Self-healing Cerium Molybdate and Copper Oxide Nanomaterials for Protection of Metal Alloys for Marine Applications

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1. Introduction
2. Synthesis and loading of containers
3. Synthesis of the hybrid organic-inorganic materials
4. Application and characterization of the coating
5. Self-healing evaluation
6. Conclusions

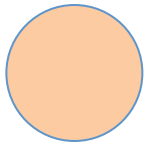
Introduction

- Corrosion of steel has an enormous economic impact.
- Alternative corrosion protection is urgent since hexavalent chromium provokes human disease.
- The current developed coating system consists of hybrid organic-inorganic containers composed of corrosion inhibiting compounds.
- These structures exhibit self-healing due to the supramolecular polymers shell formed on the inorganic surface, properties.
- The inorganic containers can be loaded with the preferred corrosion inhibitors, prior to the polymer shell formation.

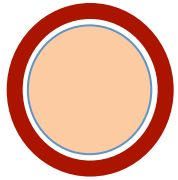
Preparation of cerium molybdate containers

Three Step Process:

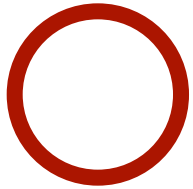
i) Production of polystyrene spheres via polymerization in emulsion



ii) Coating of polystyrene spheres via the sol-gel method to form an inorganic shell

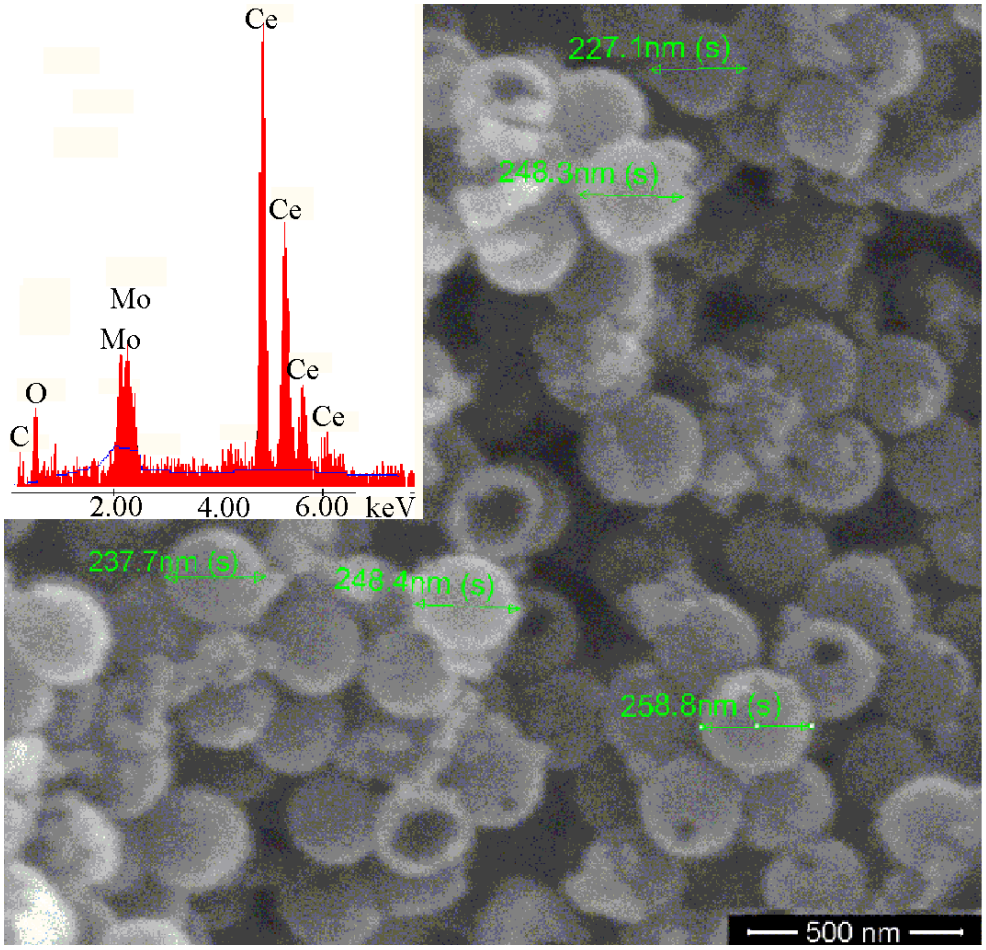


iii) Calcination of the coated containers



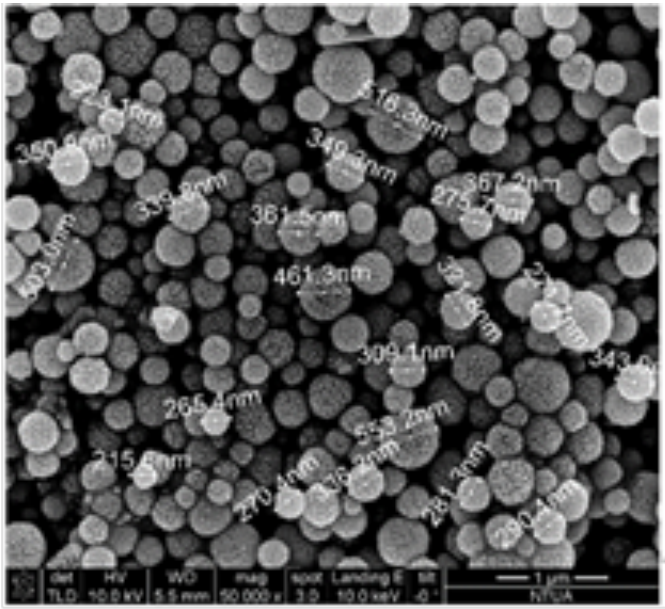
Cerium molybdate containers

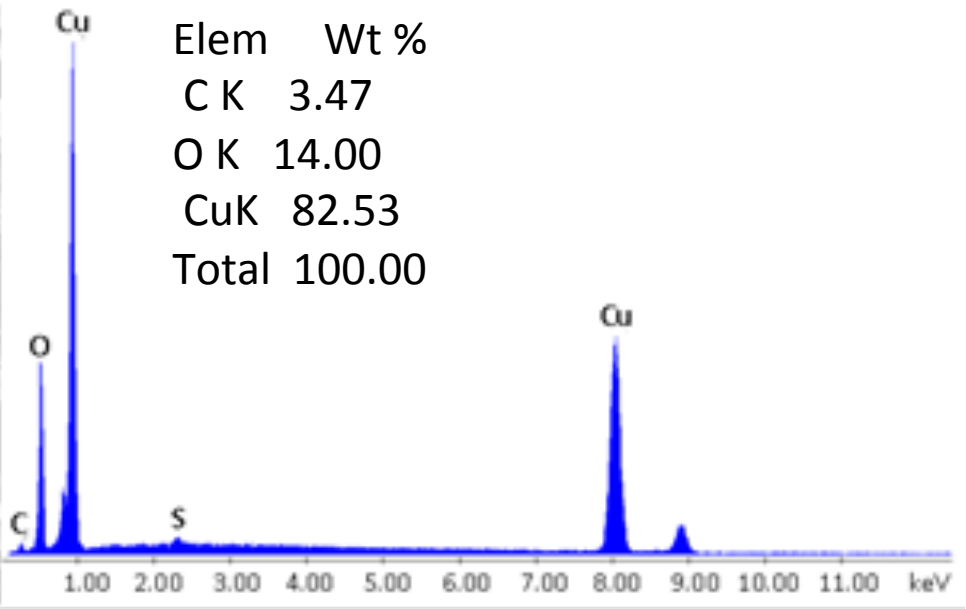
Elem	Wt %
C K	3.30
O K	4.20
MoL	5.33
CeL	87.16
Total	100.00



Cuprous oxide microspheres

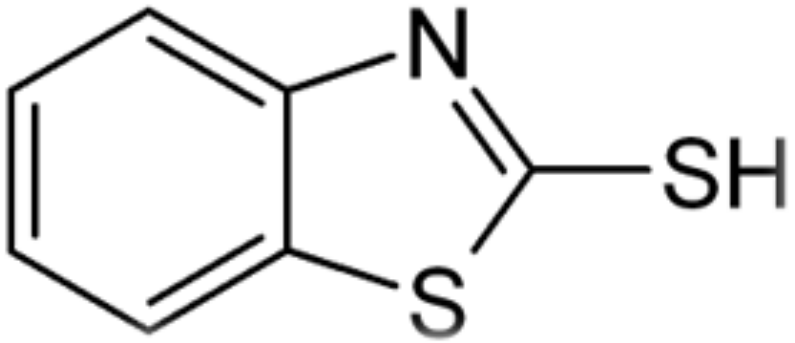
SEM image and EDS spectrum

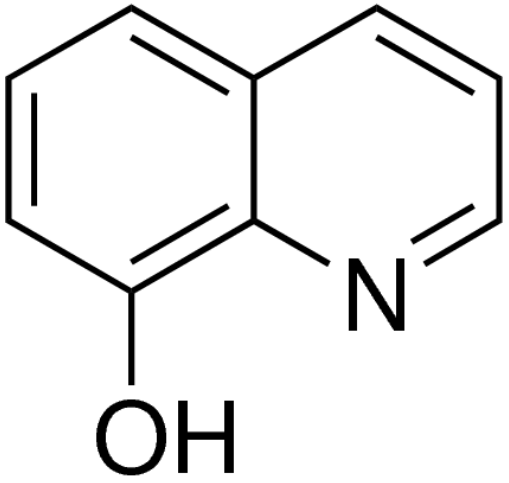




Elem	Wt %
C K	3.47
O K	14.00
CuK	82.53
Total	100.00

Anodic Inhibitors 2-mercaprobenzothiazole (MBT) and 8-HQ used for loading of nanocontainers



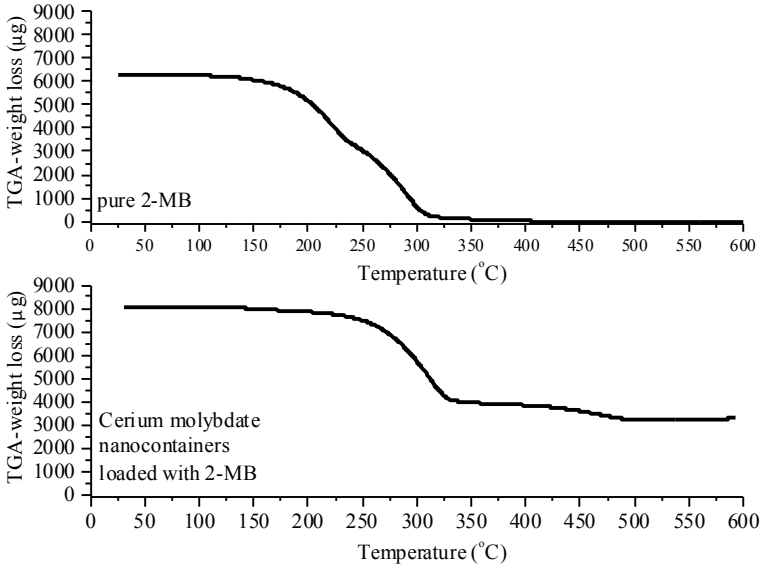


Anodic Inhibitors:

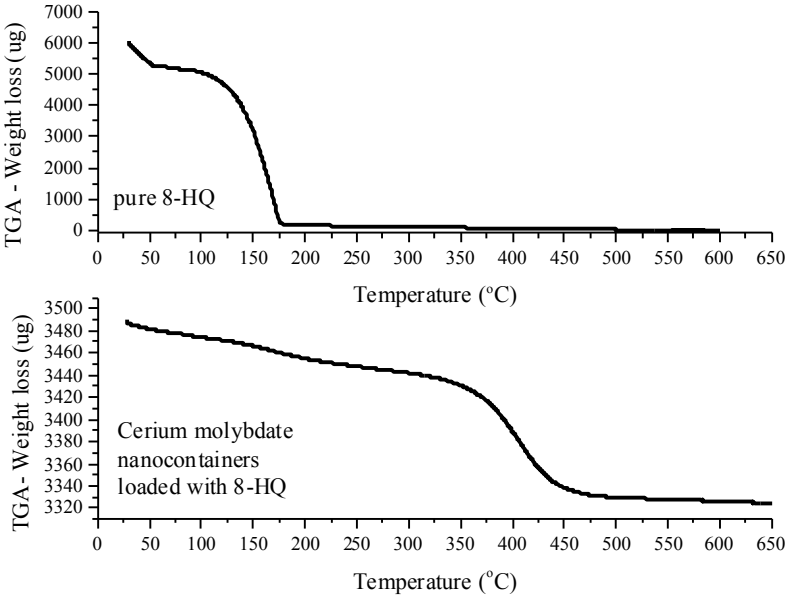
- Build a thin protective film along the anode, increasing the potential at the anode and slowing the corrosion reaction.
- The film is initiated at the anode although it may eventually cover the entire metal surface.
- The film is not visible to the naked eye ⇒ the appearance of the metal is unchanged.

Thermogravimetric Analysis: MBT and 8HQ Loaded Nanocontainers

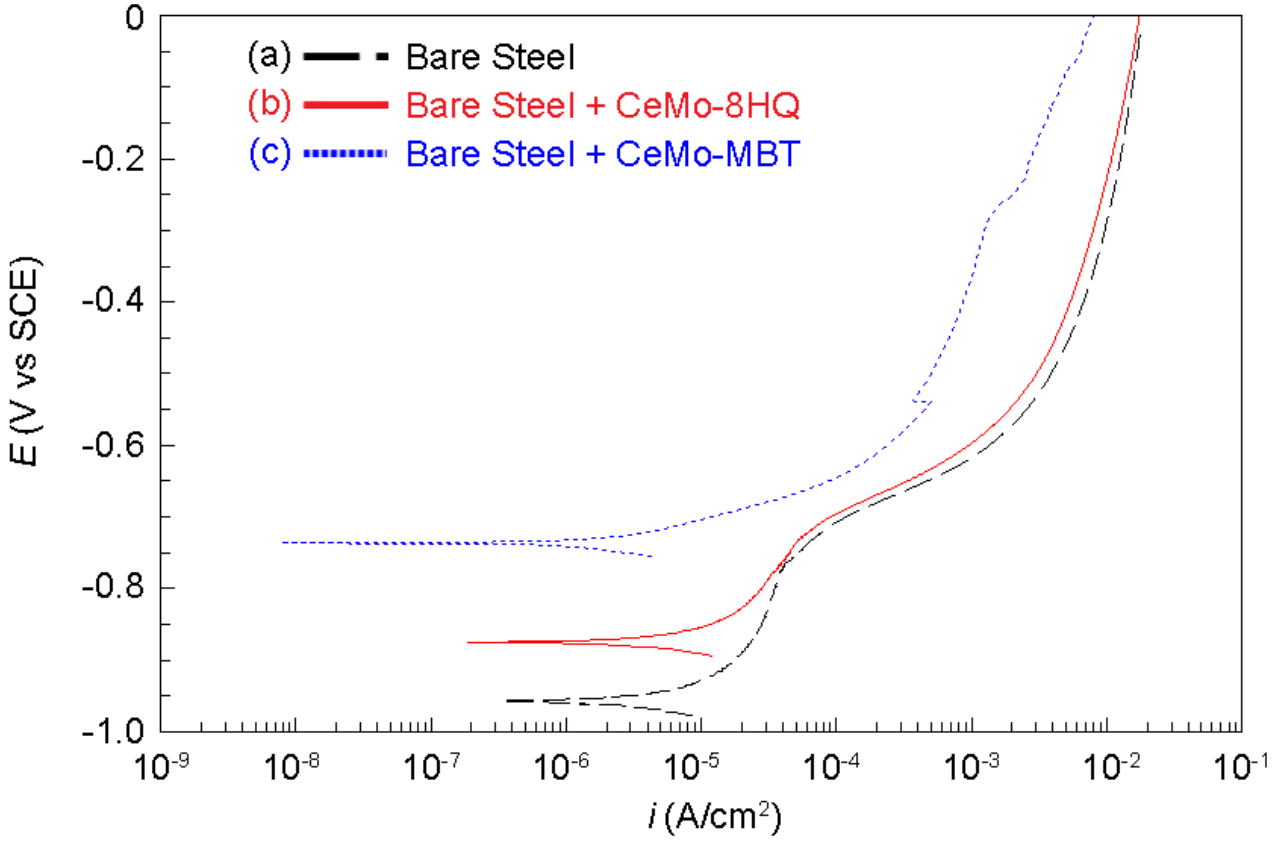
58.08% w/w loading



31.8% w/w loading



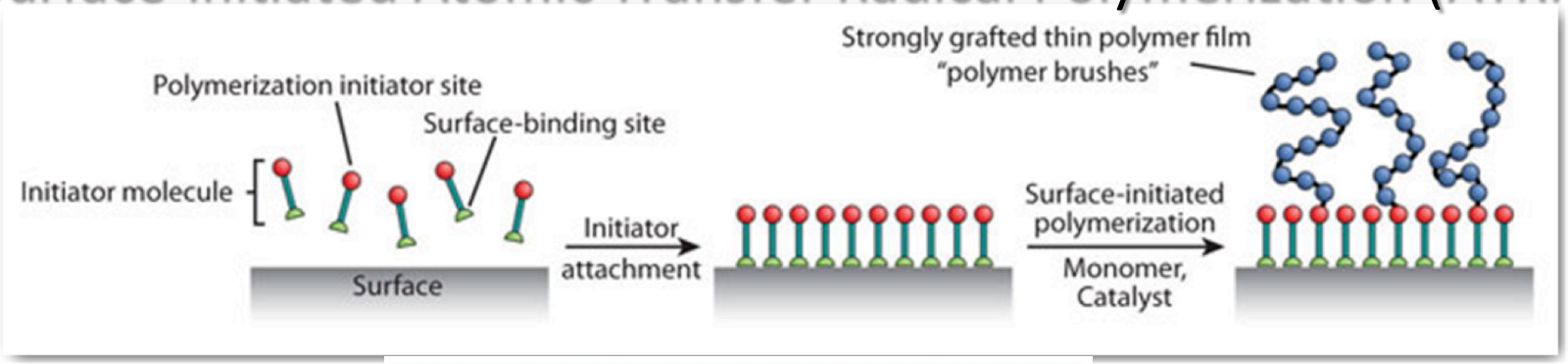
Potentiodynamic Polarization Measurements

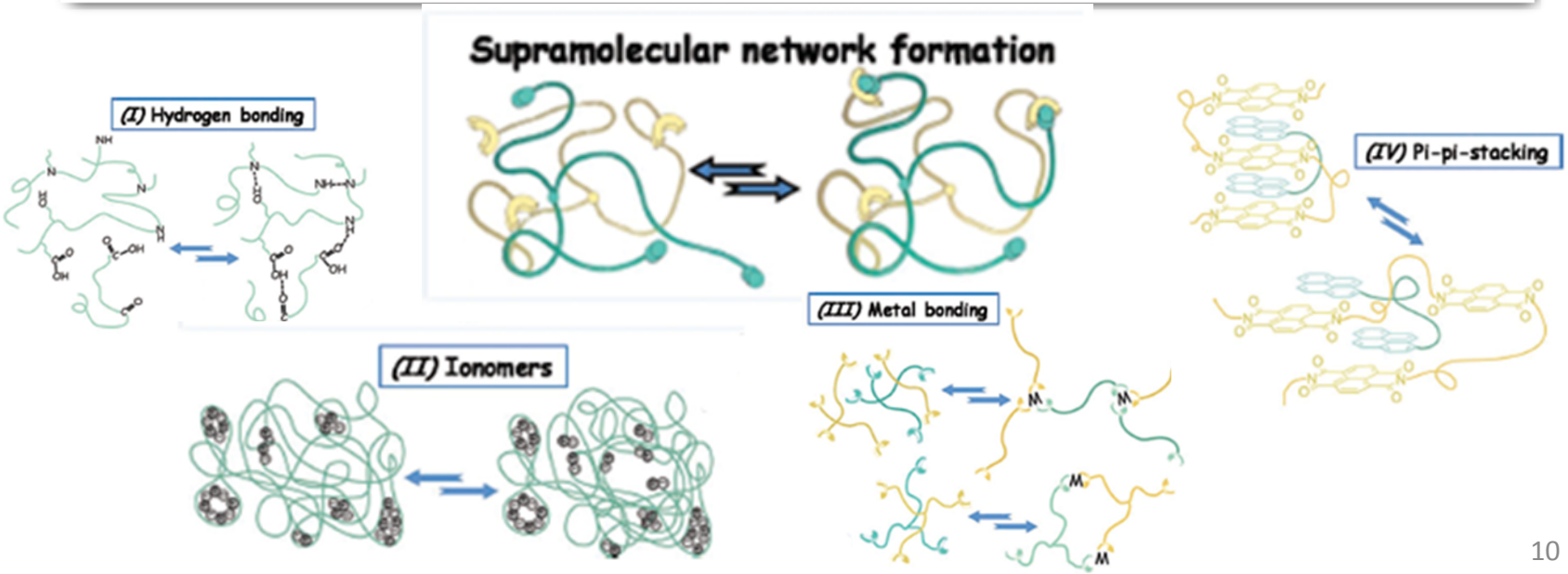


- CeMo NCs in combination with the selected corrosion inhibitors increase the overall performance of steel substrates under corrosive conditions

Synthesis of hybrid organic-inorganic materials

Surface-initiated Atomic Transfer Radical Polymerization (ATRP)

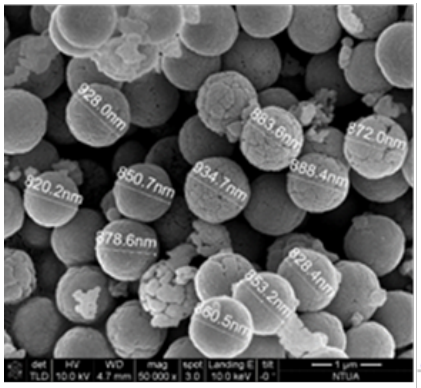


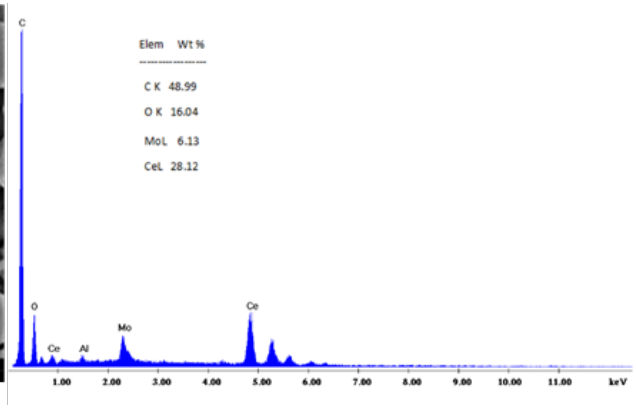


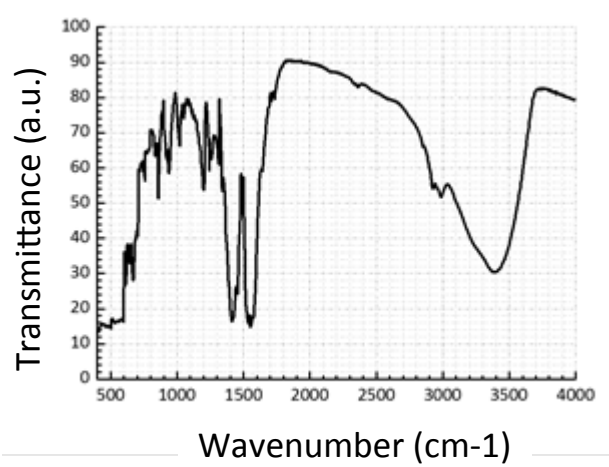
Morphological and chemical characterization of the hybrid organic-inorganic materials

Cerium molybdate containers coated with P(nBA-co-AA)

SEM images and FT-IR spectrum



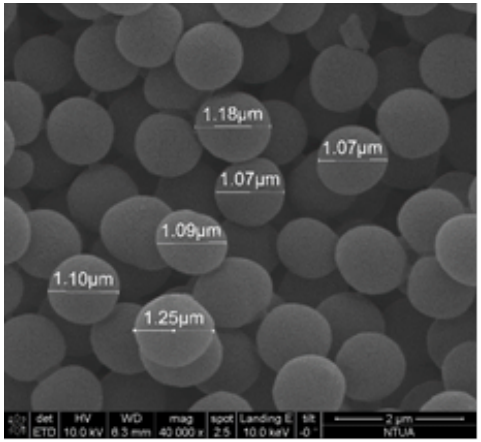


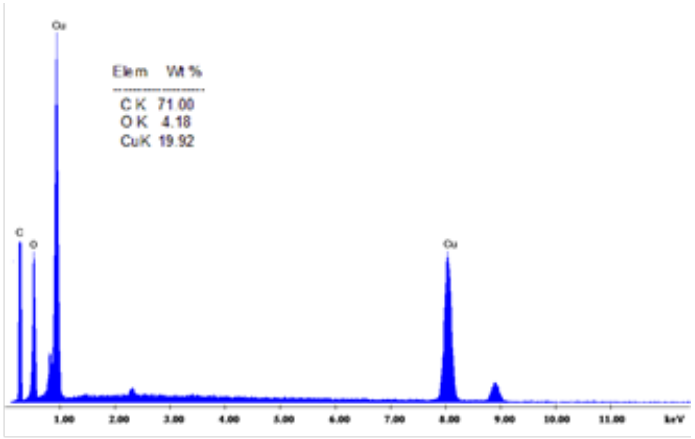


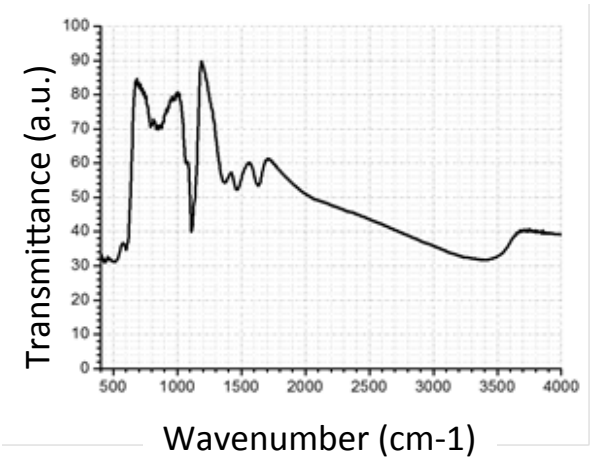
Morphological and chemical characterization of the hybrid organic-inorganic materials

Cuprous oxide microspheres coated with P(nBA-co-AA)

SEM images and FT-IR spectrum

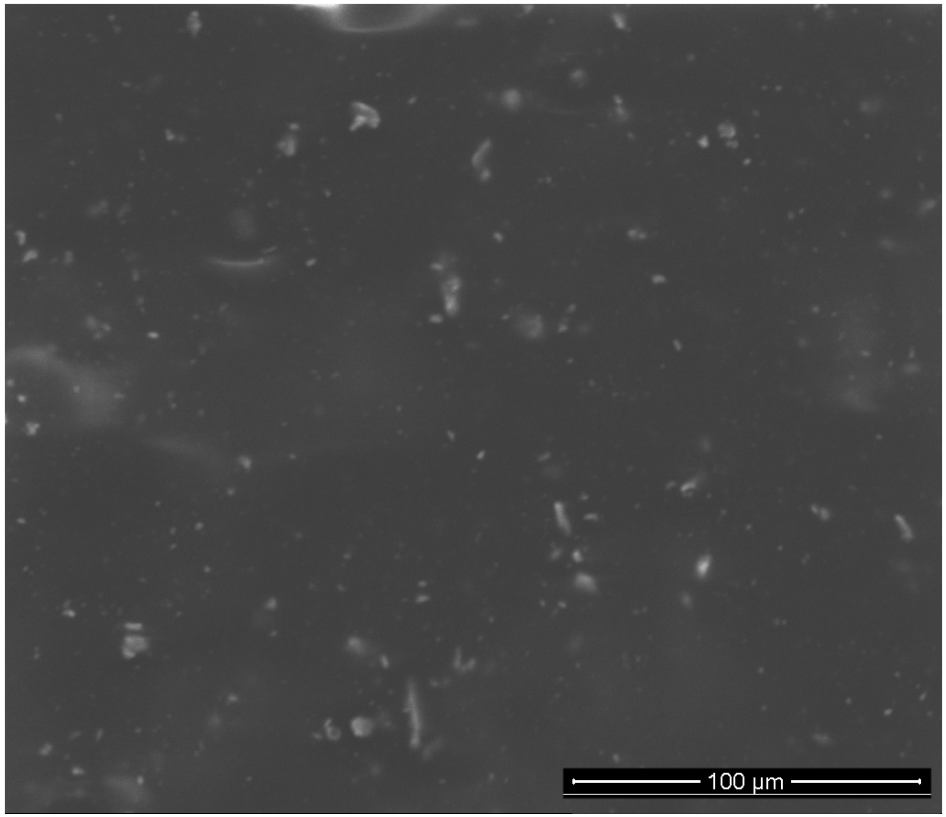


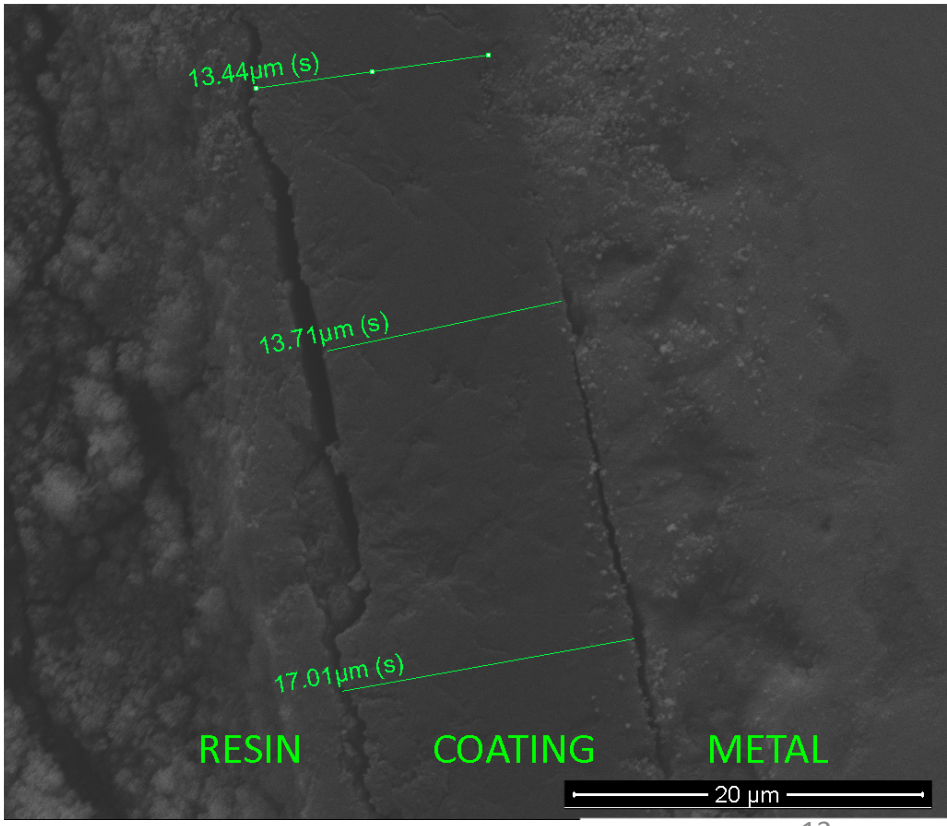




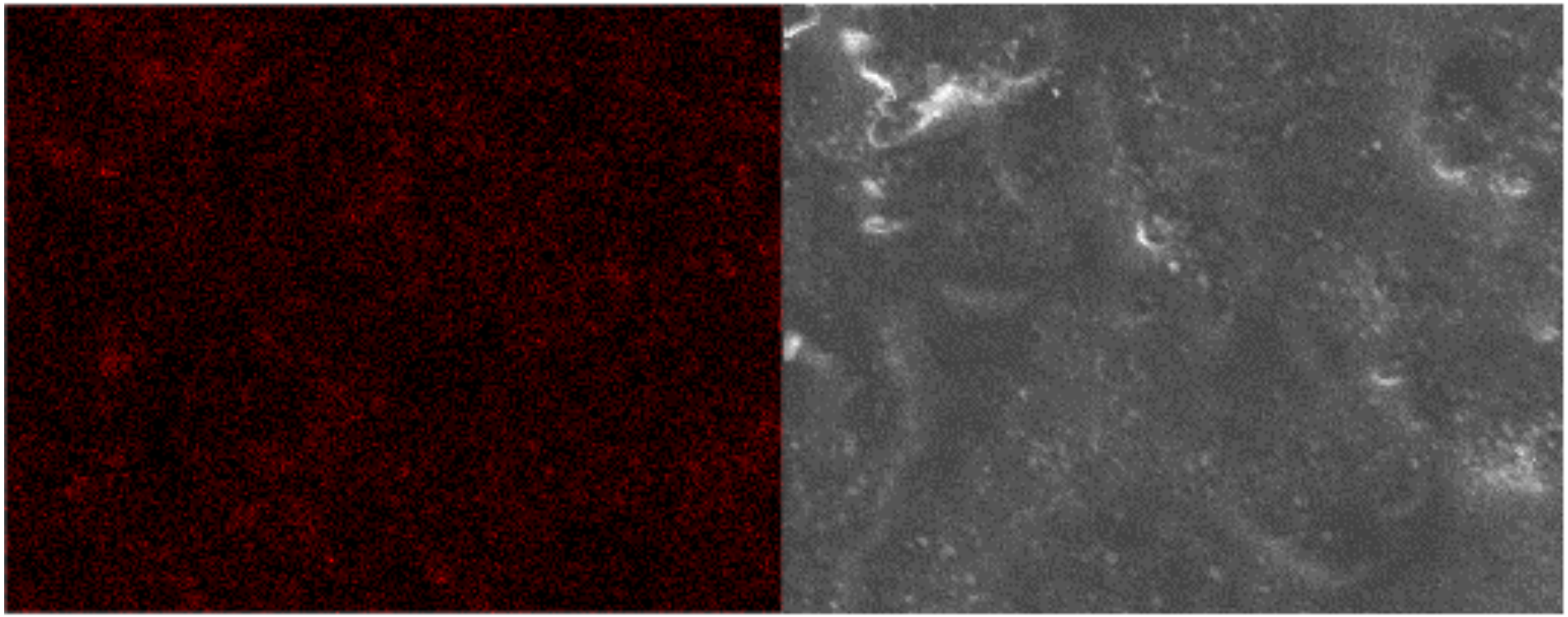
Morphological characterization of the final coating

- For the coating application on the HDG steel substrates a bar film applicator with 30um gap size was used

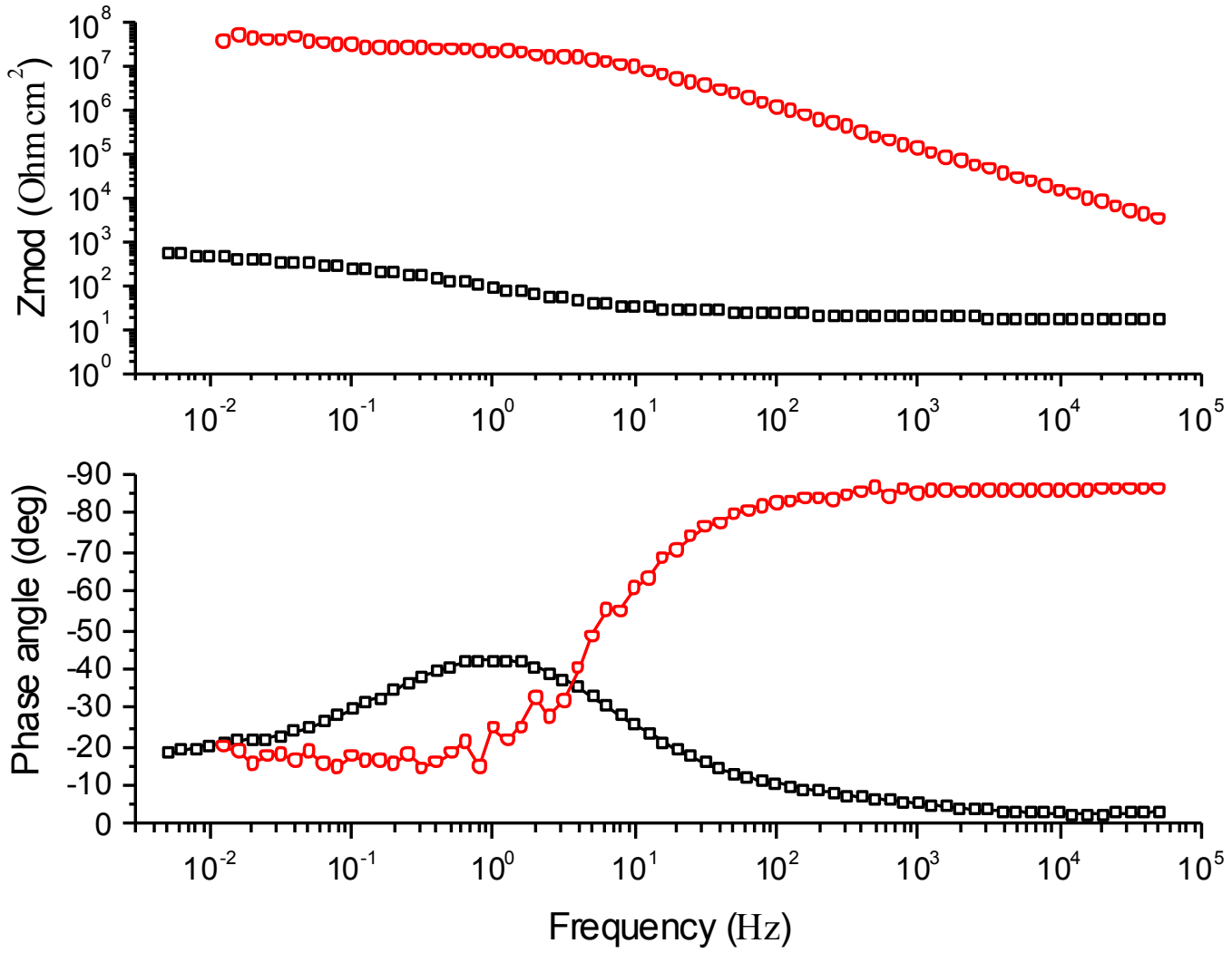




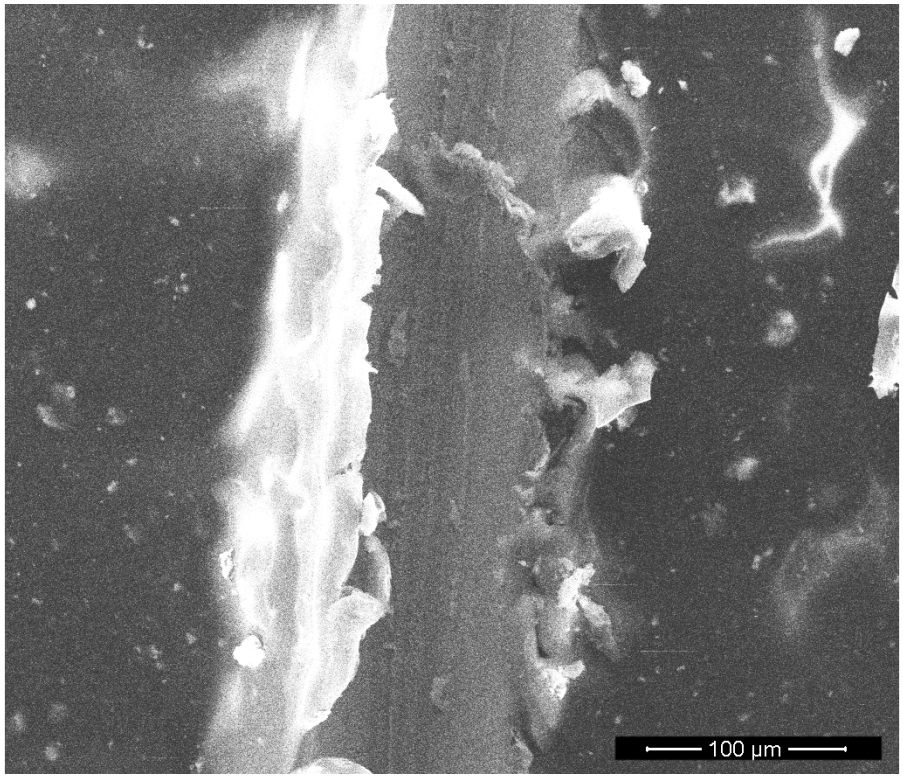
Elemental mapping at the microstructural level by SEM with energy dispersive X-ray spectrometry (EDS)

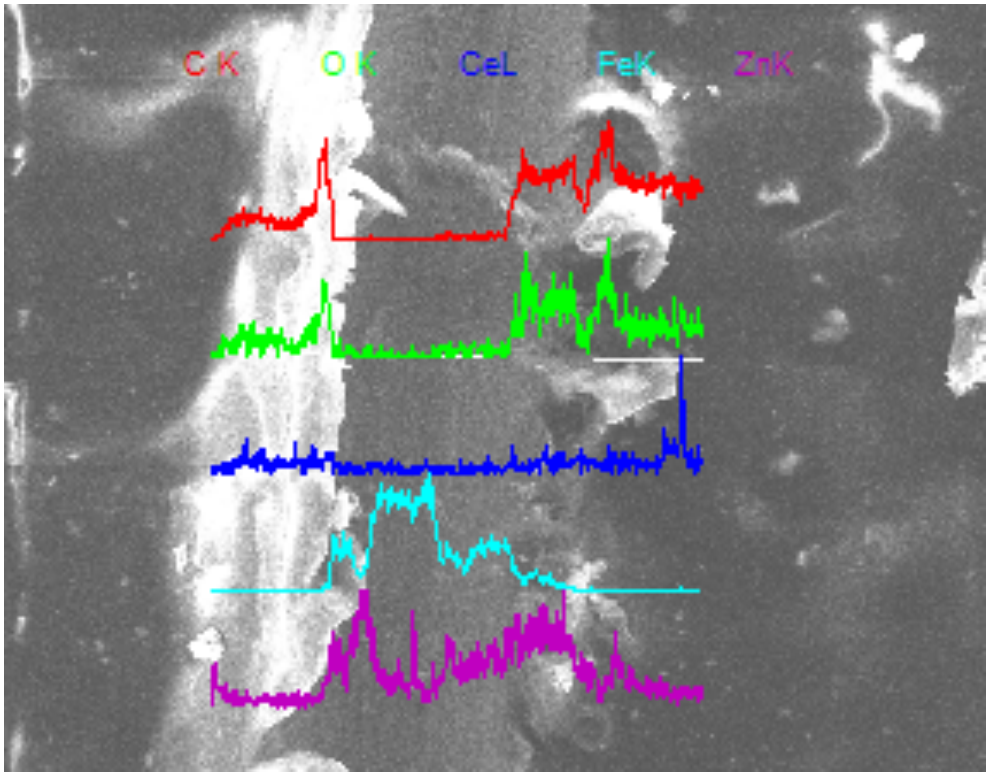


EIS Bode plots after 20 days in 0.5M NaCl solution

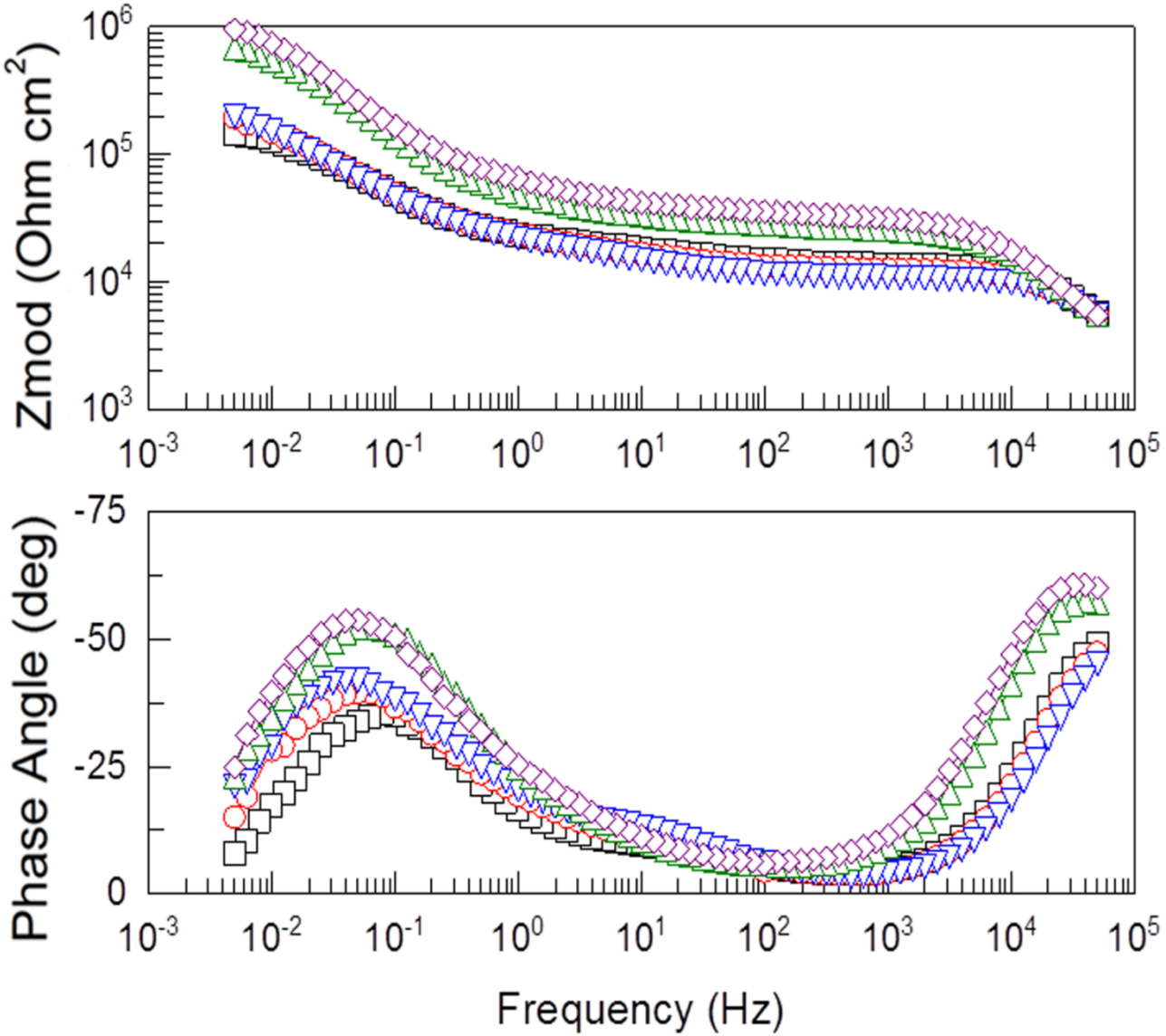


Elemental mapping at the artificial defect region



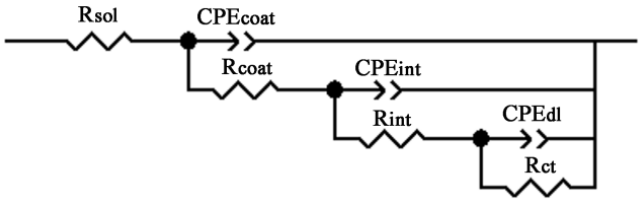


EIS Bode plots after the **artificial defect formation** in 5 mM NaCl solution

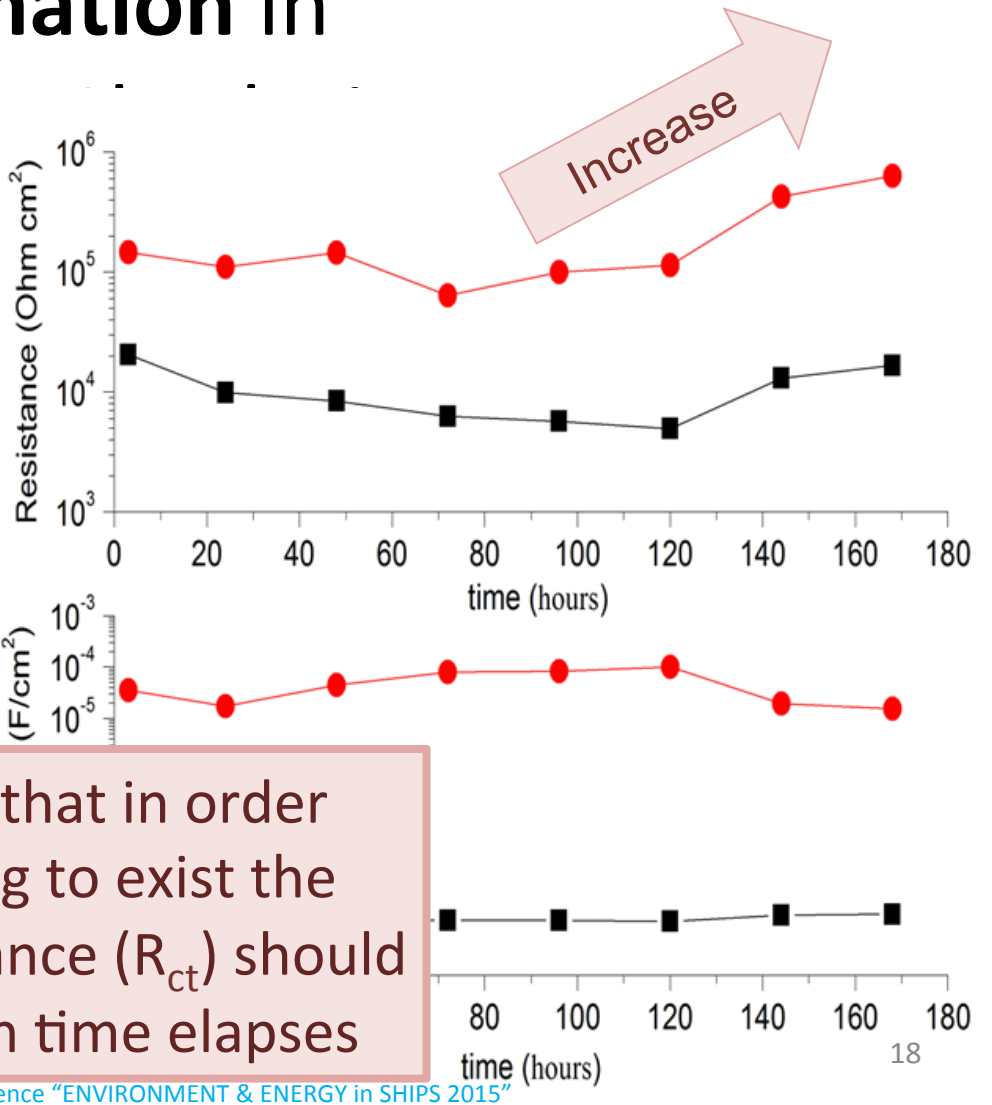


(□) 3 days
(○) 4 days
(∇) 5 days
(Δ) 6 days
(◊) 7 days

Evolution of the EIS fitting parameters after **artificial defect formation** in



(■) coating resistance,
(●) charge transfer resistance,
(■) coating capacitance,
(●) double layer capacitance



In literature, it is mentioned that in order partial recovery of the coating to exist the values of charge transfer resistance (R_{ct}) should be increased as the immersion time elapses

Conclusions

- A new system has been developed for the corrosion protection of HDG steel.
- EIS results showed improved corrosion protection after immersion in 0.5 M NaCl solution for 20 days.
- The coating presented partial recovery action of the defected area after immersion in 5 mM NaCl solution.

Future Plans

Improvement of coating process and corrosion protection properties by:

- decrease of solvents (e.g. thermal spraying)
- addition of different types and sizes of containers (e.g. chloride ion traps)
- In-depth analysis of the formatted polymer shell
- Identification of the possible self-healing mechanism

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