Finanziato dall'Unione europea NextGenerationEU
Ministero dell'Università e della Ricerca
Italiadomani PIANO NAZIONALE DI RIPRESA E RESILIENZA
POLITECNICO MILANO 1863
UNIVERSITÀ DI TRENTO

(PRIN 2022, COD. PROTOCOLLO: 2022H3S28T, CUP MASTER: D53D23005410006) FINANZIATO DALL'UNIONE EUROPEA – NEXT GENERATION EU, PNRR - MISSIONE 4 "ISTRUZIONE E RICERCA" - COMPONENTE C2 INVESTIMENTO 1.1 "FONDO PER IL PROGRAMMA NAZIONALE DI RICERCA E PROGETTI DI RILEVANTE INTERESSE NAZIONALE (PRIN)" D.D. N. 104/2022 "BANDO PRIN 2022". PE11 Engineering of Metals and alloys.

EuroCorr 2024
Paris | 1st – 5th September 2024

Plasma Electrolytic Oxidation (PEO) corrosion resistant coatings on aluminium 2024 texturized with a riblet-like surface for aeronautical applications

M. Gamba[1], A. Brenna[1], F. Ceriani[1], M. Ormellese[1], M. Fedel[2], A. Cristoforetti[2]

[1] Dipartimento di Chimica, Materiali ed Ingegneria Chimica "Giulio Natta", Politecnico di Milano
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Plasma Electrolytic Oxidation (PEO) corrosion resistant coatings on aluminium 2024 texturized with a riblet-like surface for aeronautical applications

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MAKO: *Biomimetic Corrosion Resistant Aluminium for Aeronautics*

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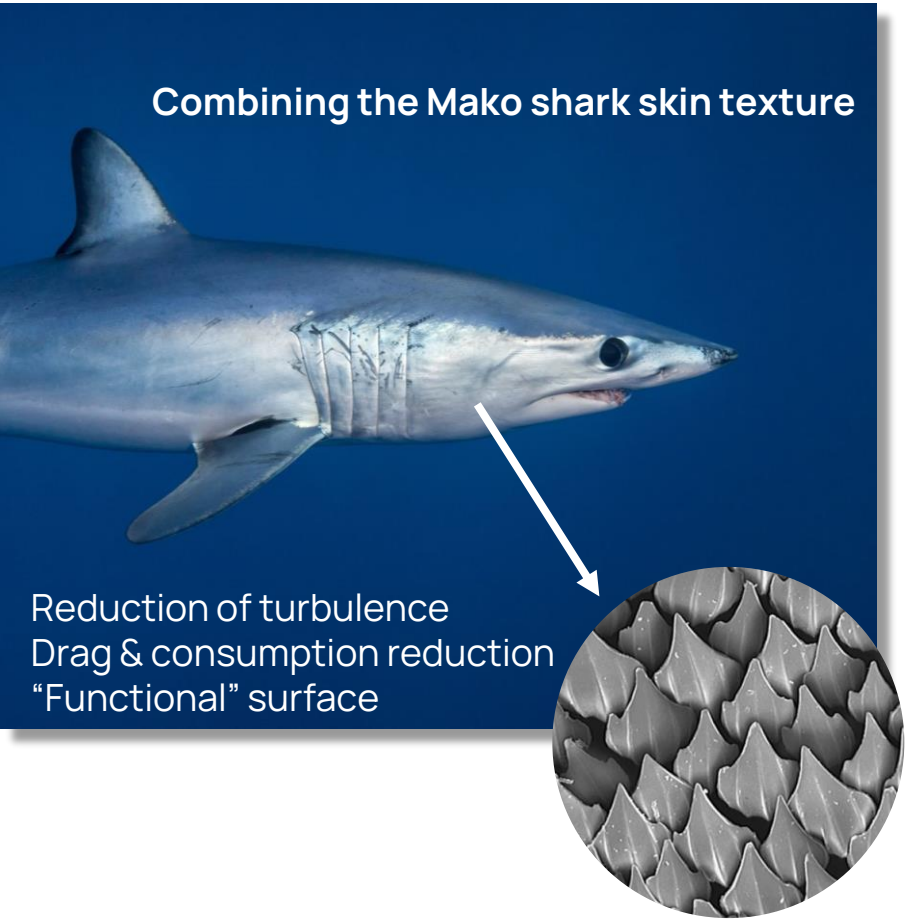

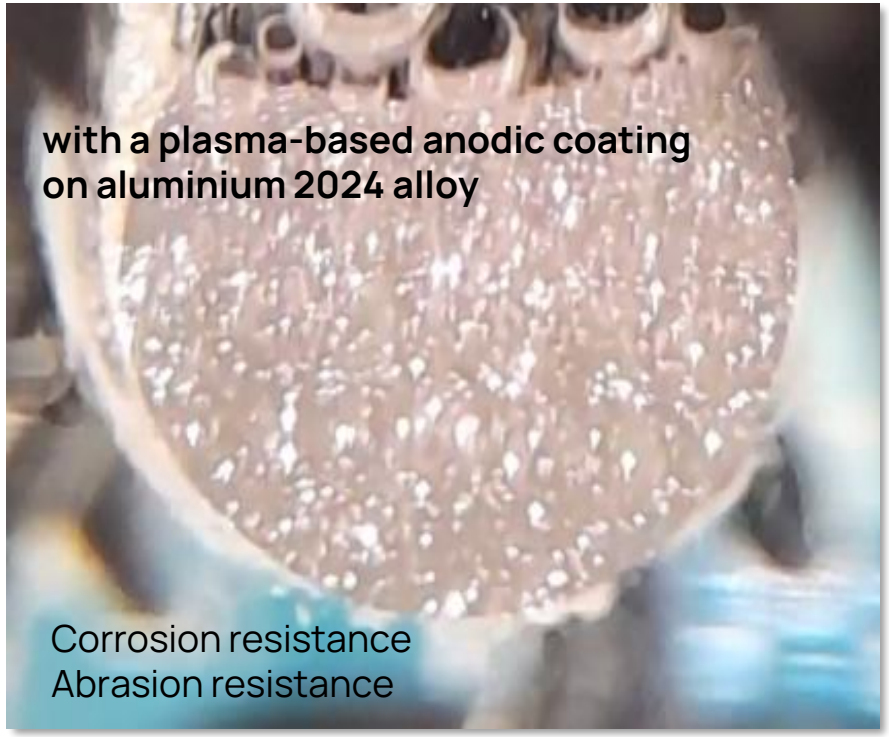

Project Outline

- WP1. Texture definition
- WP2. Riblets production
- WP3. PEO coating
- WP4. Corrosion testing

The research activity is co-funded by the European Union – Next Generation EU, PNRR - mission 4 “instruction and research” - D.D. N. 104/2022 “BANDO PRIN 2022”.

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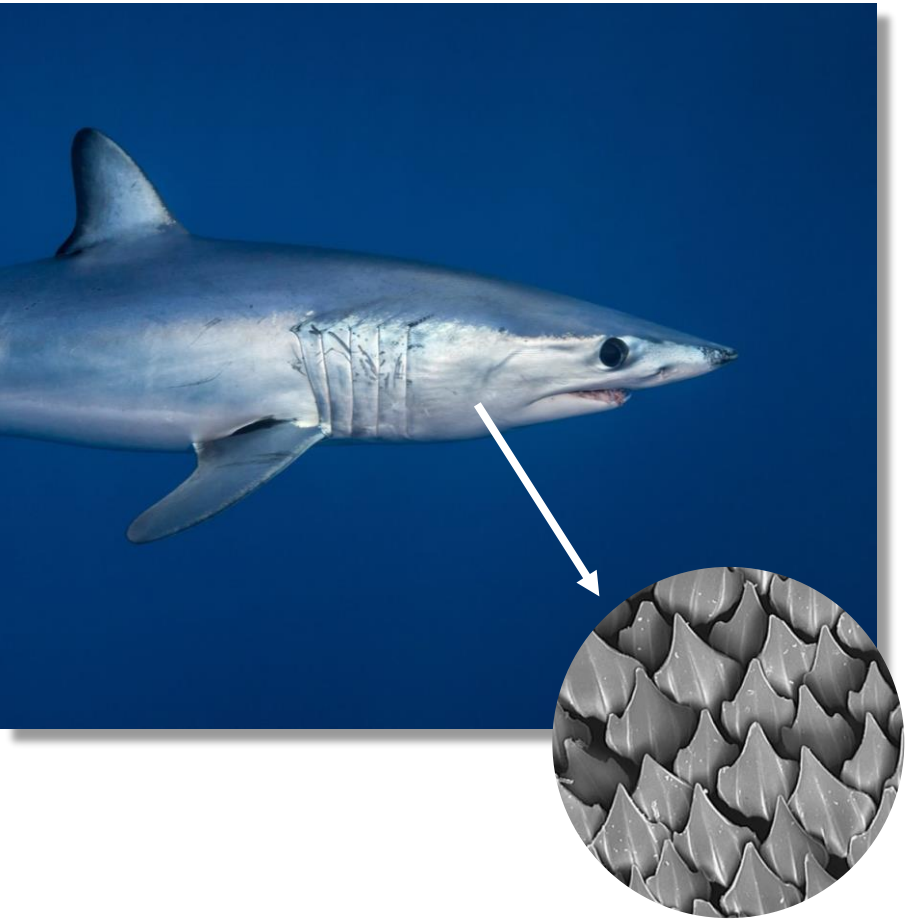
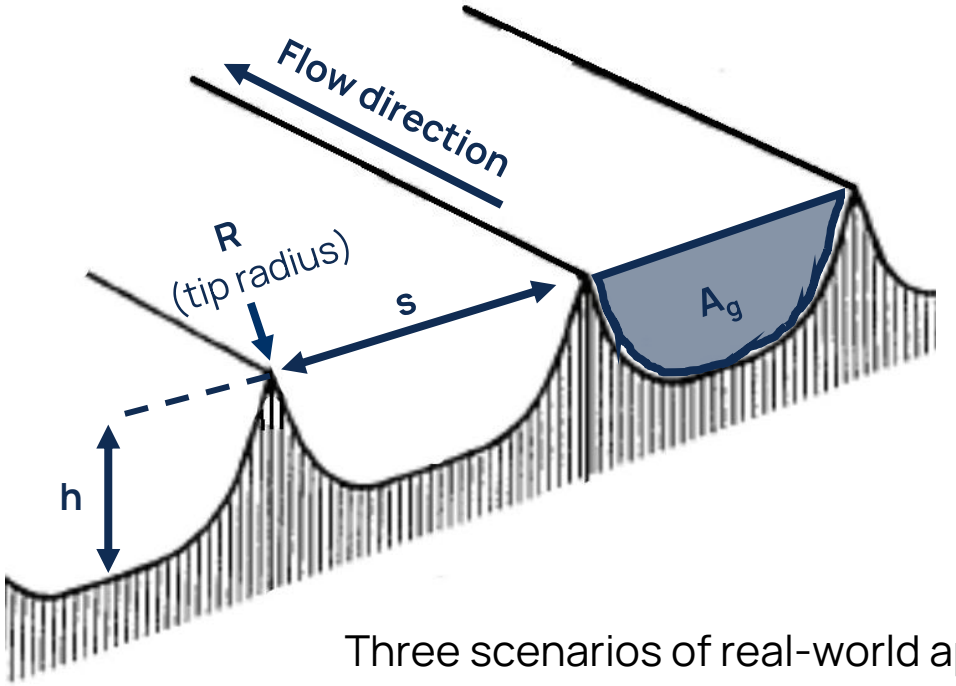
Definition of the biomimetic texture





Three scenarios of real-world application:

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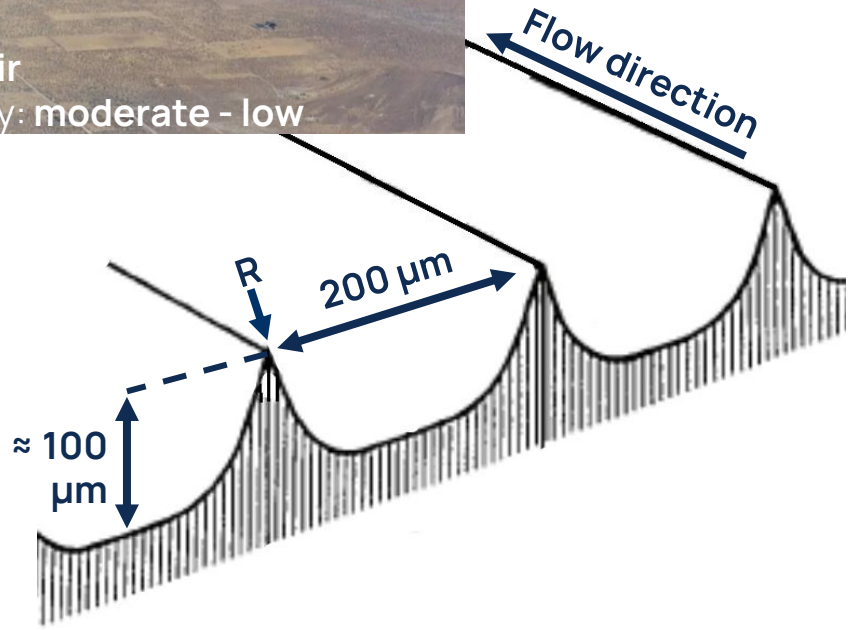
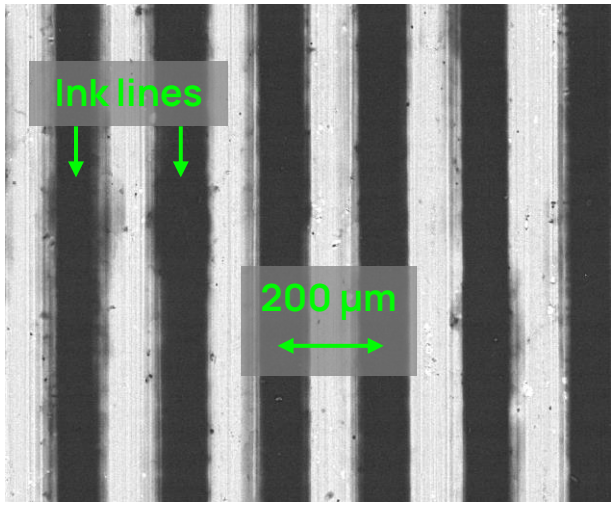
WP1 activities have been developed in collaboration with prof. Maurizio Quadrio, Department of Aerospace Science and Technology, Politecnico di Milano.

Biomimetic texture production on AA2024 alloy

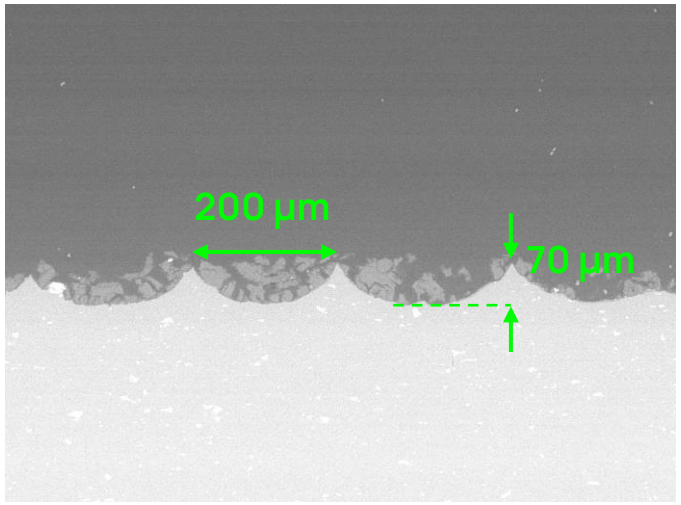


Riblets have been produced by **through-mask electrochemical etching** (TMEMM)



Dielectric mask ink-jet printing
UV curing
Build-up of 10-20 layers

Electrochemical etching
144 s at 2,5 A/cm^2
DC or pulsed DC
in 1,17 mol/L $NaNO_3$



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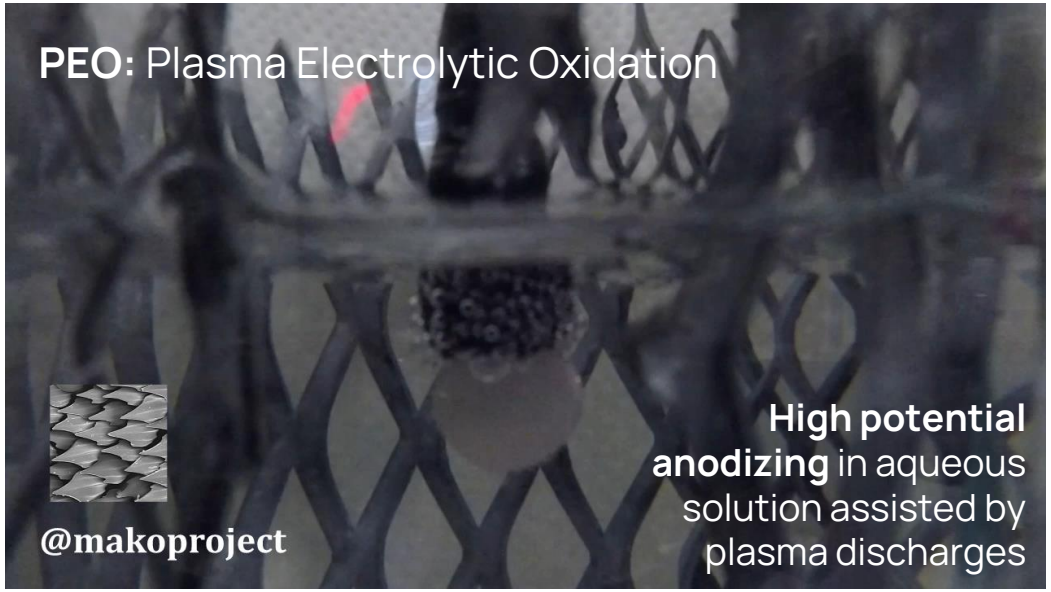
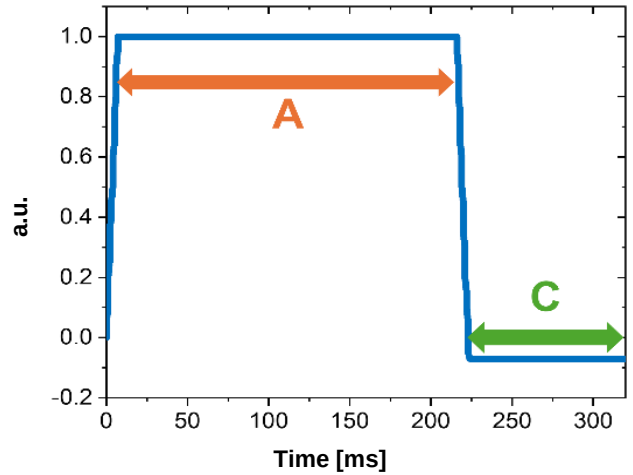
PEO coating optimization: *Methods and procedure*



Potentiostatic PEO in **AC mode** with 60-40-7 square waves



60% anodic
40% cathodic
7% cathodic vs anodic peak

- Definition of the **electrical input**
- Effect of the **electrolyte composition**
  - Sodium silicate (Na_2SiO_3)
  - Sodium hydroxide (NaOH)
  - Solution alkalinity
- Identification of the **best recipes**

PEO coating optimization: *Electrical input definition*

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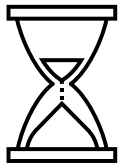
Current density → Growth rate

Applied potential

Must allow sparking onset
Current is proportional to him



Maintenance time

Maintenance allows coating growth
Decreasing current during growth
Larger sparks at longer times

Process A: Short process (9'), thin coating

Step 1	120 s ramp	300 V_{rms}
Step 2	120 s ramp	310 V_{rms}
Step 3	180 s ramp + 120 s maintenance	340 V_{rms}

Process B: Long process (14'), thick coating

Step 1	120 s ramp	300 V_{rms}
Step 2	120 s ramp	310 V_{rms}
Step 3	180 s ramp + 200 s maintenance	330 V_{rms}
Step 4	100 s ramp + 100 s maintenance	350 V_{rms}

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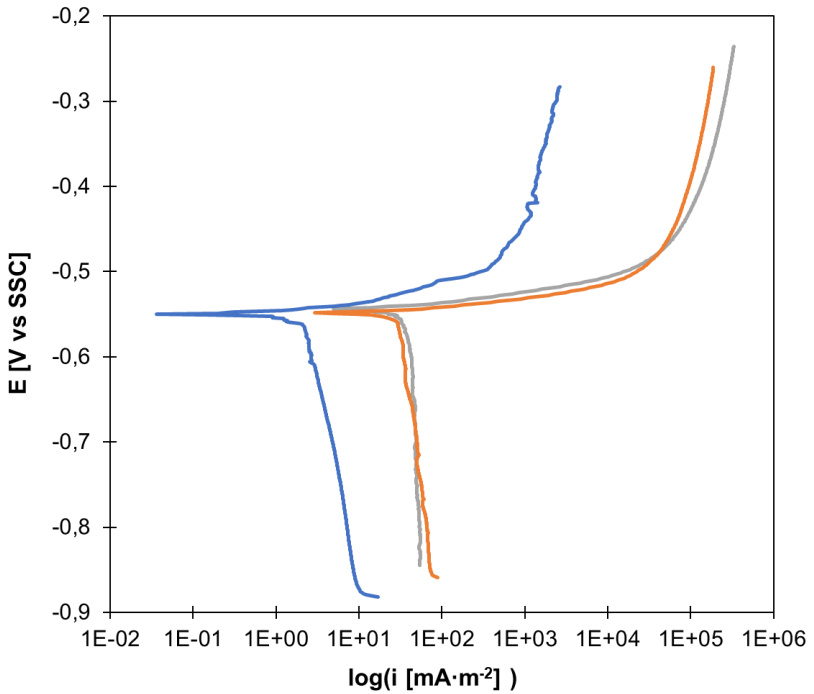
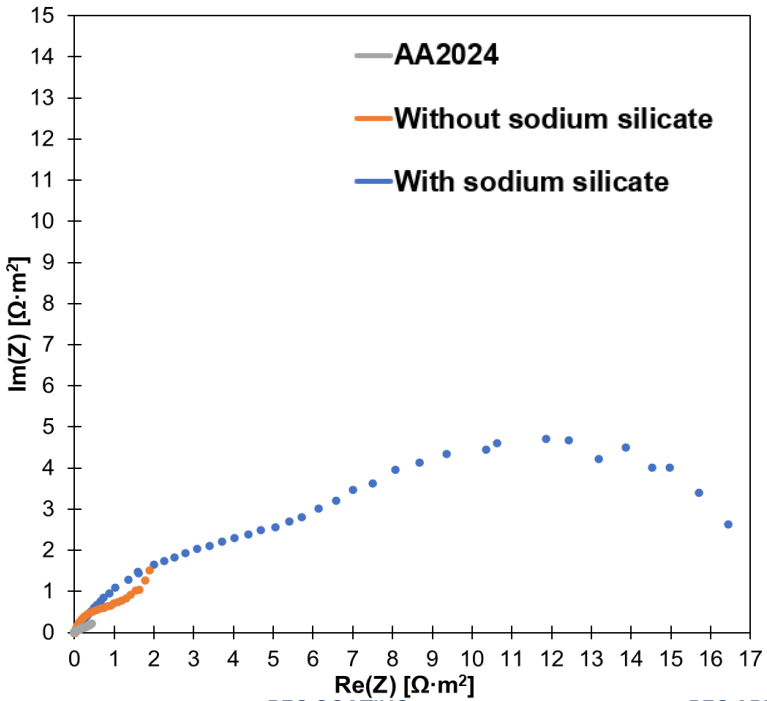
PEO electrolyte optimization: *Sodium silicate (Na_2SiO_3)*

Electrolyte	KOH [mol/L]	Na_2SiO_3 [g/L]	Glycerin [g/L]	Thickness (proc.B)	R_p (EIS) [$\Omega \cdot m^2$]	i_{corr} [$mA \cdot m^{-2}$]
0.20 K	0.20	-	10	**20.43 µm (± 11%)**	**3.7**	**62**
0.20 KS	0.20	**10**	10	**43.15 µm (± 11%)**	**18.5**	**7**





Development of the **porous layer**

Increase in coating **thickness** at constant standard deviation

Corrosion resistance improvement

For conciseness, only results obtained on process B specimens are given.
Electrochemical tests executed in 3.5% w/w NaCl after 1h immersion.

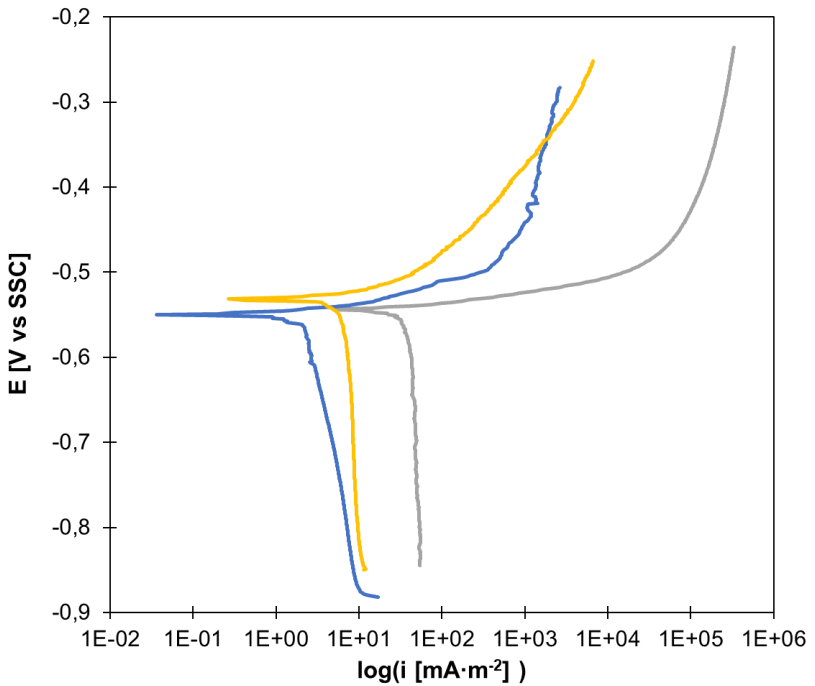
PEO electrolyte optimization: *Sodium hydroxide (NaOH)*

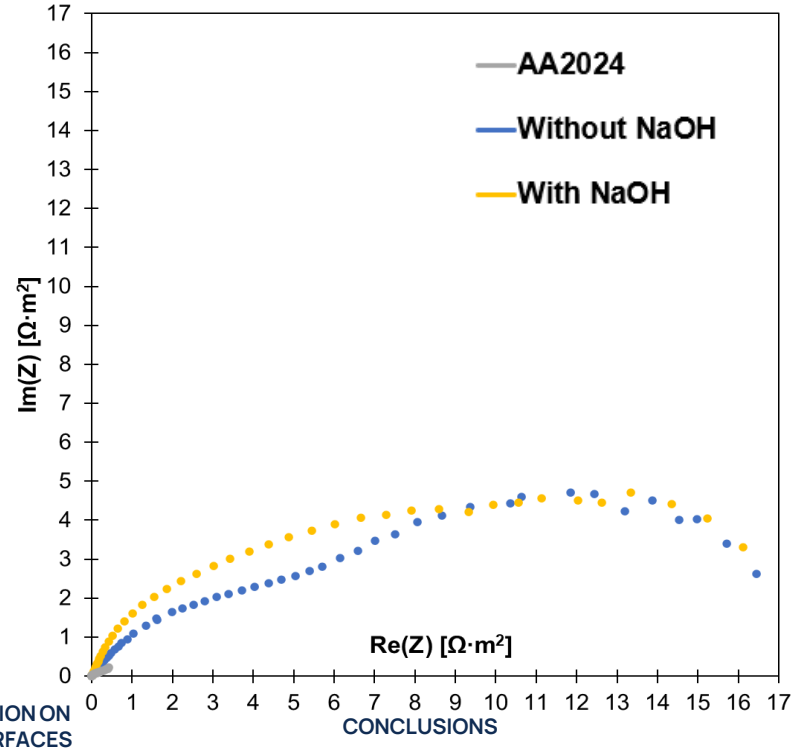
Electrolyte	OH^- [mol/L]	KOH [mol/L]	NaOH [mol/L]	Na_2SiO_3 [g/L]	Glycerin [g/L]	Thickness (B)	R_p [$\Omega \cdot m^2$]	i_{corr} [$mA \cdot m^{-2}$]
0.20 KS	0.20	0.20	-	10	10	**43.15 µm (± 11%)**	**18.5**	**7**
0.20 KNS	0.20	0.04	**0.16**	10	10	**34.32 µm (± 5%)**	**23.6**	**9**

Slight decrease in coating **thickness** at constant/lower standard deviation

Larger R_p value

Higher slope of the anodic branch





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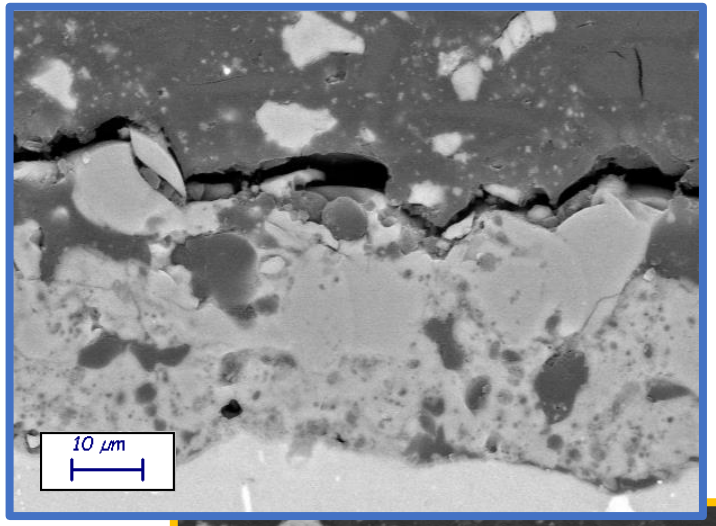
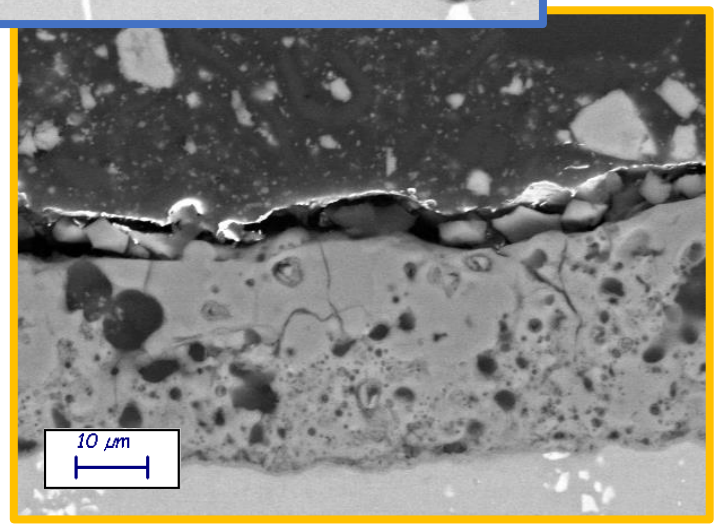
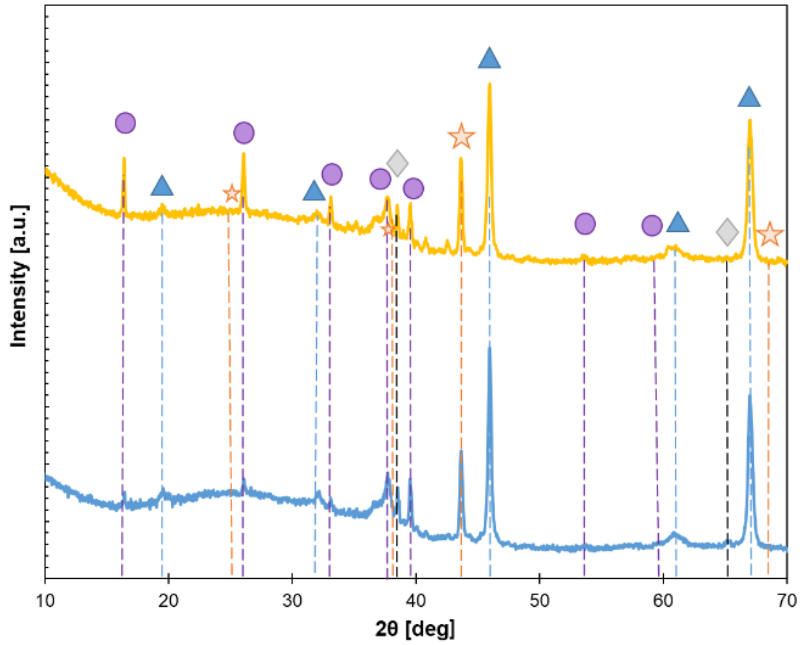
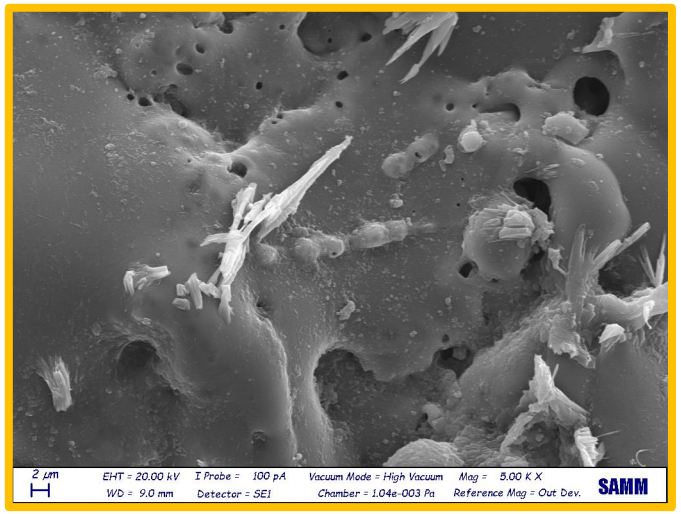
For conciseness, only results obtained on process B specimens are given.
Electrochemical tests executed in 3.5% w/w NaCl after 1h immersion.

PEO electrolyte optimization: *Sodium hydroxide (NaOH)*









Coating compaction

Large uptake of **amorphous silica**

Sodium aluminates needles on the surface

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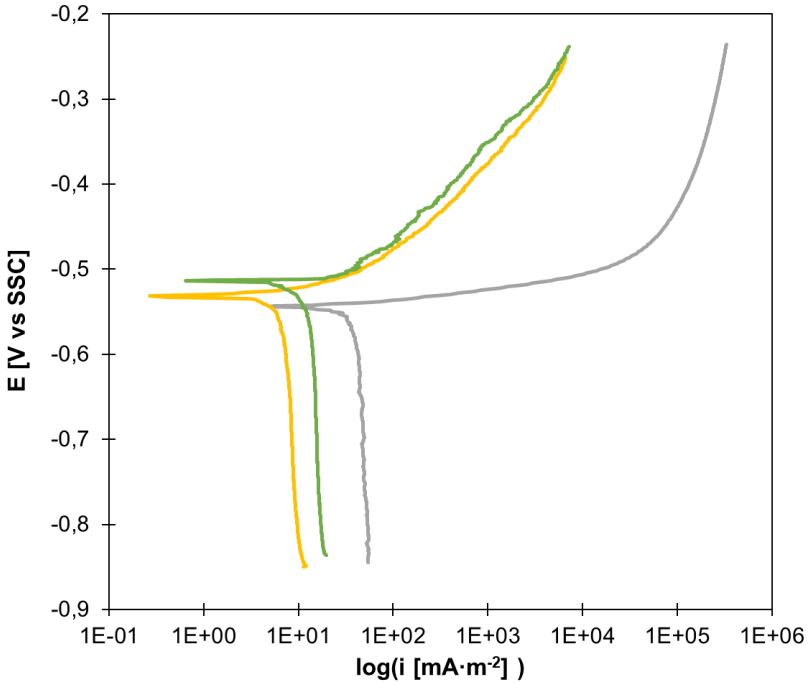
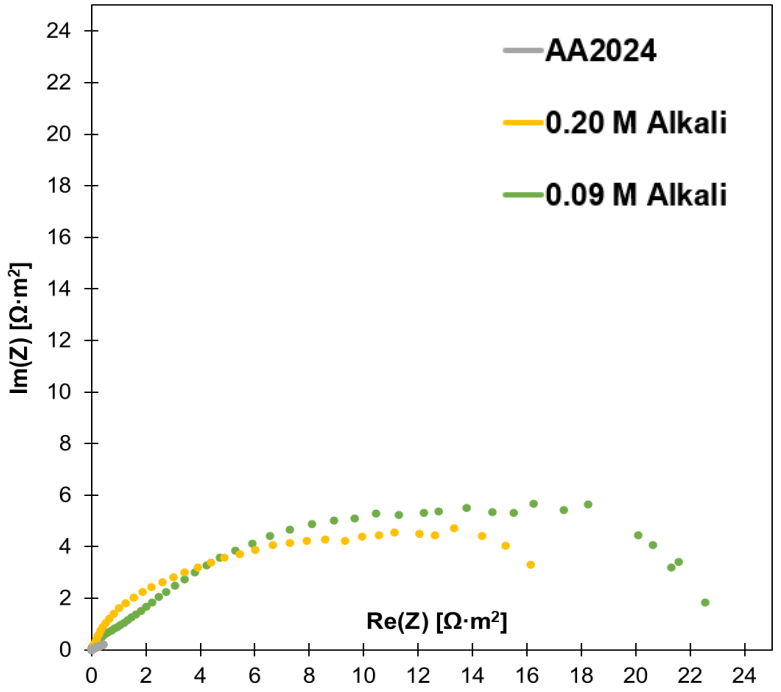
PEO electrolyte optimization: *Alkalinity (OH^-)*

Electrolyte	OH^- [mol/L]	KOH [mol/L]	NaOH [mol/L]	Na_2SiO_3 [g/L]	Glycerin [g/L]	Thickness (B)	R_p [$\Omega \cdot m^2$]	i_{corr} [$mA \cdot m^{-2}$]
0.20 KNS	**0.20**	0.04	0.16	10	10	**34.32 µm (± 5%)**	**23.6**	**9**
0.09 KNS	**0.09**	0.014	0.076	10	10	**13.01 µm (± 12%)**	**25.3**	**16**





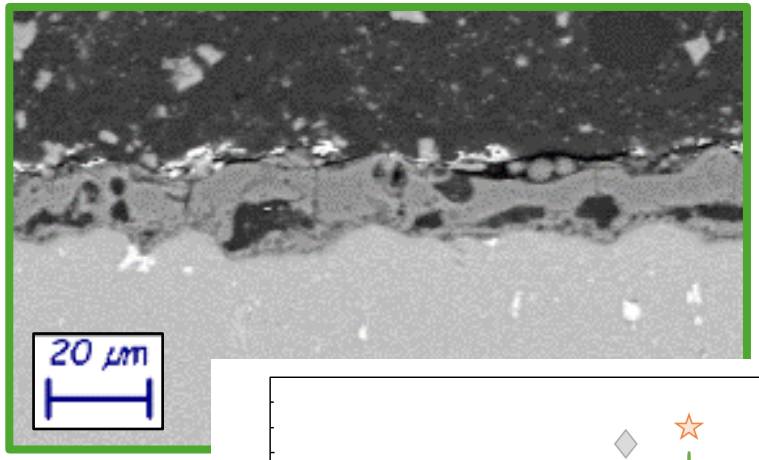
Lower coating **thickness**

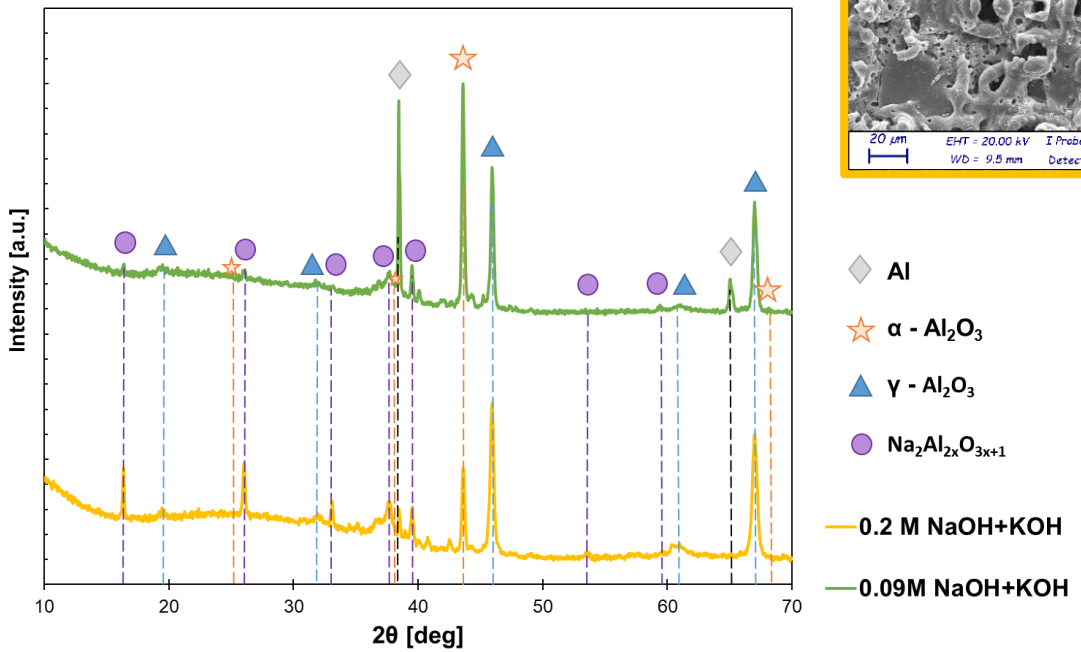
Slight increase in R_p value

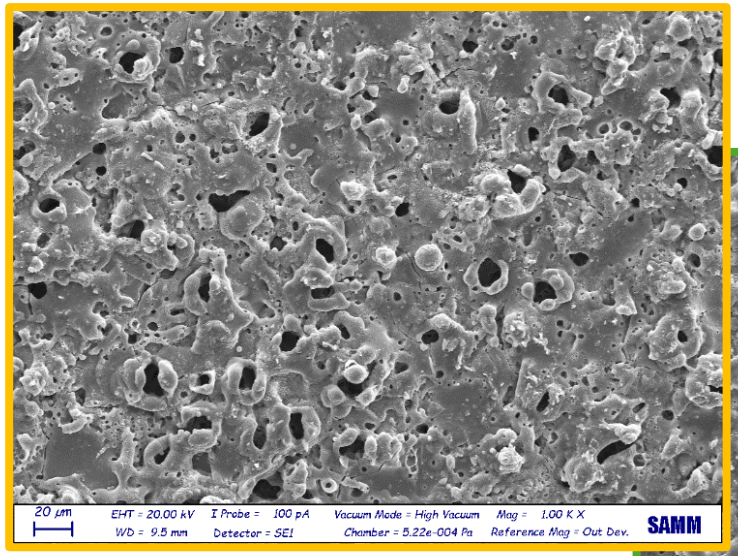
Very similar anodic branch and limit current density

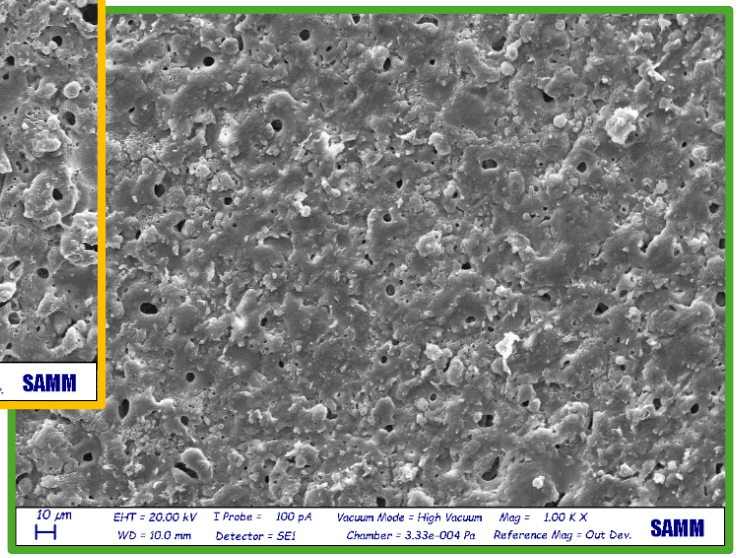
For conciseness, only results obtained on process B specimens are given.
Electrochemical tests executed in 3.5% w/w NaCl after 1h immersion.

PEO electrolyte optimization: *Alkalinity (OH^-)*







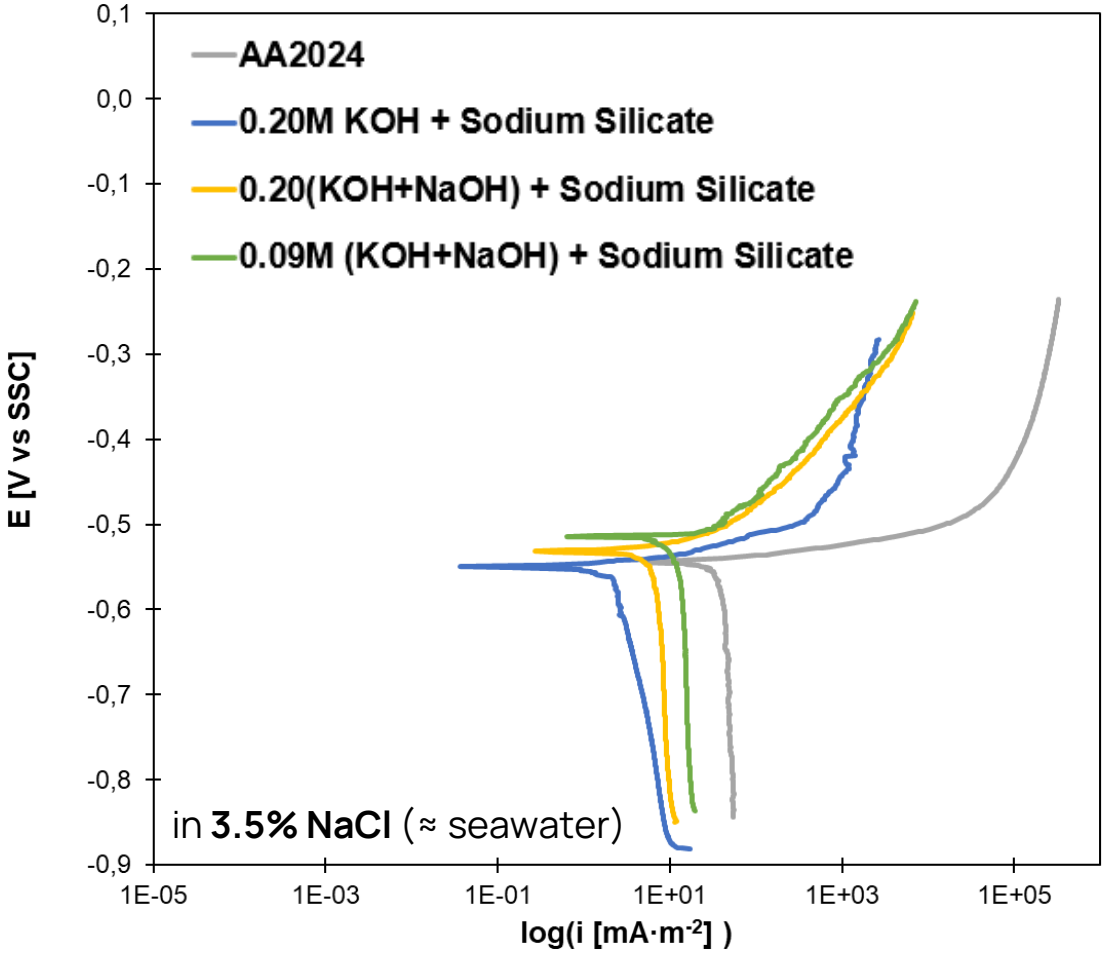


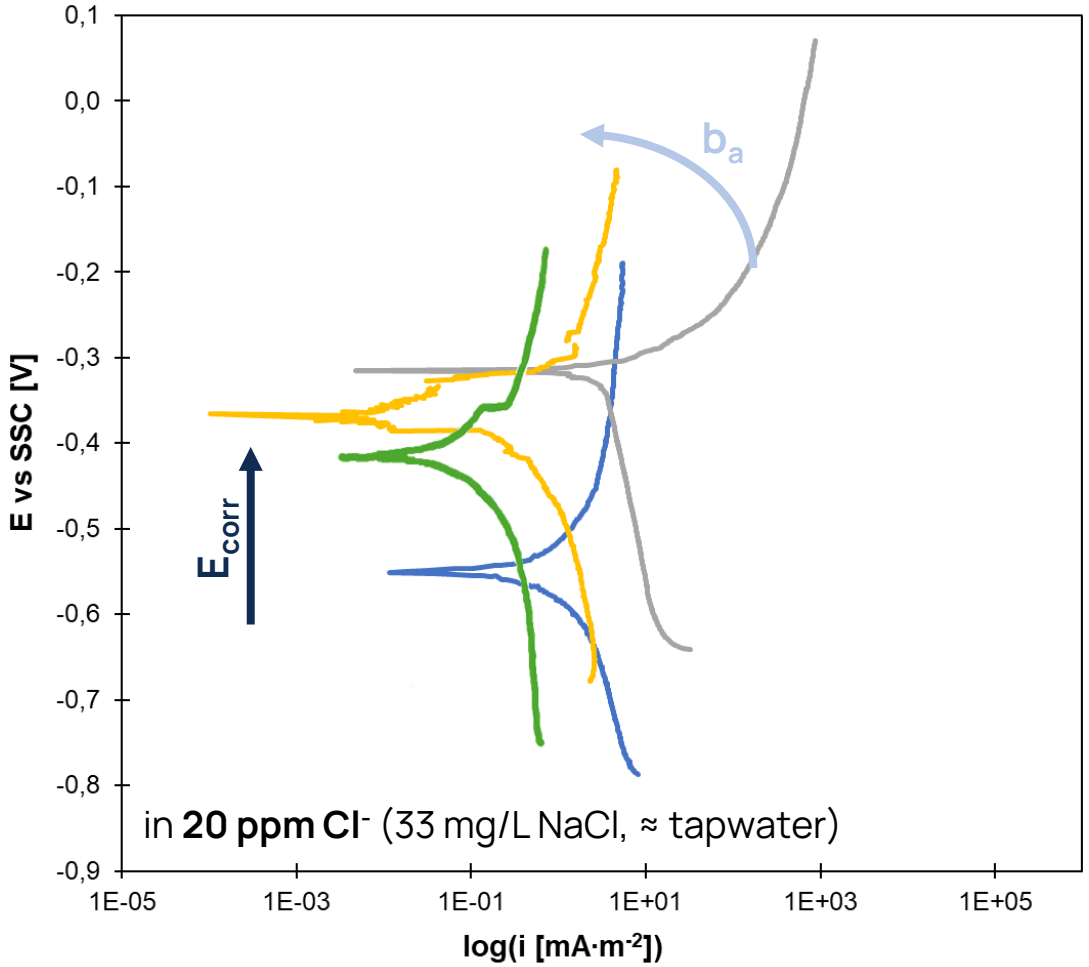
Smaller and less connected pores

Lower **amorphous silica**, higher alumina

Less **sodium aluminates** detected

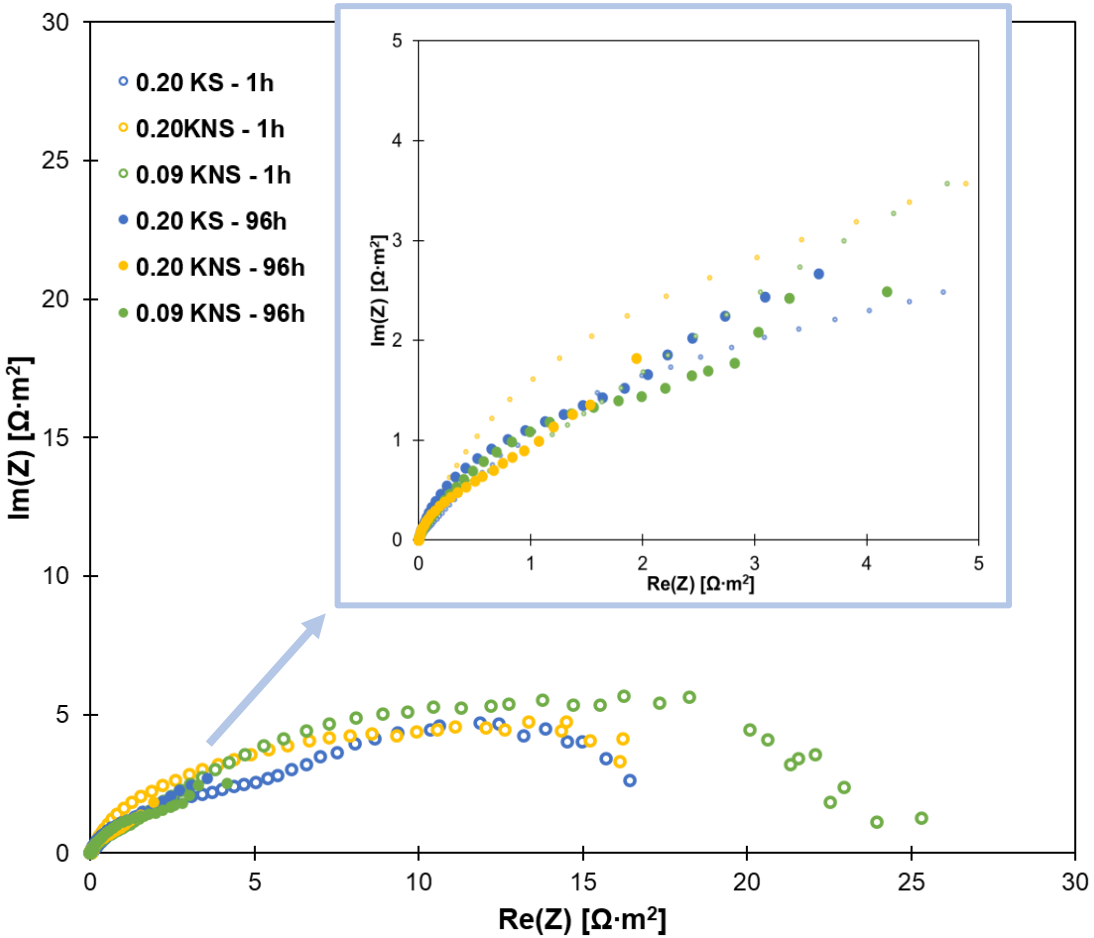
Identification of the best procedure: *Effect of the environment*

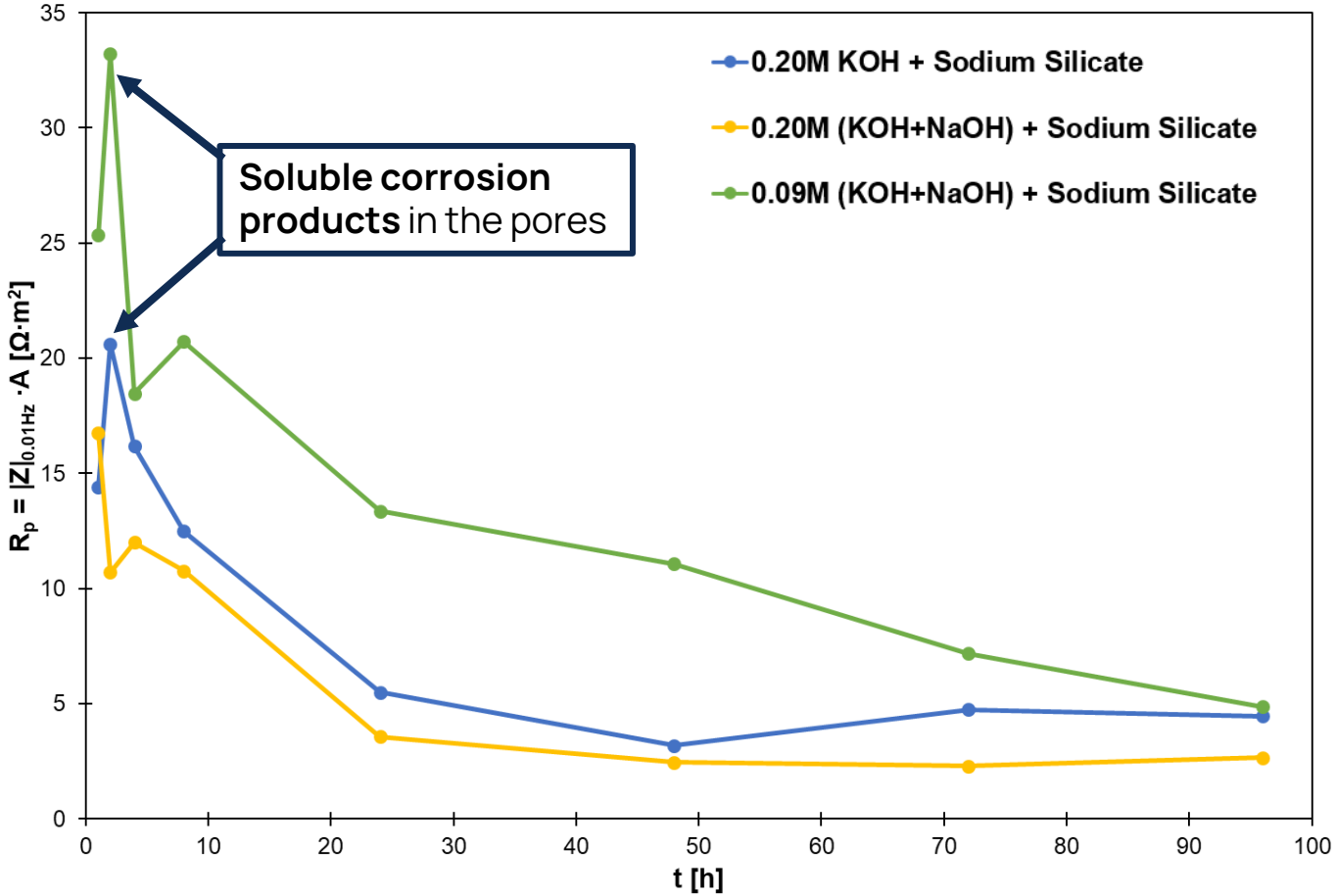




Identification of the best procedure: *Long-term behaviour*

The three coatings selected above have been **exposed for 96h** in 3.5% w/w NaCl simulating **seawater**.





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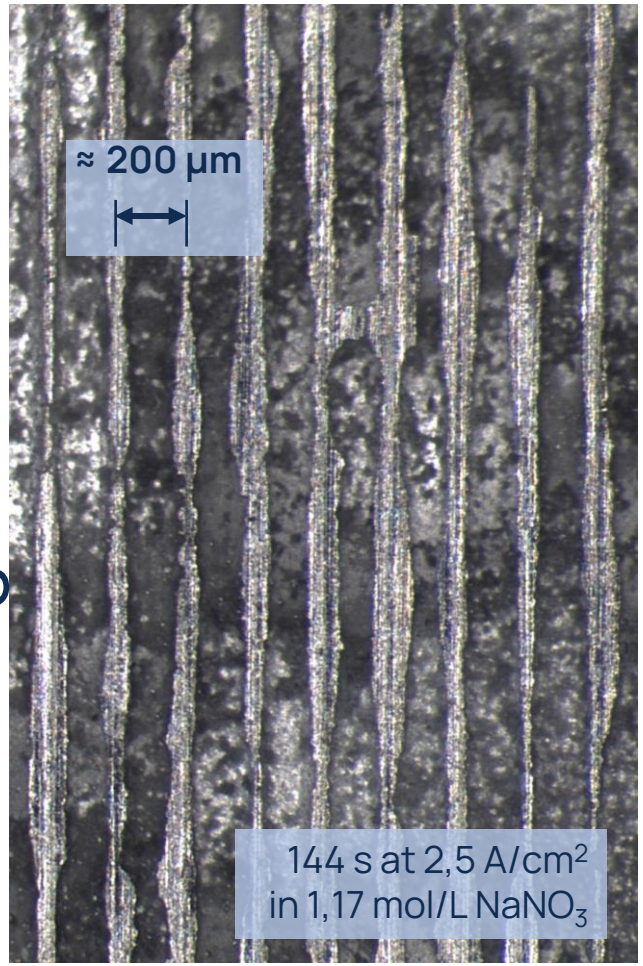
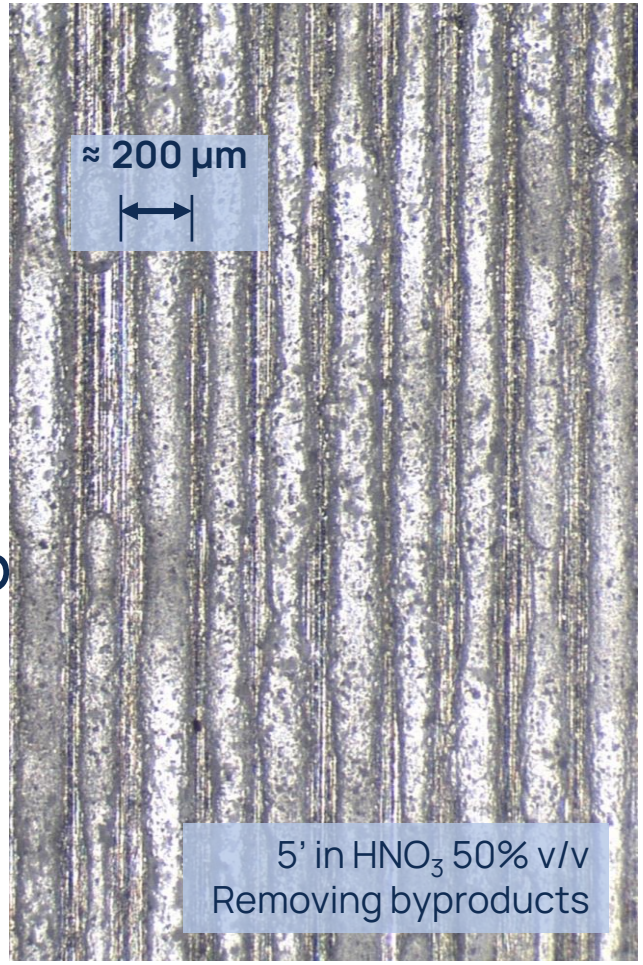
Coating application to the textured surfaces

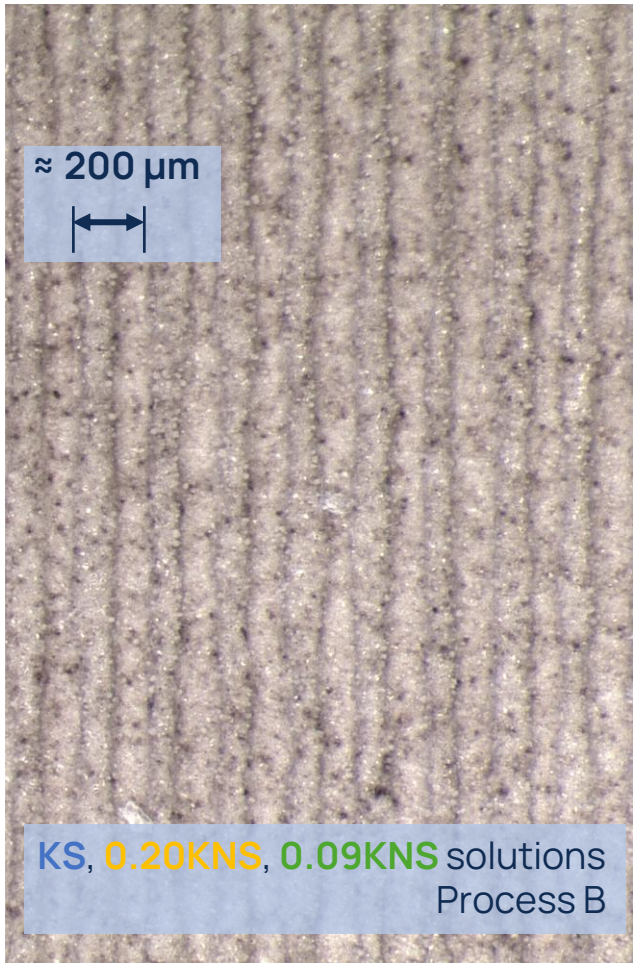
01. Etching



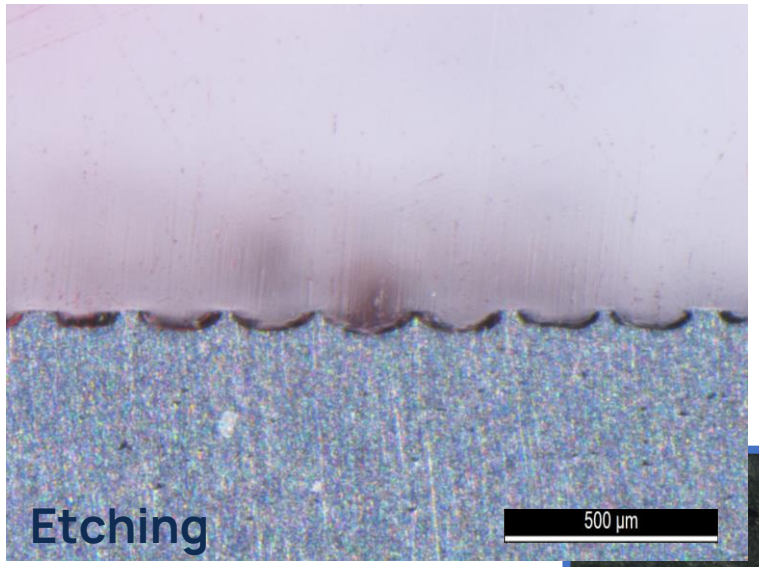
02. Pickling

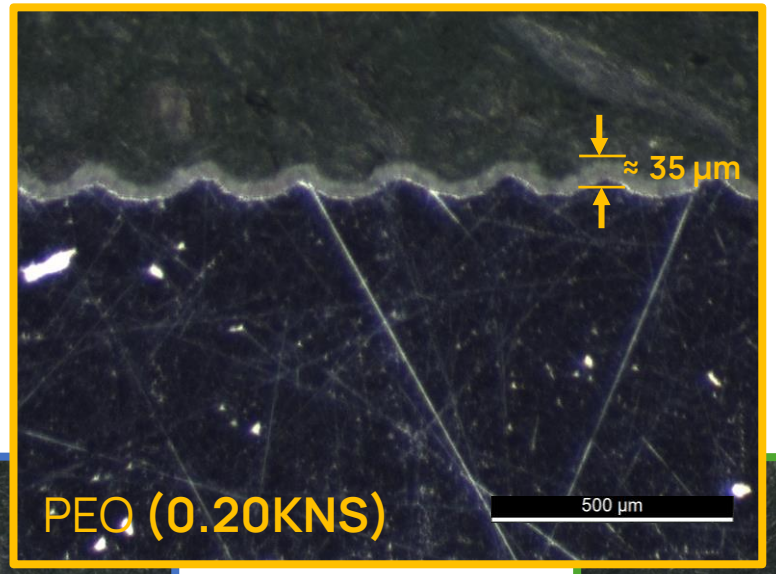


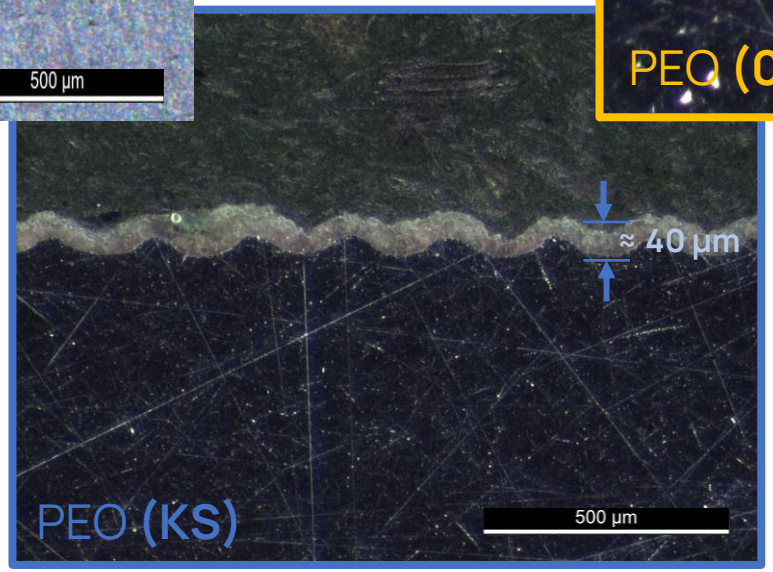
03. PEO

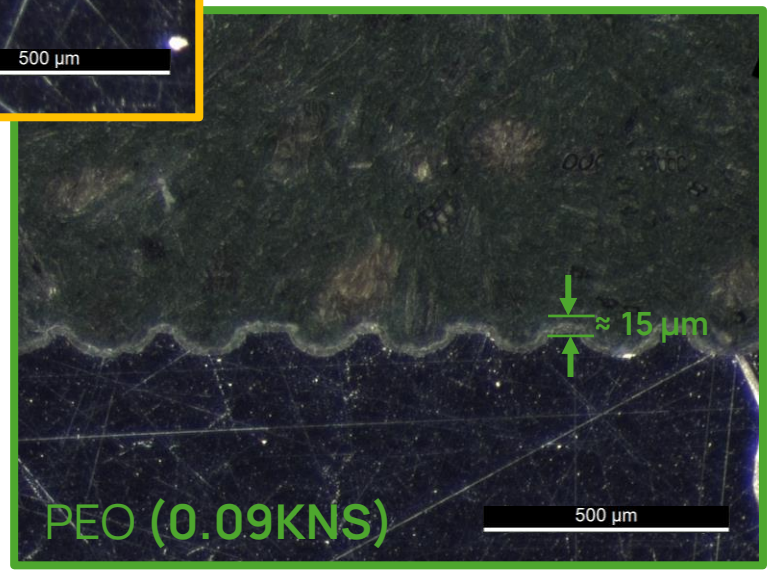


Coating application to the textured surfaces









A comprehensive comparison between the PEO processes

Electrolyte	Alkali [mol/L]	Na_2SiO_3 [g/L]	Thickness	Corrosion	Porosity	Durability	Texture
0.20 K	KOH, 0.20	-	☆	☆	-	-	-
0.20 KS	KOH, 0.20	10	☆☆☆☆	☆☆	☆	☆☆	☆☆
0.20 KNS	KOH+NaOH, 0.20	10	☆☆☆	☆☆☆	☆☆☆	☆☆	☆☆☆☆
0.09 KNS	KOH+NaOH, 0.09	10	☆☆	☆☆☆	☆☆☆☆	☆☆☆	☆☆☆☆

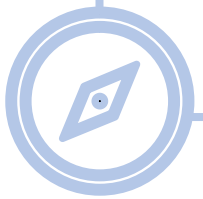
Sodium silicate-free process has been **discarded**.

Sodium hydroxide-free process is **not accurate enough** at reproducing the biomimetic texture.

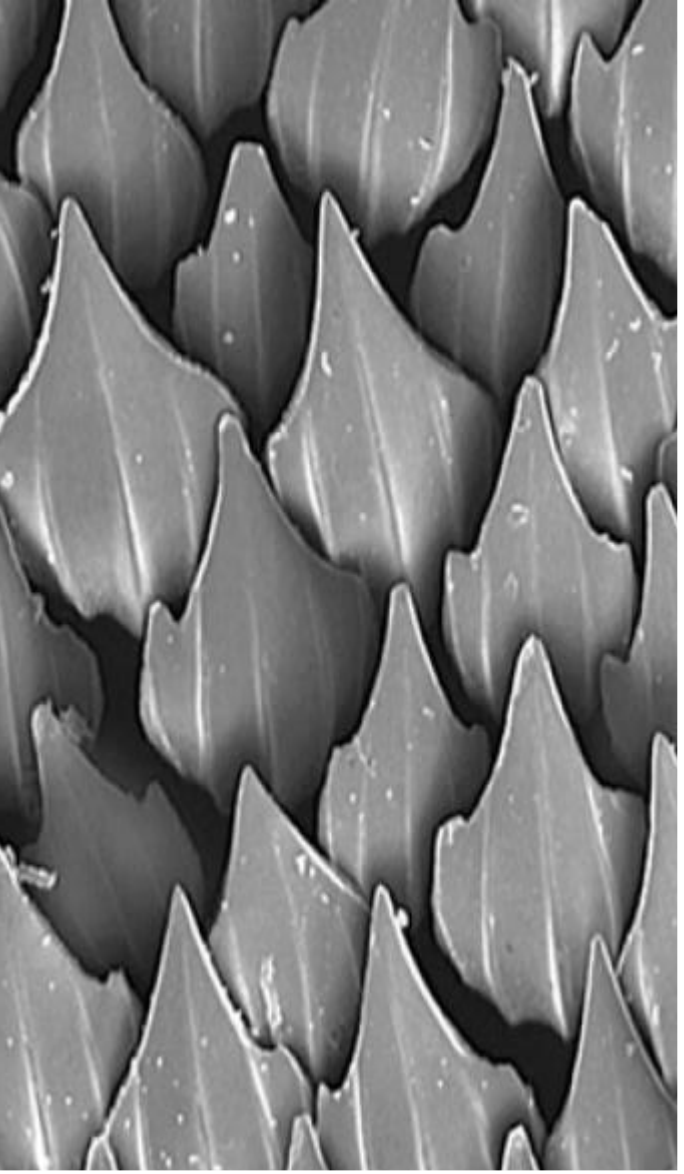
Low-alkali process shows a **slightly larger durability** due to the improved **microstructure**.

Conclusions and future developments

- **Sodium silicate (Na_2SiO_3)** help developing thick and corrosion resistant coatings.
- **Sodium hydroxide (NaOH)** offers a compaction effect, increasing corrosion resistance.
- A **reduction of alkalinity (OH^-)** leads to a better microstructure, but with a reduced growth rate.
- All the coatings show a **quite fast degradation** when exposed to aggressive environments.
- PEO can **reproduce the biomimetic texture**, with an accuracy depending on the electrolyte.



- Studying the corrosion resistance of the textured and coated surfaces.
- Implementing a pore sealing post-treatment for reducing porosity.
- Addressing the riblets tip rounding issue during PEO.



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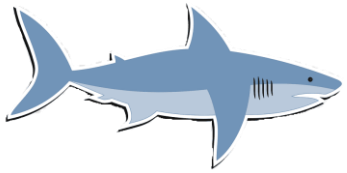
Thanks for your attention!

Follow the shark!



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The research activity is co-funded by the European Union – Next Generation EU, PNRR - mission 4 “instruction and research” - D.D. N. 104/2022 “BANDO PRIN 2022”.

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