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Unveiling the self-healing effect of cerium ions in PMMA-silica coatings on AA7075: A comparative study of Ce(III) and Ce(IV)

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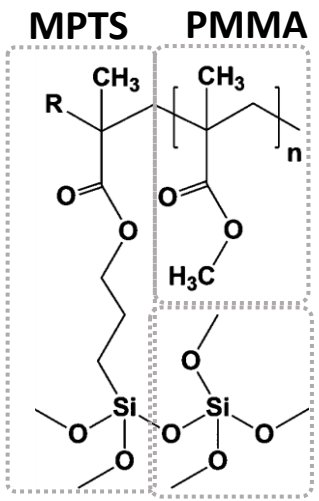
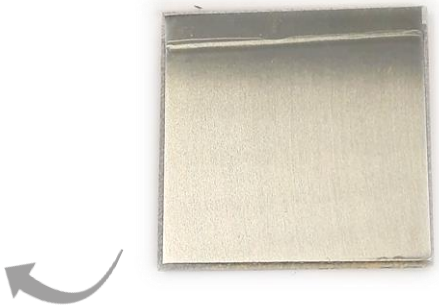
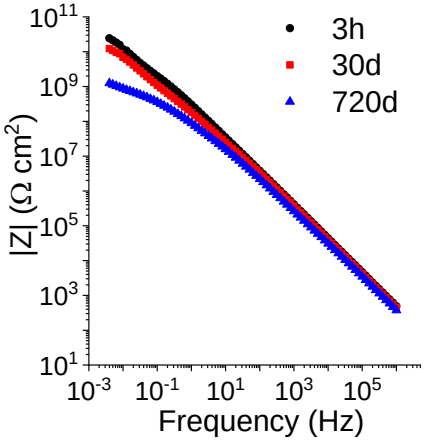
PMMA-silica-Ce(III)/Ce(IV) coatings

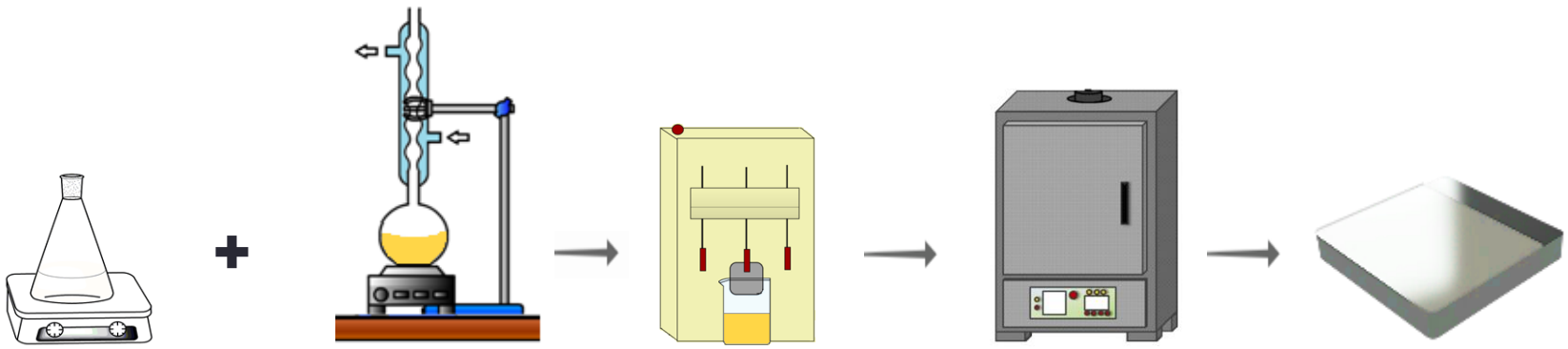
- Hybrid coatings combine properties of polymeric and sol-gel materials
- Aluminum AA7075: widely used in aircrafts
- > 720 days of stability in 3.5% NaCl
- Thickness 5~ µm
- Ce(III) vs. Ce(IV): Role of the oxidation state in active corrosion inhibition







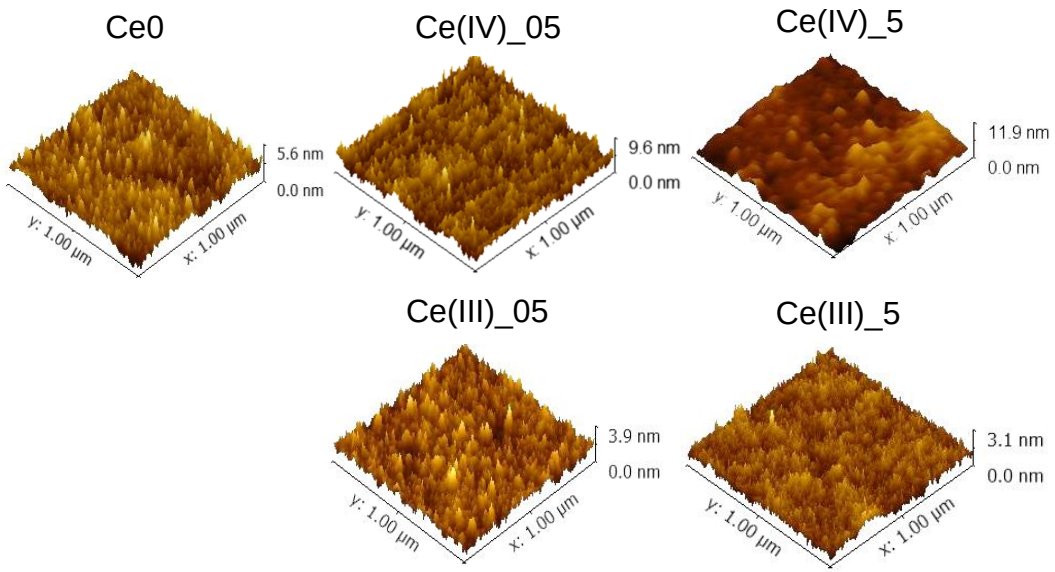
PMMA-silica-Ce(III)/Ce(IV) synthesis

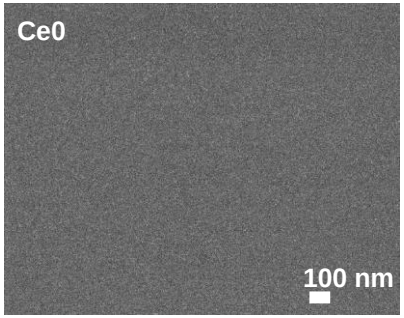


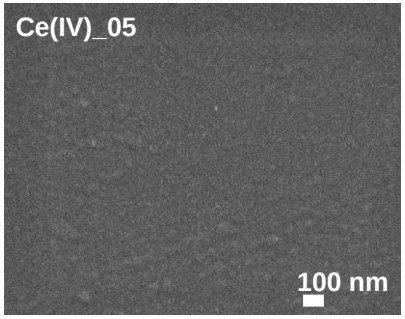
Sol-gel	Polymerization	Dip-coating	Drying and curing	Characterization
- TEOS - Ethanol - H_2O (pH 1) - $((NH_4)_2Ce(NO_3)_6)$ - $(Ce(NO_3)_3.6H_2O)$	- MMA (monomer) - BPO (thermal initiator) - MPTS (coupling agent)	- 3 immersions	- 60 °C / 24 h - 160 °C / 3 h	Ce0 Ce(III)_05 (500 ppm) Ce(III)_1 (1000 ppm) Ce(III)_3 (3000 ppm) Ce(III)_5 (5000 ppm) Ce(IV)_05 Ce(IV)_1 Ce(IV)_3 Ce(IV)_5

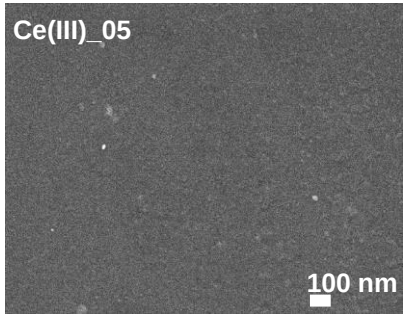
Surface Morphology of PMMA-silica-Ce(III)/Ce(IV) – AFM and SEM

- Roughness in the nm range (0.3 to 6.7 nm)
- Higher Ce(IV) content: Increased R_{RMS}
- Absence of pores and cracks

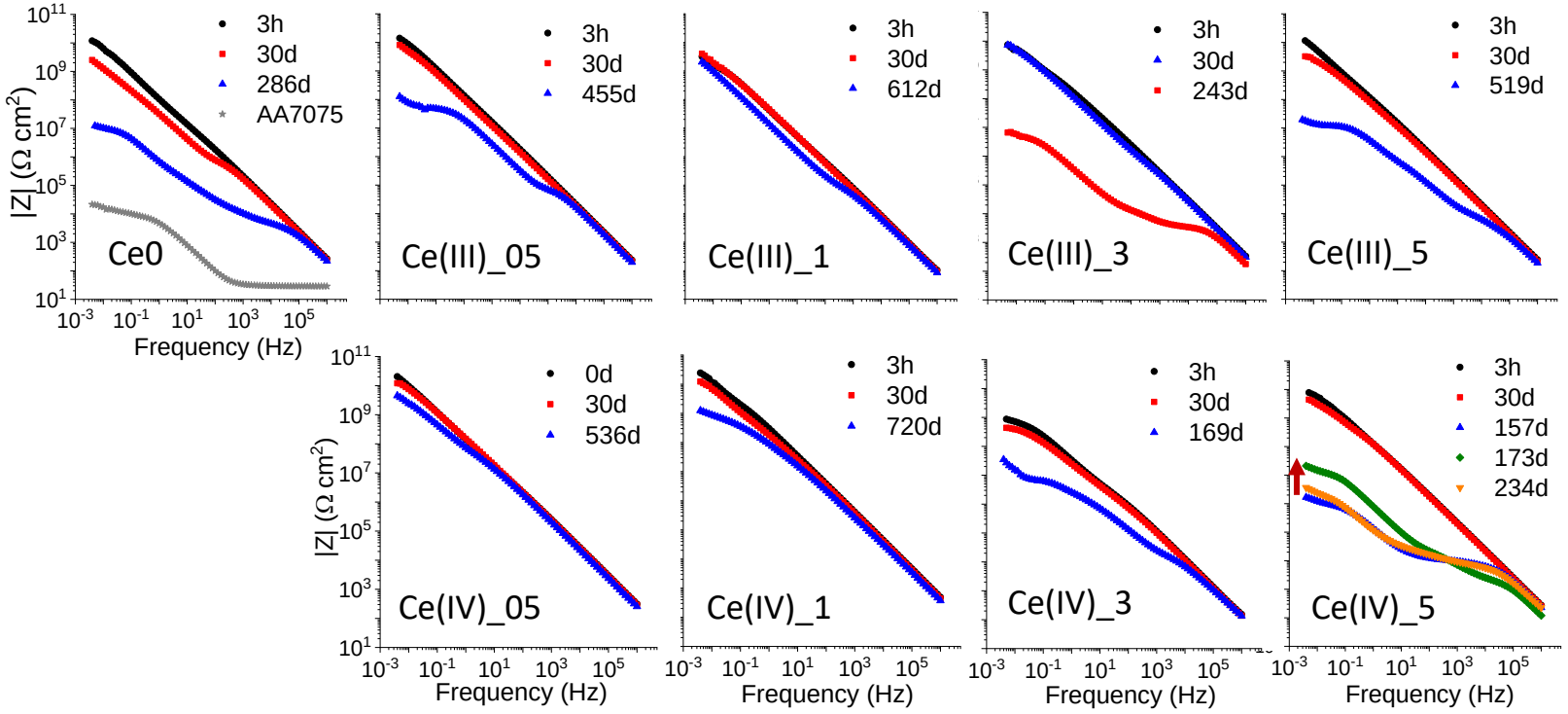






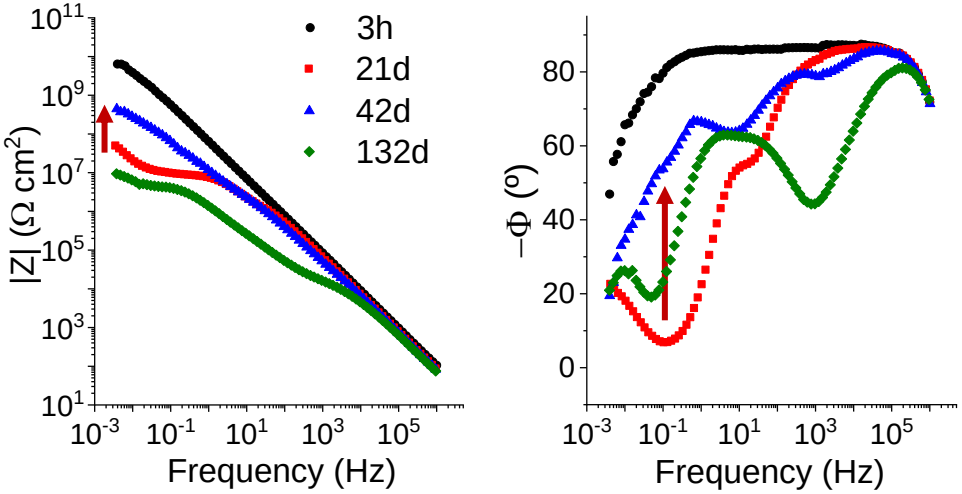


Electrochemical response over time – EIS



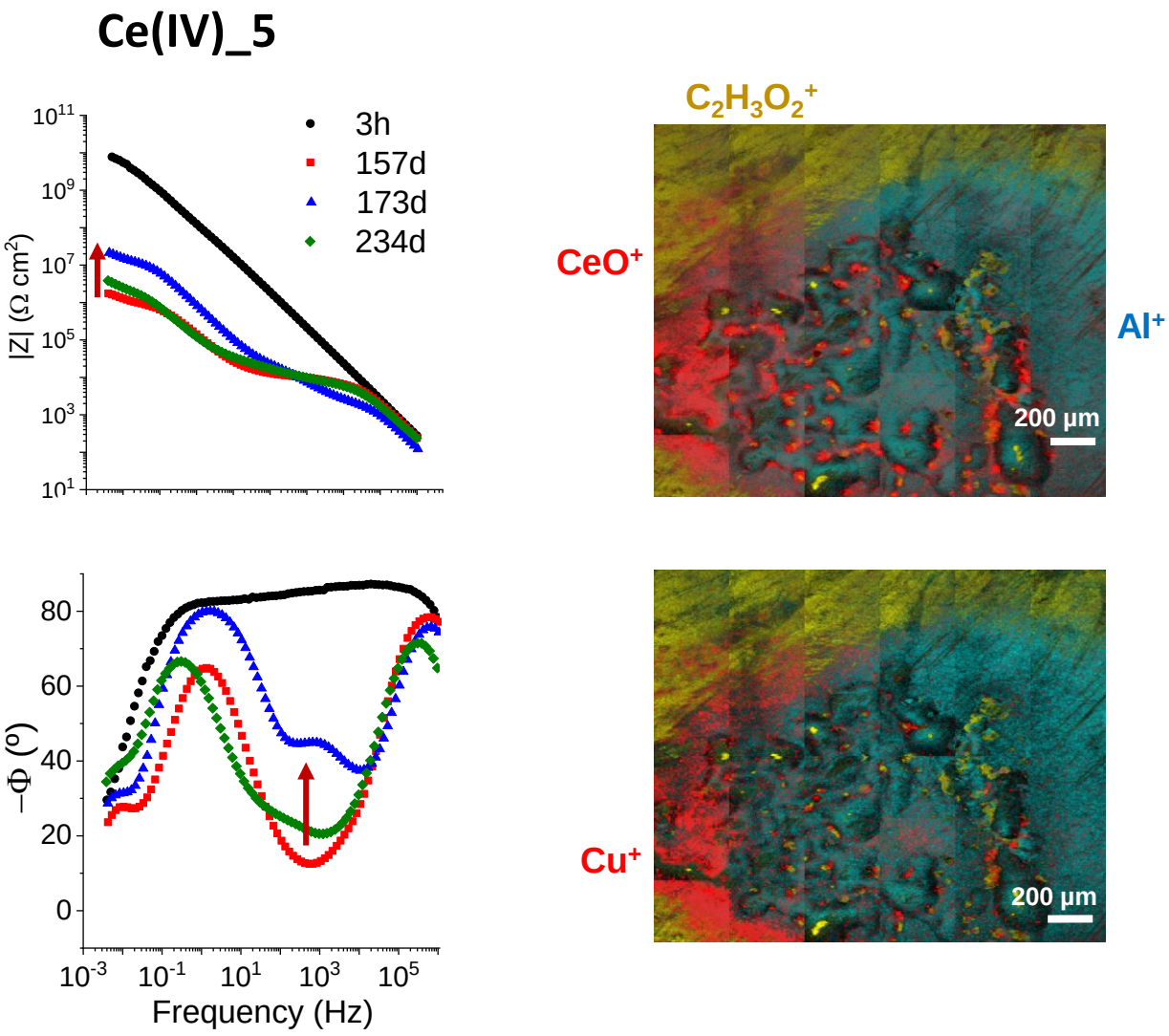
- High low-frequency impedance modulus ~ *24 GΩ cm² in 3.5% NaCl*
- Ce(IV)_05 and Ce(IV)_5: *Increased lifespan due to self-healing activity*

Electrochemical response over time – EIS



- **Ce(IV)_05**: Activity on pits of corrosion
- Suppression of the charge transfer process at the interface

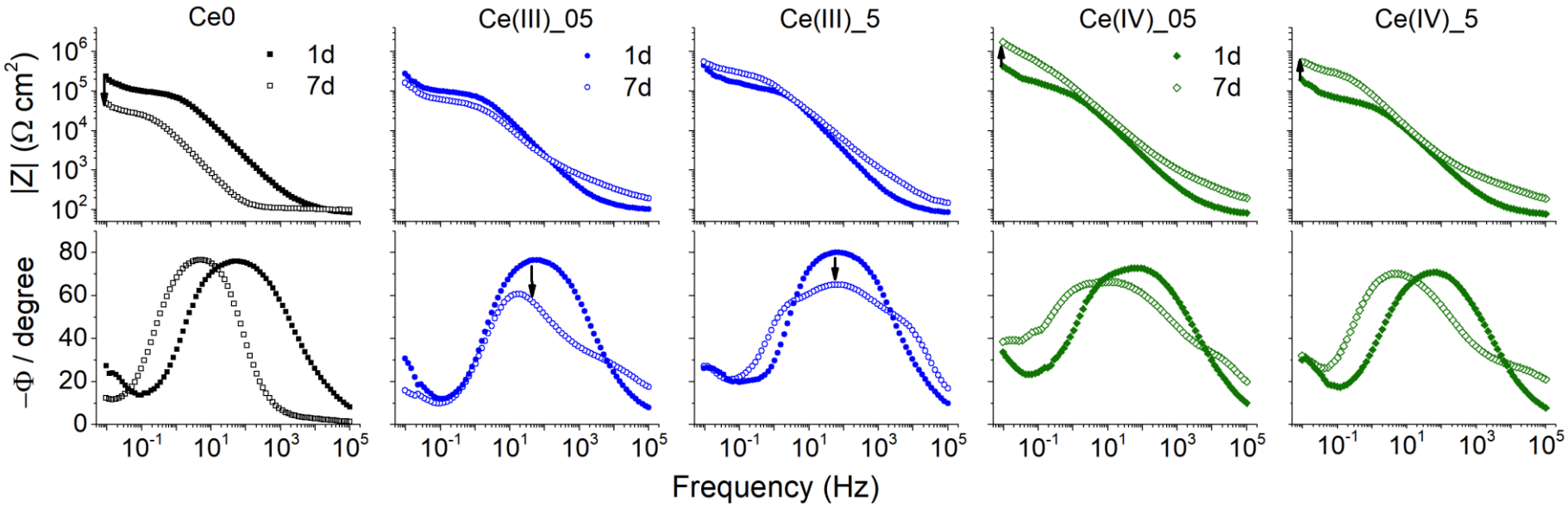
Proposed mechanism – EIS and SIMS



- Self-healing effect: formation of insoluble oxides/hydroxides
- CeO^+ is formed preferentially in Cu^+ (intermetallic of AA7075)

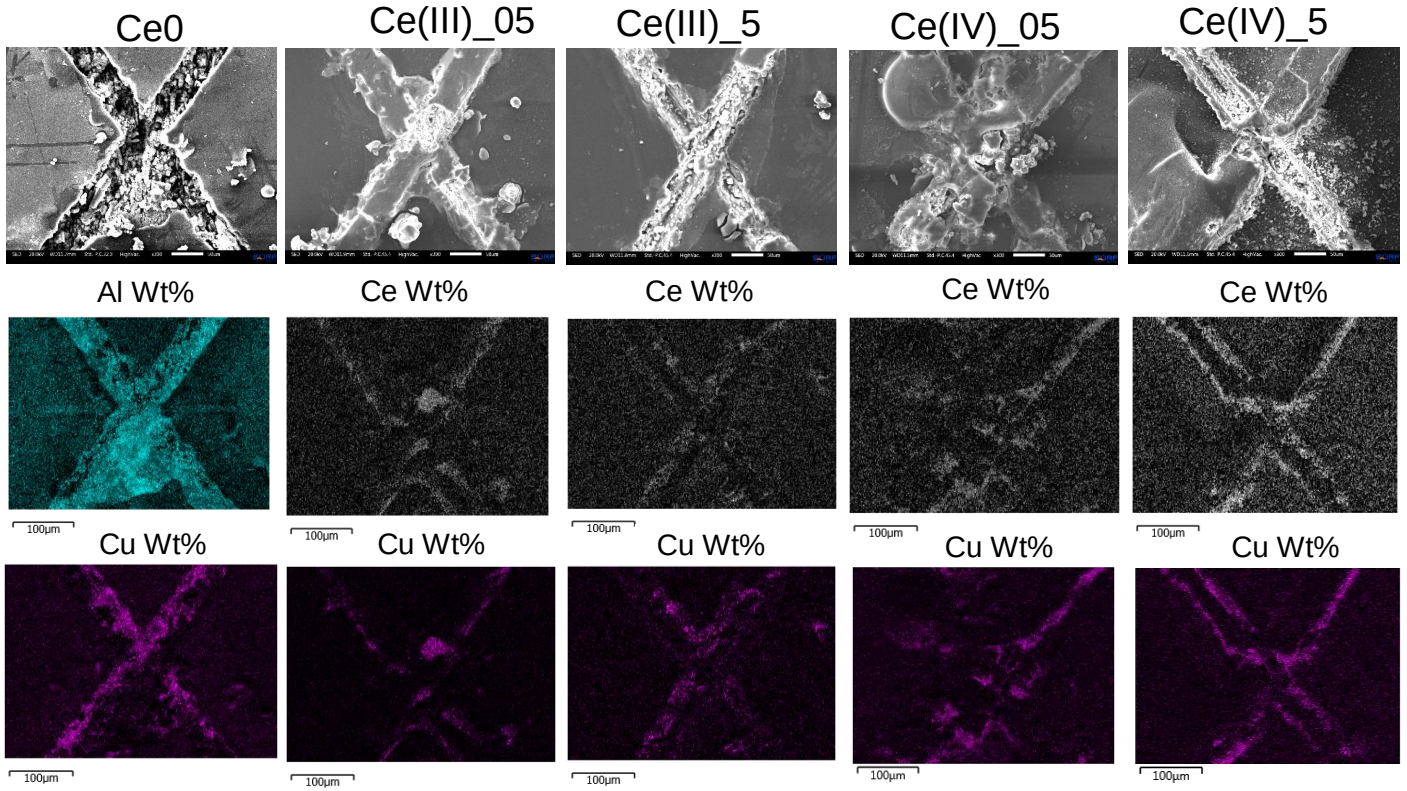
Active protection – accelerated corrosion tests / EIS

- Ce0 and Ce(III): decrease / similar |Z| after 7 days, respectively
- Ce(IV): recovery of |Z| → inhibitory effect



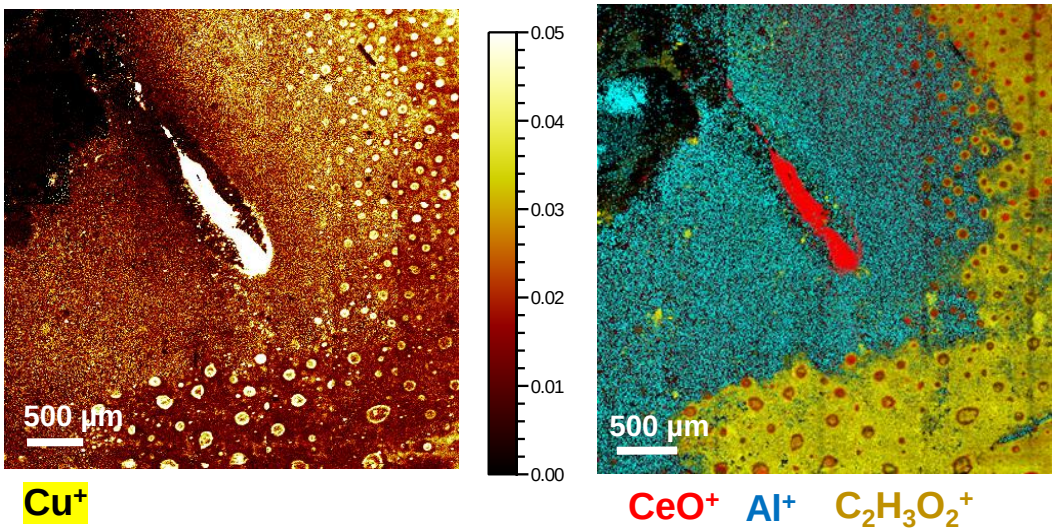
Active protection – SEM / EDS

- Ce0: Al products → main composition of the scratch
- Ce(III) and Ce(IV): correlation with Cu at the scratch edges



Active protection – SIMS

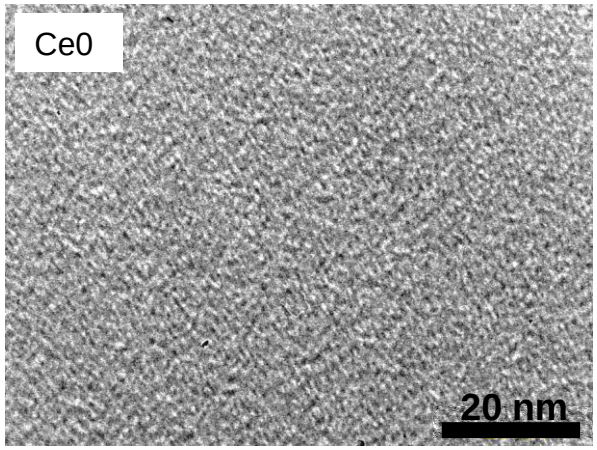
Ce(IV)_5

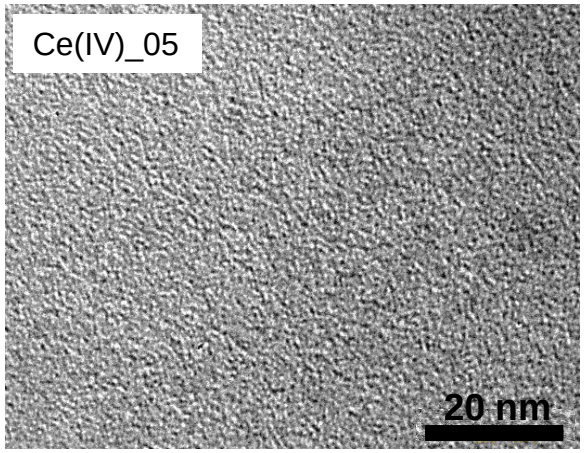


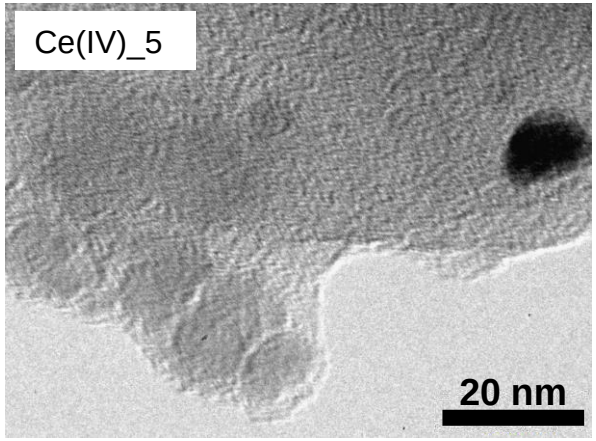
- Higher activity on intermetallic particles
- Correlation of CeO^+ and Cu^+ at the scratch track
- Leached Ce(IV) ions from adjacent walls formed a protective layer

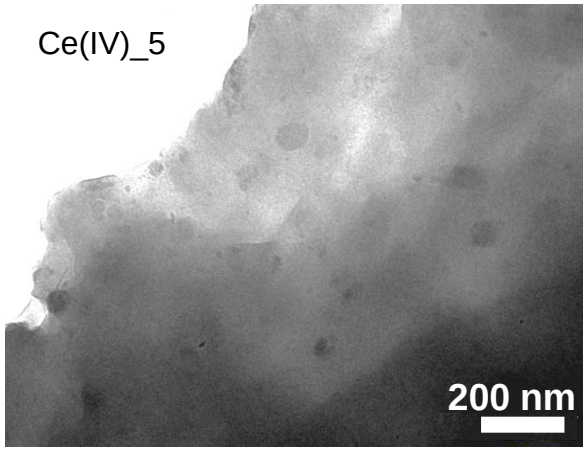
Nanostructural analysis of silica and cerium nanoparticles – TEM

- Ce0 and Ce(IV)_05: homogeneous distribution
- Ce(IV)_3 and Ce(IV)_5: larger cerium oxide/hydroxide particles (30 - 100 nm)





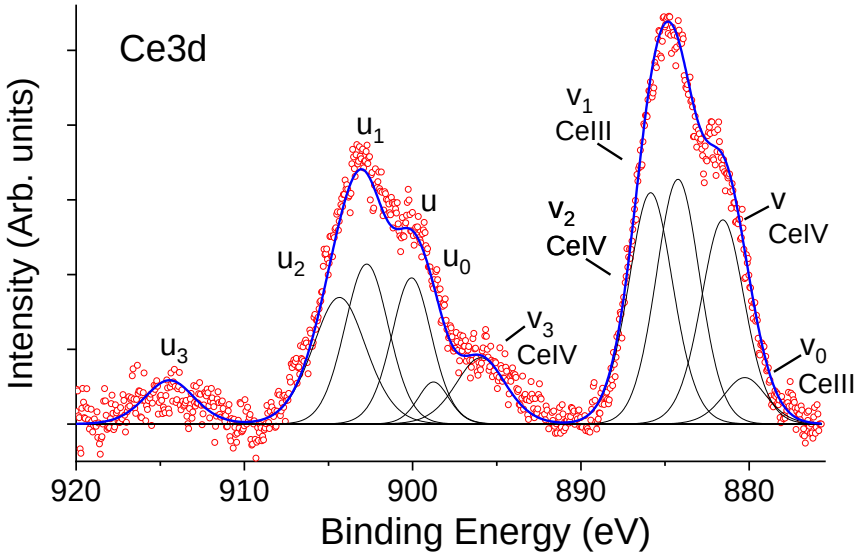




Surface Chemistry of PMMA-silica-Ce(III)/Ce(IV) – XPS

- **Ce(IV)_5**: 64% of Ce(IV)
- **Ce(III)_5**: 41% of Ce(IV)
- Ce(IV) reacts faster with OH^- from oxygen reduction reaction

→ insoluble oxides and hydroxides



$$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$

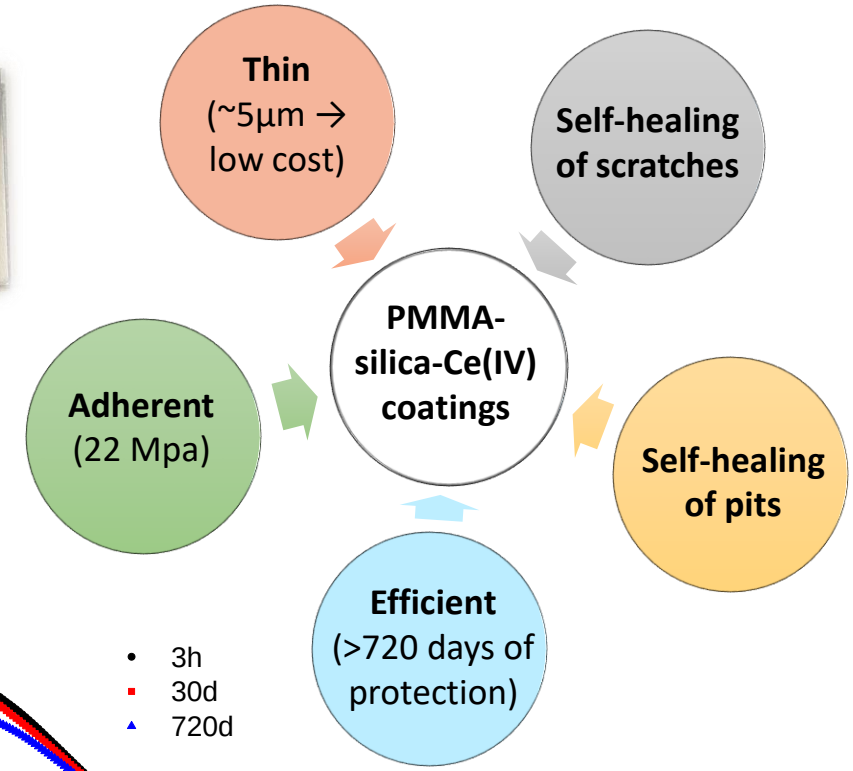
$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

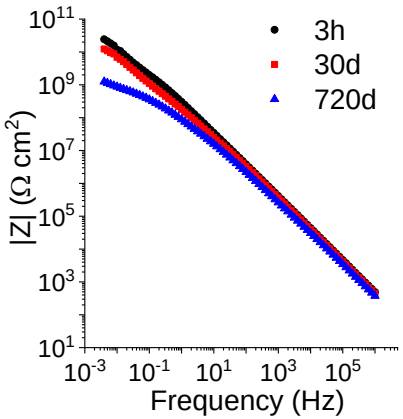
$$Ce^{4+} + 4OH^- \rightarrow Ce(OH)_4 \downarrow$$

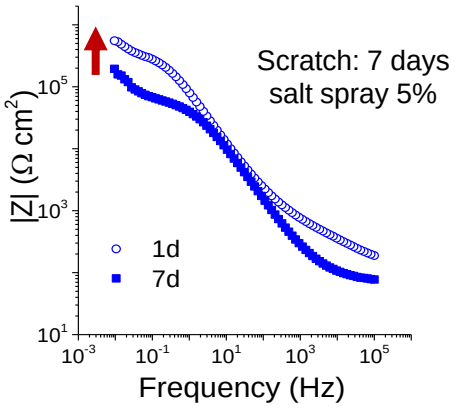
$$Ce(OH)_4 \leftrightarrow CeO_2 + H_2O$$

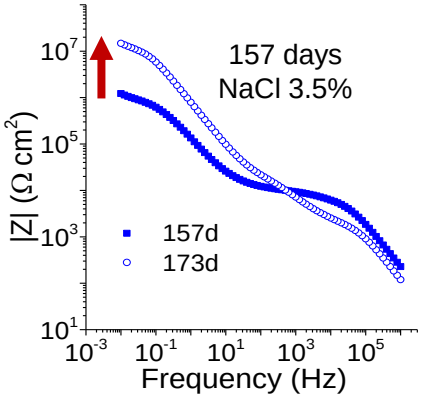
*K.A. Yasakau, et al. J. Phys. Chem. B 110 (2006) 5515-5528

Current hypothesis









Thank you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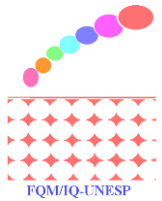
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