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Active protective coatings based on "smart" nanocontainers

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Resumo

A função principal dos revestimentos orgânicos contra a protecção da corrosão é fornecer uma barreira contra as espécies corrosivas. Contudo o processo de corrosão pode desenvolver-se por baixo do revestimento após a sua danificação. Deste modo uma protecção activa contra a corrosão, baseada na auto-reparação dos defeitos nos revestimentos é necessária para conferir protecção a longo prazo. Neste trabalho pretende-se dopar os revestimentos com espécies de protecção activas usando nano-reservatórios. Os nano-reservatórios são estruturas nanométricas que podem armazenar agentes activos e fornecê-los de uma maneira controlada. Vários tipos de nano-contentores foram produzidos, introduzidos nos revestimentos e testados em termos de protecção activa. O inibidor libertado pode reagir com a superfície metálica, parando a propagação da corrosão e fornecendo um efeito de reparação que termina quando a corrosão da superfície para.

Palavras-chave: corrosão, revestimentos, nano-reservatórios

Active collaborators

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Corrosion protection of metallic structures

Passive corrosion protection

Use of coatings

+Good barrier against corrosive species
+Tailored surface properties

-Lack of self-healing

Active corrosion protection

Employment of inhibiting species

+Decrease of corrosion rate
+Self-healing of defects

-Should be added to corrosive medium

Passive + active

Coating + Corrosion Inhibitor

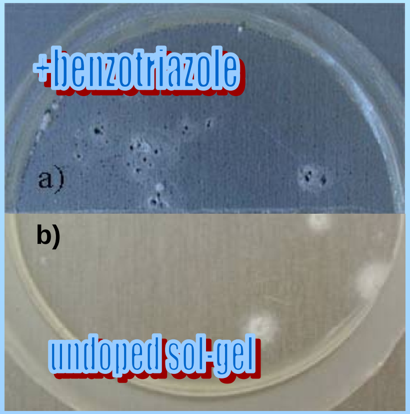
+Combination of barrier and self-healing

-Negative effect of inhibitor on coating stability
-Deactivation of inhibitor in coating
-Uncontrollable release of inhibitor

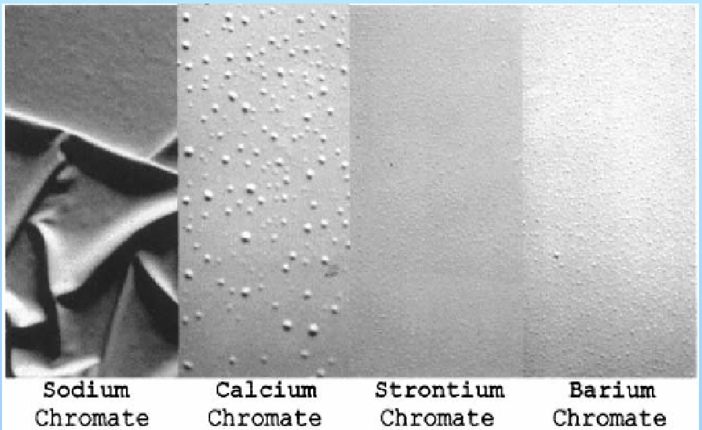
Immobilization of Healing Agents

Active agent must be encapsulated in order to prevent its interaction with components of coatings!!!

Examples of negative effect of active agents



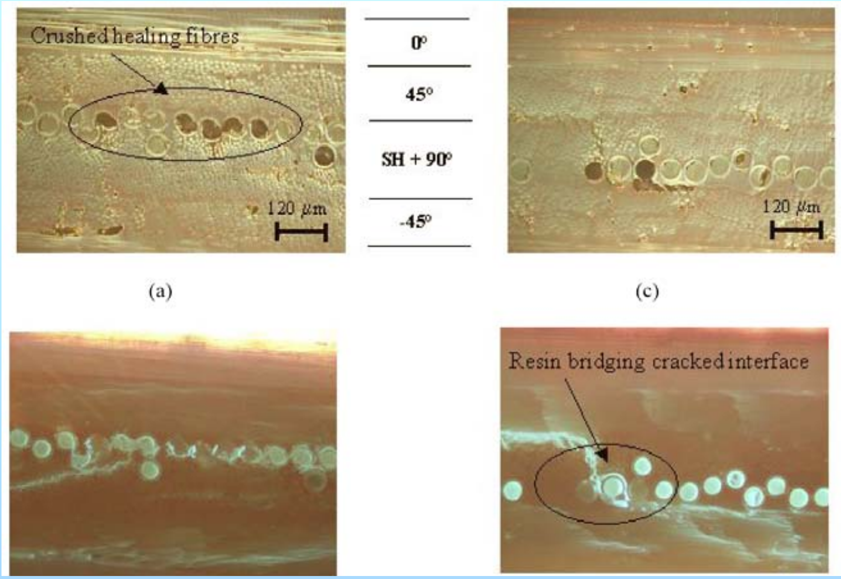
Lower hydrolytical stability

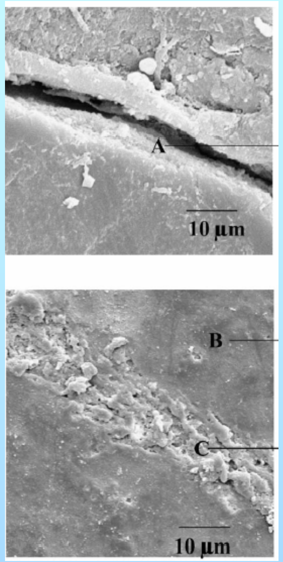


Osmotic blistering

Self-Healing Protective Coatings

The classical understanding of self-healing is based on the complete recovery of the coating functionalities due to a real healing of the defect retrieving initial coating integrity.



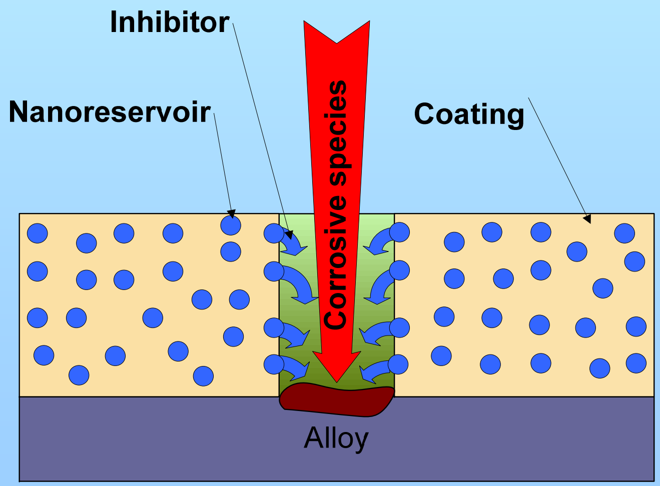


The hindering of the corrosion activity in the defect by the coating itself employing any mechanisms can be already considered as self-healing, because the corrosion protective system recovers its main function, namely the corrosion protection, after being damaged.

•R.S. Trask, G.J. Williams, I.P.Bond, *J. R. Soc. Interface.* 2007, *4,*363-371.
•T. Sugama, K. Gawlik, *Mater. Lett.* 2003*, 57,*4282-4290.

Idea

To nano-encapsulate corrosion inhibitors before addition to the coating



Possible Advantages

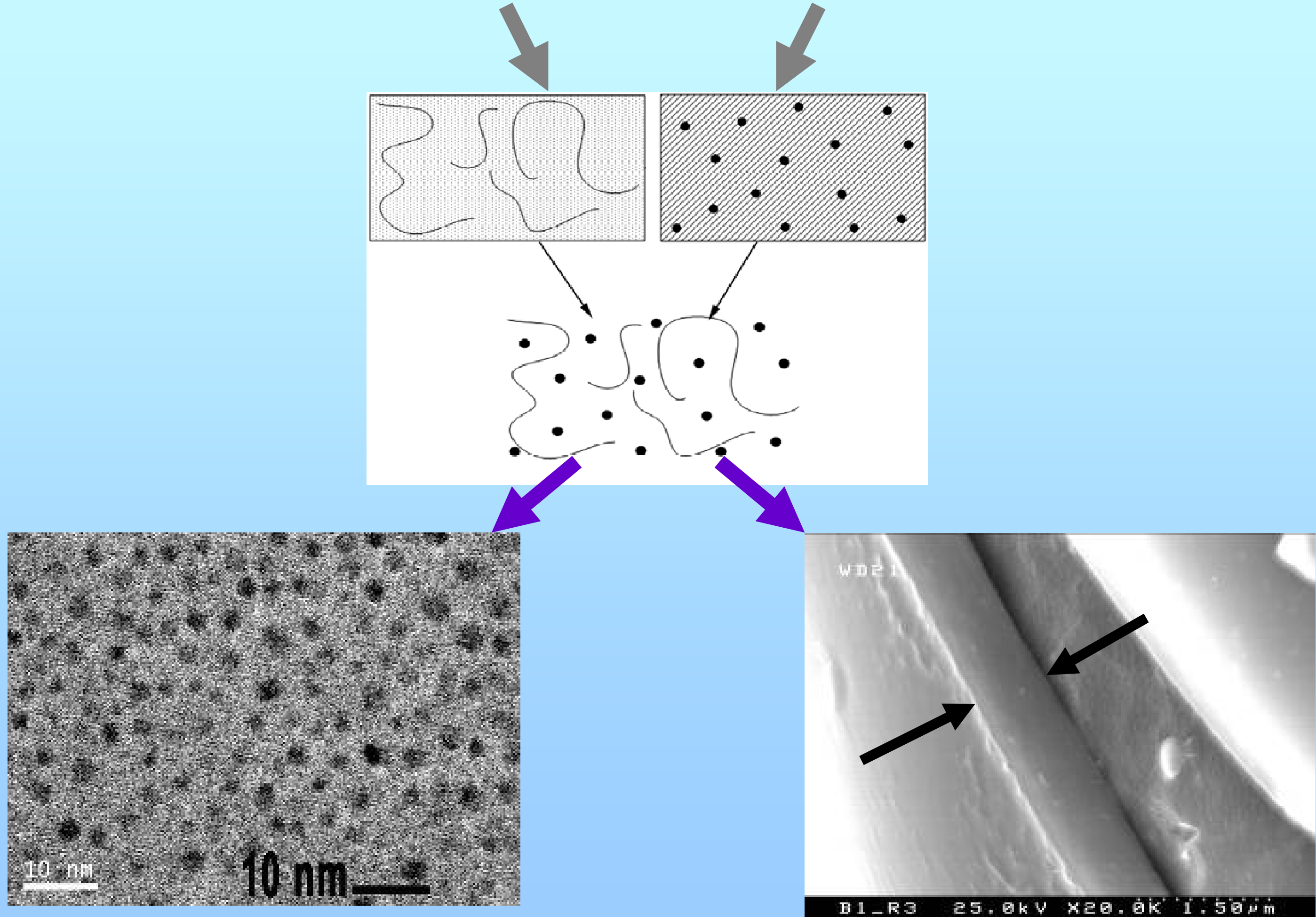
- ✓ Prevention of inhibitor deactivation due to interaction with coating components
- ✓ Reduction of negative effect of the inhibitor on coating
- ✓ Controllable release of inhibitor on demand

Types of Nanoreservoirs

- Oxide nanoparticles
- Porous nanostructured layers
- LbL constructed nanocontainers
- LDH nanocontainers

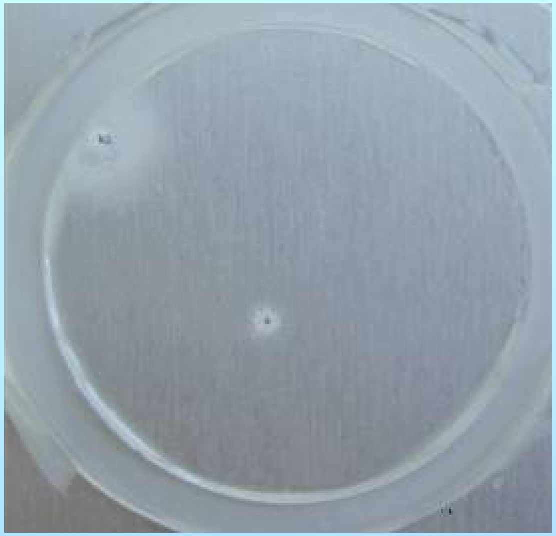
In-situ formed oxide nanopartcles as reservoirs of corrosion inhibitors

GPTMS + 2-propanol+H_2O **TPOZ + H_2O + Ce^{3+}**



Corrosion protection performance of nanocomposite films

without inhibitor

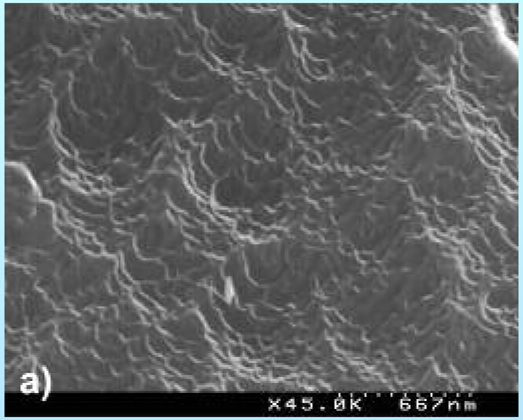


with inhibitor

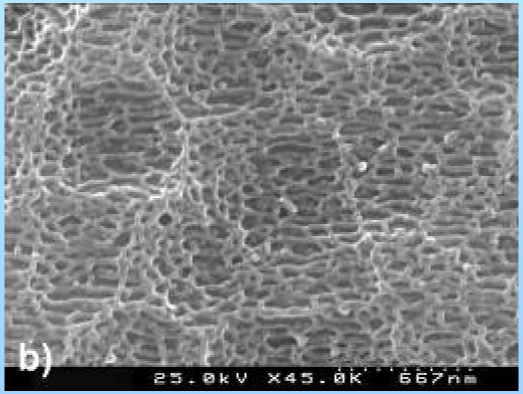
1 month immersion in 3% NaCl solution

Porous layer as nanostructured reservoir of corrosion inhibitor

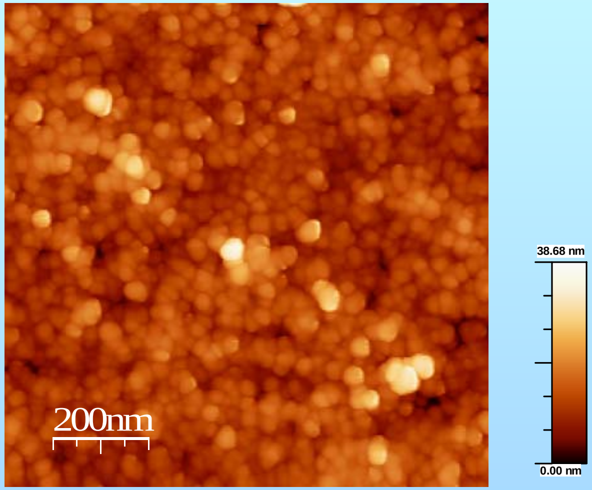
Structure of the nano-titania layer deposited on polished and etched alloy



Etched alloy



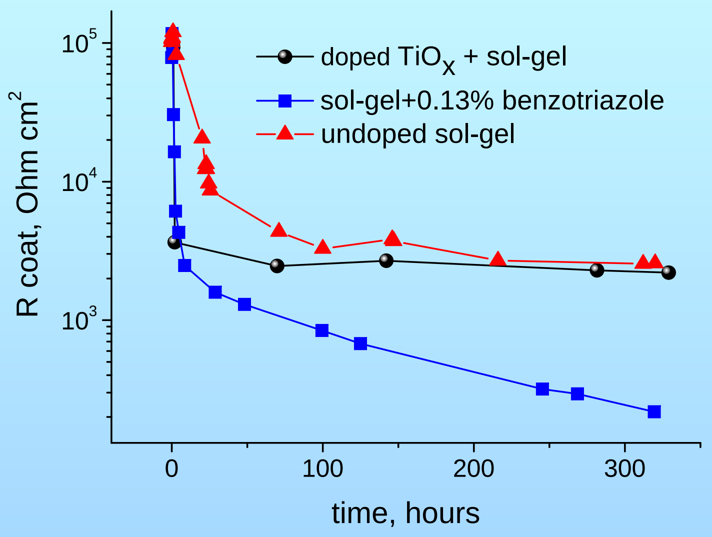
Etched alloy + titania



The micelle-template approach can be used to obtain porous nanostructured titania pre-layer before hybrid film deposition

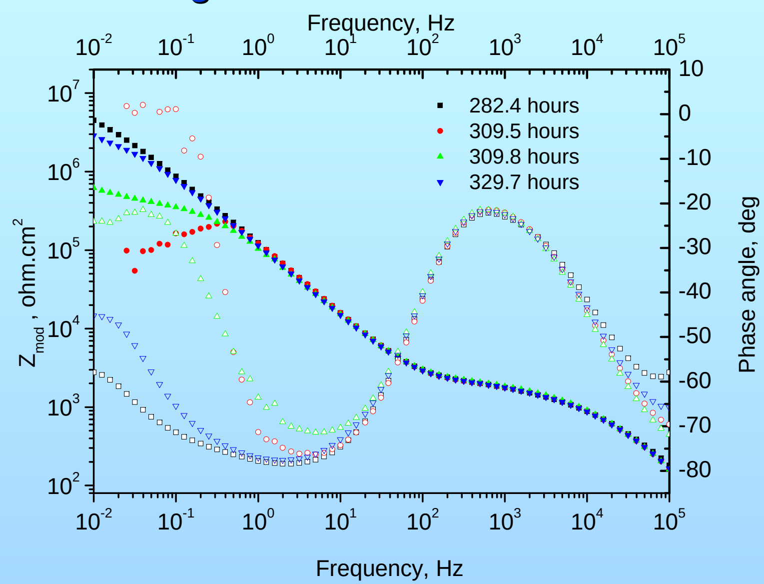
Porous layer as nanostructured reservoir of corrosion inhibitor

Evolution of pore resistance for different hybrid films



Use of nanostructured porous reservoir prevents degradation of sol-gel film due to introduction of inhibitor

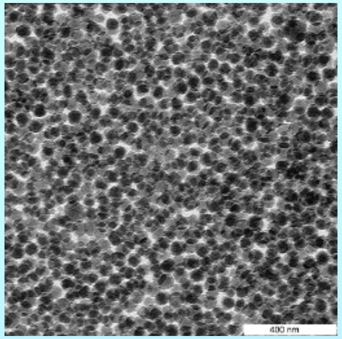
Bode diagrams for two-layer system after long immersion in 0.05 M NaCl

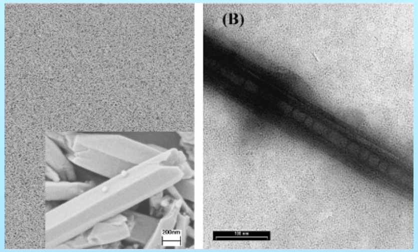


Increase of low frequency impedance is originated from defect passivation

Two-layer system demonstrates promising results with signs of self-healing effect

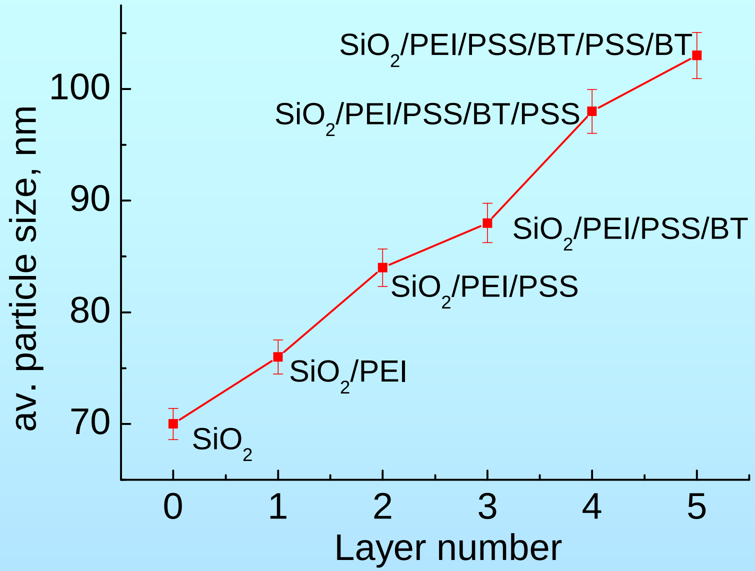
LbL polyelectrolyte shells

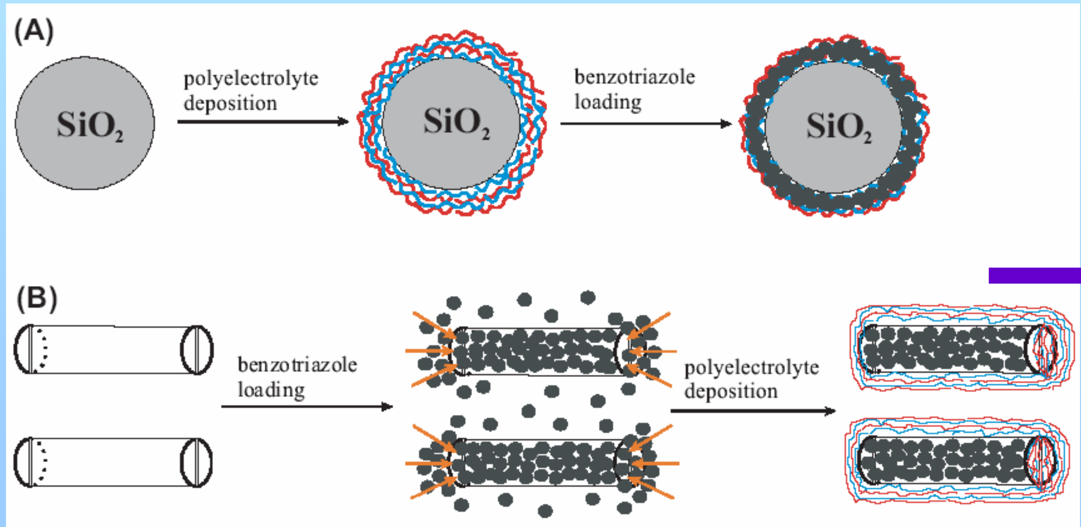


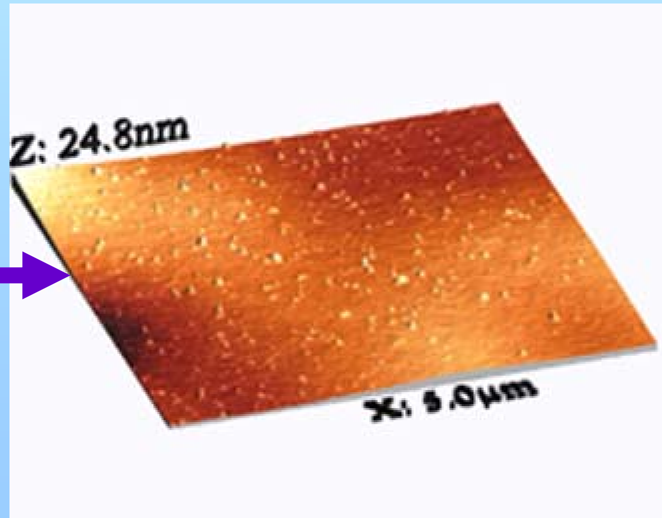


Layer by Layer

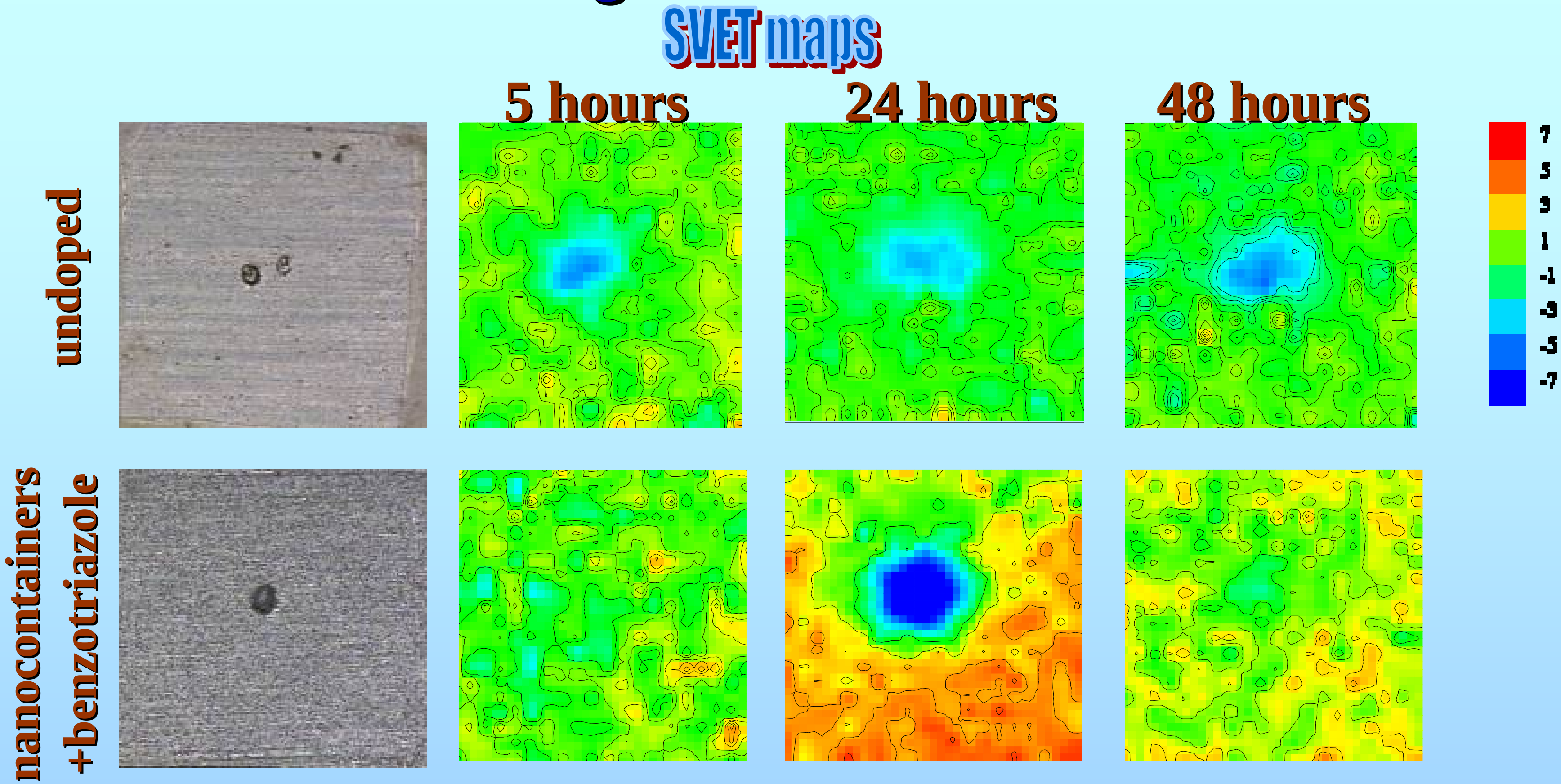
assembling process





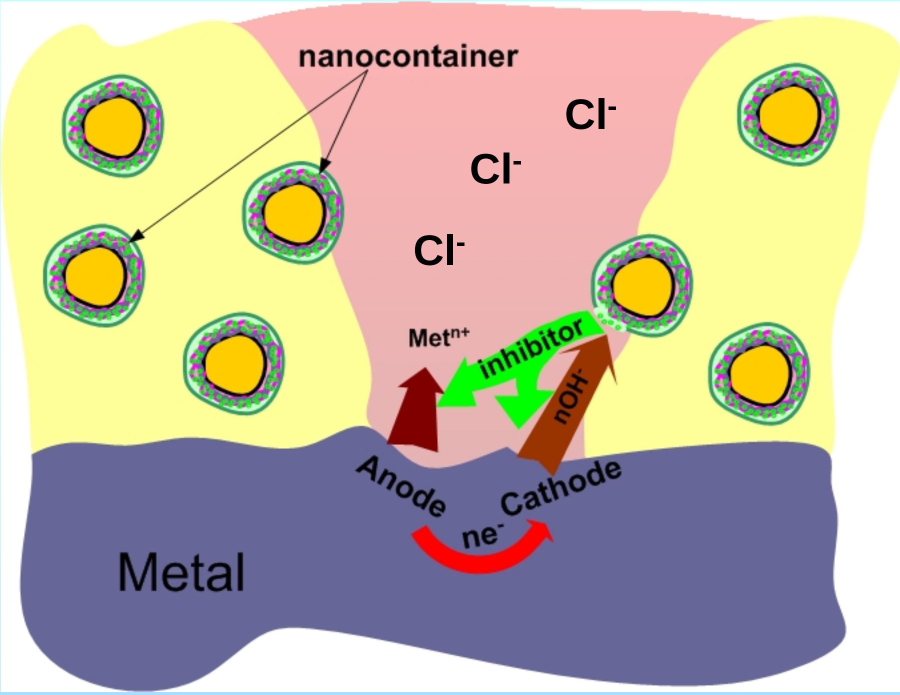


Self-healing of an artificial defect



Suppression of the active corrosion processes demonstrates self-healing of artificial defect in sol-gel film doped with nanocontainers loaded with benzotriazole

Mechanism of “smart” self-healing



Induced defect opens pathway for chloride ions

Corrosion processes start on the alloy surface

Cathodic reactions generate hydroxyls leading to local increase of pH:

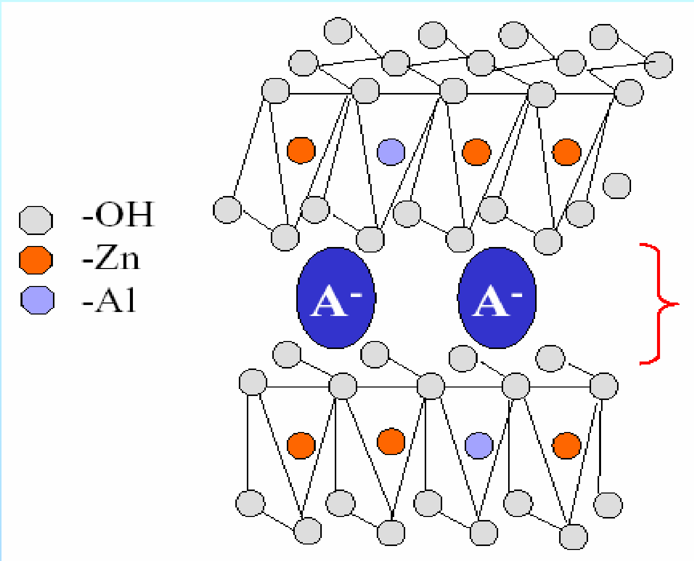
$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \uparrow$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Raise of pH increases permeability of polyelectrolyte shell leading to release of inhibitor

Released benzotriazole hinders corrosion activity healing the defect

LDH pigments



Zn-Al layered double hydroxide (LDH) powders

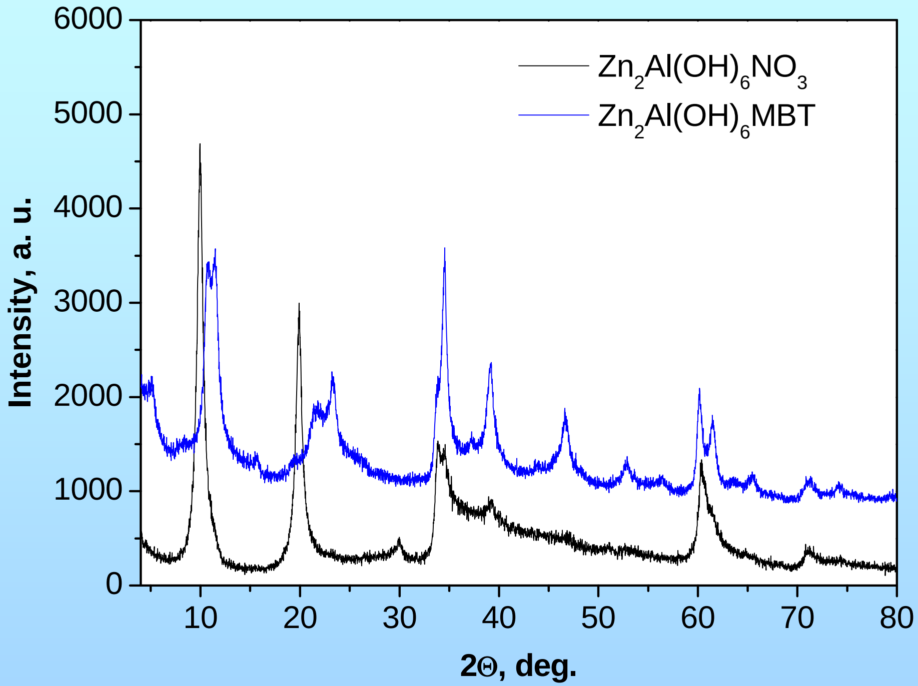
Inhibiting anions: (A^-)

- **Mercaptobenzothiazole (MBT)**
- **vanadate**

Two ways of pigment preparation:

- **direct synthesis (-formation of insoluble salts);**
- **ion-exchange**

Zn-Al LDH pigments

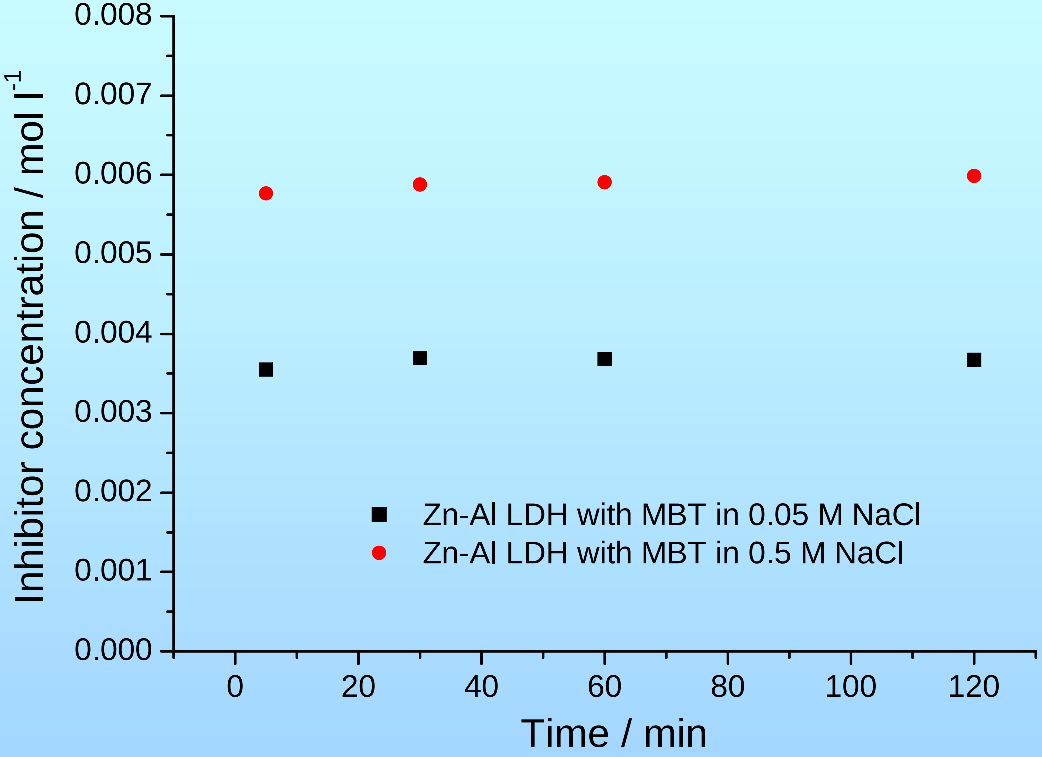


d(003)

$Zn_2Al(OH)_6VO_3$ - 0.8892 nm

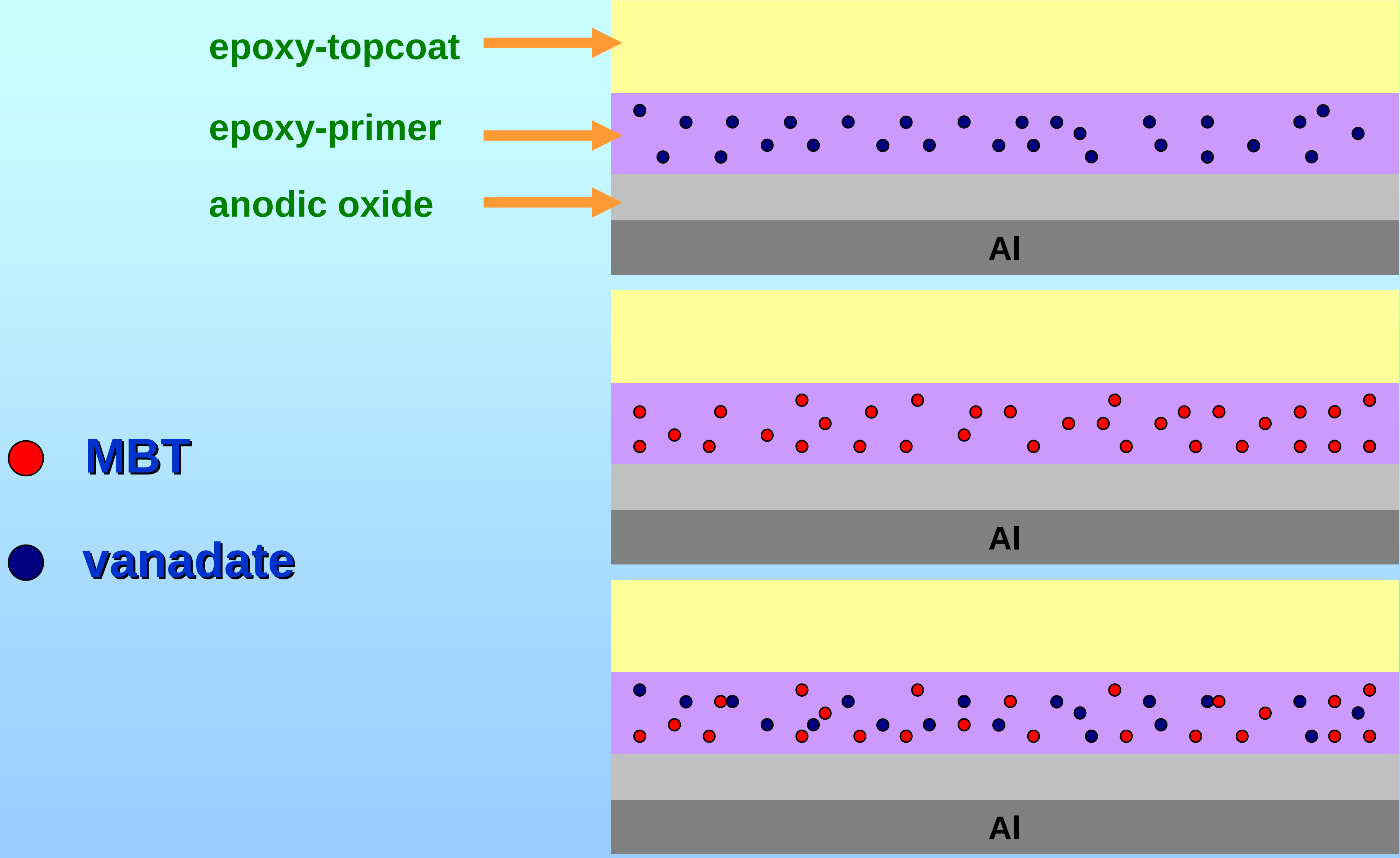
$Zn_2Al(OH)_6MBT$ - 1.71 nm

Release of inhibitors from LDH pigments



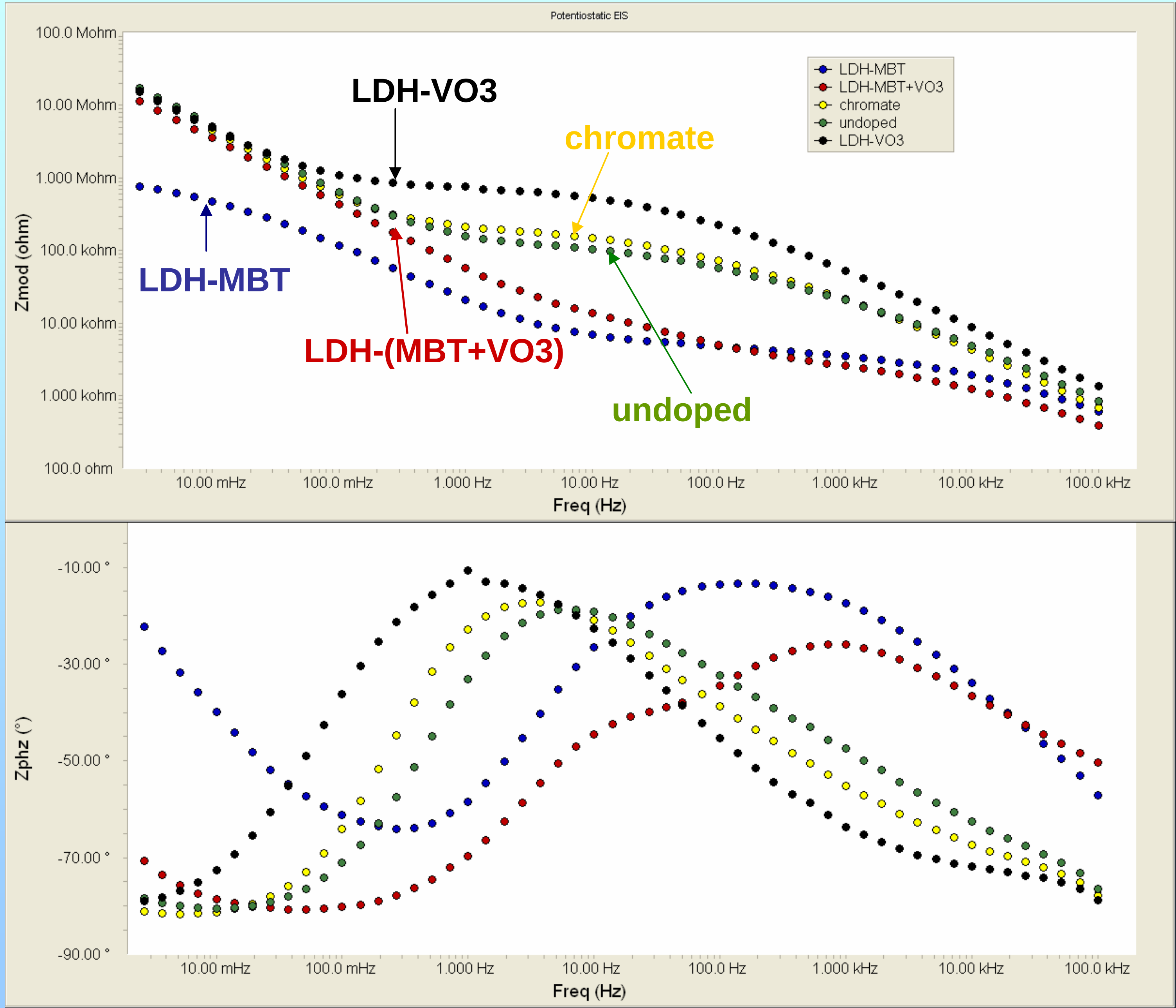
- **LDH pigments demonstrate fast release-response**
- **Release of inhibitor is triggered by chloride ions**

LDH pigments in aerospace coatings



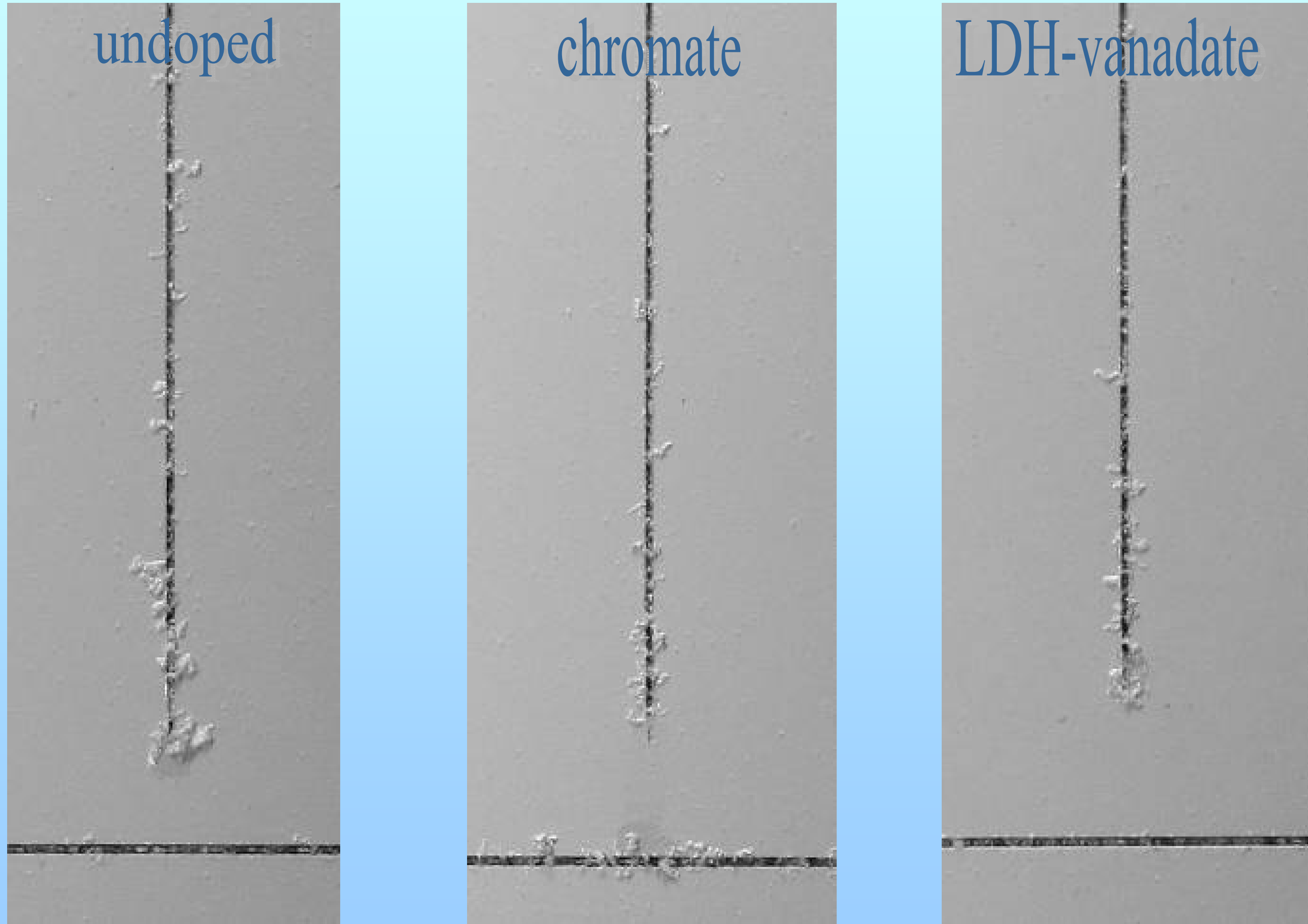
LDH pigments in aerospace coatings

2 months in 0.5 M NaCl



LDH pigments in aerospace coatings

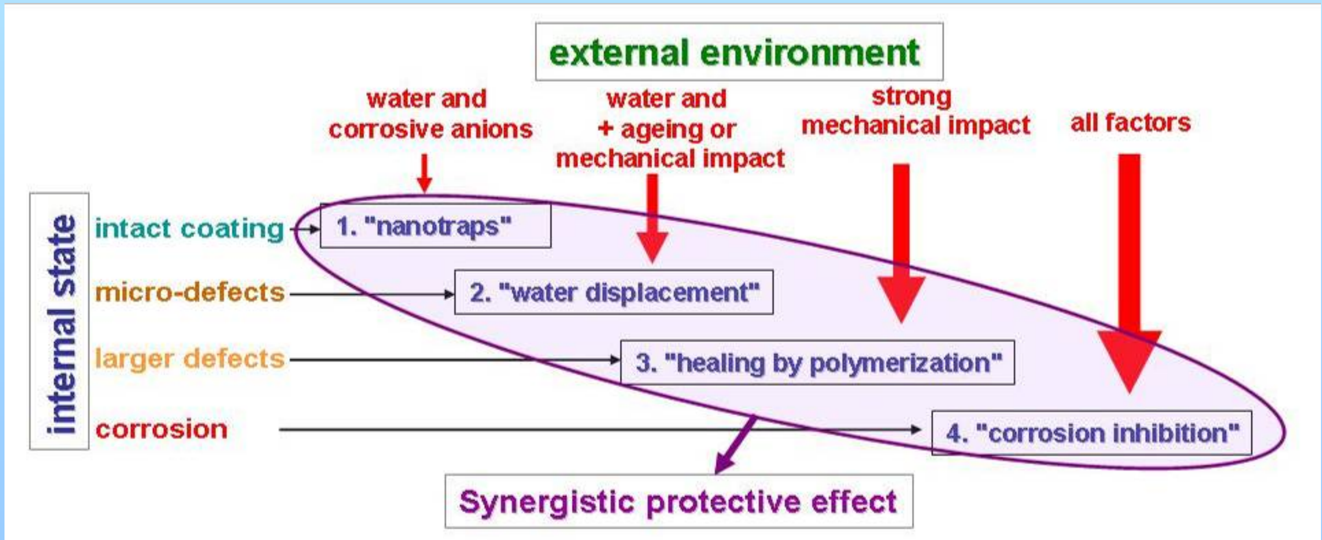
960 h of filiform corrosion tests



New approach

MULTI-LEVEL ACTIVE PROTECTION

- Active feed-back of the coatings depends on the internal state of the coating system and the external environmental conditions
- Different levels of active protection are working as response to different impacts



Conclusions

- *Several new approaches of corrosion inhibitor delivery on demand are proposed conferring “intelligent” self-healing ability to the protective films. Controllable delivery is achieved incorporating nanocontainers of corrosion inhibitor in the coatings;*
- *Porous nanostructured layers and oxide nanoparticles containing corrosion inhibitors confer self-healing ability revealing active corrosion protection;*
- *Nanocontainers of corrosion inhibitors based on LDH nanopigments are developed demonstrating effective corrosion protection and self-healing ability;*
- *“Smart” nanoreservoirs of corrosion inhibitors are also produced using polyelectrolyte shells assembled by LbL approach. This containers are pH-sensitive providing release of corrosion inhibitor on demand.*

Acknowledgements

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Thank you for attention!