SELF-HEALING COATINGS WITH MULTI-LEVEL PROTECTION BASED ON ACTIVE NANOCONTAINERS

*Mario Ferreira**", Mikhail Zheludkevich*

**University of Aveiro, CICECO,Ceramics and Glass Eng., Aveiro, Portugal*
"Instituto Superior Técnico, DEQB, Lisboa, Portugal

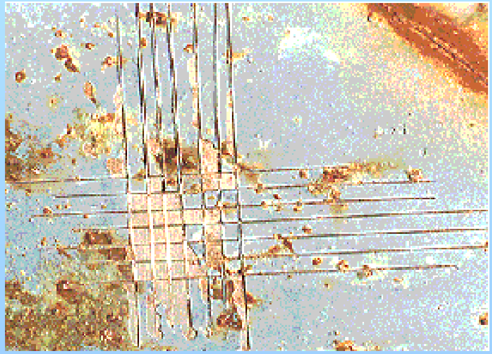
2009 U.S. Army Corrosion Summit

Report Documentation Page					*Form Approved* *OMB No. 0704-0188*
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE **FEB 2009**		2. REPORT TYPE			3. DATES COVERED **00-00-2009 to 00-00-2009**
4. TITLE AND SUBTITLE **Self-Healing Coatings with Multi-Level Protection Based on Active Nanocontainers**					5a. CONTRACT NUMBER
					5b. GRANT NUMBER
					5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)					5d. PROJECT NUMBER
					5e. TASK NUMBER
					5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **University of Aveiro,CICECO, Ceramics and Glas Engineering,Aveiro, Portugal,**					8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)					10. SPONSOR/MONITOR’S ACRONYM(S)
					11. SPONSOR/MONITOR’S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release; distribution unlimited**					
13. SUPPLEMENTARY NOTES **2009 U.S. Army Corrosion Summit, 3-5 Feb, Clearwater Beach, FL**					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**42**	

Protective coatings on metallic substrates

+Aesthetic properties
+Tailored surface properties
+Good barrier against corrosive species

-Lack of self-healing



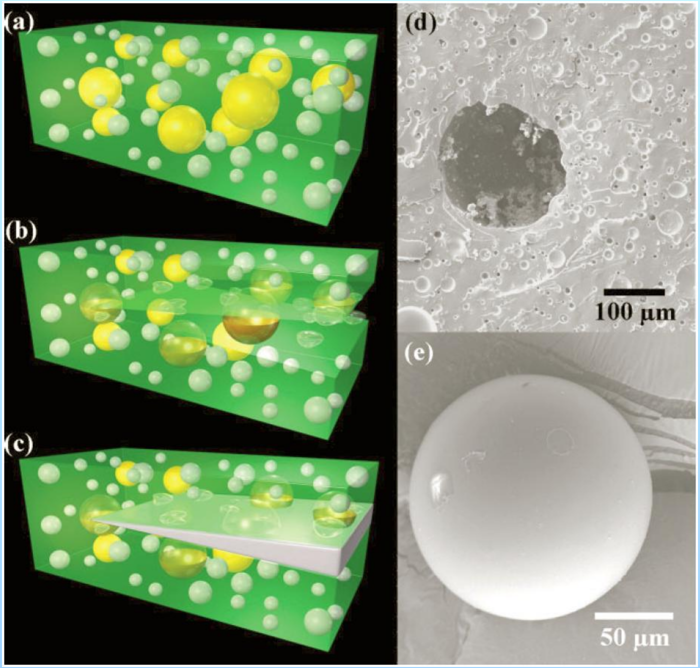
Passive + active

Coating + Active Healing Agent

+Combination of barrier and self-healing

Definition of Self-Healing

The term "self-healing" in materials science means self-recovery of the mechanical integrity and initial properties of the material after destructive actions of external environment or under influence of internal stresses.



Self-healing composite consisting:

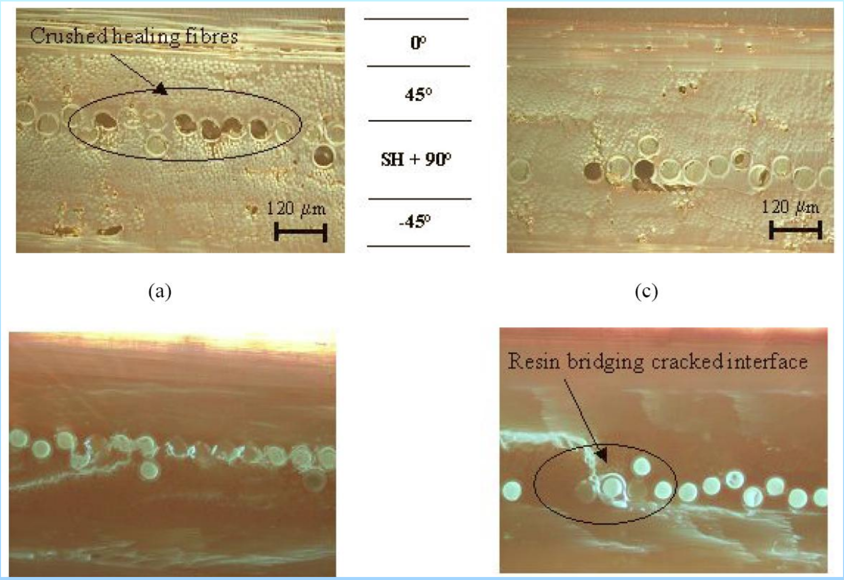
- **microencapsulated catalyst (yellow)**
- **phase-separated healing-agent droplets (white)**
- **matrix (green)**

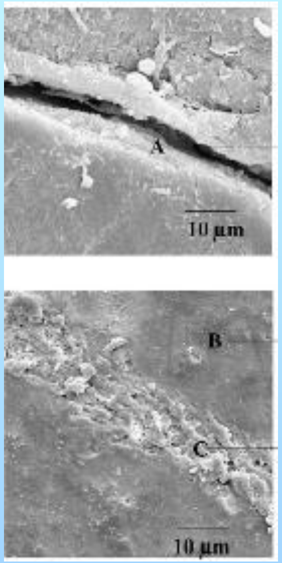
B.S.H. Cho, H.M. Andersson, S.R. White, N.R. Sottos, P.V. Braun, *Adv. Mater.* **2006, *18*,**997-1000.

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

GFRP HGF+Re





•coating

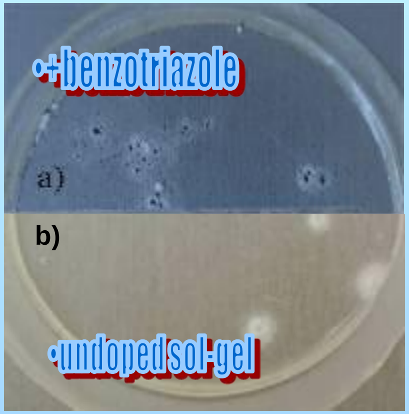
•bohemite

•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.

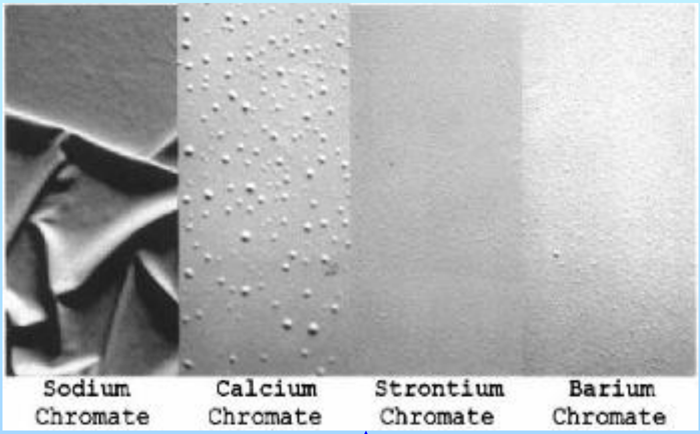
CORROSION SELF-HEALING

The hindering of the corrosion activity in a defect in a coating by any mechanism can be considered as corrosion self-healing

•Examples of negative effect of active agents



Low hydrolytical stability

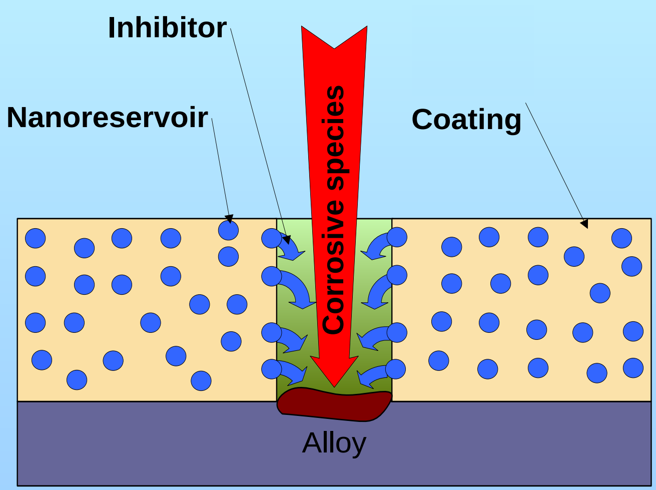


Osmotic blistering

M.L. Zheludkevich, Self-healing anticorrosion coatings, in “Self-healing materials”, Edited by S.K. Ghosh, Wiley-VCH, 2008

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

Nano-encapsulation of corrosion inhibitors before addition to the coating



Possible Advantages

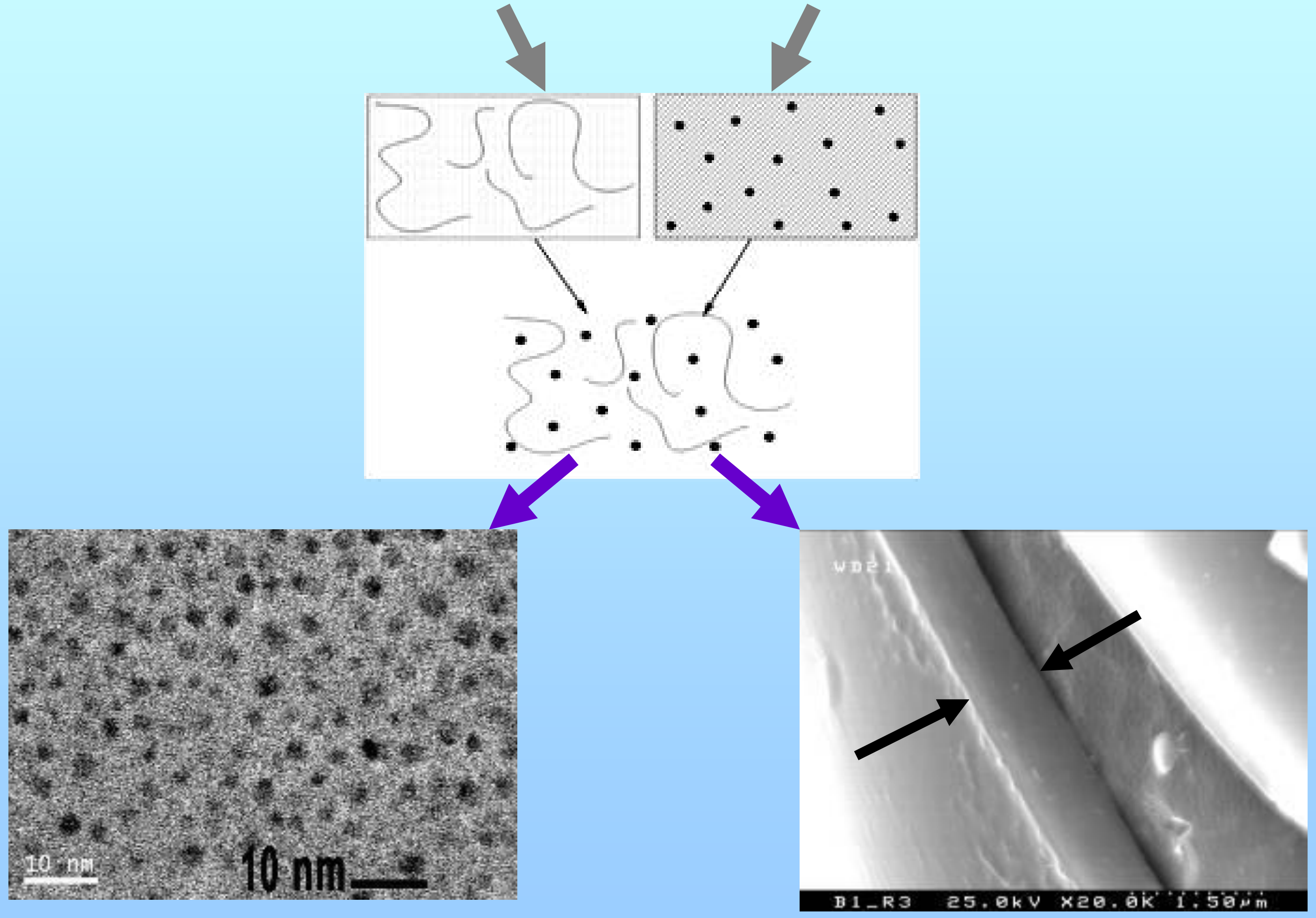
- ✓ Reduction of negative effect of the inhibitor on coating
- ✓ Prevention of inhibitor deactivation due to interaction with coating components
- ✓ Controllable release of inhibitor on demand

Types of Nanocontainers

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

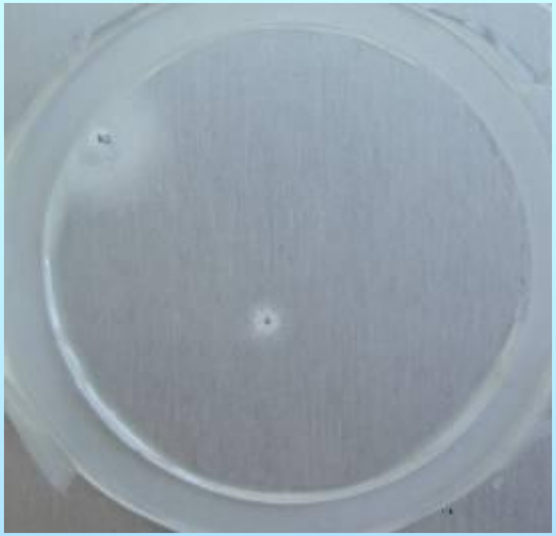
In-situ formed oxide nanopartcles as reservoirs of corrosion inhibitors

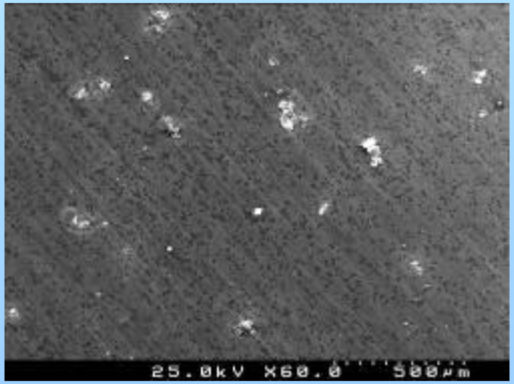
GPTMS + 2-propanol+H_2O **TPOZ + H_2O + Ce^{3+}**



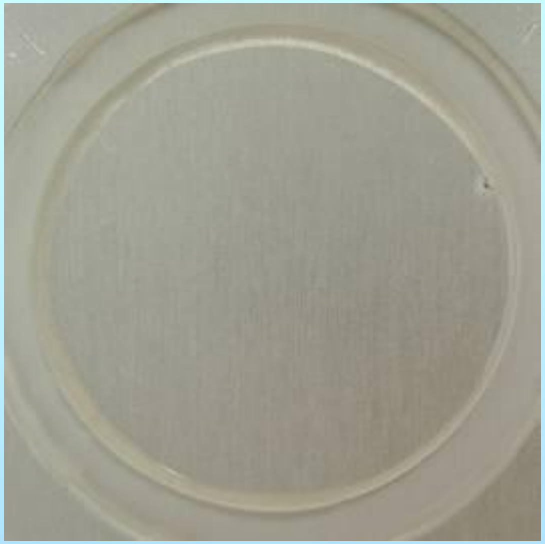
Corrosion protection performance of nanocomposite films

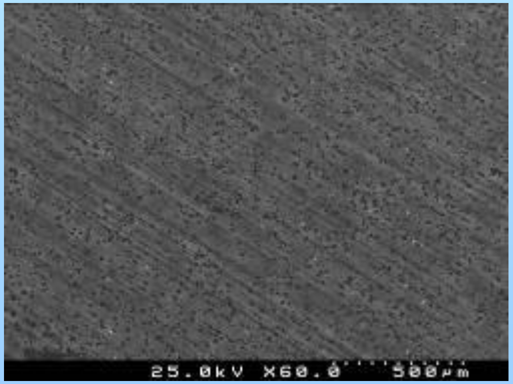
without inhibitor





with inhibitor

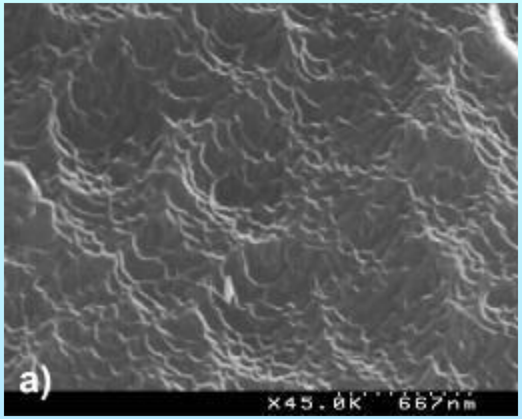




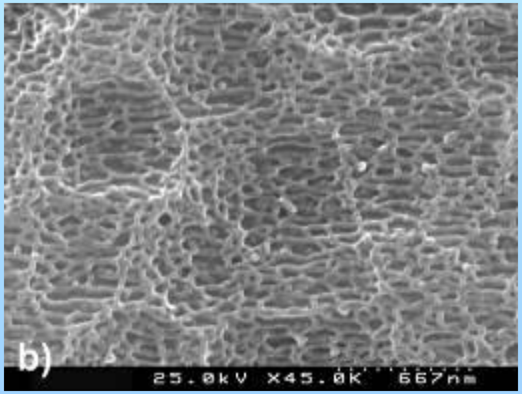
1 month immersion in 3% NaCl solution

Porous layer as nanostructured reservoir of corrosion inhibitor

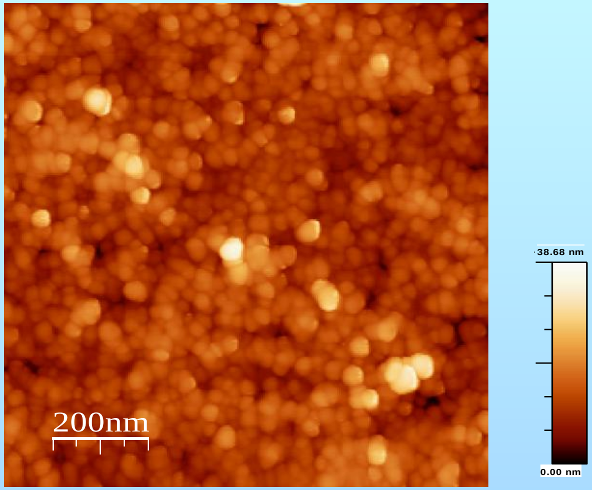
• Structure of the nano-titania layer deposited on polished and etched alloy



• Etched alloy



• Etched alloy + titania

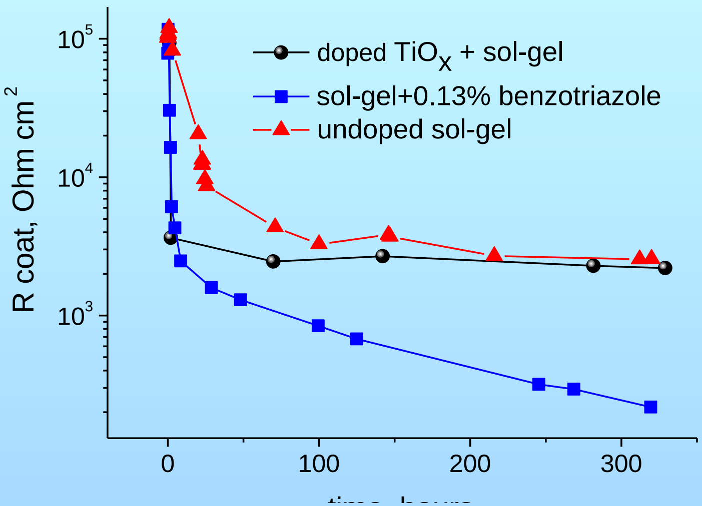


The micelle-template approach can be used to obtain porous nanostructured titania pre-layer before hybrid film deposition

S.V. Lamaka, M.L. Zheludkevich, K.A. Yasakau, M.F. Montemor, P. Cecílio, M.G.S. Ferreira, *Electrochemistry Communications*, 8 (2006) 421-428.

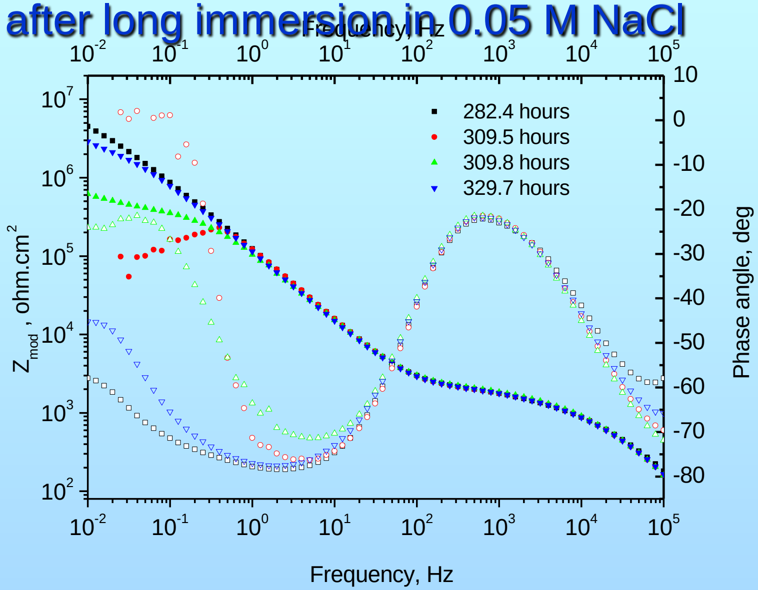
Porous layer as nanostructured reservoir of corrosion inhibitor

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

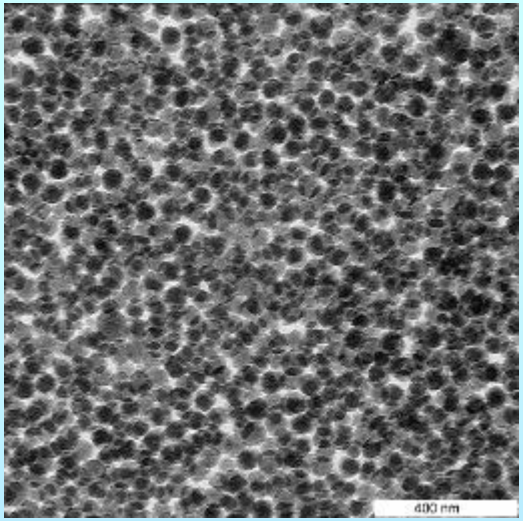


Increase of low frequency impedance is originated from defect passivation

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

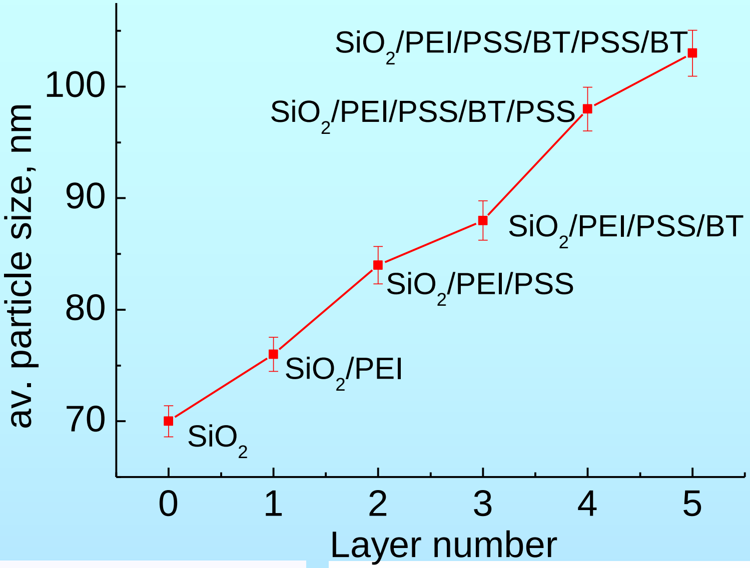
S.V. Lamaka, M.L. Zheludkevich, K.A. Yasakau, R. Serra, S.K. Poznyak, M.G.S. Ferreira,, *Progress in Organic Coatings*, 58 (2007) 127-135.

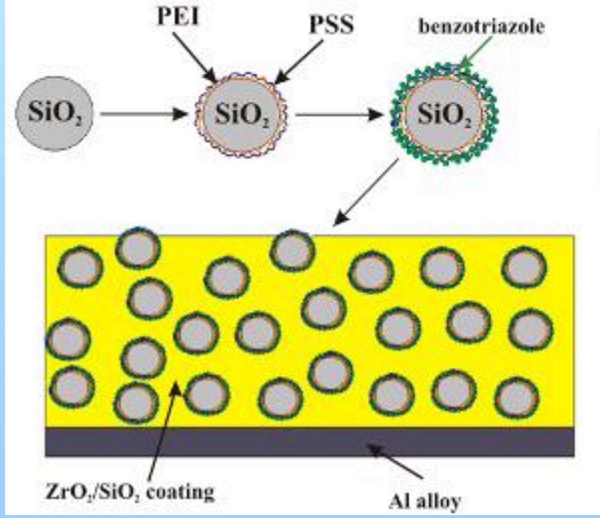
LbL polyelectrolyte nanocontainers for inhibitor encapsulation

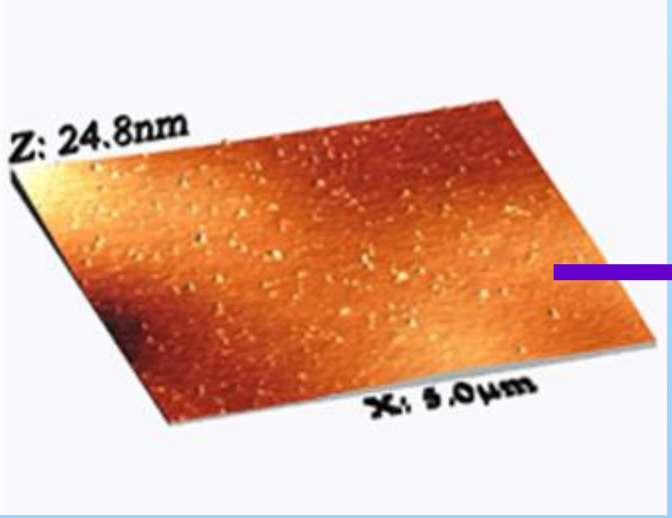


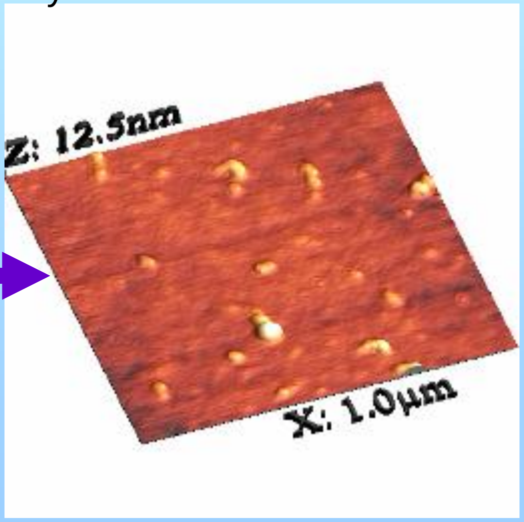
Layer by Layer

assembling process





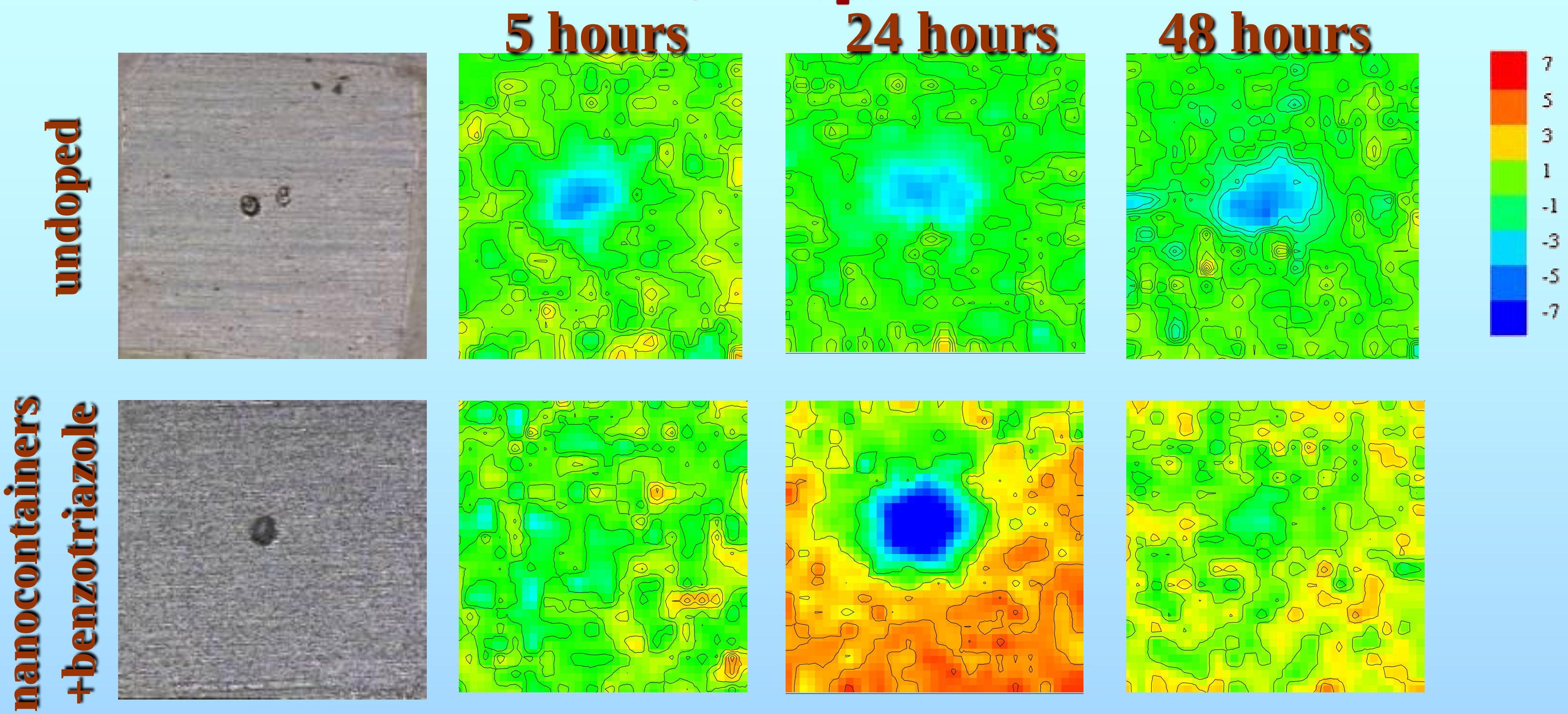




M.L.Zheludkevich, D.G.Shchukin, K.A.Yasakau, H.Möhwald, M.G.S. Ferreira, *Chemistry of Materials*, 19 (2007) 402-411
D.G.Shchukin, M.Zheludkevich, K.Yasakau, S.Lamaka, H.Möhwald, M.G.S.Ferreira, *Advanced Materials*, 18, 2006, 1672–1678.

Self-healing of an artificial defect

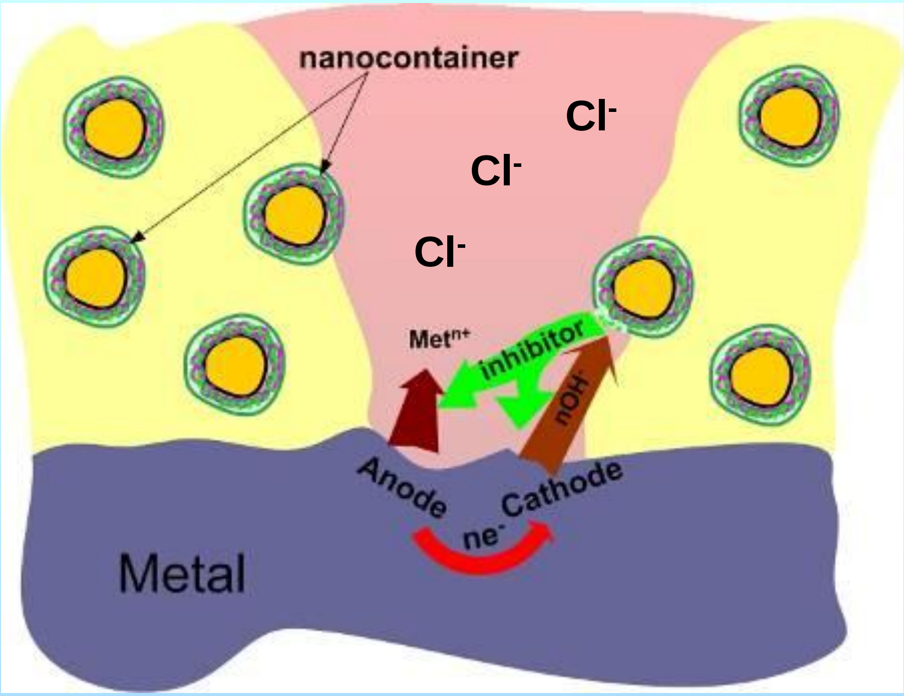
•SVET maps



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

M.L.Zheludkevich, D.G.Shchukin, K.A.Yasakau, H.Möhwald, M.G.S. Ferreira, *Chemistry of Materials*, 19 (2007) 402-411
D.G.Shchukin, M.Zheludkevich, K.Yasakau, S.Lamaka, H.Möhwald, M.G.S.Ferreira, *Advanced Materials*, 18, 2006, 1672–1678.

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

⇓

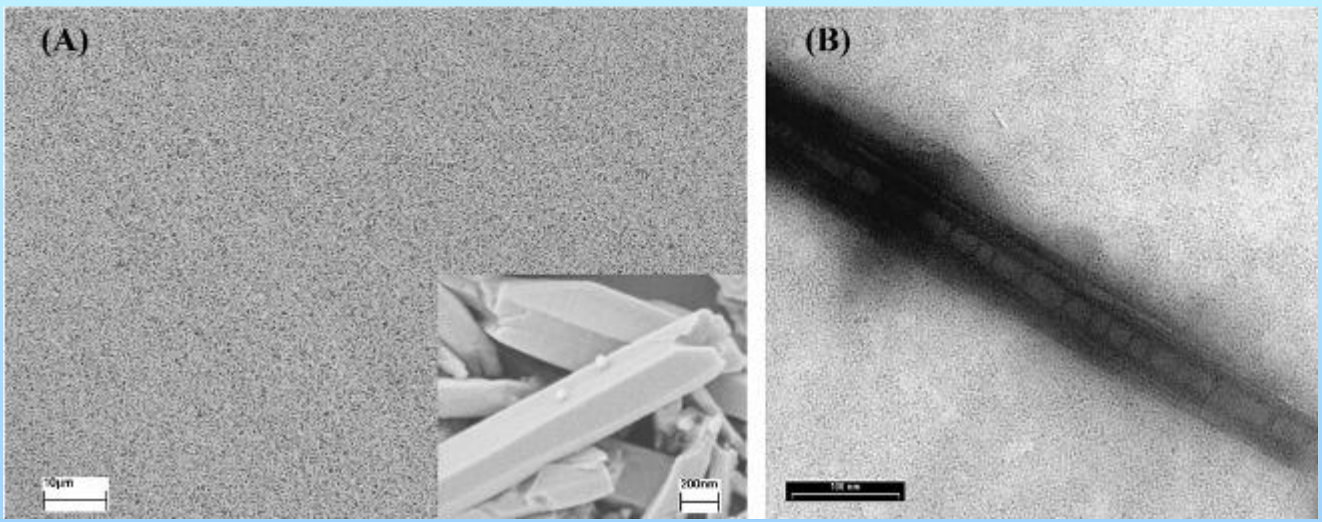
Released benzotriazole hinders corrosion activity healing the defect

M.L.Zheludkevich, D.G.Shchukin, K.A.Yasakau, H.Möhwald, M.G.S. Ferreira, *Chemistry of Materials*, 19 (2007) 402-411
D.G.Shchukin, M.Zheludkevich, K.Yasakau, S.Lamaka, H.Möhwald, M.G.S.Ferreira, *Advanced Materials*, 18, 2006, 1672–1678.

Halloysite as nanocontainers of corrosion inhibitor

Halloysite is defined as a two-layered aluminosilicate, which has a hollow tubular structure in the submicrometer range.

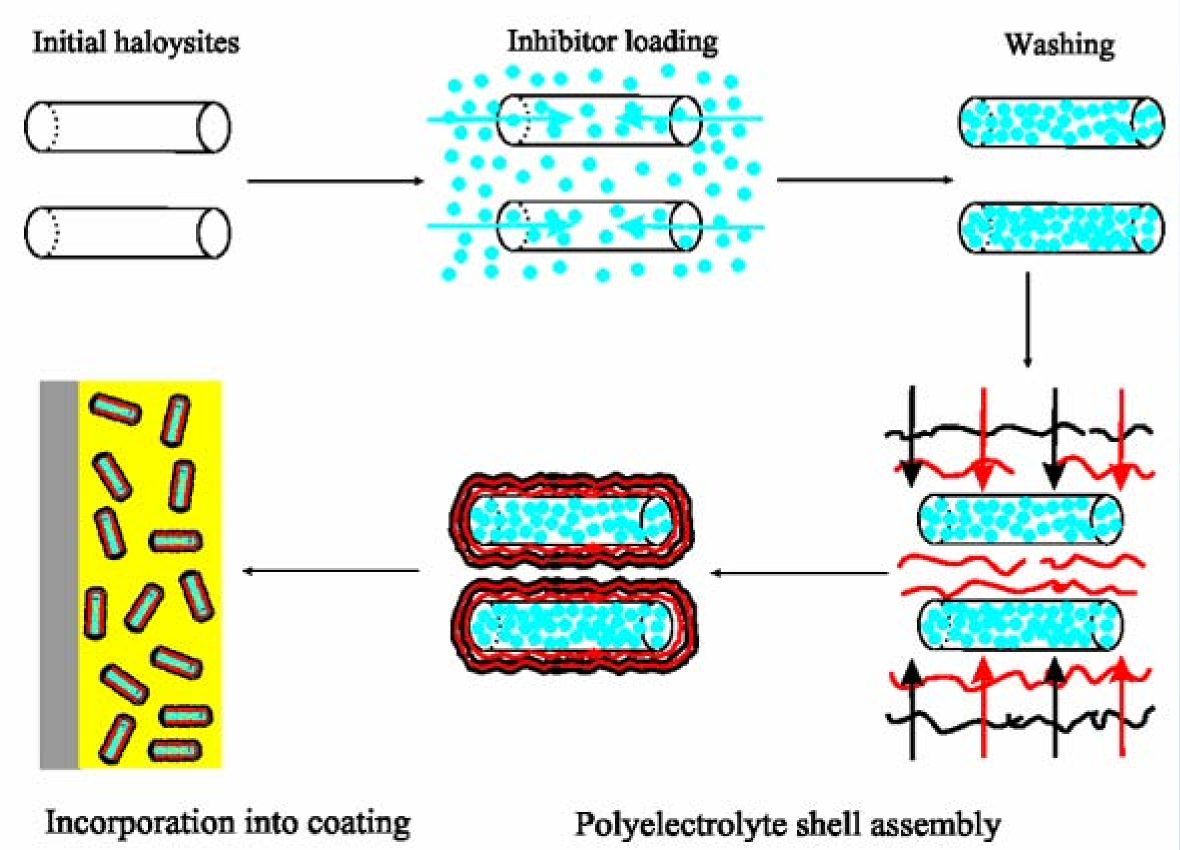
The halloysite tubules are very small with a typical size of less than 3.0 μm long×0.3 μm outer diameter and have an inner diameter of 10– 150 nm depending on the types.



SEM (A) and TEM (B) images of the halloysite nanotubes

D.G. Shchukin, S.V. Lamaka, K.A. Yasakau, M.L. Zheludkevich, H. Möhwald, M.G.S. Ferreira, *Journal of Physical Chemistry C*, 112 (2007) 958-964.

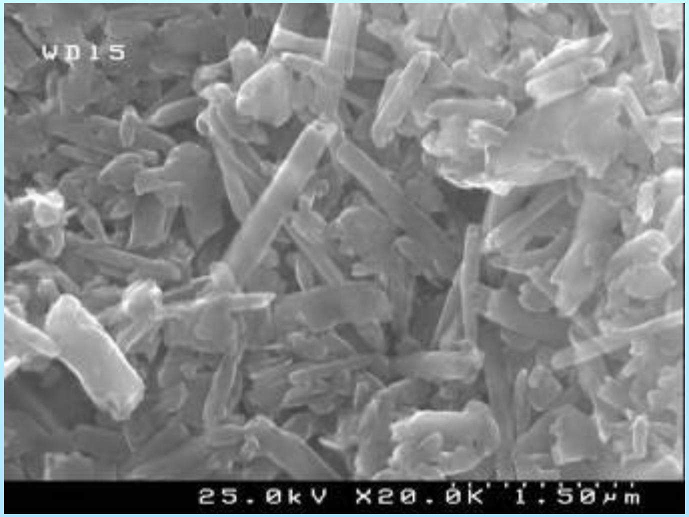
Halloysite as nanocontainers of corrosion inhibitor



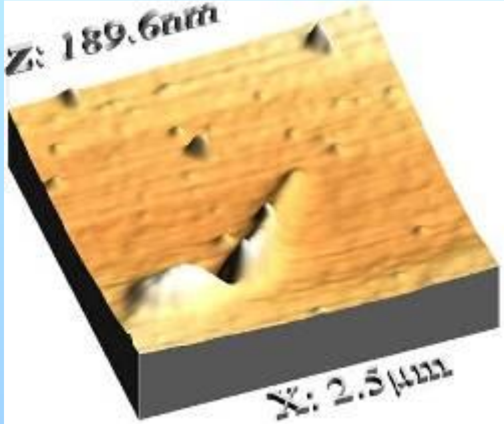
Fabrication of 2-mercaptobenzothiazole-loaded halloysite/polyelectrolyte nanocontainers

D.G. Shchukin, S.V. Lamaka, K.A. Yasakau, M.L. Zheludkevich, H. Möhwald, M.G.S. Ferreira, *Journal of Physical Chemistry C*, 112 (2007) 958-964.

Halloysites nanocontainers with PE shell



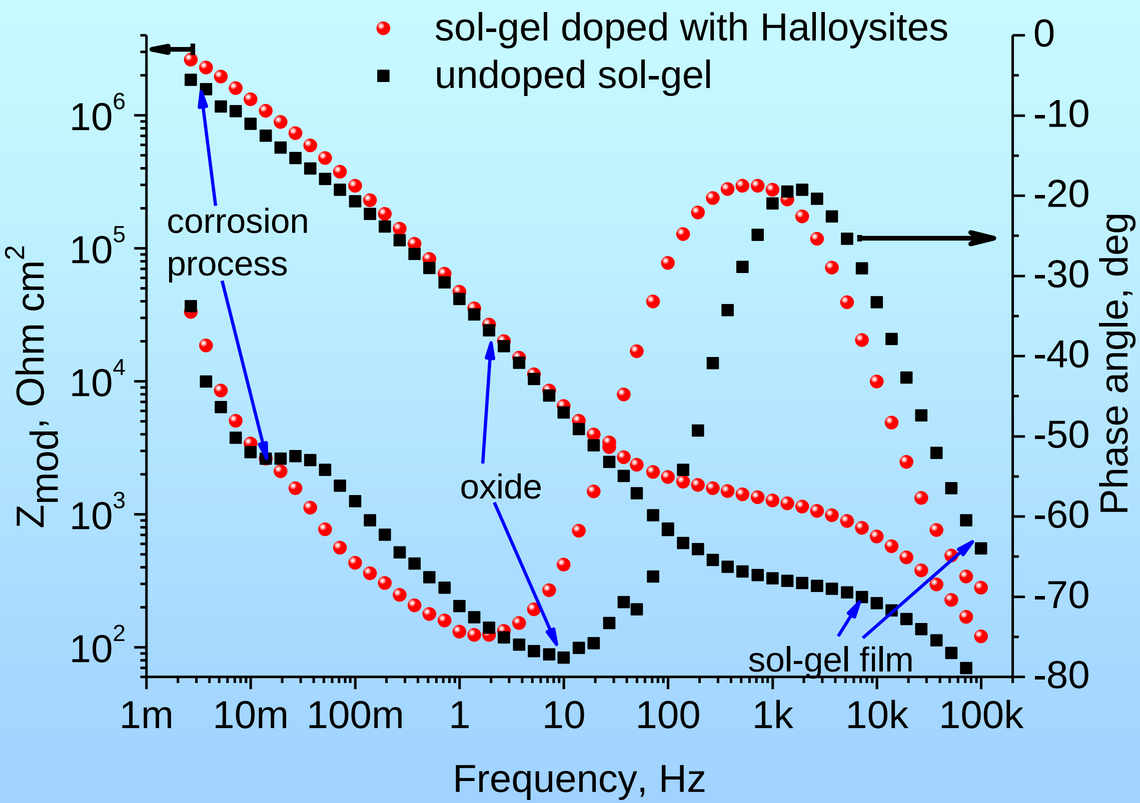
2-mercaptobenzothiazole-loaded halloysite/polyelectrolyte nanocontainers



Nanocontainers in hybrid coating

D.G. Shchukin, S.V. Lamaka, K.A. Yasakau, M.L. Zheludkevich, H. Möhwald, M.G.S. Ferreira, *Journal of Physical Chemistry C*, 112 (2007) 958-964.

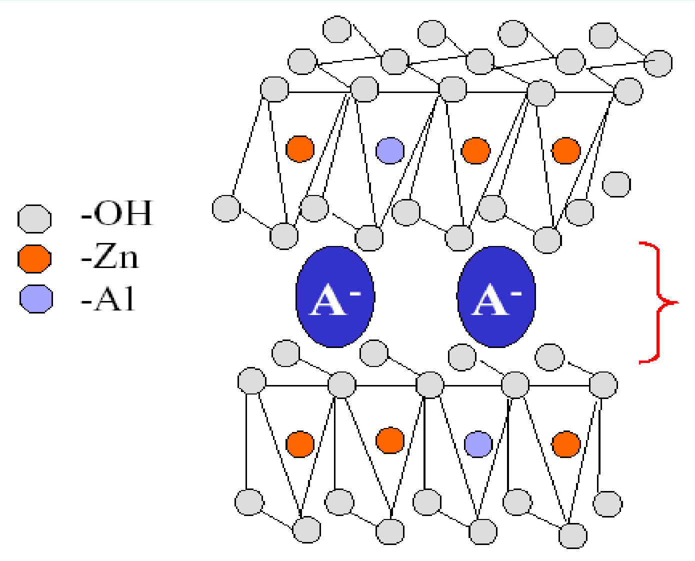
Corrosion protection properties of hybrid films doped with halloysite nanocontainers



Impedance spectra of undoped and halloysites doped sol-gel coatings after 2 week immersion test in 3% NaCl

D.G. Shchukin, S.V. Lamaka, K.A. Yasakau, M.L. Zheludkevich, H. Möhwald, M.G.S. Ferreira, *Journal of Physical Chemistry C*, 112 (2007) 958-964.

LDH nanocontainers



Layered double hydroxide (LDH) powders:

1) Mg^{2+}/Cr^{3+} (2:1)
2) Mg^{2+}/Al^{3+} (2:1)
3) Zn^{2+}/Al^{3+} (2:1)

Inhibiting anions:

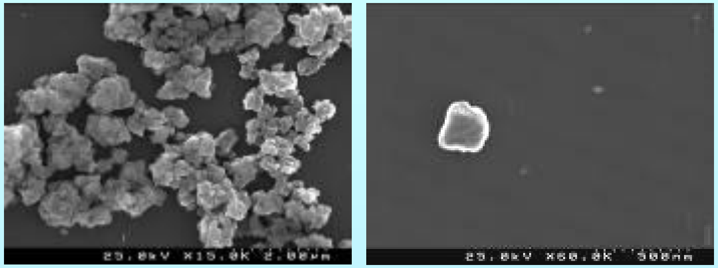
- **Mercaptobenzothiazole (MBT)**
- **Quinaldic acid (QA)**
- **Vanadate**
- **Tungstate**
- **Molibdate**

Two ways of pigment preparation:

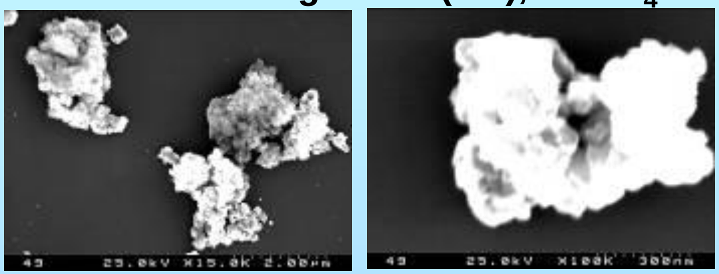
- **direct synthesis (-formation of insoluble salts/complexes)**
- **ion-exchange**

Mg/Cr LDH pigments

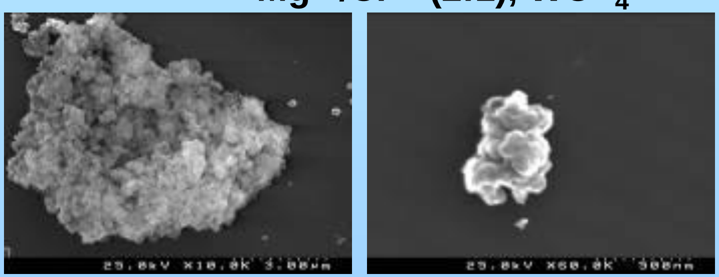
Mg^{2+}/Cr^{3+} (2:1) , Cl



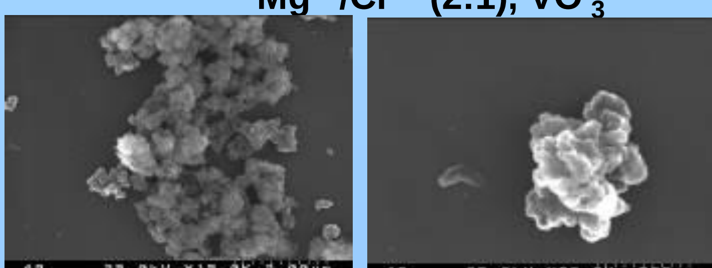
Mg^{2+}/Cr^{3+} (2:1), MoO^{2-}_4



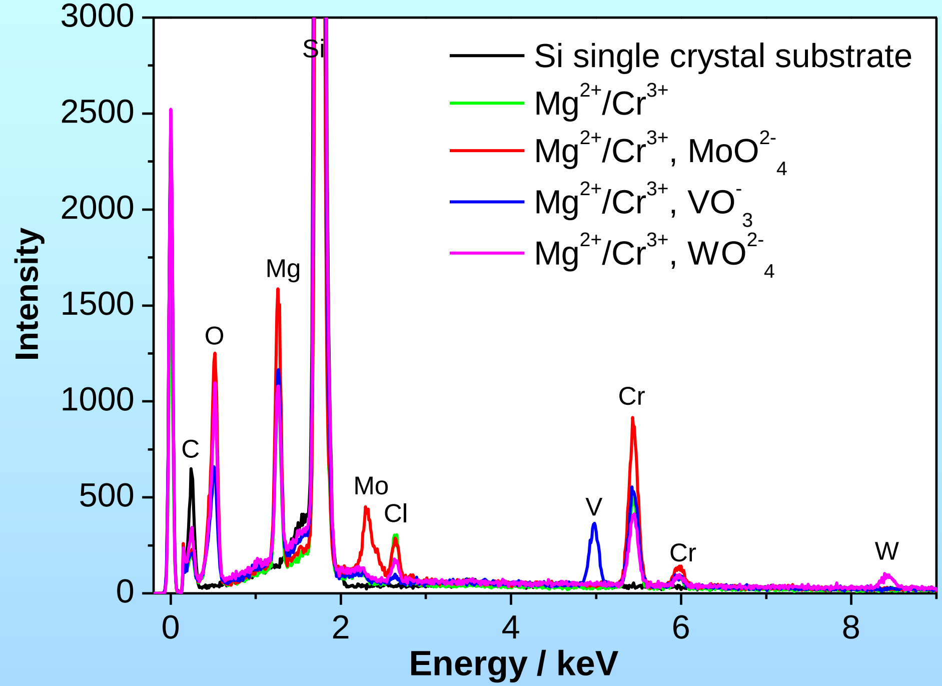
Mg^{2+}/Cr^{3+} (2:1), WO^{2-}_4



Mg^{2+}/Cr^{3+} (2:1), VO^-_3



EDS of initial LDH powders :



Composition of LDH powders in at. % by EDS.

Powder	Mg	Cr	Mo	V	W	O
Mg/Cr, Cl^-	4.73	2.37	---	---	---	91.90
Mg/Cr, MoO_4^{2-}	10.02	7.28	4.48	---	---	76.84
Mg/Cr, WO_4^{2-}	2.50	1.24	---	---	0.32	95.67
Mg/Cr, VO_3^-	3.55	1.65	---	1.03	---	93.72

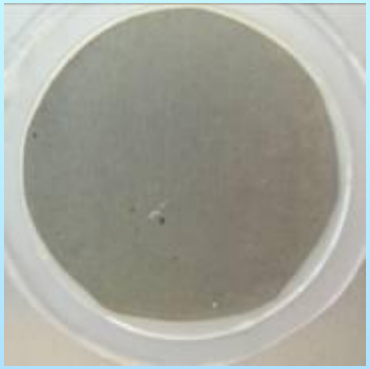
Mg/Cr LDH pigments

Photos of AA2024 samples after corrosion tests during 14 days
(50 mg of LDH was added to 10 ml of 0.05 M NaCl)

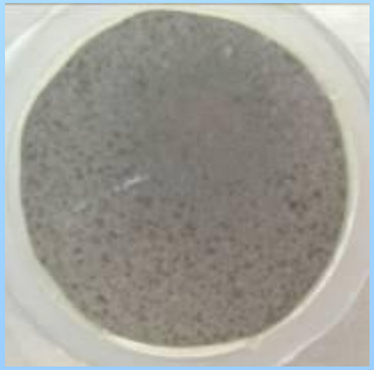
0.05M NaCl

0.05M NaCl + Mg^{2+}/Cr^{3+}, Cl^-

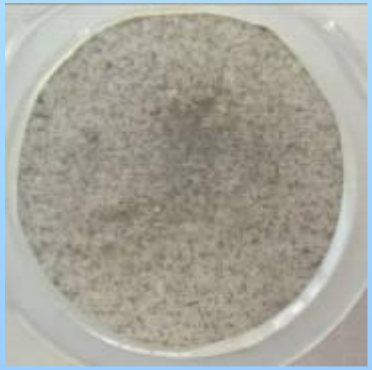
0.05M NaCl + Mg^{2+}/Cr^{3+}, MoO_4^{2-}



0.05M NaCl + Mg^{2+}/Cr^{3+}, WO_4^{2-}

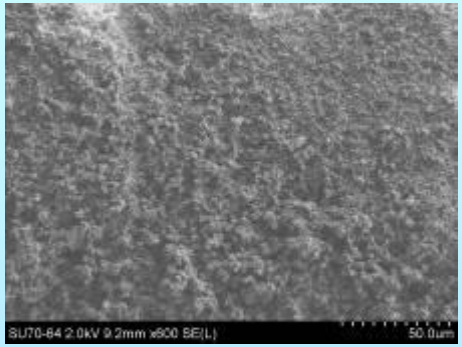


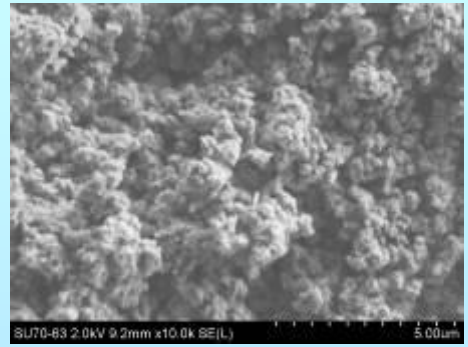
0.05M NaCl + Mg^{2+}/Cr^{3+}, VO_3^-



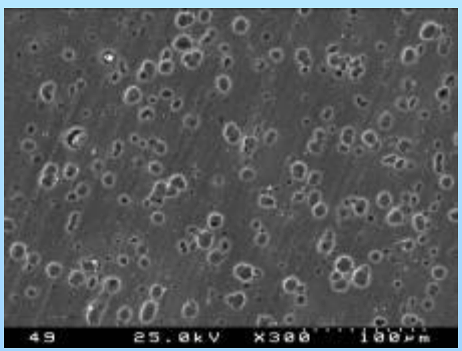
Mg/Cr LDH pigments

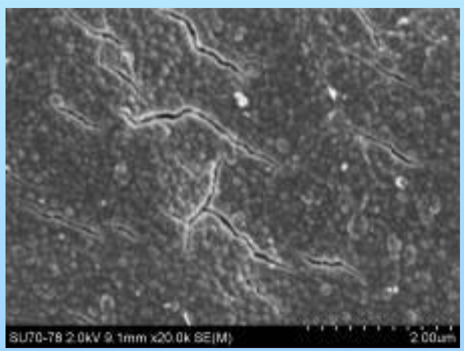
Al in 0.05M NaCl



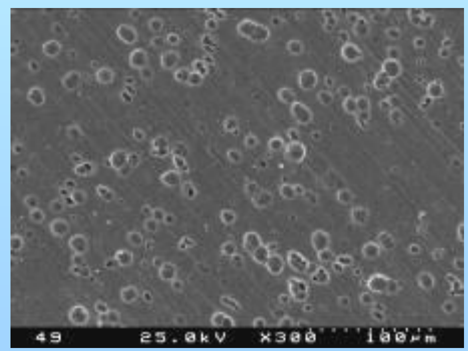


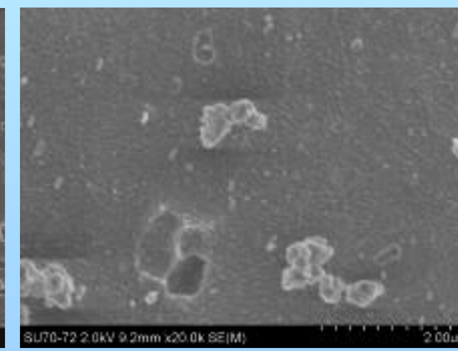
Al in 0.05M NaCl + Mg^{2+}/Cr^{3+}, MoO^{2-}_4



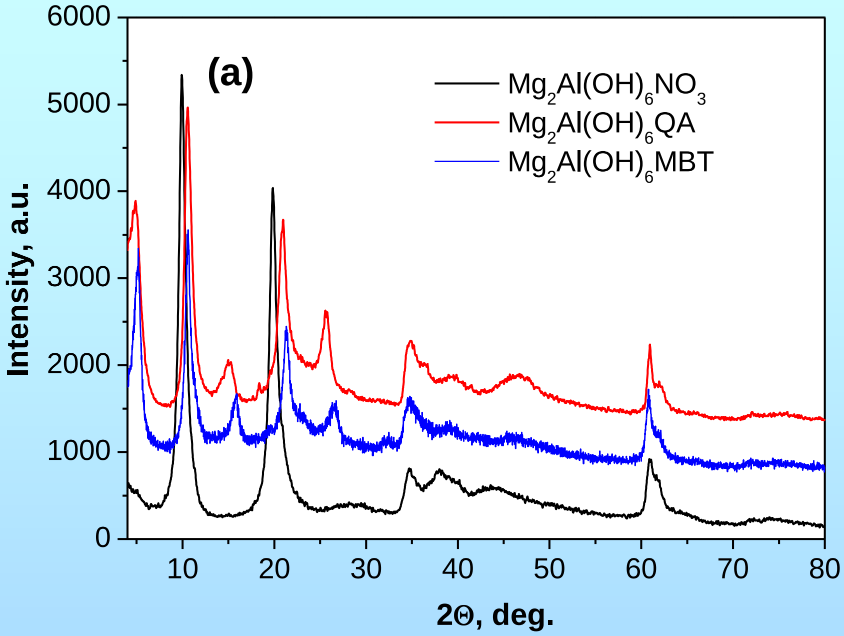


Al in 0.05M NaCl + Mg^{2+}/Cr^{3+}, VO^{-}_3





Mg-Al LDH pigments



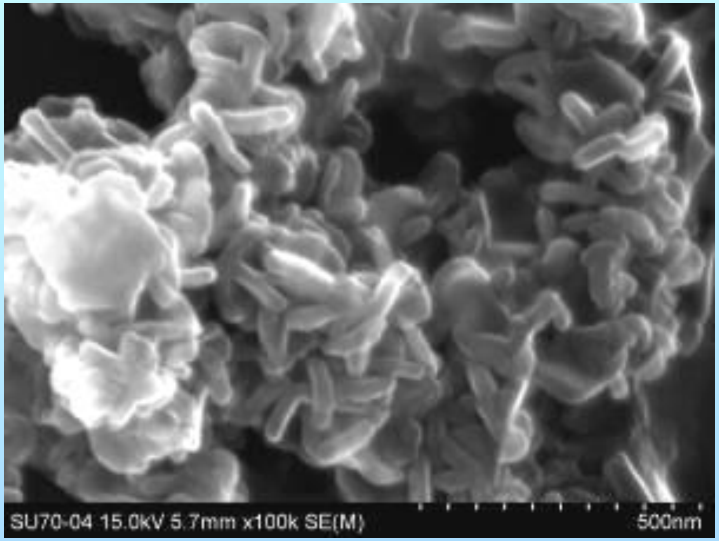
d(*003*)

- $Mg_2Al(OH)_6NO_3$ - 0.8909 nm
- $Mg_2Al(OH)_6QA$ - 1.78 nm
- $Mg_2Al(OH)_6MBT$ - 1.71 nm

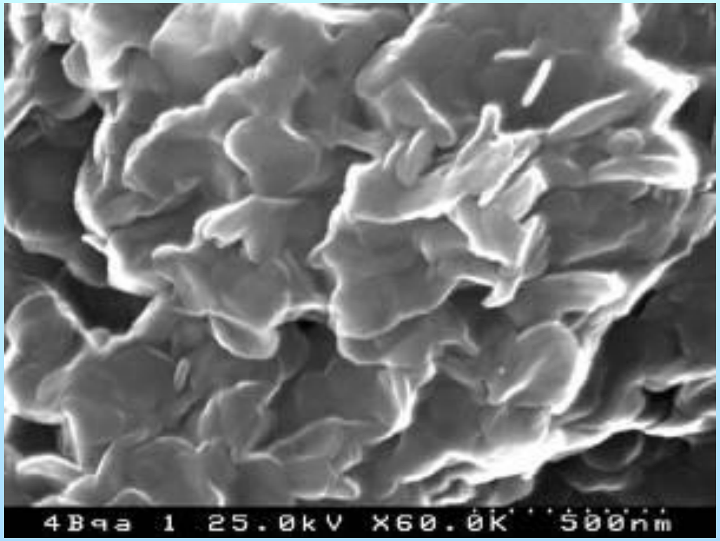
The average size of LDH nanocrystallites:

- 12 nm - $Mg_2Al(OH)_6NO_3$
- 14 nm - $Mg_2Al(OH)_6QA$
- 14 nm - $Mg_2Al(OH)_6MBT$

Mg-Al LDH pigments



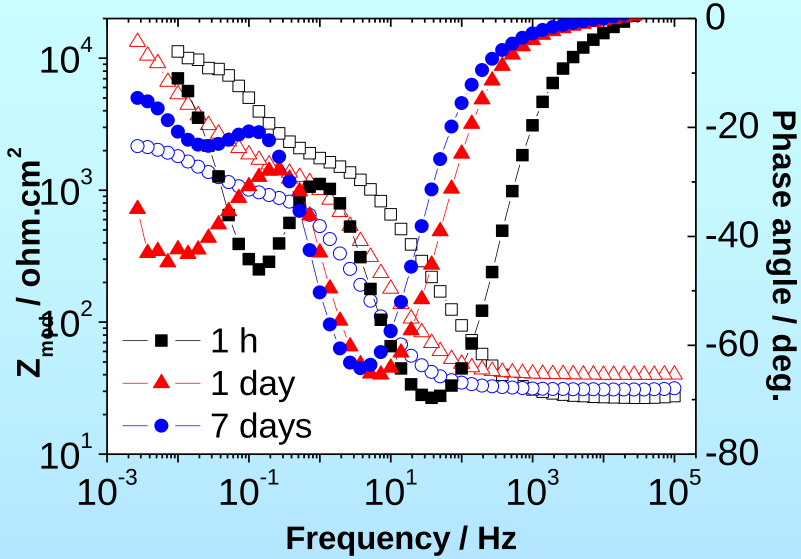
$Mg_2Al(OH)_6NO_3$



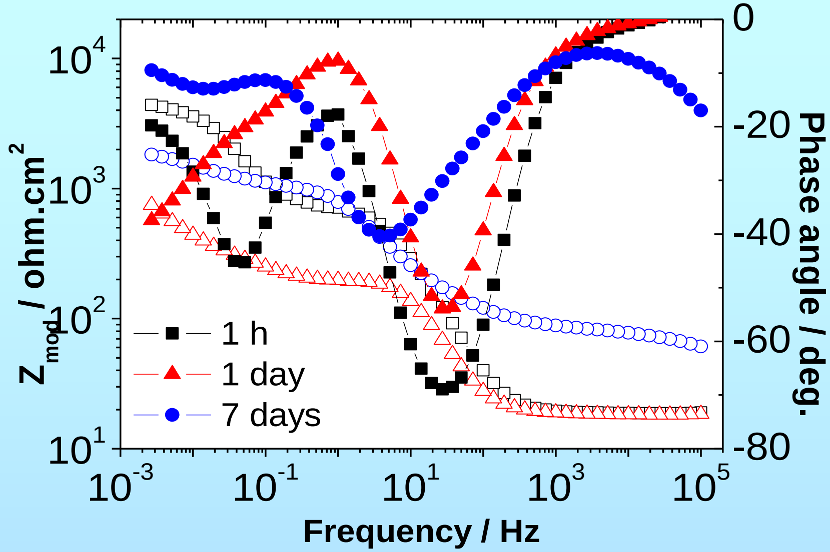
$Mg_2Al(OH)_6QA$

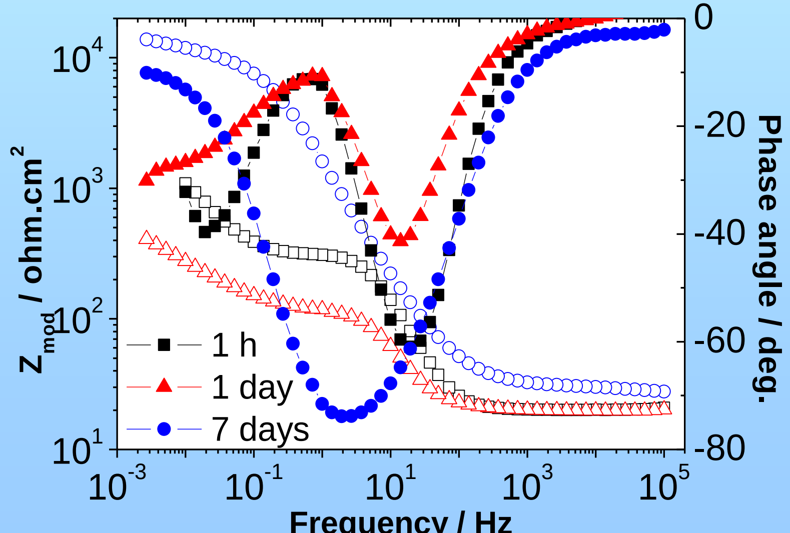
Corrosion efficiency of LDH pigments

0.05 M NaCl



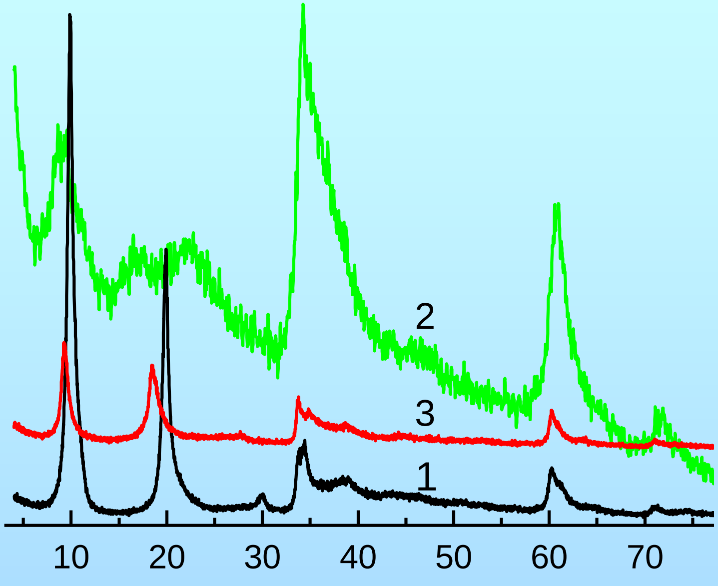
$Mg_2Al(OH)_6QA$ + 0.05 M NaCl

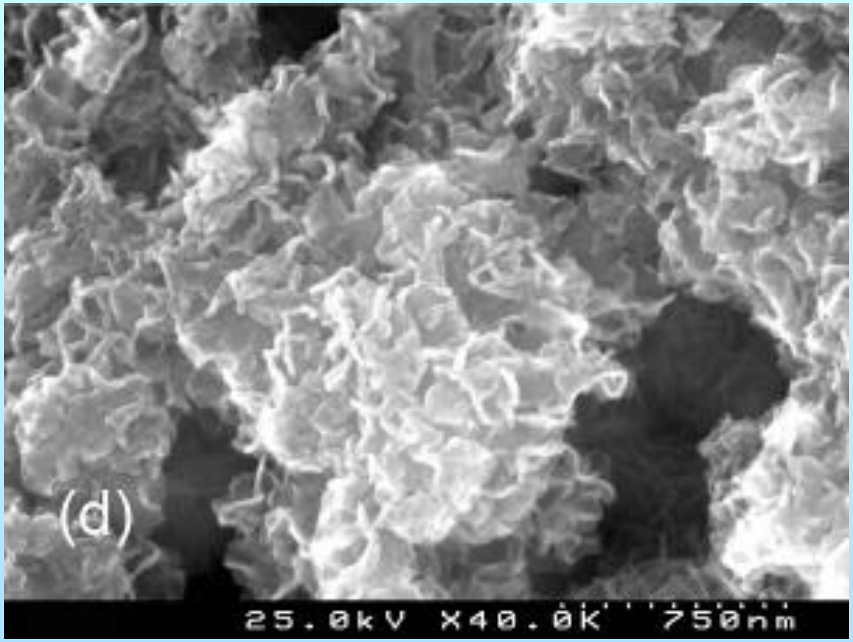


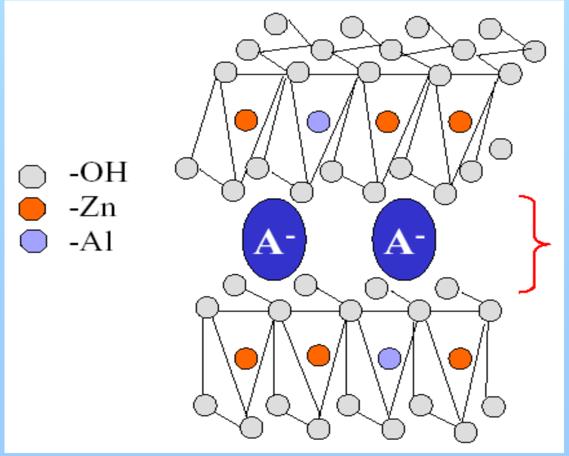


$Mg_2Al(OH)_6MBT$ + 0.05 M NaCl

Zn-Al LDH pigments





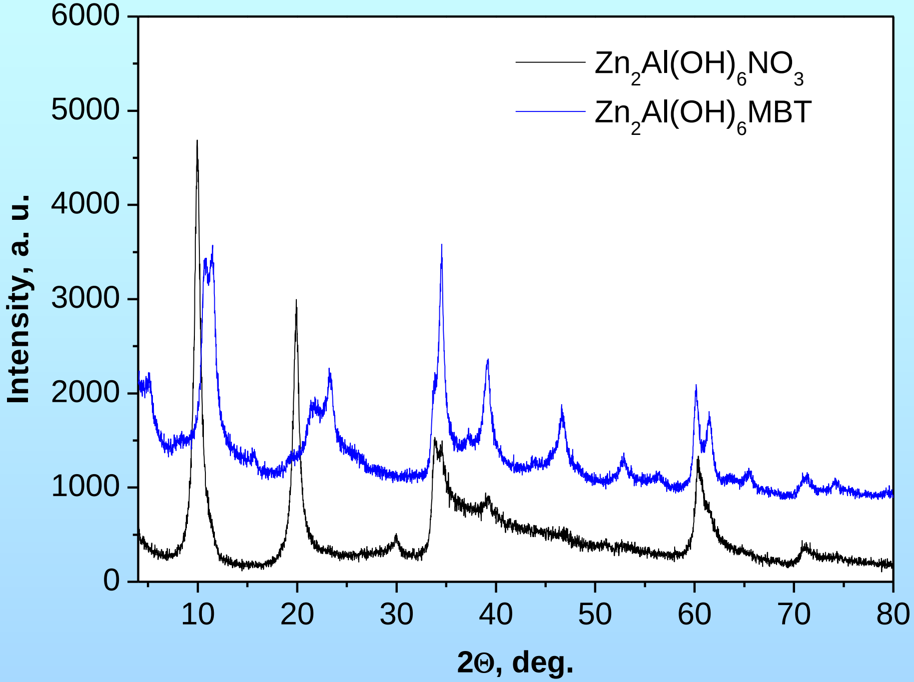


X-ray diffraction patterns for Zn-Al LDHs

- **1 – NO^{3-}** **d(003) 0.8892nm**
- **2 - VO^{3-} by direct synthesis**
- **3 - VO^{3-} by anion exchange**

d(003) 0.9262nm

Zn-Al LDH pigments

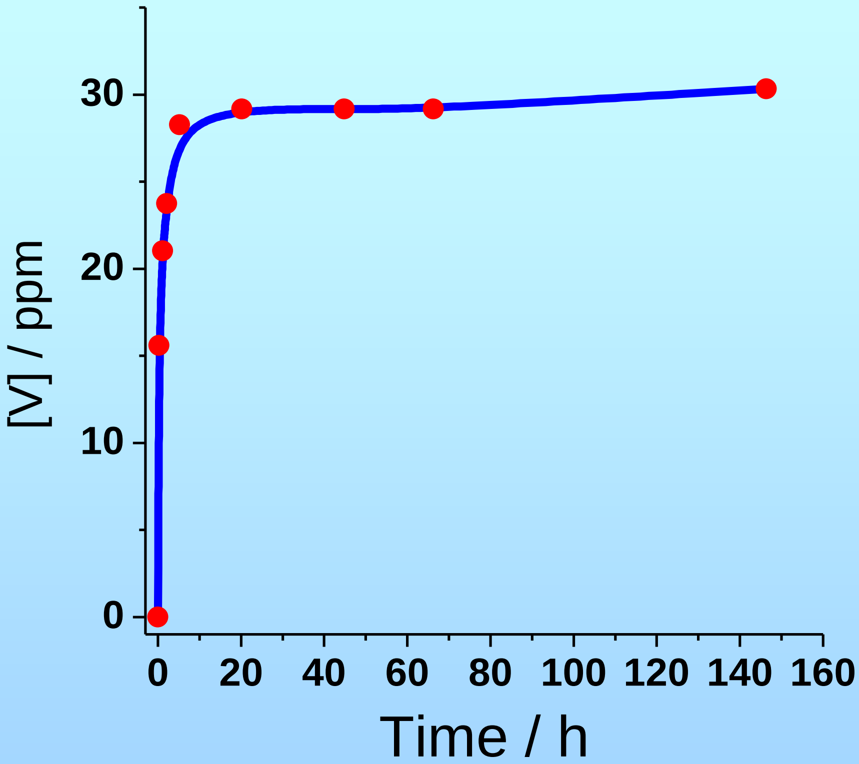


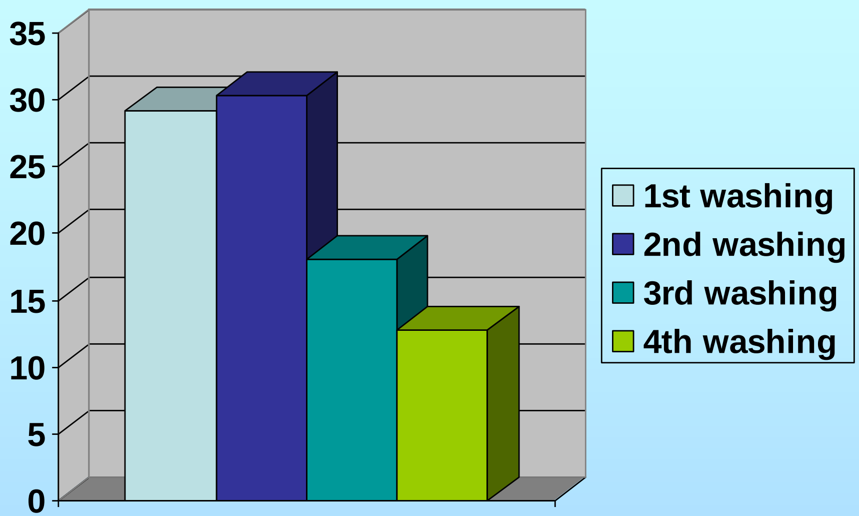
d(003)

$Zn_2Al(OH)_6NO_3$ - 0.8892 nm

$Zn_2Al(OH)_6MBT$ - 1.71 nm

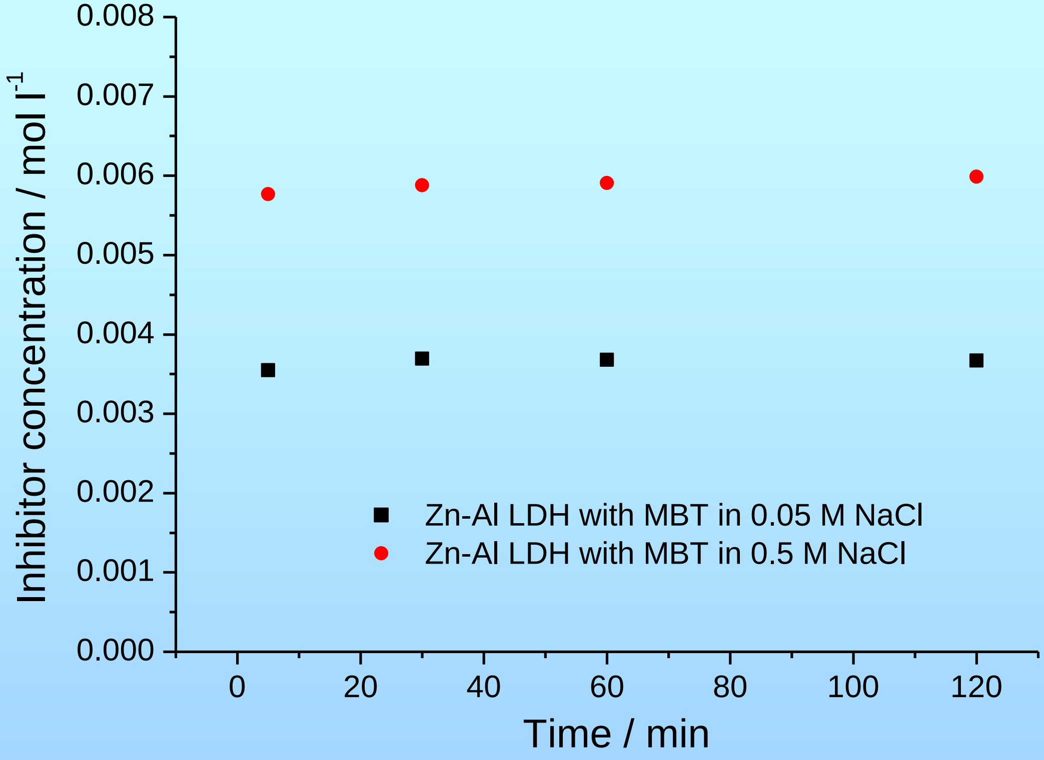
Release of vanadate from LDH pigments





Concentration of released vanadium vs. time plots for $Zn_2Al(OH)_6VO_3$ LDH in 0.5 M NaCl solutions (200 mg LDH per 25 ml of solution).

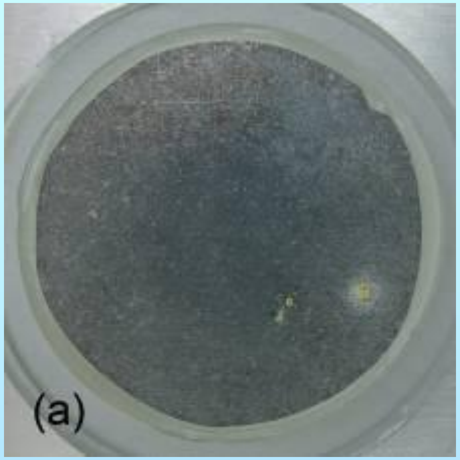
Release of inhibitors from LDH pigments



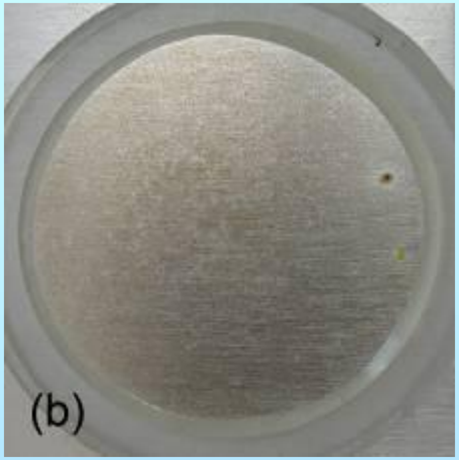
- **LDH pigments demonstrate fast release-response**
- **Release of inhibitor is triggered by chloride ions**

Corrosion efficiency of LDH pigments

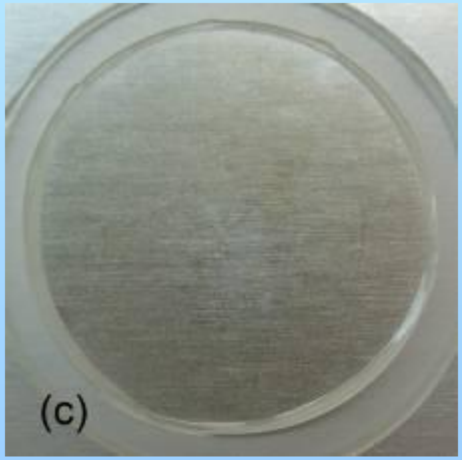
$Mg_2Al(OH)_6VO_3$ + 0.05 M NaCl



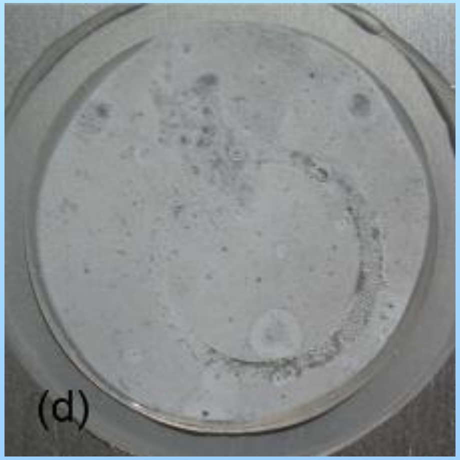
$Zn_2Al(OH)_6VO_3$ (direct)+ 0.05 M NaCl



•2 weeks

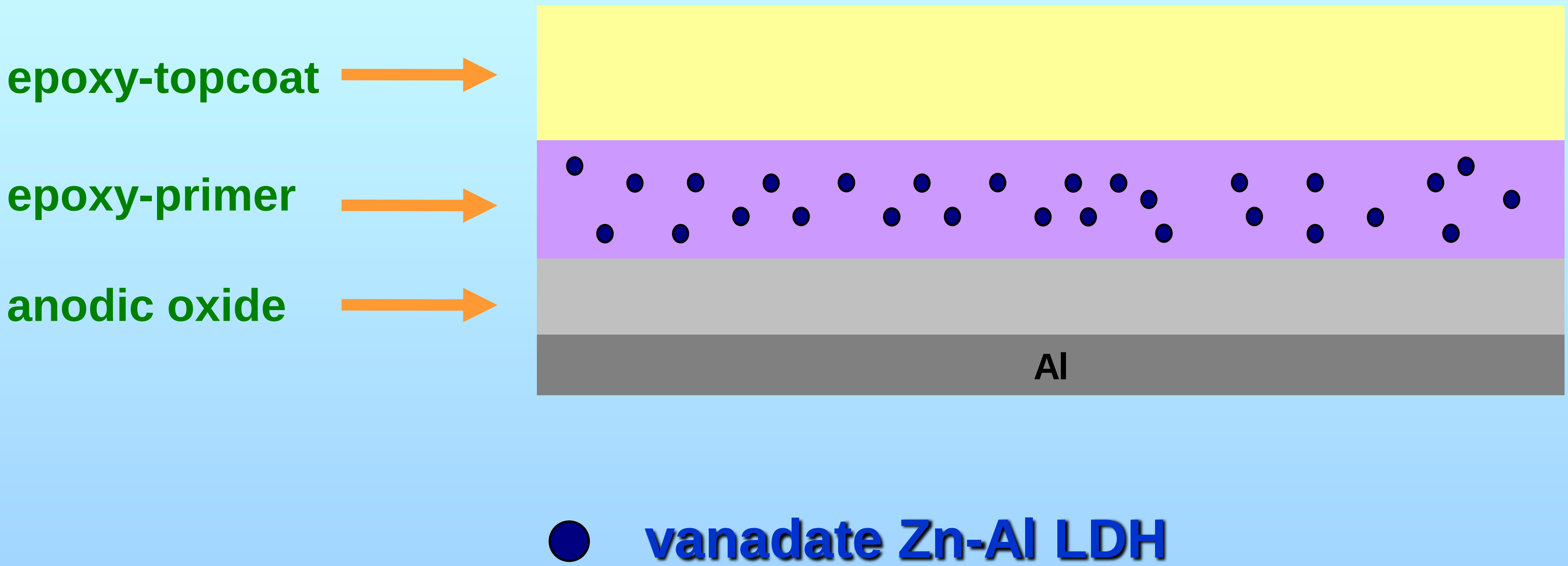


$Zn_2Al(OH)_6VO_3$ (exch.)+ 0.05 M NaCl



0.05 M NaCl

LDH pigments in aerospace coatings



In collaboration with EADS IW, Germany

LDH pigments in aerospace coatings

960 h of filiform corrosion tests

In collaboration with EADS IW, Germany

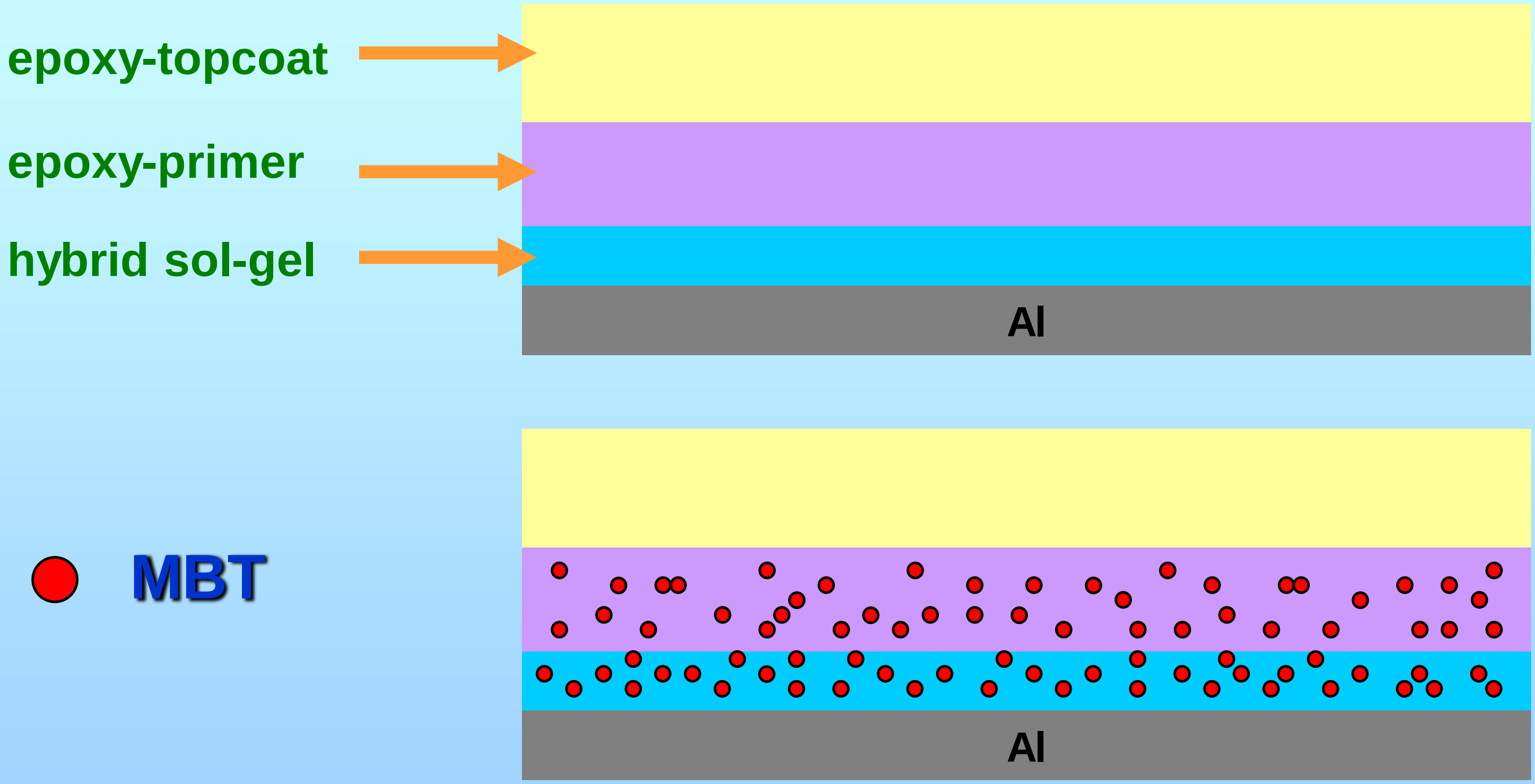
LDH pigments in aerospace coatings

results of filiform corrosion tests

Sample	960 h		336 h	
	Max Filament length [mm]	Amount M1…M5	Max Filament length [mm]	Amount M1…M5
Zn_2AlVO_3 LDH - 1	1,6	M3	1,0	M2
Zn_2AlVO_3 LDH - 2	2,0	M3	1,0	M2
Undoped - 1	2,3	M3-4	1,4	M2
Undoped - 2	2,5	M3	1,2	M3
Chromate - 1	1,6	M3	0,7	M3
Chromate - 2	1,9	M3	0,8	M3

In collaboration with EADS IW, Germany

LDH pigments in aerospace coatings



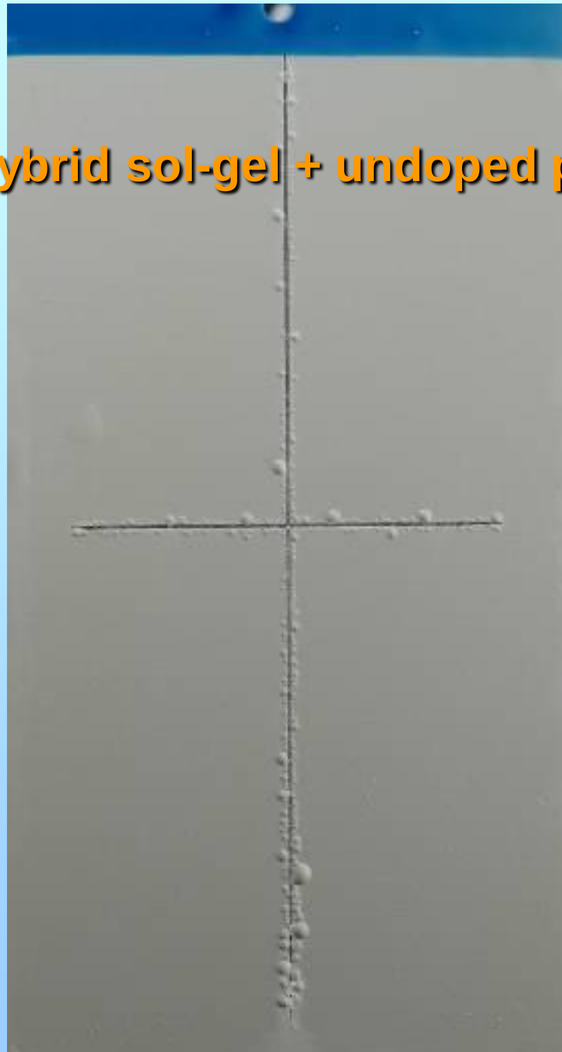
In collaboration with EADS IW, Germany

Aerospace coatings with LDH nanocontainers of organic inhibitors

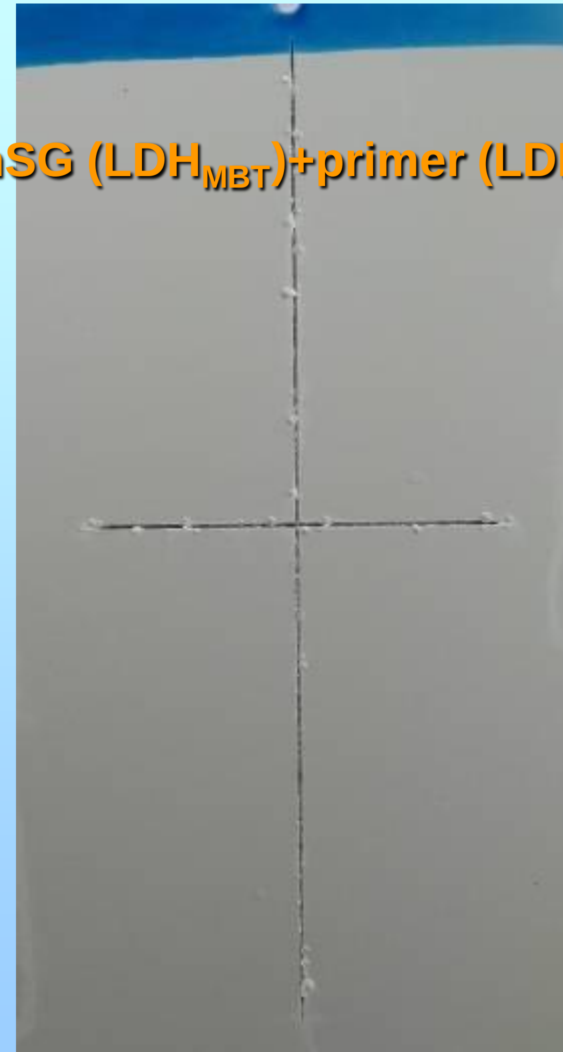
- EN ISO 3665

336 h SST

hybrid sol-gel + undoped primer



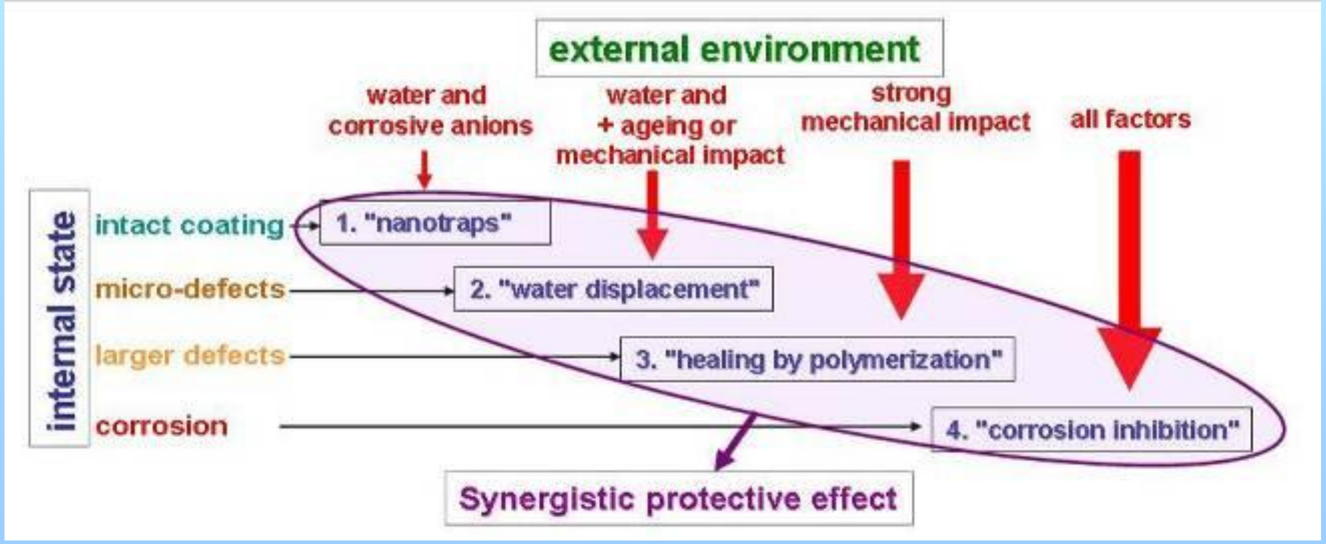
hSG (LDH_{MBT})+primer (LDH_{MBT})



In collaboration with EADS IW, Germany

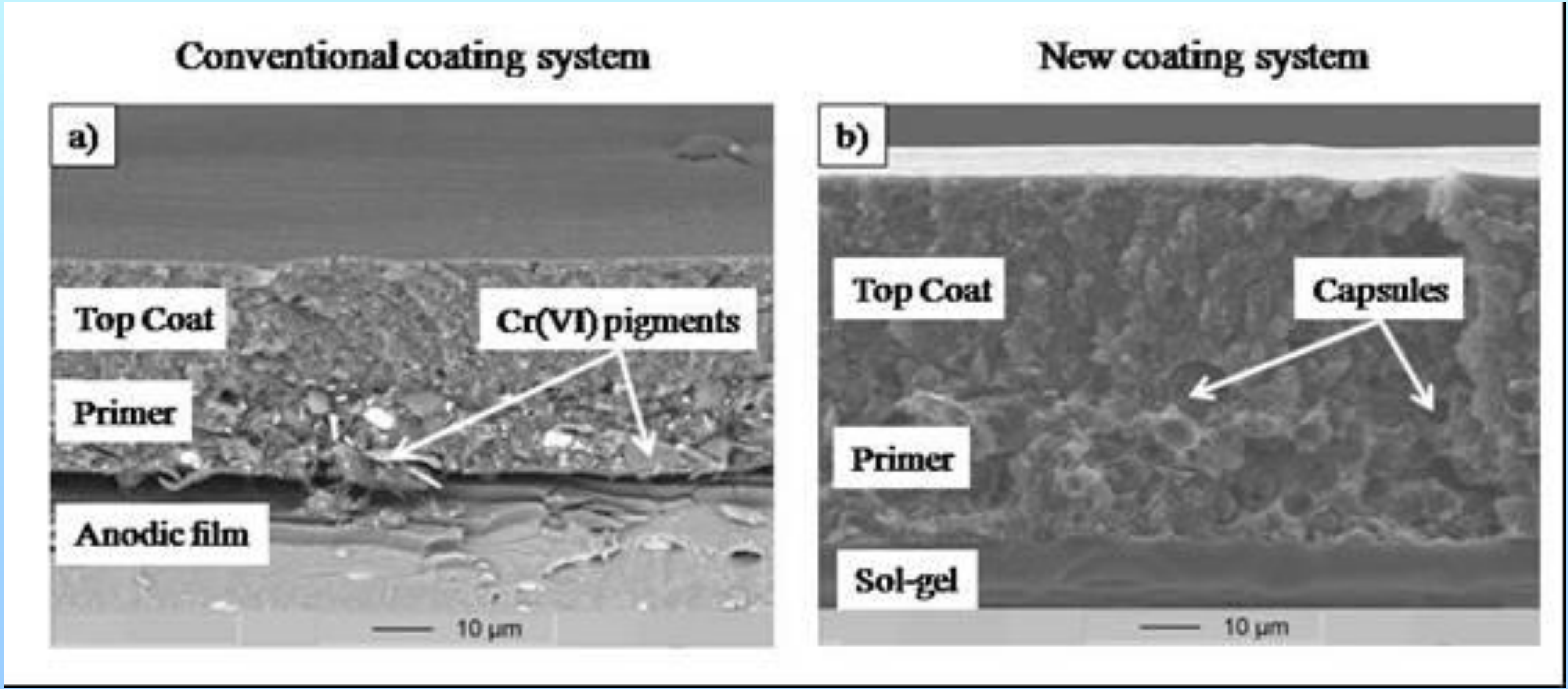
MULTI-LEVEL ACTIVE PROTECTION

- 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



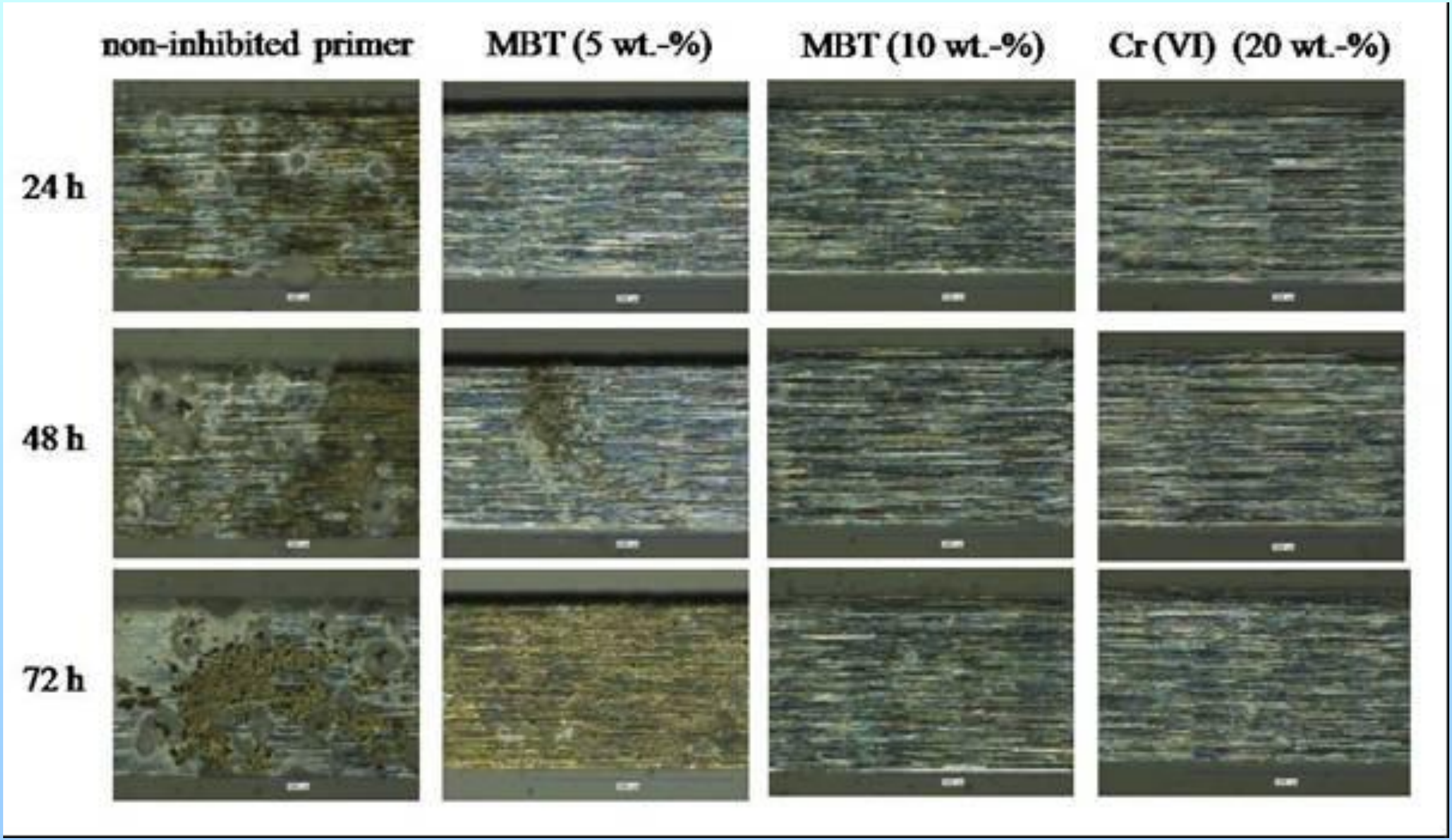
2^{nd} and 4^{th} level: water displacement + corrosion inhibition

Capsules of water displacing agent (diisopropylnaphthaline) and corrosion inhibitor (MBT) produced by microemulsion interfacial polymerization.



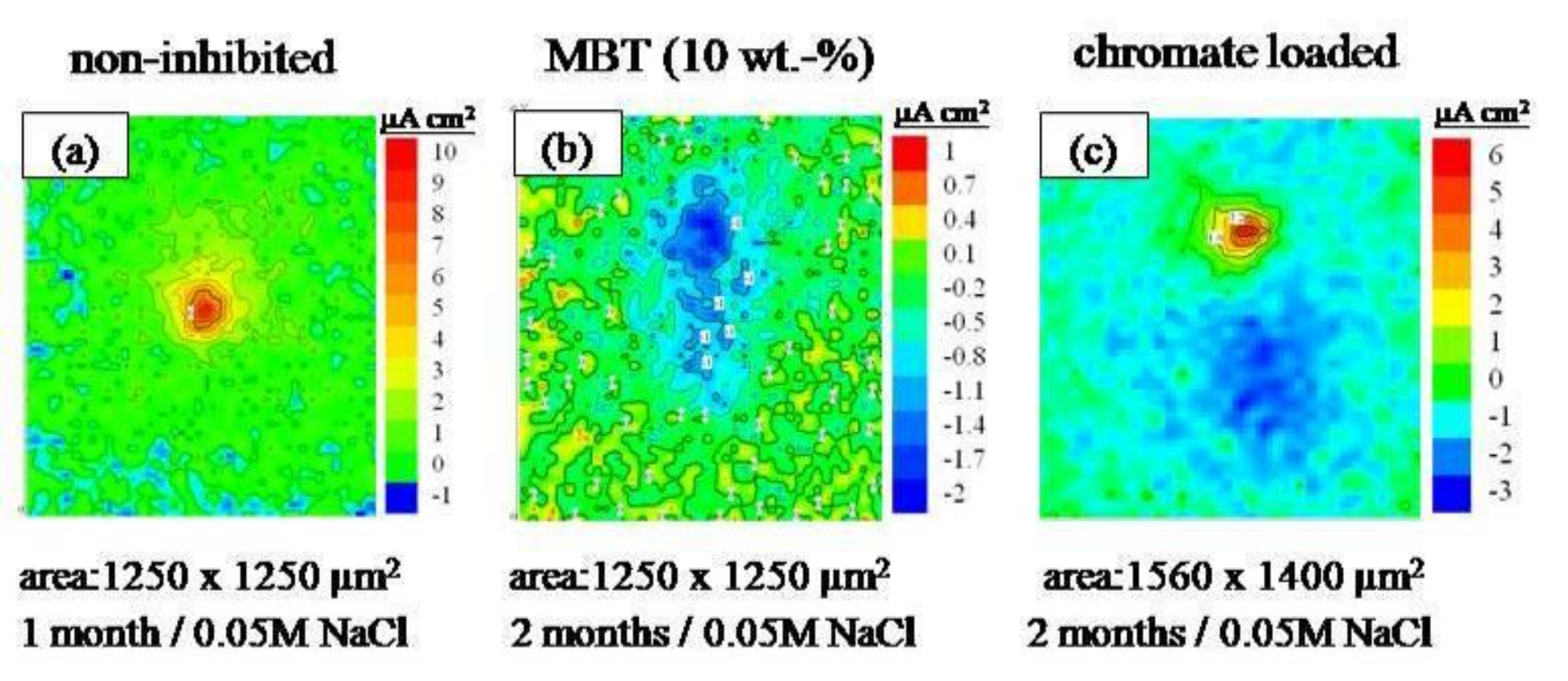
In collaboration with EADS IW, Germany

Self-healing of defects (2^{nd} + 4^{th} levels)



In collaboration with EADS IW, Germany

Self-healing of defects (2^{nd} + 4^{th} levels)



In collaboration with EADS IW, Germany

Conclusions

- ✓ *Introduction of the inhibitor in the form of nanocontainers instead of the direct addition to the sol-gel matrix prevents its interaction with components of the coating, which can negatively influence the barrier properties of the hybrid film and lead to the deactivation of the inhibitor;*
- ✓ *Several new approaches of corrosion inhibitor delivery on demand are proposed conferring intelligent self-healing ability to the protective films.*
- ✓ *"Smart" nanoreservoirs of corrosion inhibitors are produced using polyelectrolyte shells assembled by LbL approach. This containers are pH-sensitive providing release of corrosion inhibitor on demand;*
- ✓ *Nanocontainers of corrosion inhibitors based on LDH nanopigments are developed demonstrating effective corrosion protection and self-healing ability;*
- ✓ *New concept of multilevel anticorrosion system based on active nanocontainers for coatings is proposed.*

Acknowledgements

This work is supported by IP "MULTIPROTECT" Sixth Framework Program Contract N11783-2

and by IP "MUST" Seventh Framework Program

- Financial support from the FCT projects (contract # **POCI/CTM/59234/2004 and PTDC/CTM/65632/2006**) and GRICES-CAPES / CRICES-DAAD collaboration programs is gratefully acknowledged.

- Thank you for attention!