

Formulating Functional Films and Coatings IV

Wednesday 8 December 2021

Smart ceramic coatings for corrosion protection

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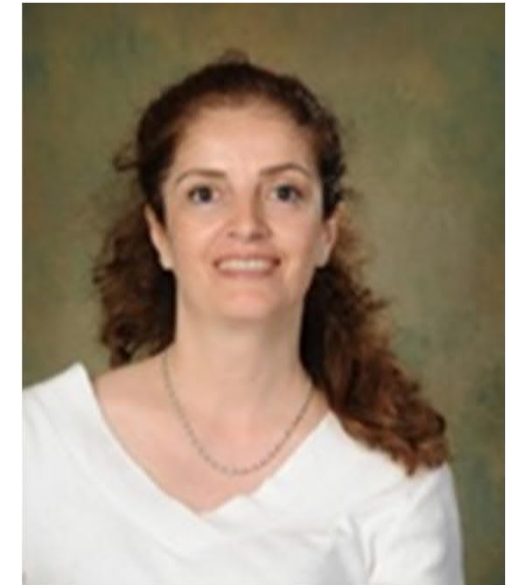


Royal Academy
of Engineering

Plasma Electrolysis Research Lab



Dr Sepideh Aliasghari

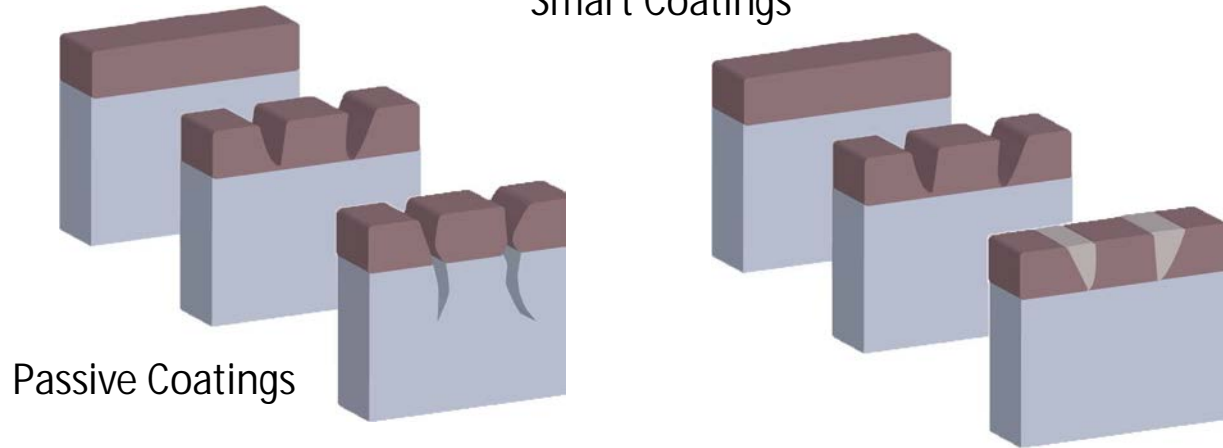


A. Matthews, A. Yerokhin, N. Laugel, S. Aliasghari, A. Rogov, D. Shore, H. Tang , Y. Li, S. Al Abri, Y. Guo

Aims and Objectives

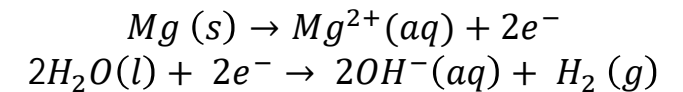
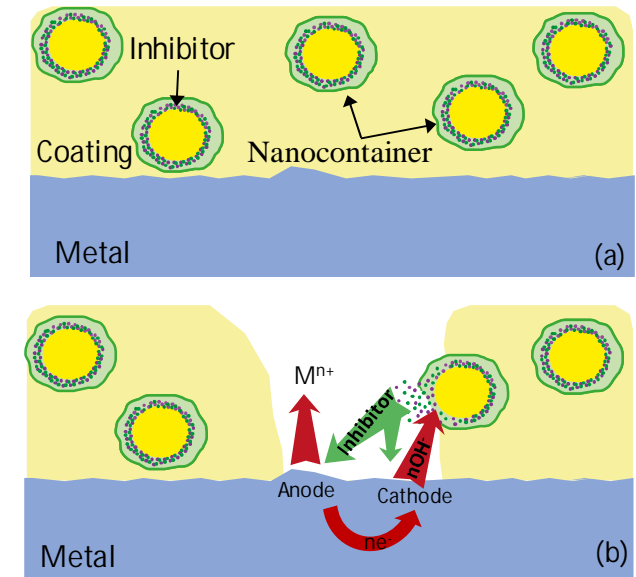
Develop an environmentally friendly coating technology capable of improving the long-term performance of lightweight components used in the transport industry

Smart Coatings



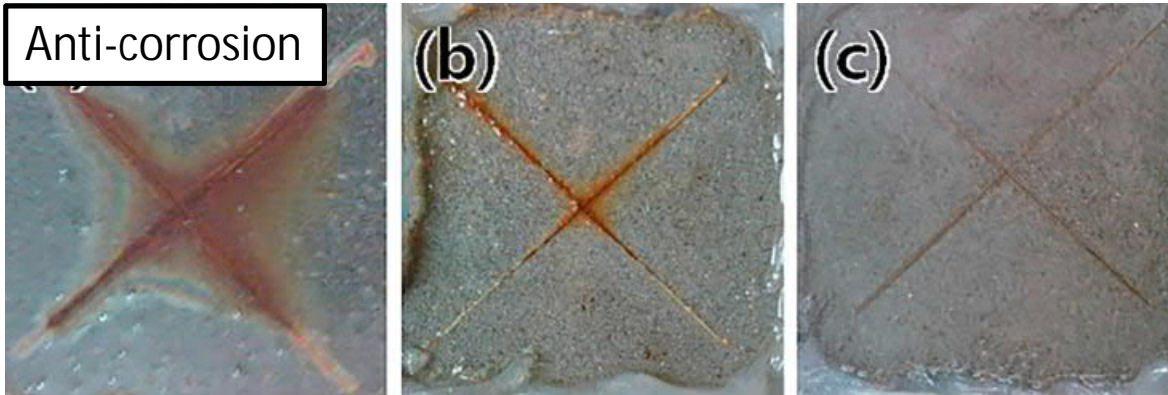
Passive Coatings

Achieve the active multi-functionalisation of ceramic coatings by incorporating encapsulated active species to provide corrosion protection and self-healing properties on-demand



Active functionalization

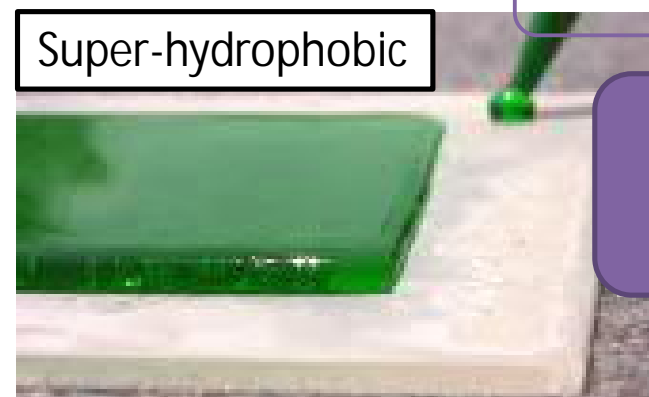
Organic coatings



2



1



Ceramic coatings

Thermal stability

Mechanical performance

Rigid and inert

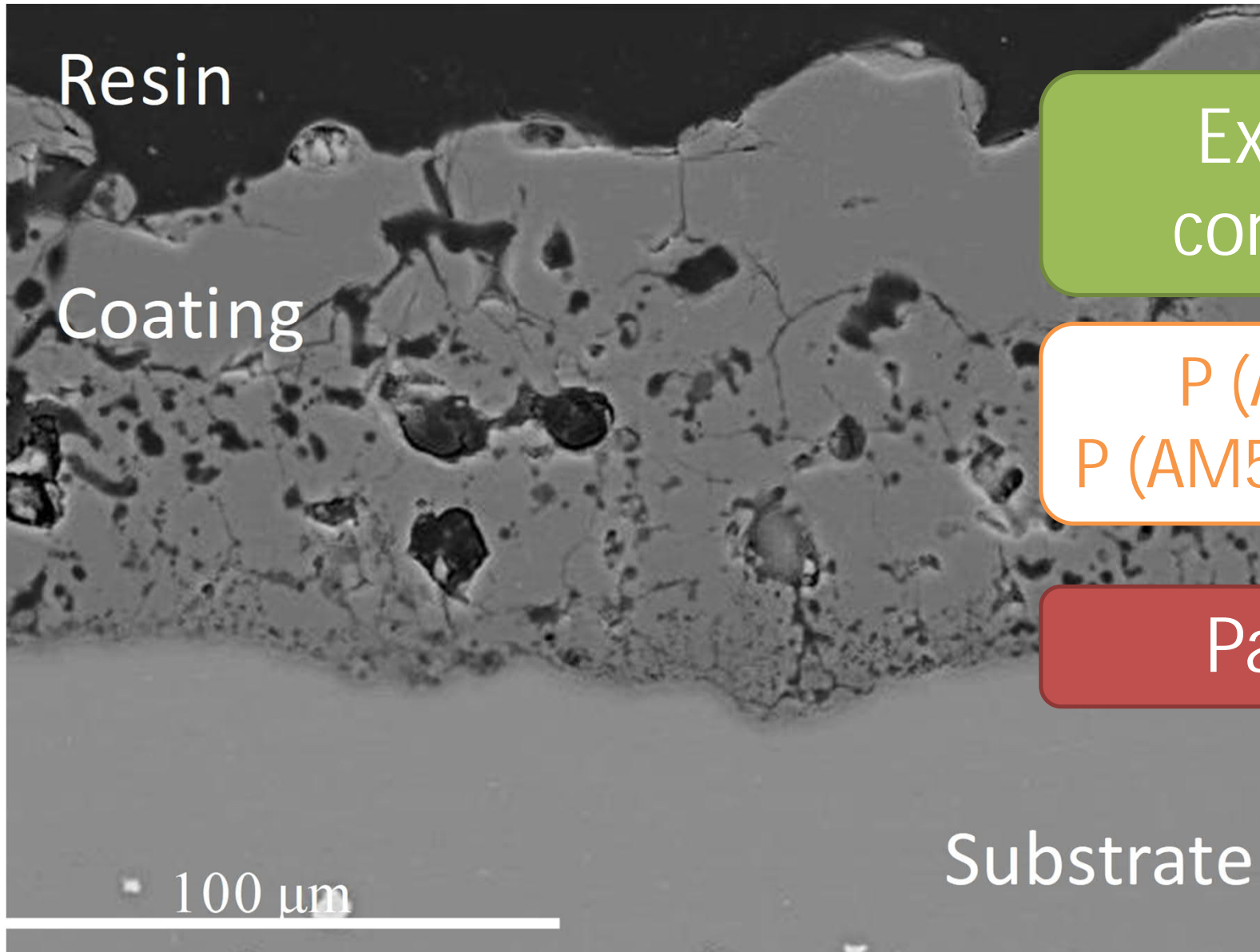
Plasma Electrolytic Oxidation
(PEO)

¹ Hanze Ying/Nature Communications 5, 3218 (2014)

² Boura/ Prog. Org. Coat., 75 (2012), pp. 292-300

³ Super hydrophobic coating (UltraTech International, Inc.) <https://www.youtube.com/watch?v=IPM8OR6W6WE>

Plasma Electrolytic Oxidation (PEO)

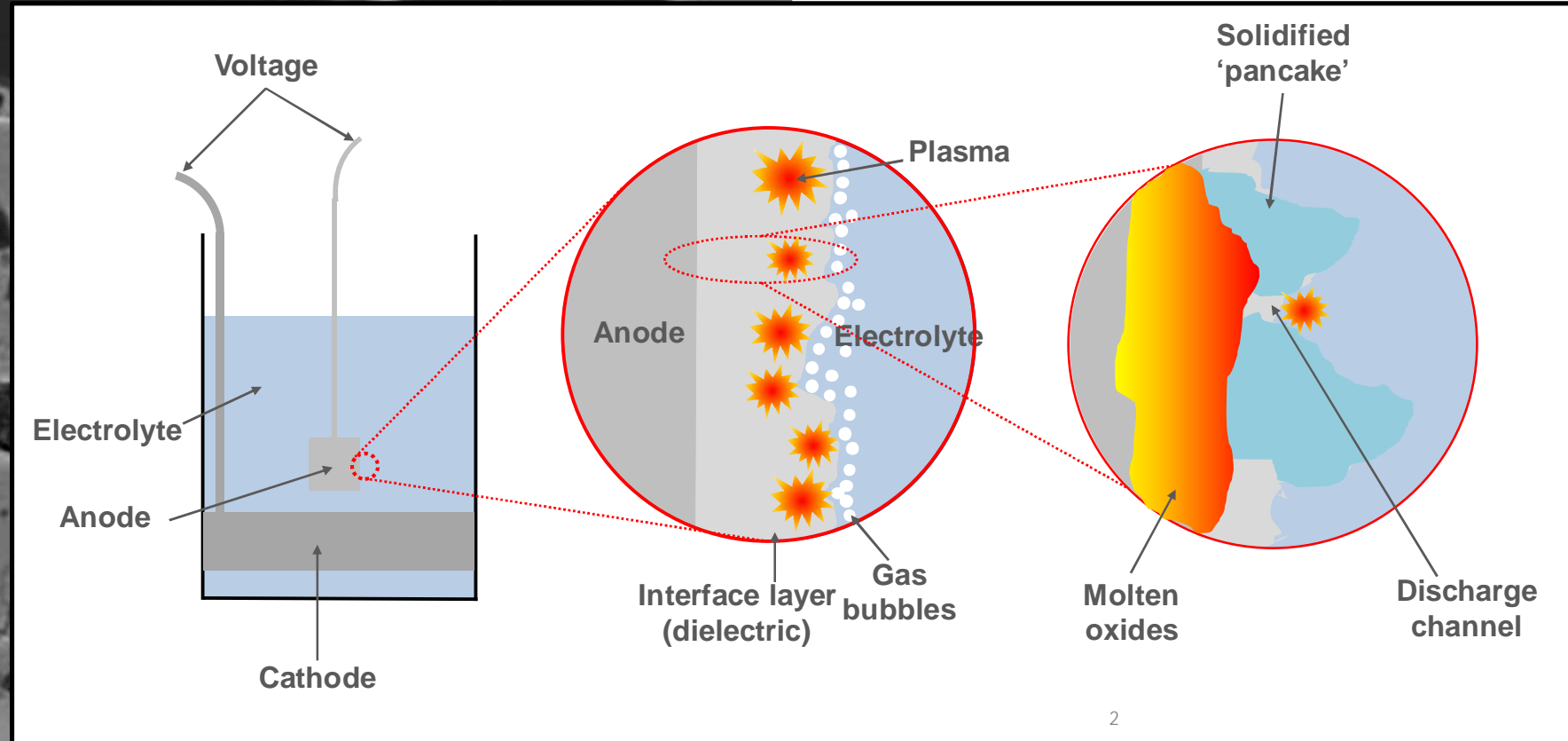
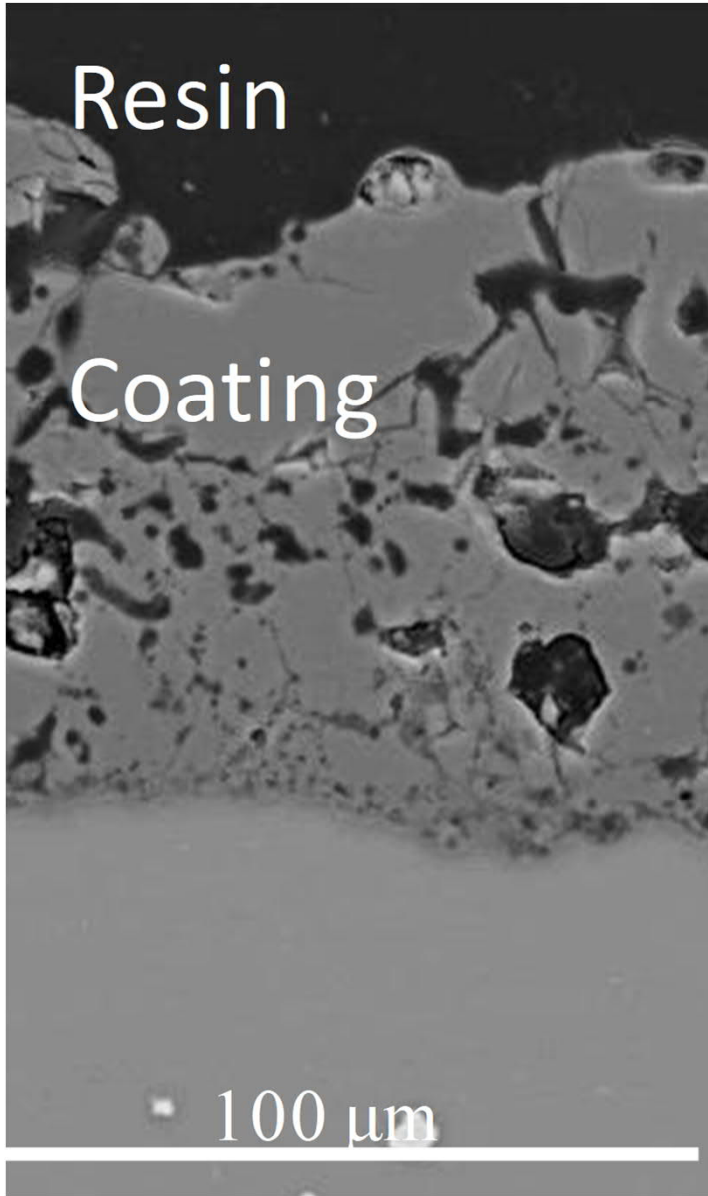


Excellent wear and corrosion properties

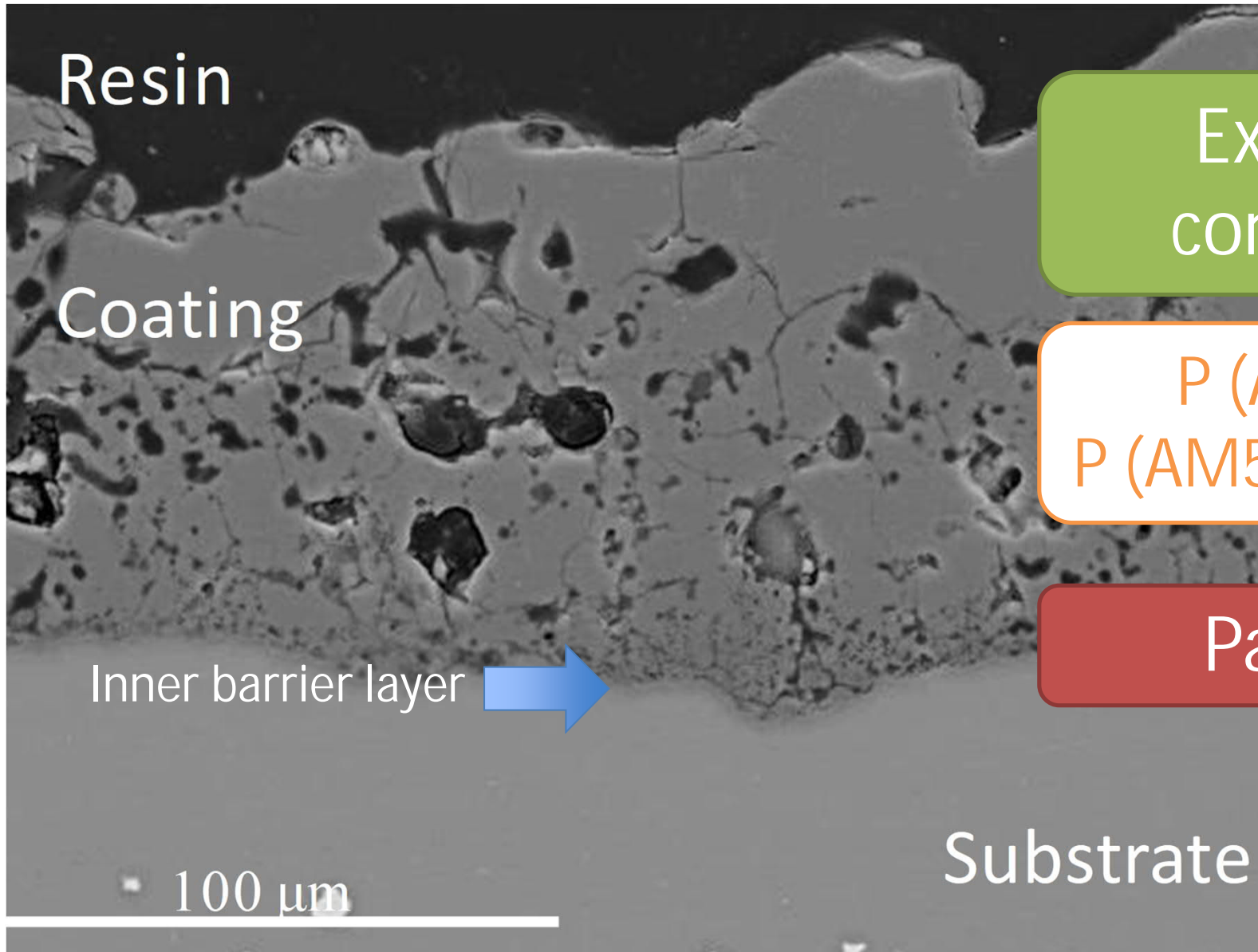
$P (AM50) = 3.21 \text{ mmy}^{-1}$
 $P (AM50+PEO) = 0.09 \text{ mmy}^{-1}$

Passive protection

Plasma Electrolytic Oxidation (PEO)



Plasma Electrolytic Oxidation (PEO)



Excellent wear and corrosion properties

$P (AM50) = 3.21 \text{ mmy}^{-1}$
 $P (AM50+PEO) = 0.09 \text{ mmy}^{-1}$

Passive protection

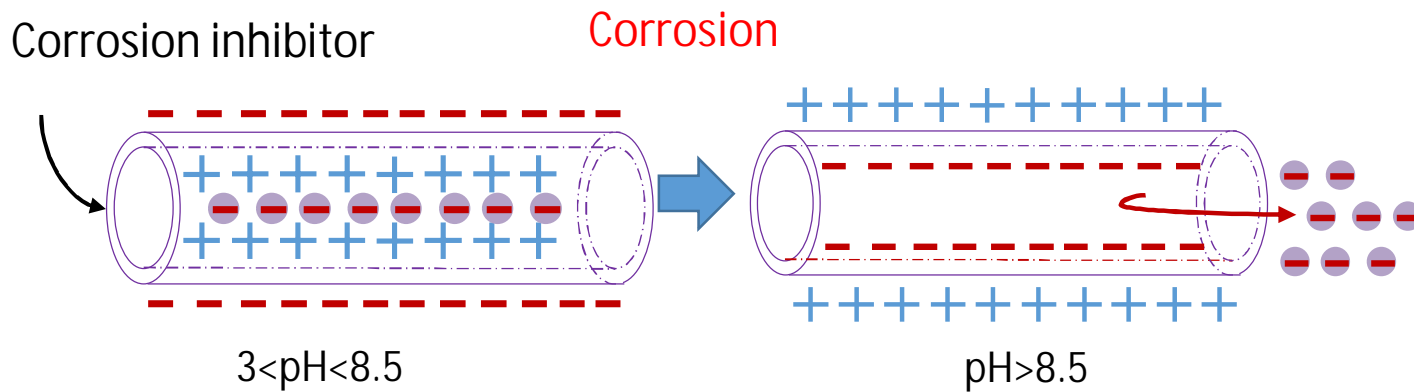
Specific Objective

Functionalization of PEO coatings

Encapsulation of corrosion inhibitors

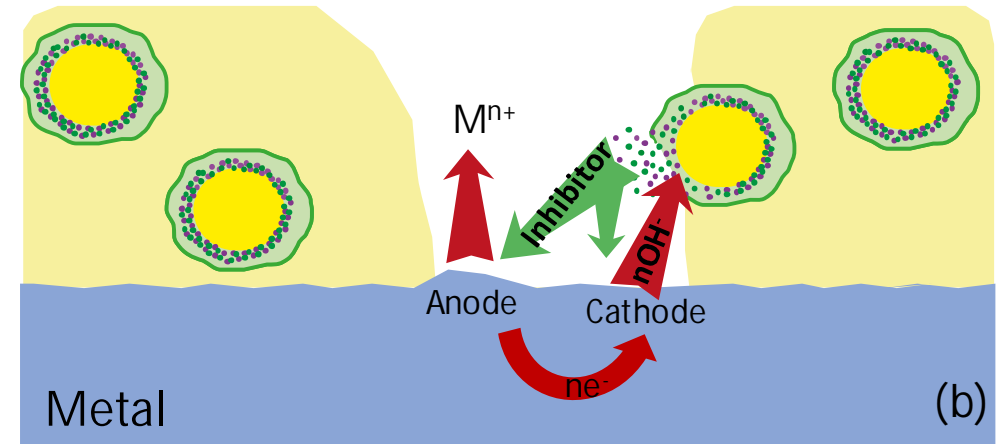
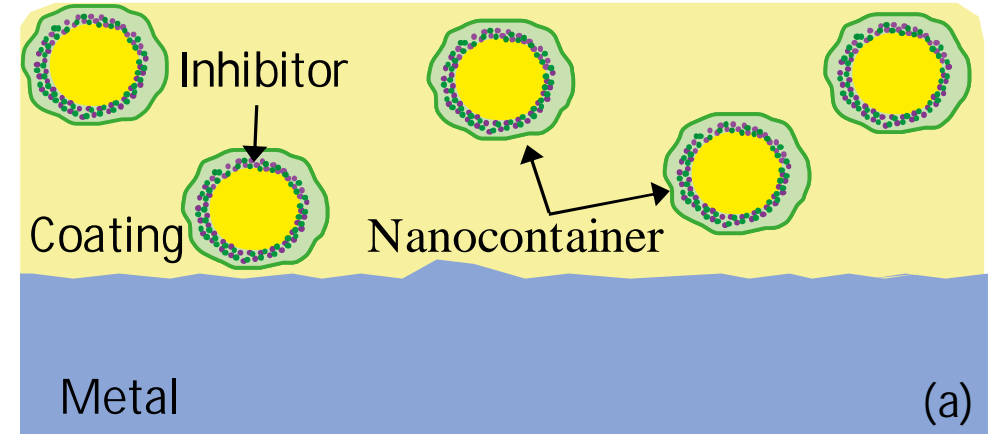
Corrosion protection on-demand

pH sensitive nanocontainers

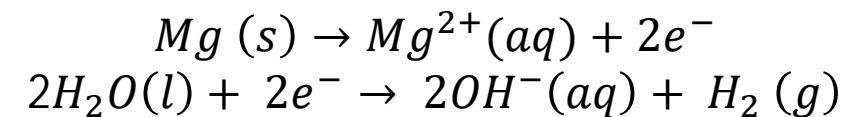


- ✓ Self-healing
- ✓ Control release

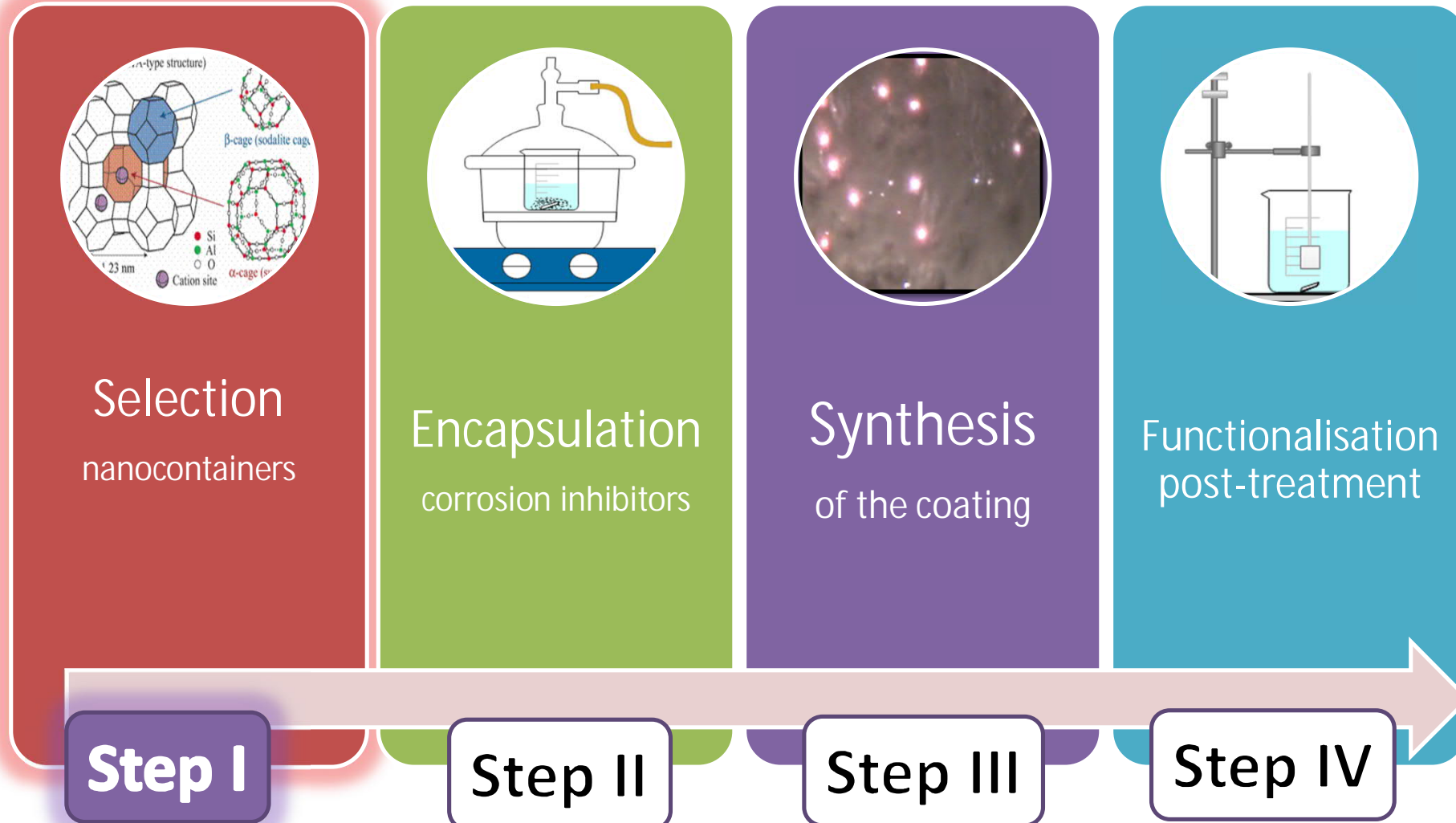
Magnesium alloy



Based on Zheludkevich/Chemistry of Materials, 19 (2007) 402-411



Active functionalization of PEO coatings

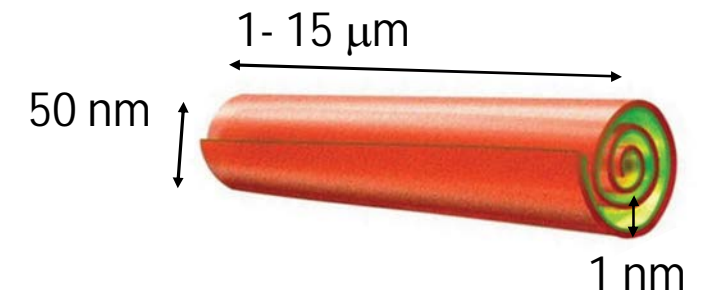
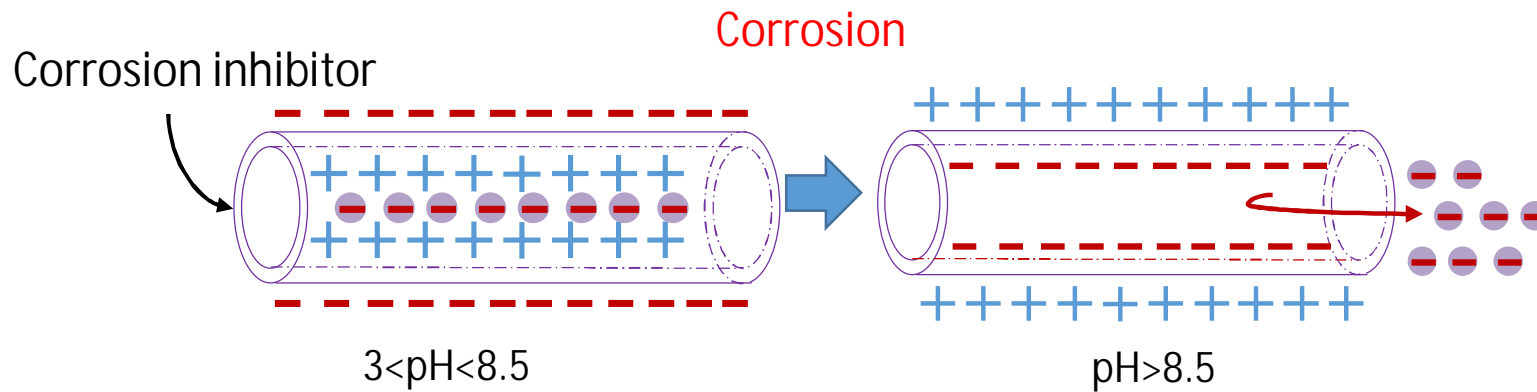
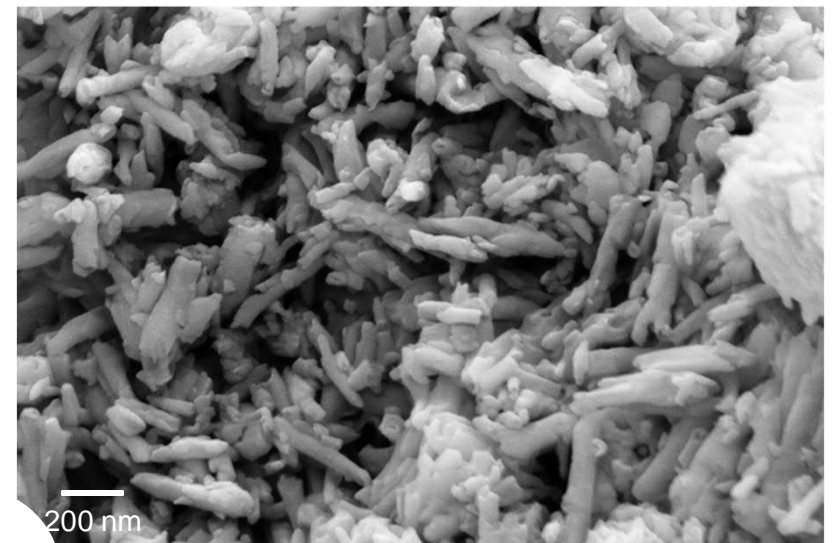
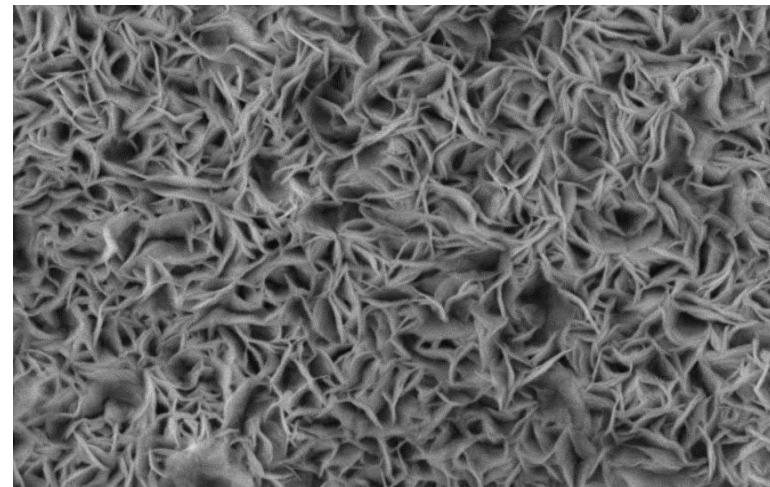
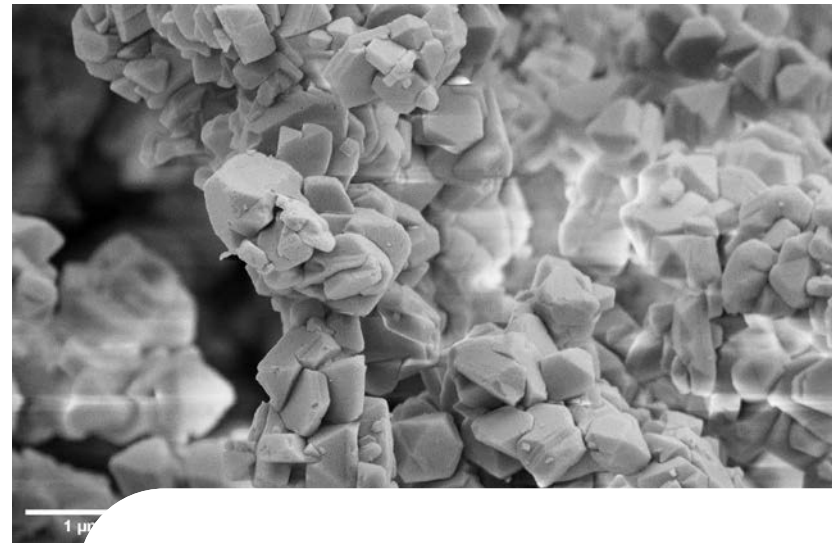


Step I: Selection of the nanocontainer

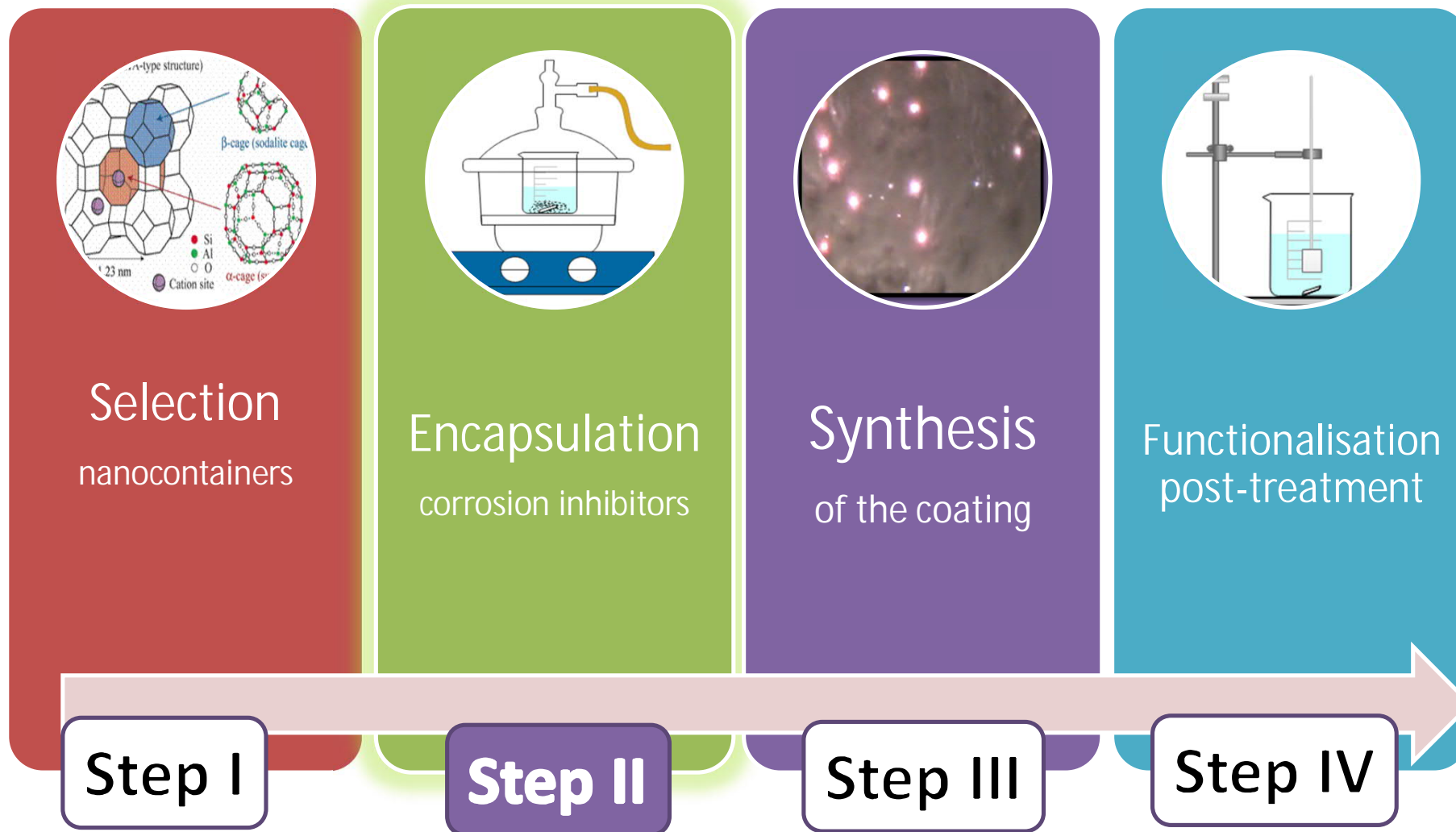
Zeolites

Layered Double Hydroxides (LDH)

Halloysite Nanotubes (HNT)



Active functionalization of PEO coatings



Step II: Encapsulation

Corrosion inhibitors

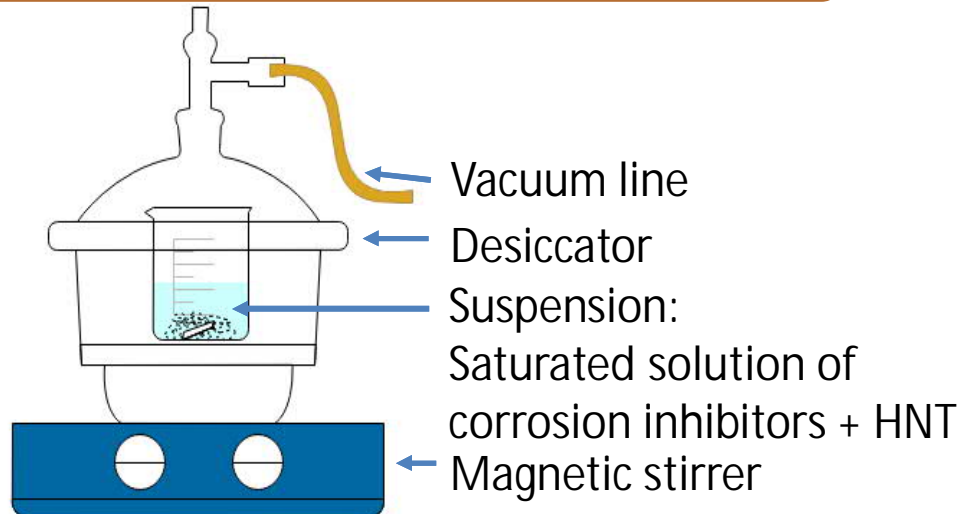
Vanadate salt (NH_4VO_3)

Molybdate salt $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$

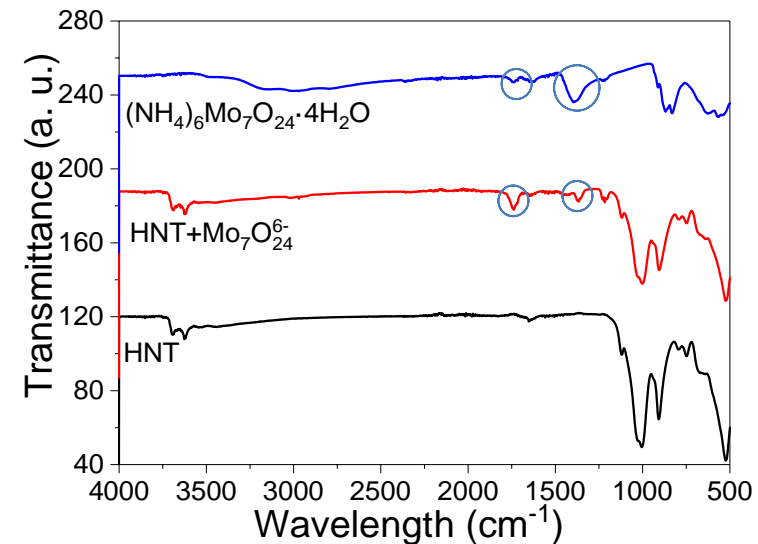
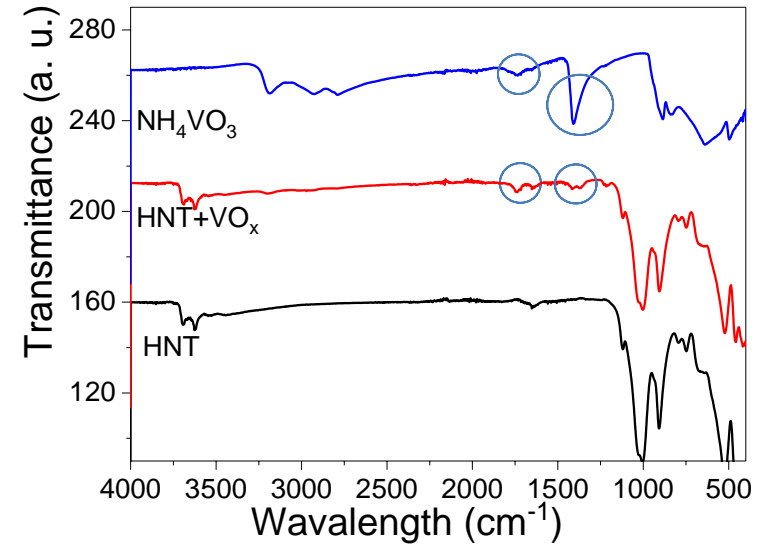
8-Hydroxyquinoline

pH
Time

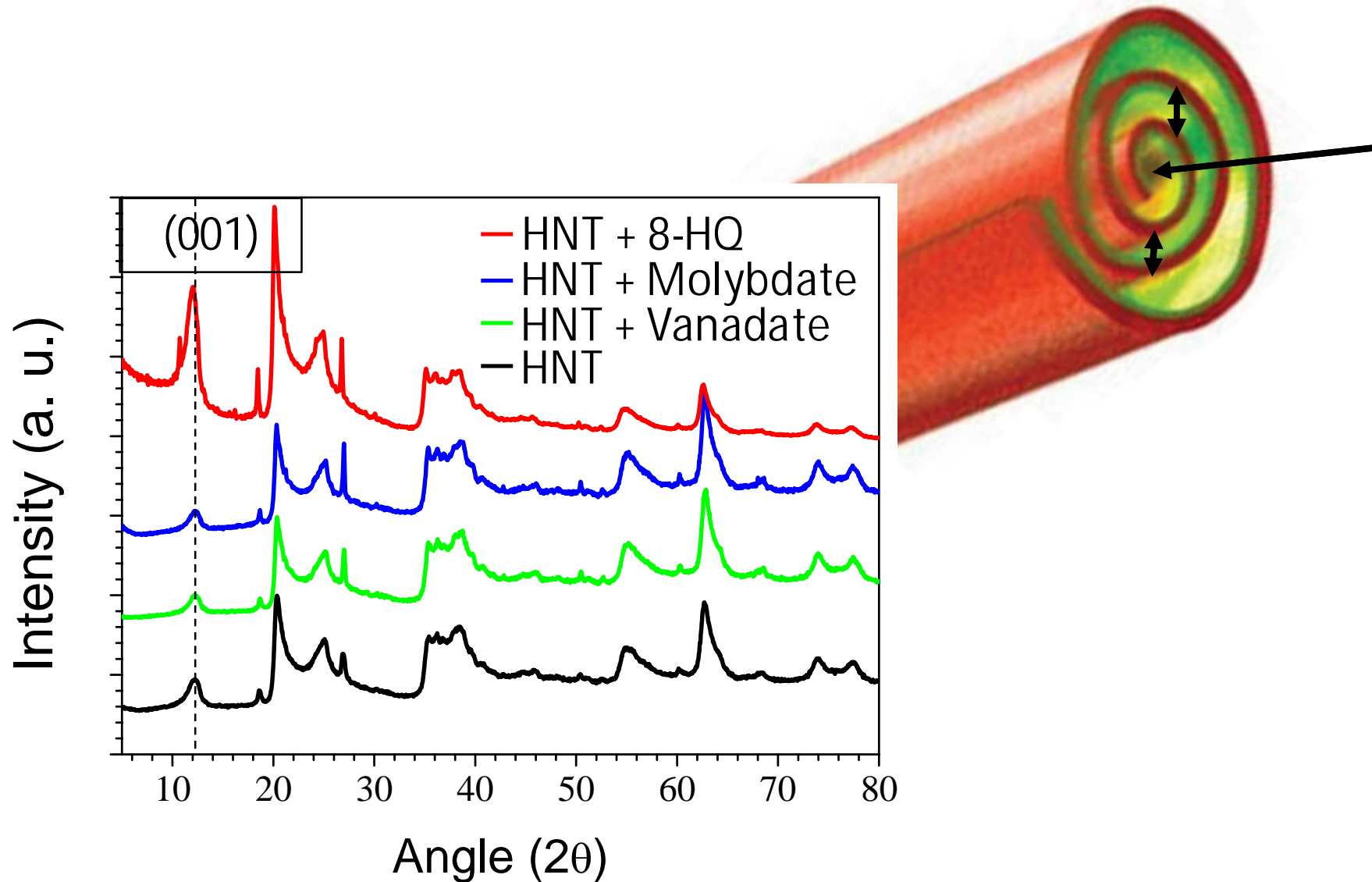
Vacuum-induced capillarity



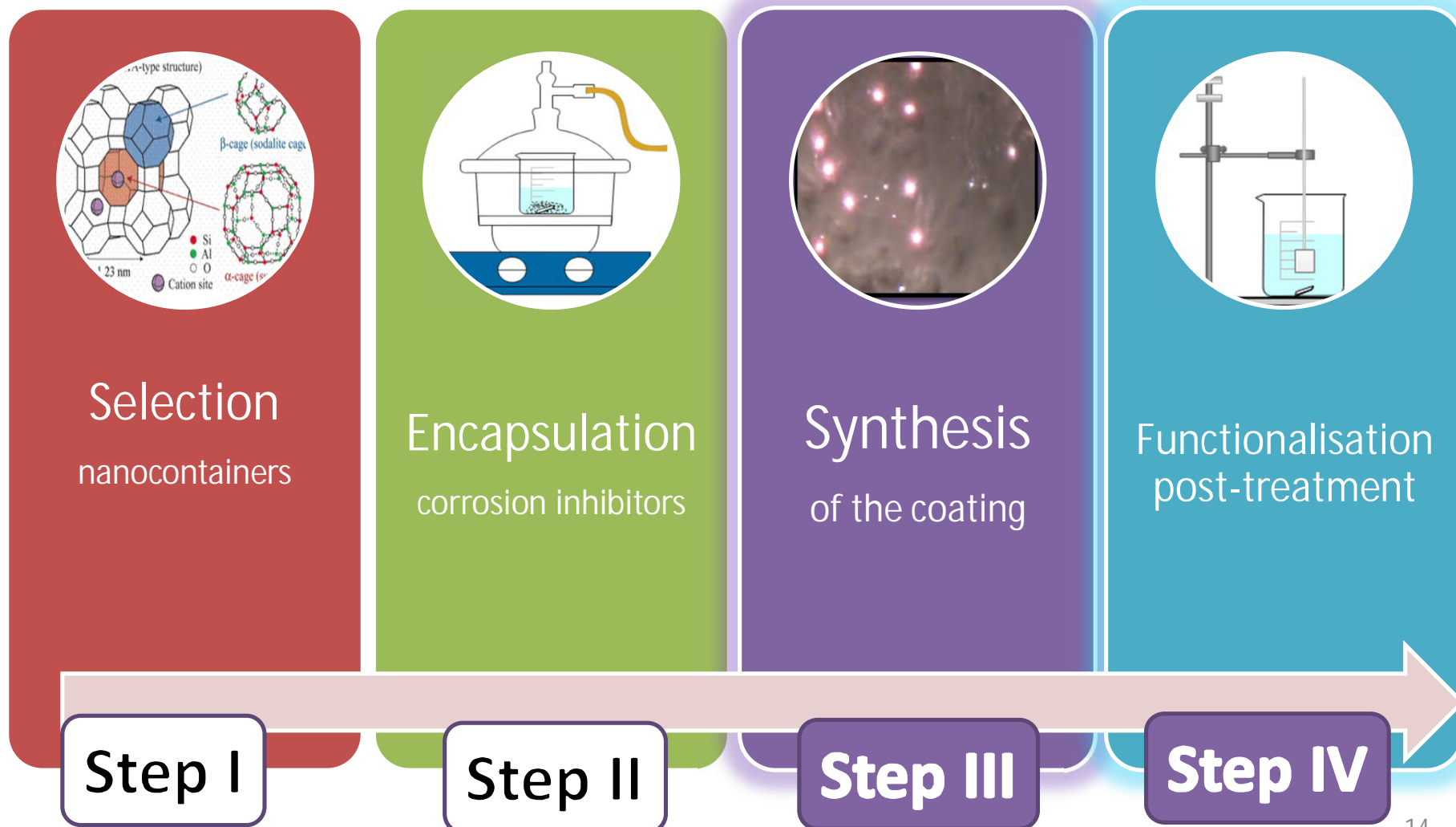
ATR-FTIR



Step II: Encapsulation



Active functionalization of PEO coatings



Step III: Synthesis of PEO coating

Single-step process

Direct functionalisation during PEO synthesis

Double-step process

Synthesis of the coating followed by functionalisation treatment

Step III: Synthesis of PEO coating

Single-step process

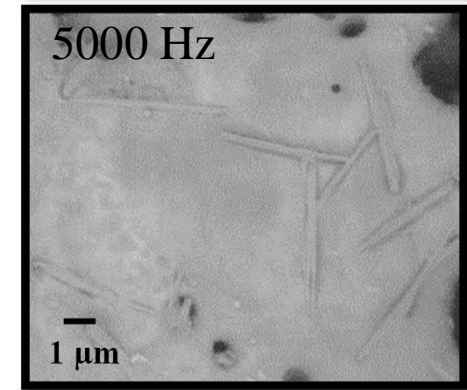
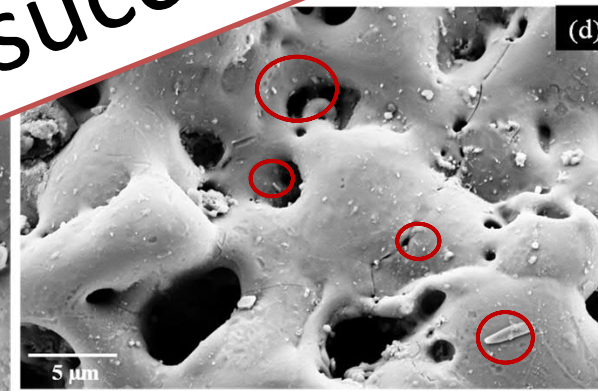
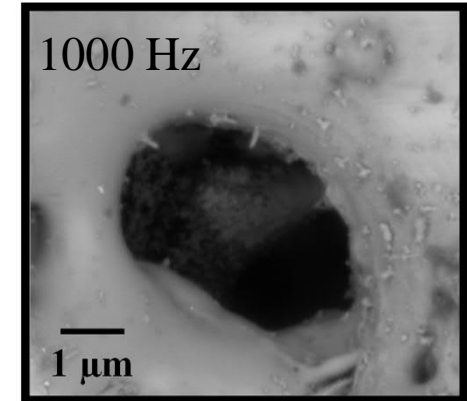
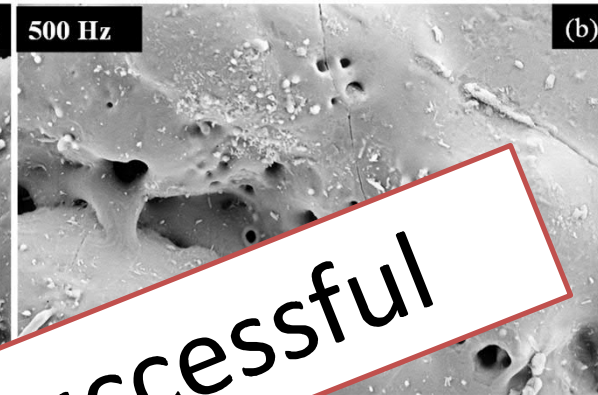
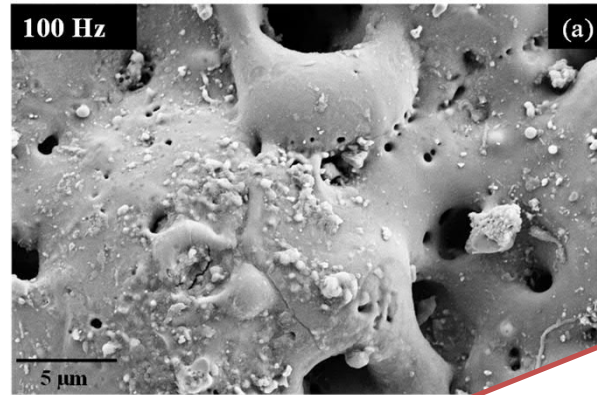
AM50

12 g/L Na_2SiO_3
2 g/L KOH
4 g/L NaF
10 g/L HNT

$i = 40 \text{ mA/cm}^2$
 $t = 5 \text{ min}$
 $\delta = 10 \%$
 $f = 100\text{-}5000 \text{ Hz}$

Reactive

Partially Reactive



Unsuccessful

Partially Reactive

Non Reactive

↑ Frequency ↑ Number of ↓ intense micro-discharges

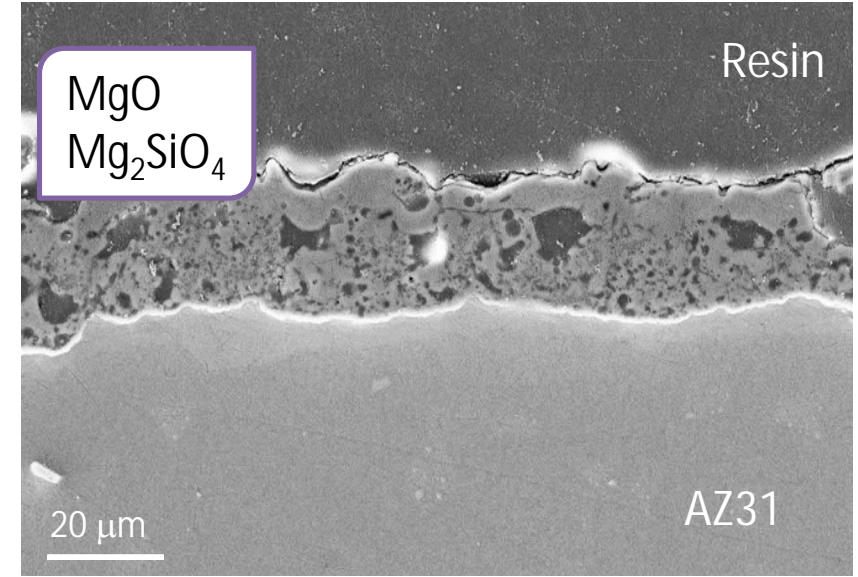
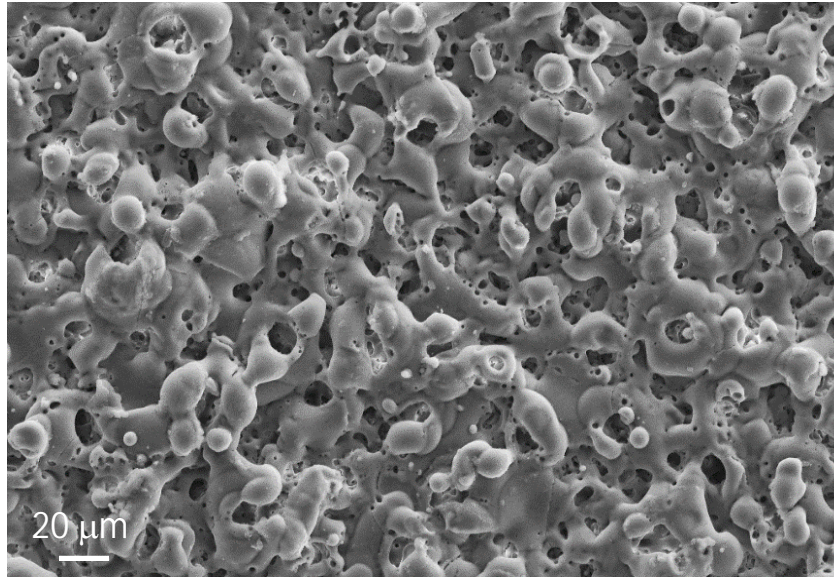
Step III: Synthesis of PEO coating

Double-step process

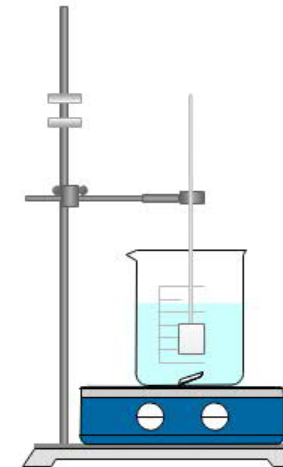
Electrolyte

12 g/L Na_2SiO_3
2 g/L KOH
4 g/L NaF

$i = 40 \text{ mA/cm}^2$
 $t = 10 \text{ min}$
 $\delta = 10 \%$
 $f = 5000 \text{ Hz}$



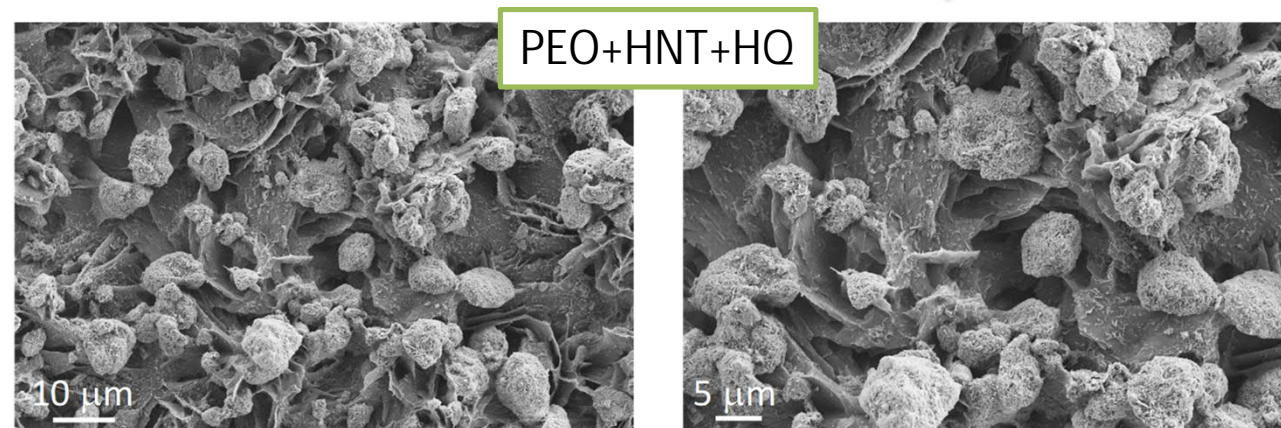
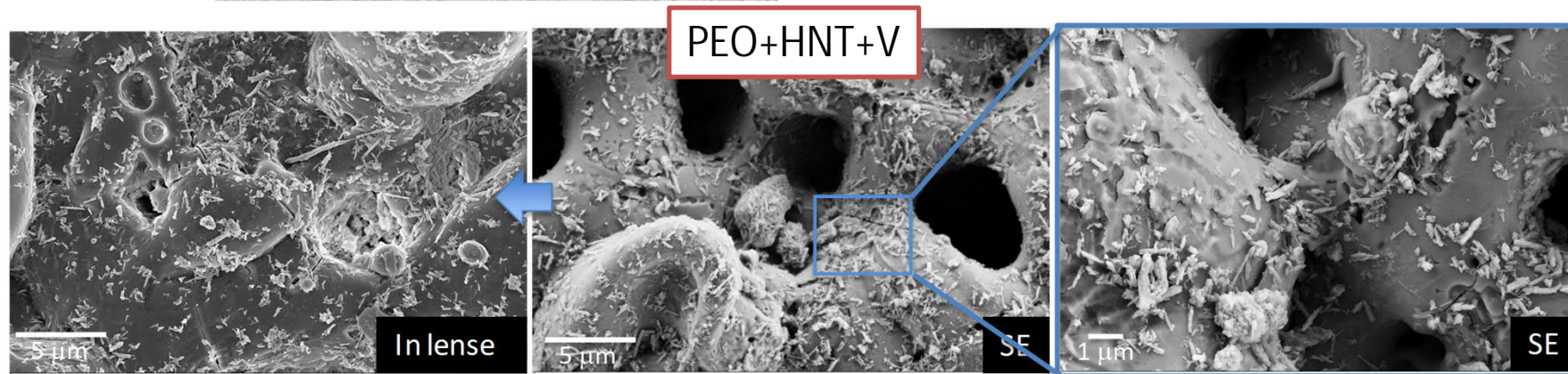
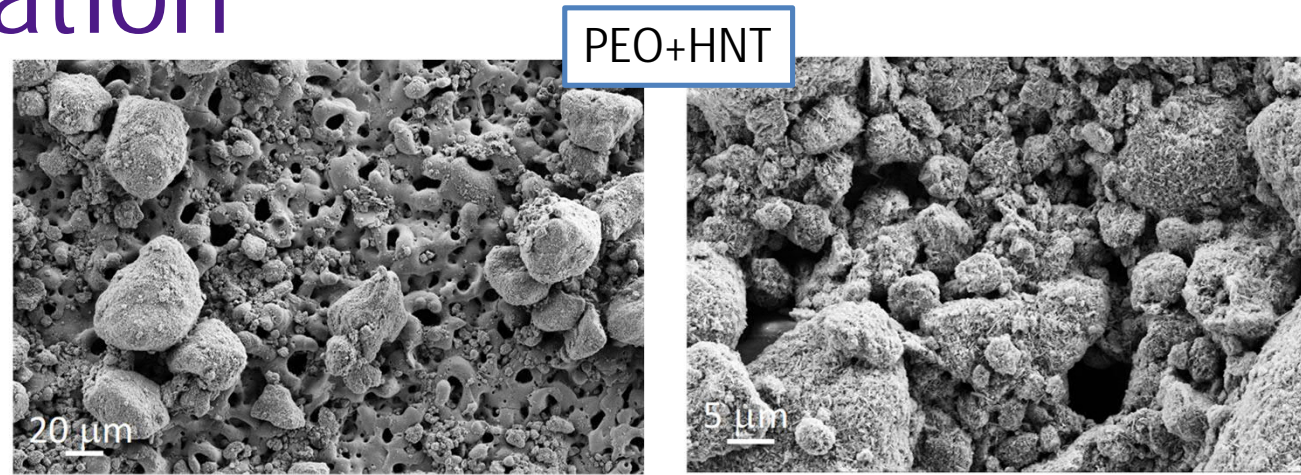
Step IV: Functionalisation post-treatment



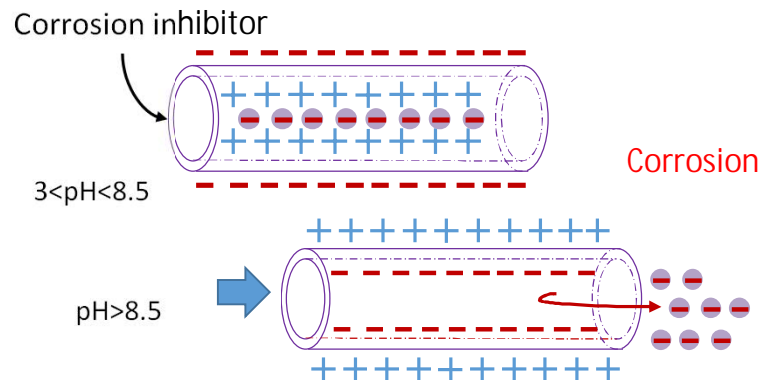
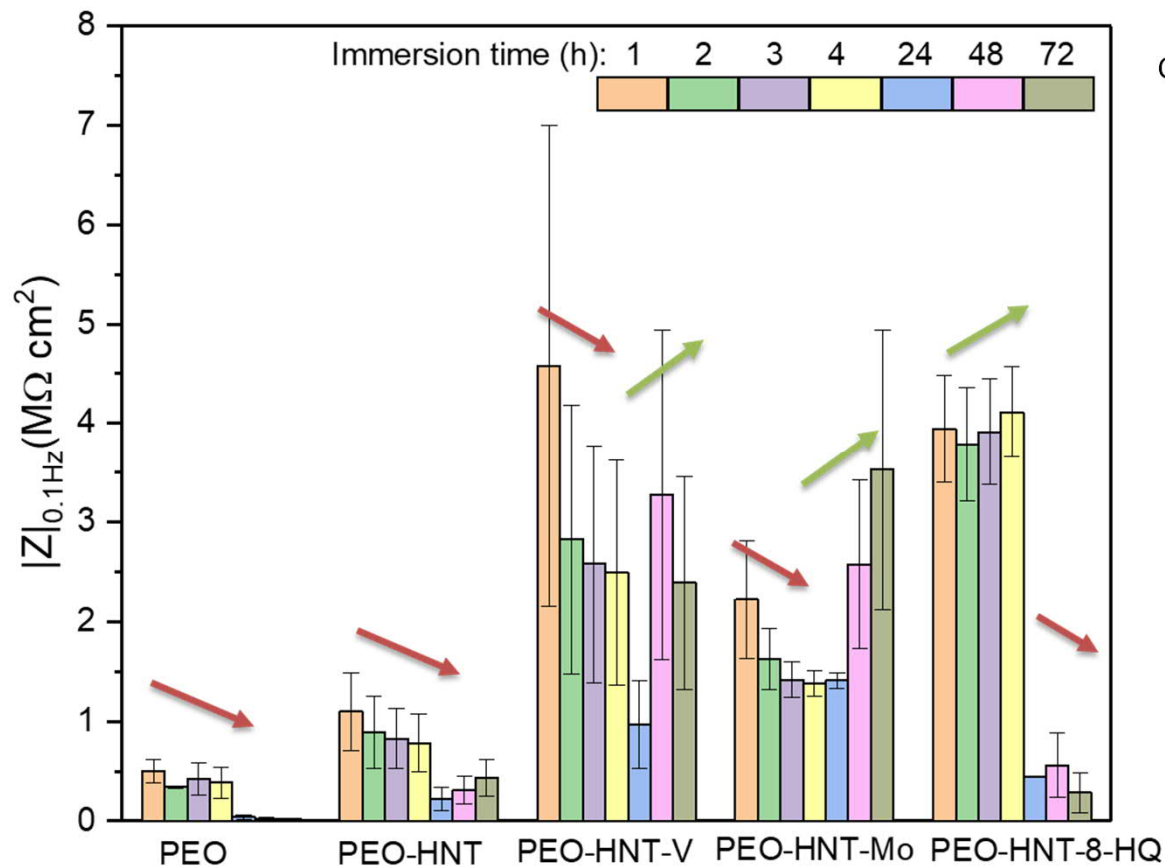
Immersion

20 g/L corrosion inhibitor-loaded HNT
10 min
pH 7-7.5

Characterisation



Evaluation of the Corrosion Resistance: Electrochemical Impedance Spectroscopy (EIS)

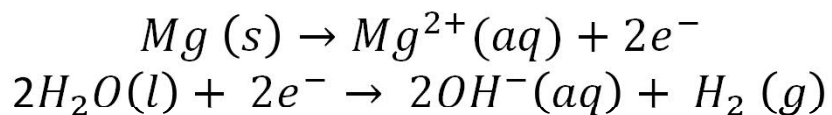
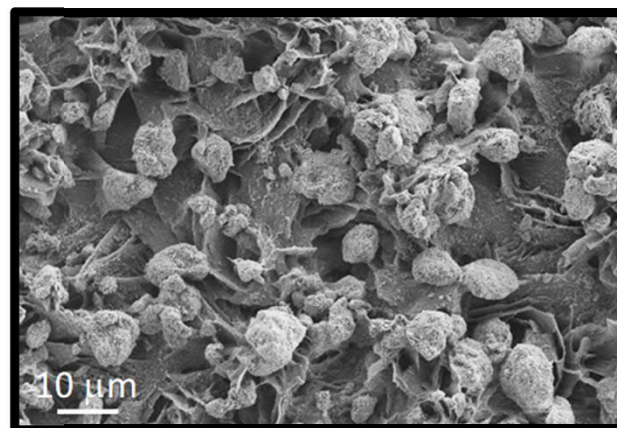


Vanadates
 HVO_4^{2-} (tetrahedral)
 Anodic type inhibitor
 Adsorption/precipitation

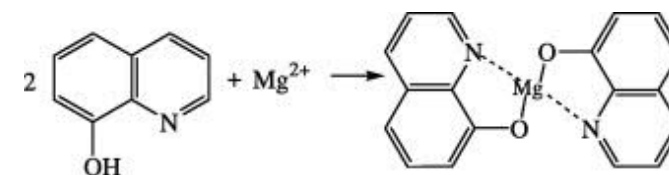
pH dependant

Molybdate
 $\text{HMoO}_4^-/\text{MoO}_4^{2-}$
 Cathodic type inhibitor
 Adsorption/precipitation

8-HQ
 Mixed type inhibitor
 Precipitation



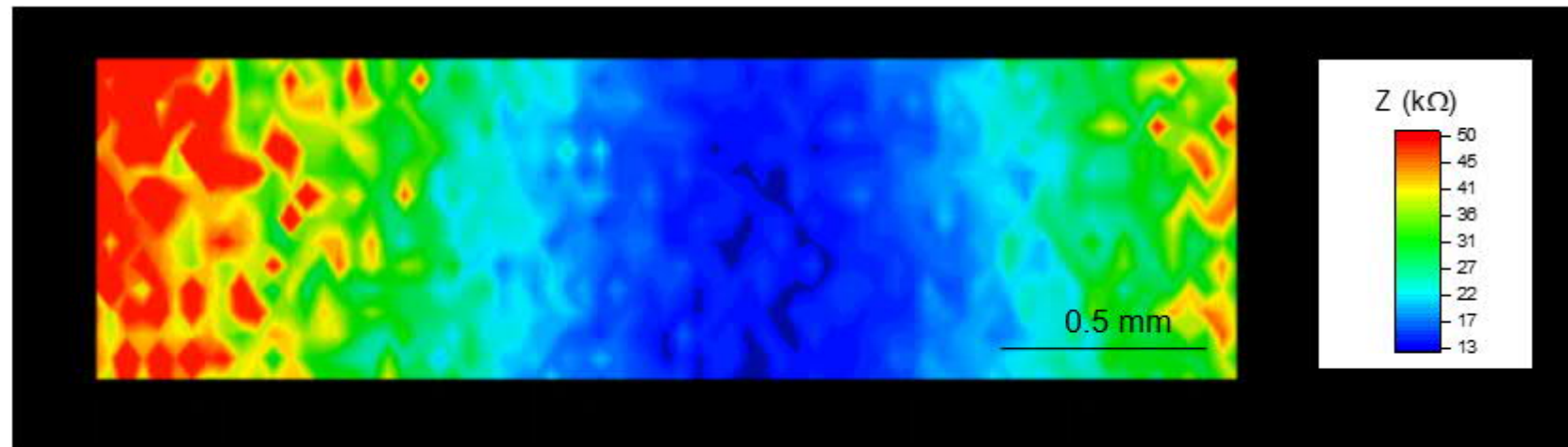
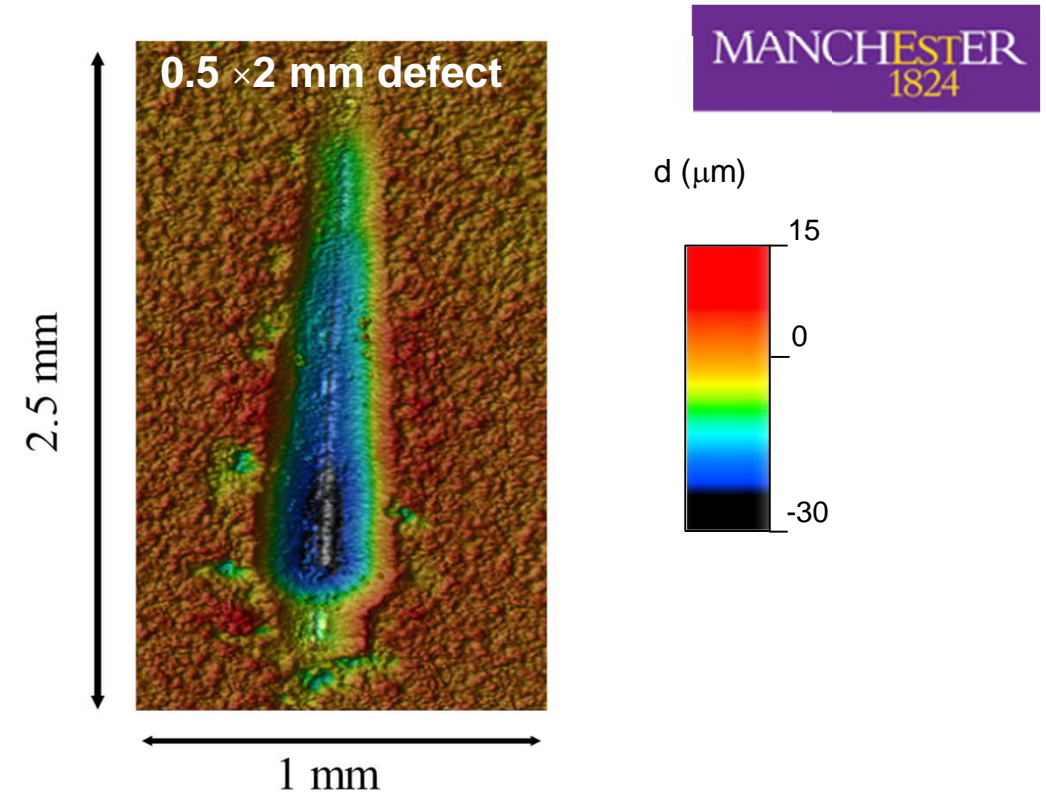
NaCl 0.5 wt. %



Localised Electrochemical Impedance Spectroscopy (LEIS)

ARTIFICIALLY DAMAGED PEO
COATING WITH INHIBITORS

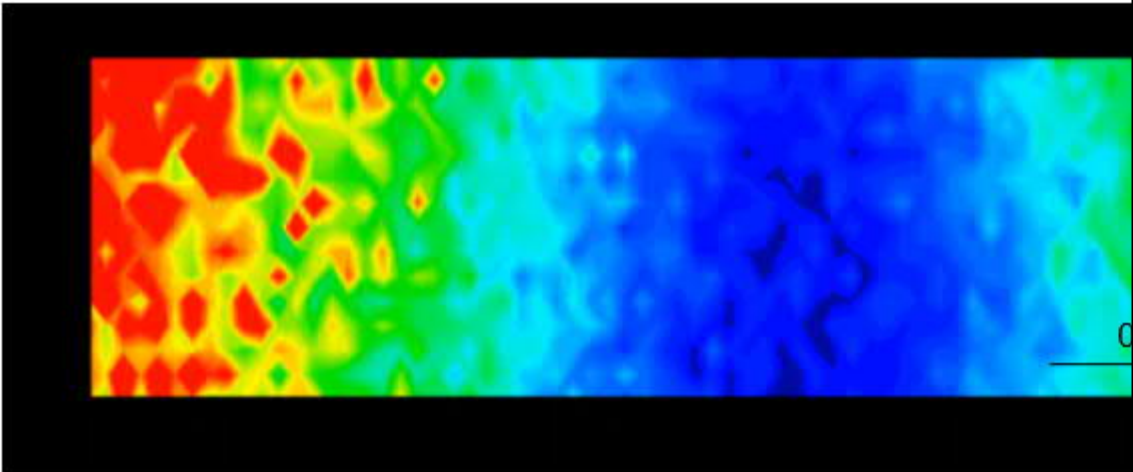
0-35 h



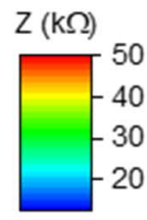
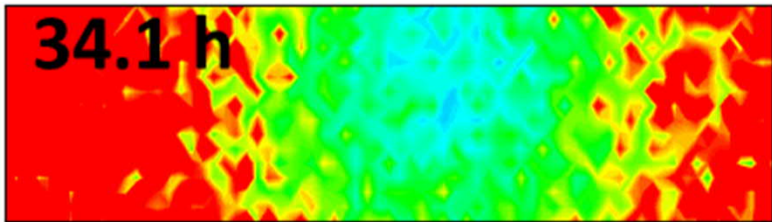
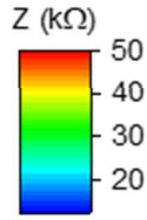
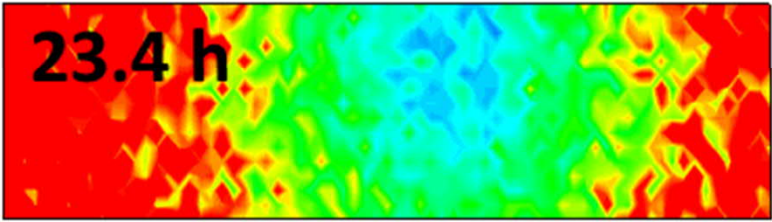
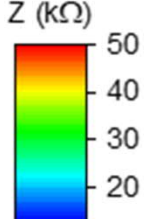
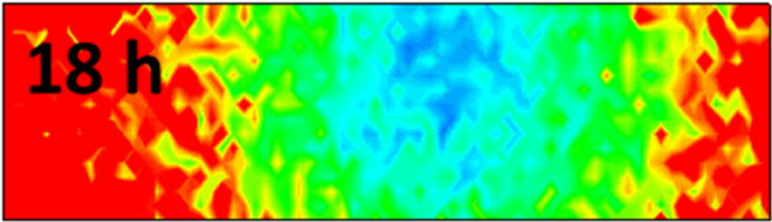
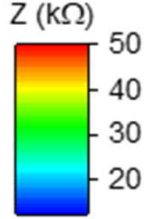
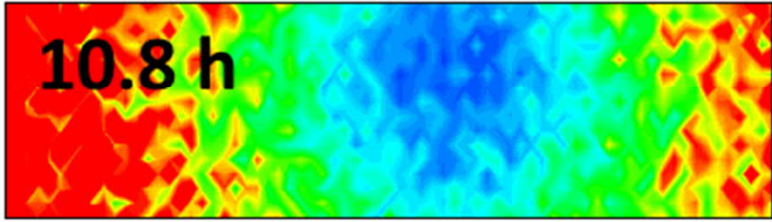
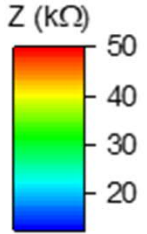
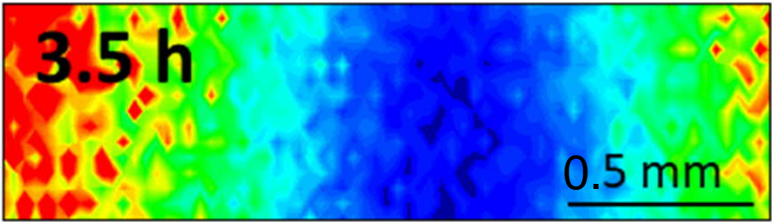
Localised Electrochemical Impedance Spectroscopy (LEIS)

ARTIFICIALLY DAMAGED PEO
COATING WITH INHIBITORS

0-35 h

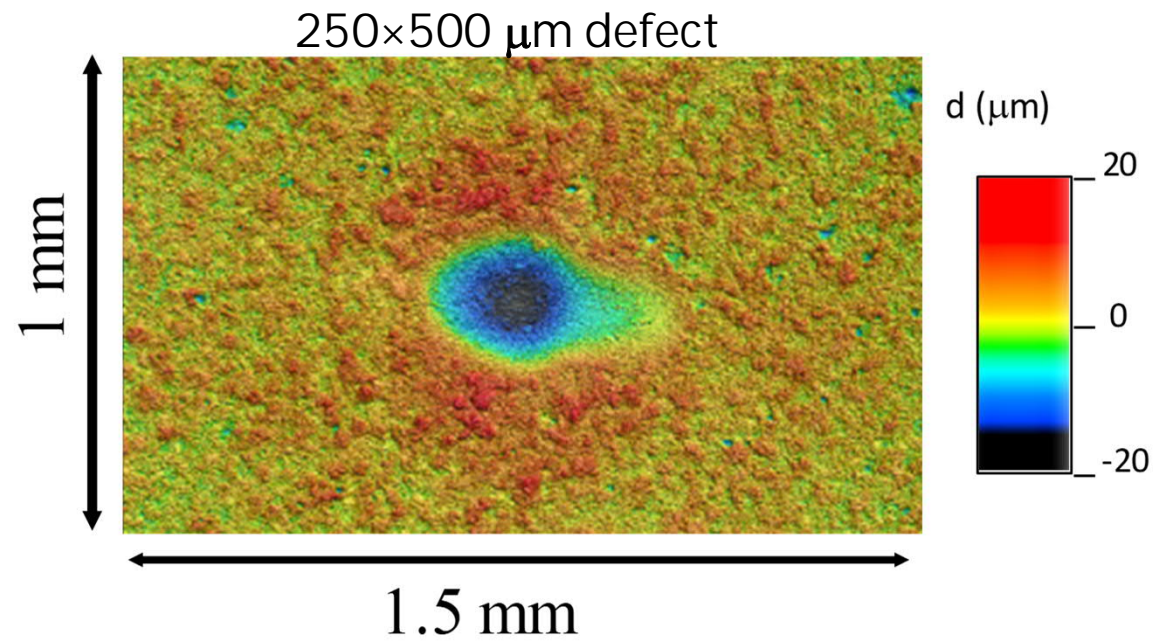


PEO-HNT-V

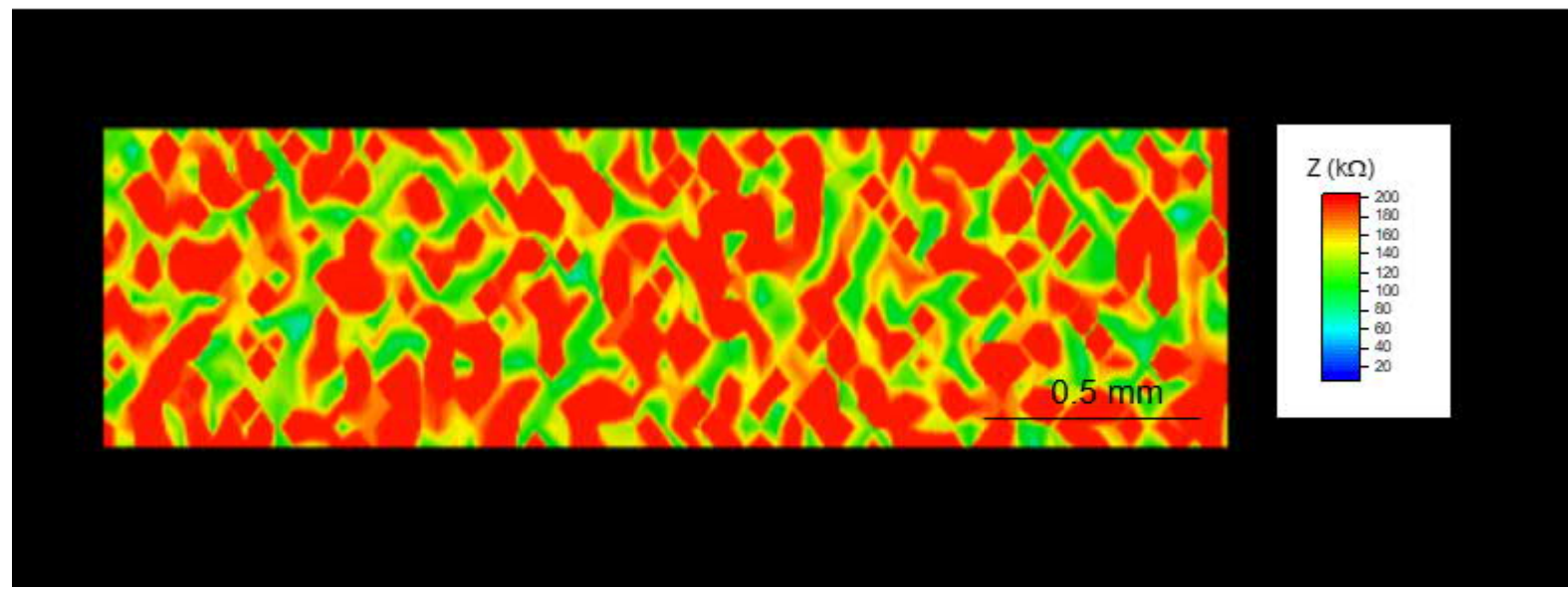


Localised Electrochemical Impedance Spectroscopy (LEIS)

ARTIFICIALLY DAMAGED
PEO COATING WITH
INORGANIC INHIBITORS

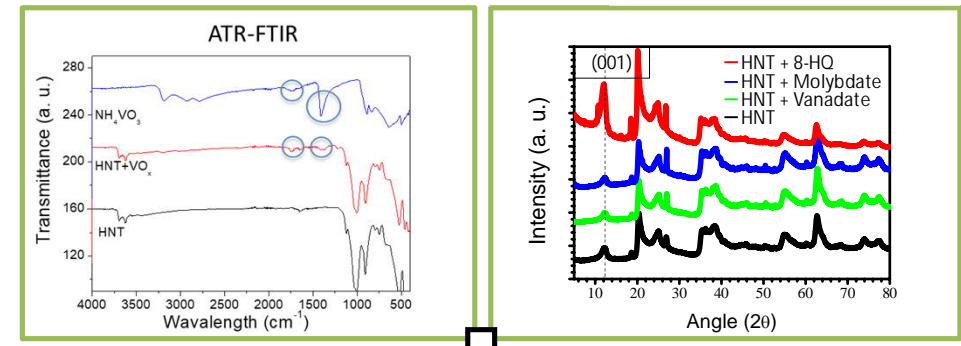


0-35 h

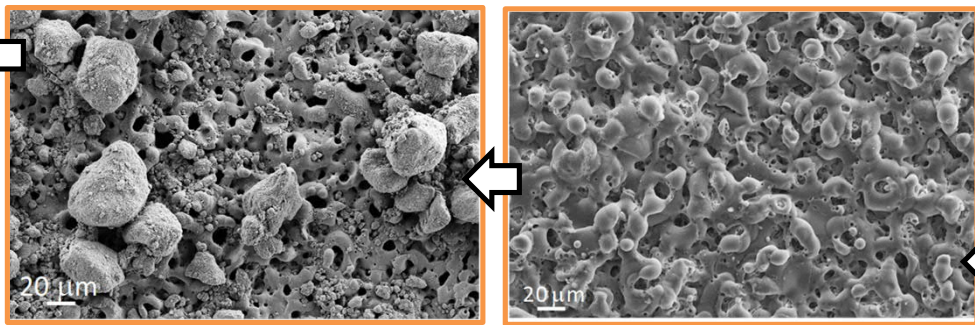
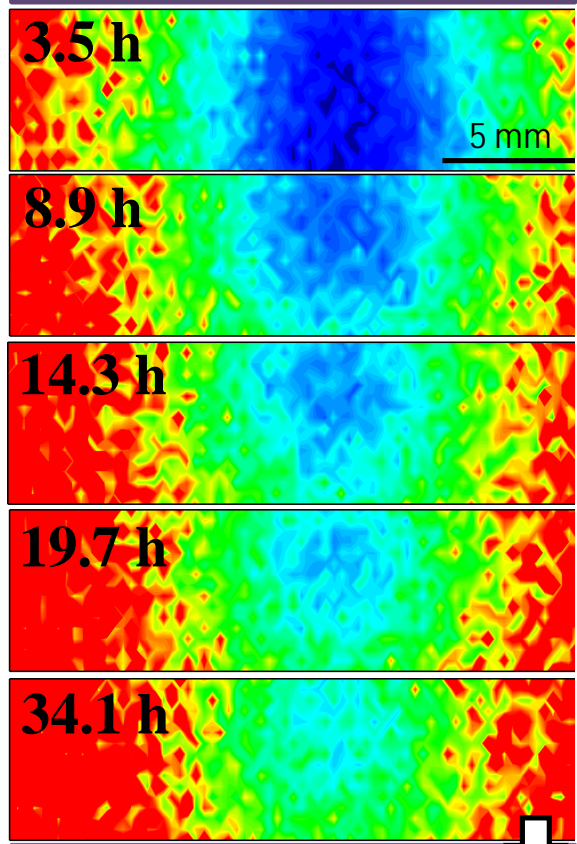


Summary

HNT were successfully loaded with three corrosion inhibitors



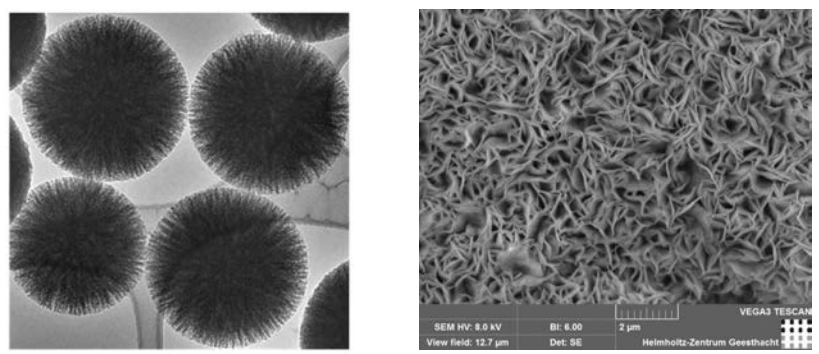
Corrosion response



Synthesis and Functionalisation of PEO coatings

Future work

Nano-containers



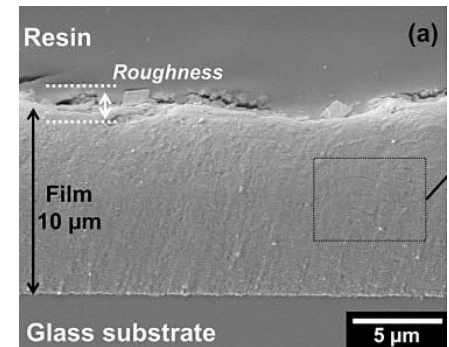
Fibrous Silica

LDH

Deposition techniques

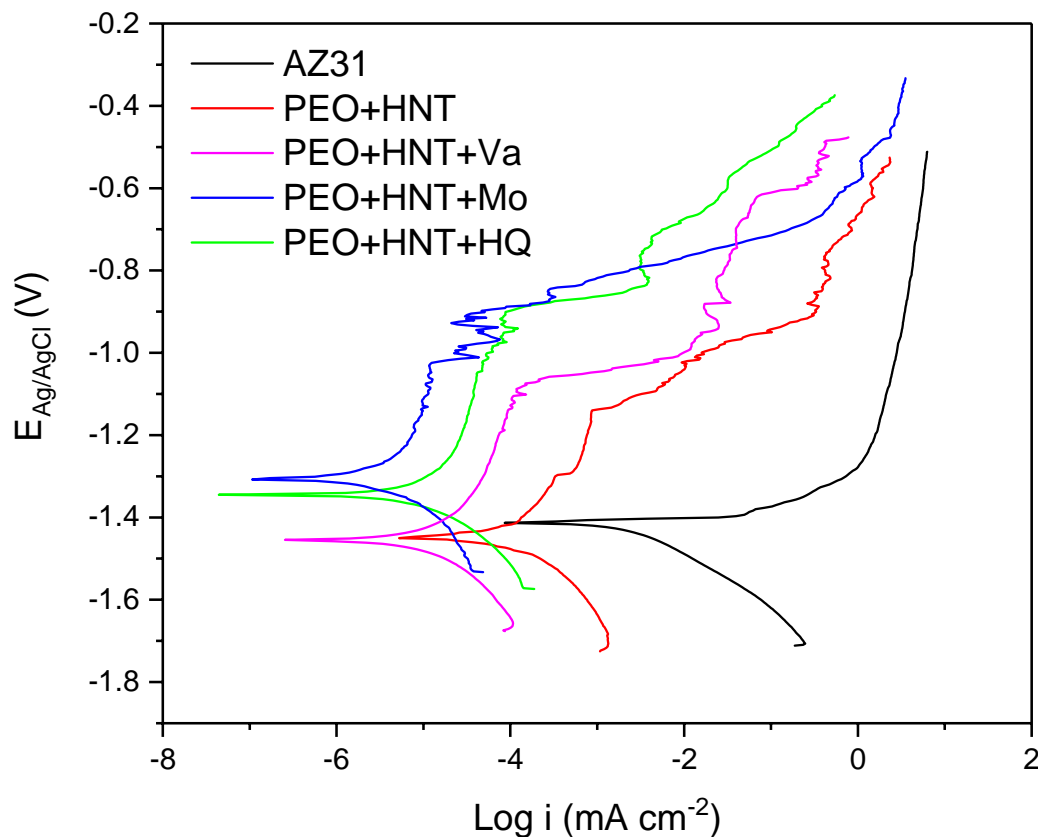
Aerosol Deposition Method

- Room temperature
- Spraying technique
- Powder precursor
- Uniform functionalisation



Smart properties

Evaluation of the Corrosion Resistance: Potentiodynamic polarisation



	E_{corr} (mV _{Ag/AgCl})	E_{hd} (mV _{Ag/AgCl})	$E_{hd}-E_{corr}$ (mV _{Ag/AgCl})
AZ31	-1432 ± 25	-1432 ± 25	0
PEO-HNT	-1302 ± 11	-1262 ± 42	40 ± 53
PEO-HNT	-1401 ± 66	-1181 ± 52	220 ± 118
PEO-HNT-V	-1454 ± 1	-1075 ± 5	379 ± 6
PEO-HNT-Mo	-1306 ± 1	-926 ± 2	381 ± 1
PEO-HNT-HQ	-1350 ± 8	-900 ± 12	450 ± 20

pH dependant

Vanadates
 HVO_4^{2-} (tetrahedral)
 Anodic type inhibitor
 Adsorption/precipitation

Molybdate
 $HMoO_4^-/MoO_4^{2-}$
 Cathodic type inhibitor
 Adsorption/precipitation

8-HQ
 Mixed type inhibitor
 Precipitation

