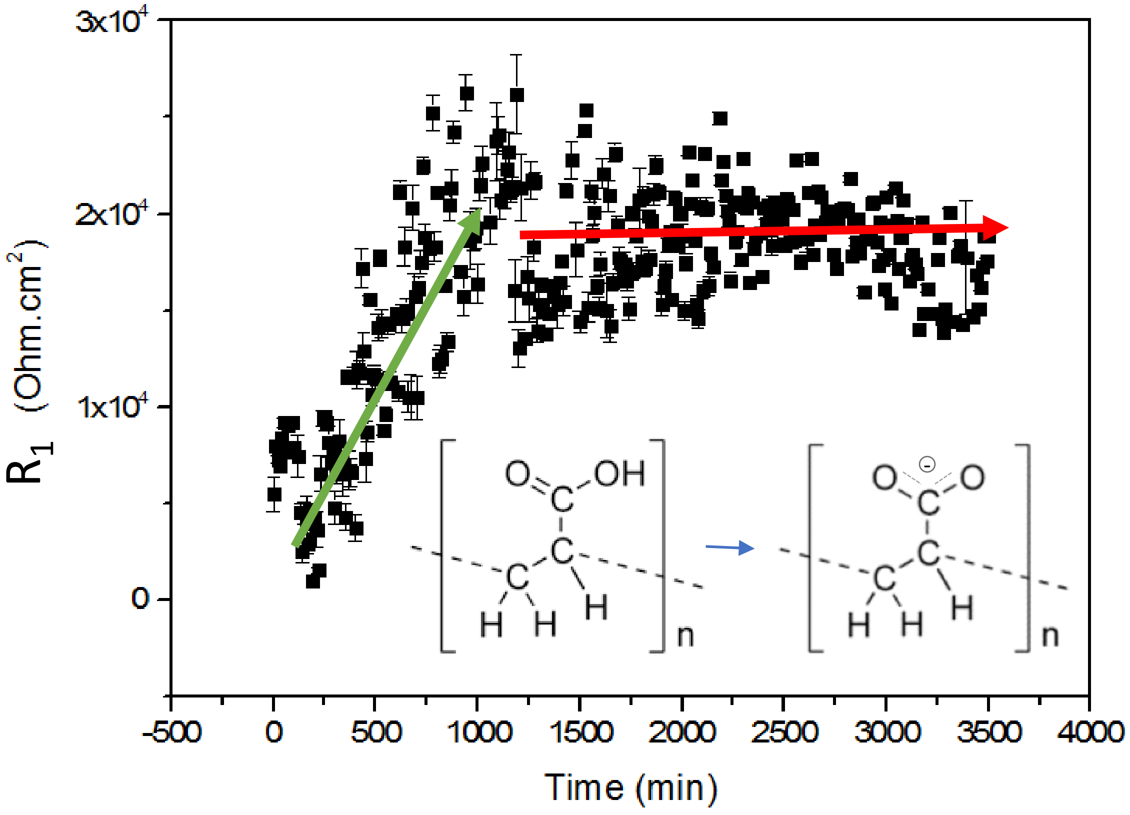
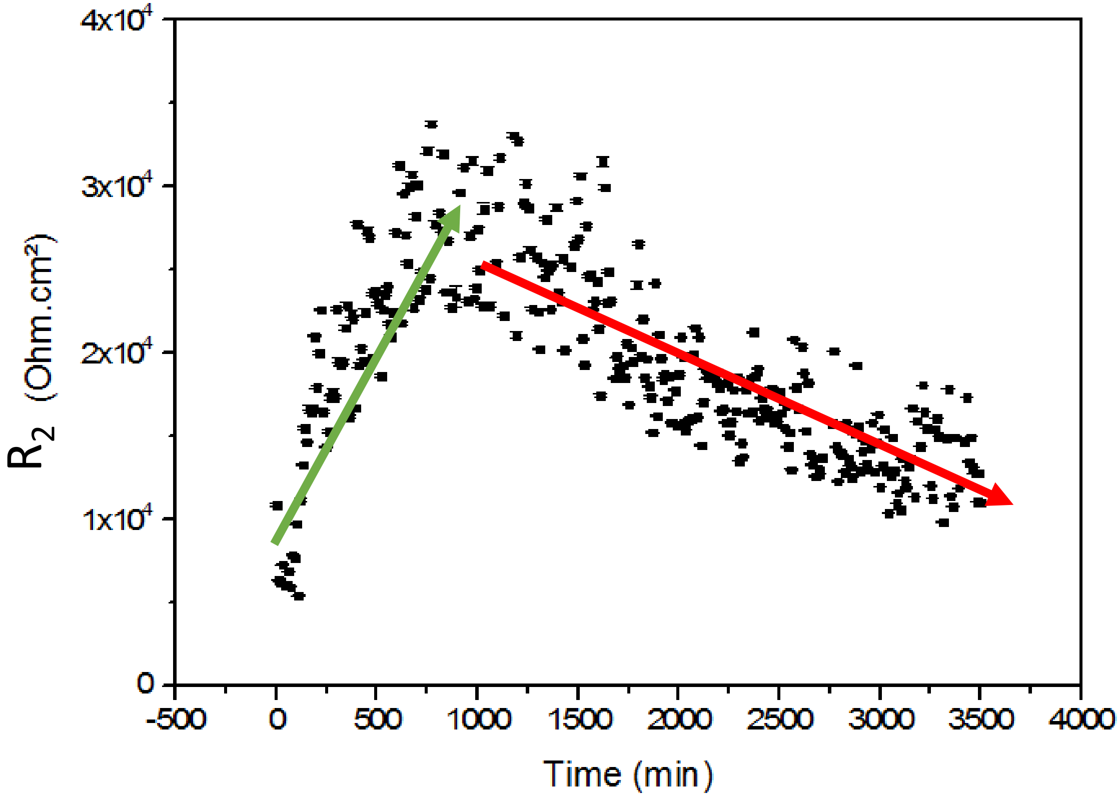
Electrochemical parameters







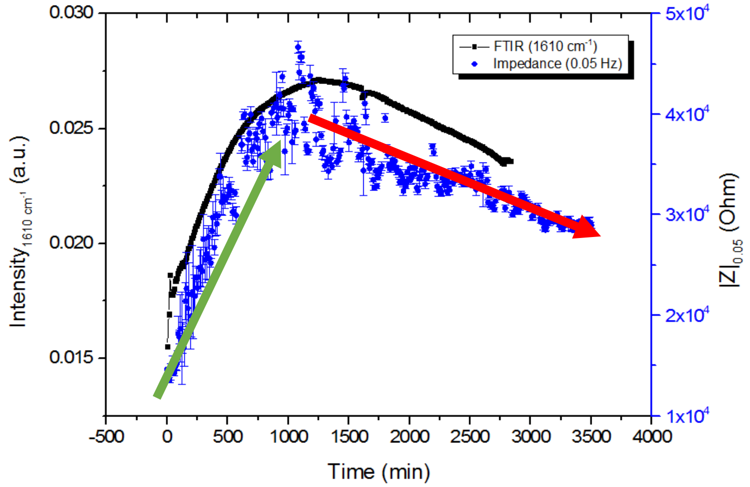
R_1 increases: functional groups deprotonate due to electrolyte diffusion. Borate buffer counters acidification. This leads to lower amount of ions → increasing resistance

$$4B(OH)_3\,(aq.) \;<\!\!-\!\!-\!\!-\!\!-\!\!-\!\!> \; B_4O_7^{2-}\,(aq.) + 5H_2O + 2H^+\,(aq.)$$

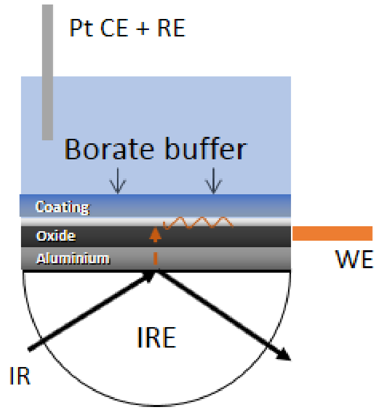
First 1000 minutes → increase in R_2 resistance (Due to bond formation, observed with IR Kretschmann)

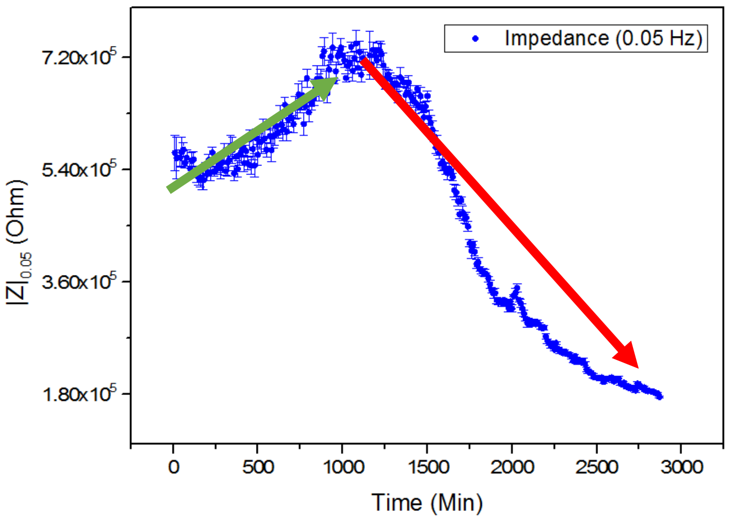
Afterwards → decrease in R_2 resistance (Due to replacement of bonds by bulk water, disappearance of IR peaks)

Comparison between systems by ORP-EIS

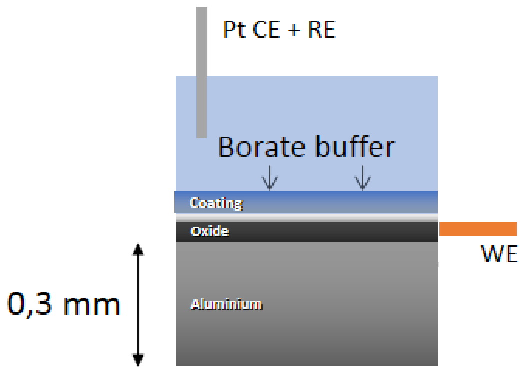


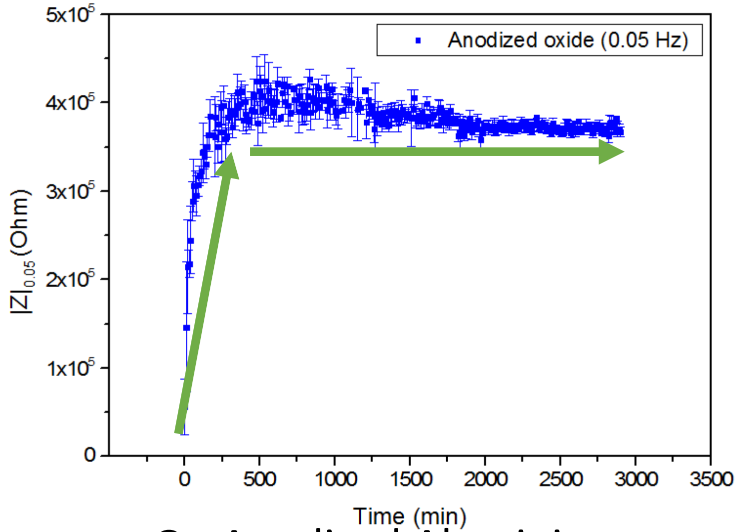
IR system on Al PVD deposited



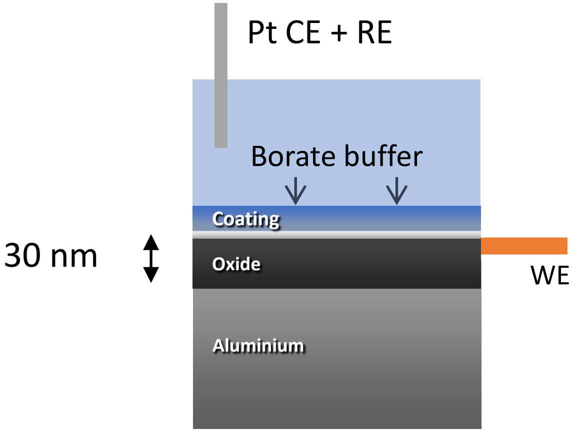


On Rolled Aluminium





On Anodized Aluminium



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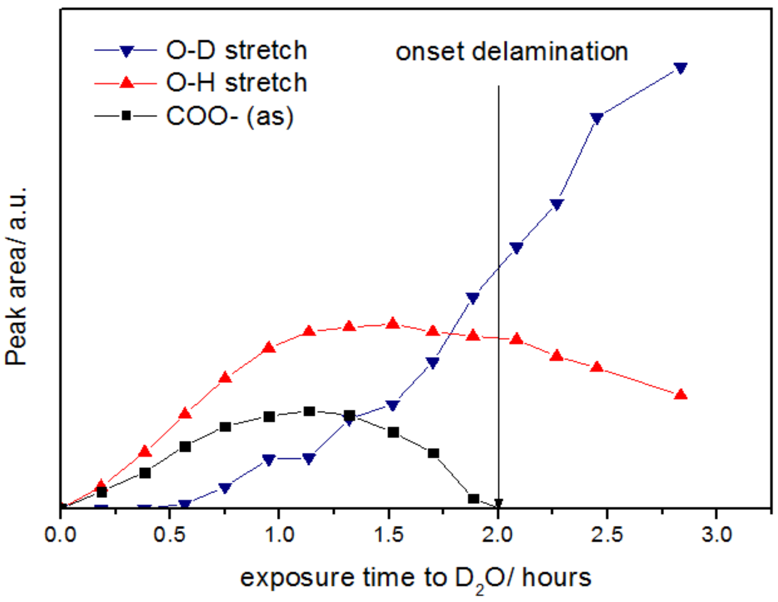
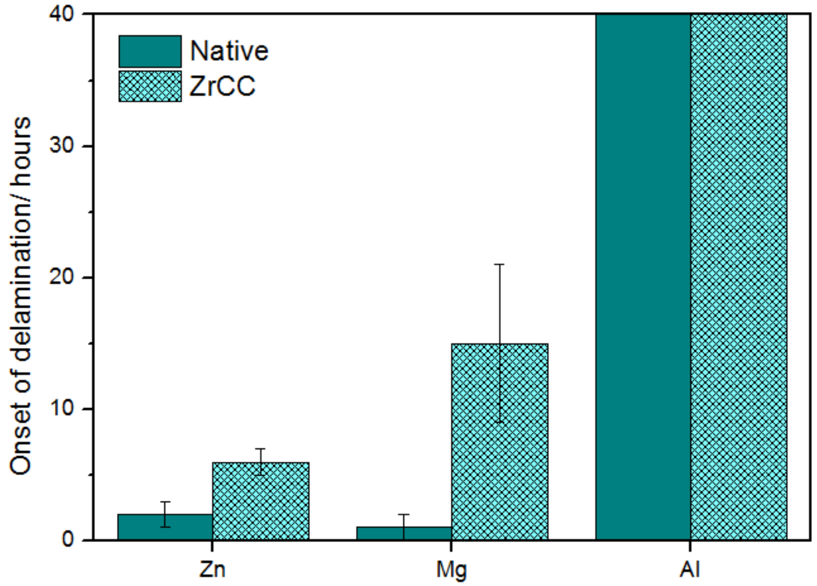
Industrial relevance: Akzo polyester coating on different (converted and non converted metals

Onset of bond changes as function of time as function nature of substrate





Onset of bond changes based on infrared peak area of asymmetric carboxylate stretchin g vibration followed in-situ during exposure to D_2O.

Effect of zirconium-based conversion treatments of zinc, aluminium and magnesium on the chemisorption of ester-functionalized molecules

Fockaert, L. I., Pletincx, S., Boelen, B., Hauffman, T., Terryn, H. & Mol, J. M. C., 1 Apr 2020, In : Applied Surface Science. 508, 145199.

Chemisorption of polyester coatings on zirconium-based conversion coated multi-metal substrates and their stability in aqueous environment

Fockaert, L. I., Pletincx, S., Ganzinga-Jurg, D., Boelen, B., Hauffman, T., Terryn, H. & Mol, J. M. C., 1 Jan 2019, In : Applied Surface Science. 508, 144771.

Conclusions

APXPS used to characterize interfacial information by using thin film approach. Environmental effects can be simulated, however limited to upper gas pressure limit. (28 % RH for this system)

Complementary information of the solid/solid interface is provided by **ATR-FTIR Kretschmann** technique.

IR Kretschmann is **combined with Impedance Spectroscopy**. Provides information of the whole hybrid system for PAA and PMMA on different types of aluminum oxide.

ORP EIS allows us to judge non stationarities/ non linearities, allows to control time window and match with the system!

Water has a **mediating role** at the interface of PAA and PMMA on aluminum oxide. PMMA has a more stable interface than PAA. Silanes we investigate at the moment. Also conversion systems.

The combined in situ IR/EIS can be used on industrial relevant systems to study interfaces of (converted) metal systems

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Locale bonds can be probed with Nano-AFM-IR (not shown in talk)

Probing the Metal Oxide/Polymer Molecular Hybrid Interfaces with Nanoscale Resolution Using AFM-IR (not shown)

Cavezza, F., Pletincx, S., Revilla, R. I., Weaytens, J., Boehm, M., Terryn, H. & Hauffman, T., 31 Oct 2019, In : Journal of Physical Chemistry C. 123, 43, p. 26178-26184 7 p.