# Micro-arc anodized magnesium AZ31 alloy: towards application in veterinary implants

O. Banakh[1], T. Journot[1], Y. Savary[1], A. Hämmerli[2], J.-C. Puippe[3]

[1]***Haute Ecole Arc Ingénierie**, La Chaux-de-Fonds, CH,*
[2] ***Kyon AG**, Zürich, CH,*
[3] ***Steiger Galvanotechnique SA**, Chatel-St.-Denis, CH*

[MEET THE EXPERT] IMPLANTS

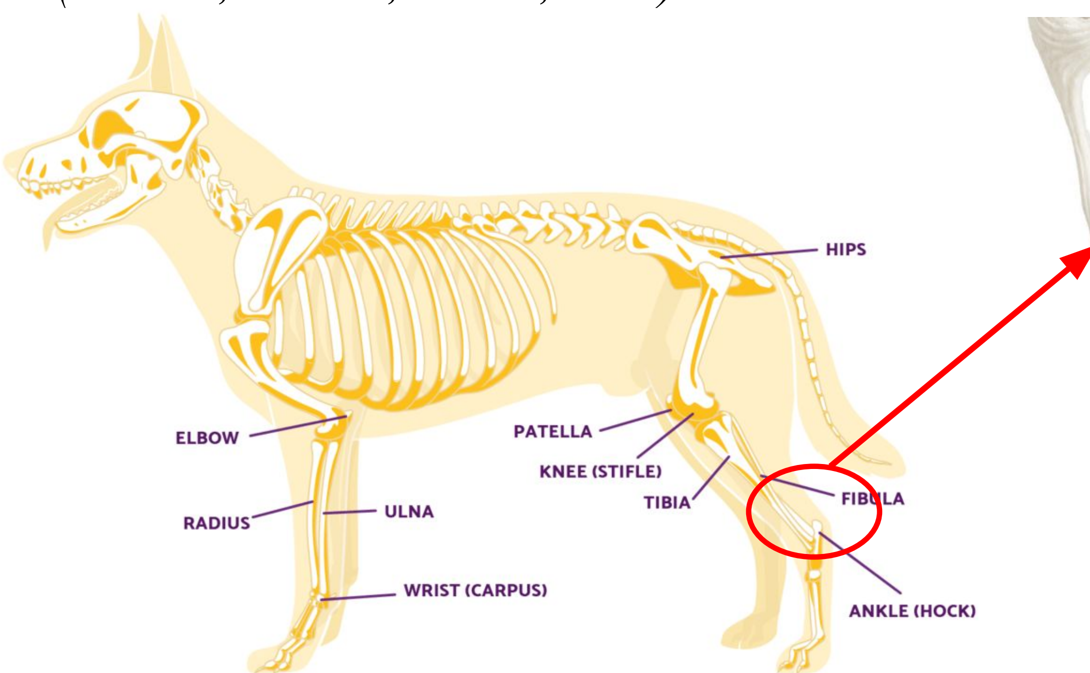
*8th September, 2022*

# Introduction

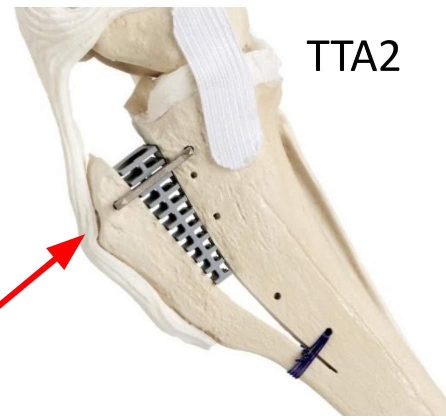
KYON is leading Swiss provider of orthopedic implants and instruments to the veterinary market.

In 2004, KYON launched TTA (Tibial Tuberosity Advancement) for Cranial Cruciate deficiency in dogs

*Rupture of the Cranial Cruciate Ligament is the most common cause of lameness in dogs. US dog owners spent **$1.3 billion** on Cranial Cruciate treatment in the US in 2003 (JAVMA, Vol 227, No. 10, 2005)*




TTA2



TTA


*www.kyon.ch/products-solutions/tta_tibial-tuberosity-advancement*

# Motivation

1st generation of KYON TTA is in **CP-4 Titanium**.

**Advantages of using a Mg-alloy (MgAl3Zn1 or AZ31):**

- bioresorbable (dissappears after several months)
- non-toxic;
- mechanical strength (290 MPa), ductility (elongation at break 15%), Young's modulus (45 GPa), machinability;
- economically affordable;
- in vivo biocompatibility*

** N. Kawamura et al., Degradation and Biocompatibility of AZ31 Magnesium Alloy Implants In Vitro and In Vivo: A Micro-Computed Tomography Study in Rats, Materials. 2020 13(2):473.*

*F. Witte et al., In vivo corrosion of four magnesium alloys and the associated bone response, Biomaterials, 2005, 26(17):3557-63.*

# Motivation

***Magmaris***® *stent from Biotronik*

***Magnezix***® *screw from Syntelllix*

*www.biotronik.com/en-de/products/coronary/magmaris*

*www.syntellix.de*

# Problem

However, Mg degrades too fast in biological medium 

$$\boxed{Mg_{(implant)} + 2H_2O \rightarrow Mg(OH)_2 + H_{2\,(gas)}}$$

- Release of hydrogen gas around the implant (rejection)
- Loss of mechanical stability

**The corrosion of a Mg implant must be carefully controlled (5 weeks)!**

# Solution

**Micro-Arc Oxidation, MAO** (also called **Plasma Electrolytic Oxidation, PEO**)

- PEO is well-established industrial anodizing process for Ti, Al, Mg;


Titanschrauben mit *Biocer* versehen (REM-Aufnahme der po-
rösen Oberflächenmorphologie).

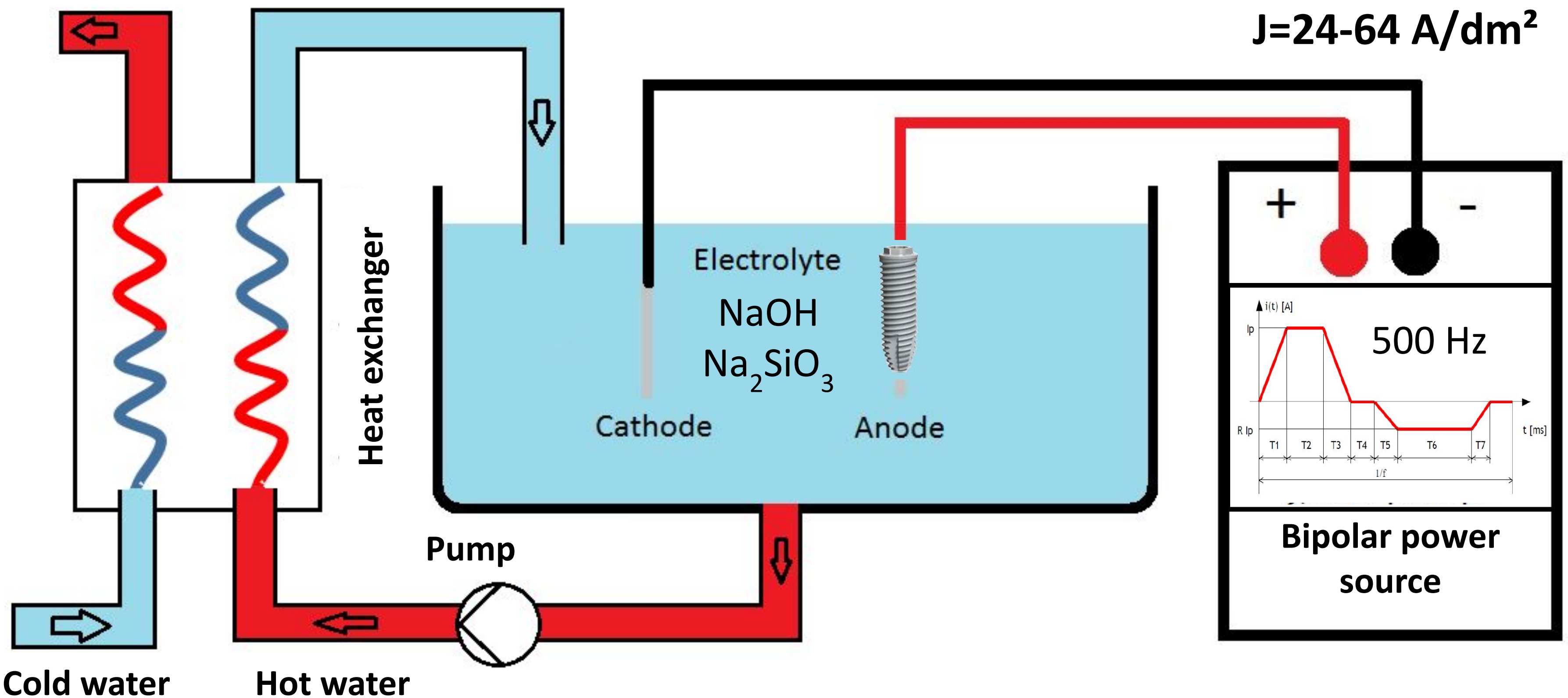
- PEO is fast and efficient (thick oxide layers in a few minutes);
- PEO uses "safe" chemicals;
- High number of publications and patents on PEO for Mg-alloys suggests its potential for implants

# Plasma Electrolytic Oxidation (PEO)

PEO is similar to conventional anodizing, but at much higher voltages (>500 V)

 Thicker (up to 200 µm) oxide layer (a breakdown threshold is overcome)

$Mg^{2+} + O^{2-}$  MgO (surface layer)

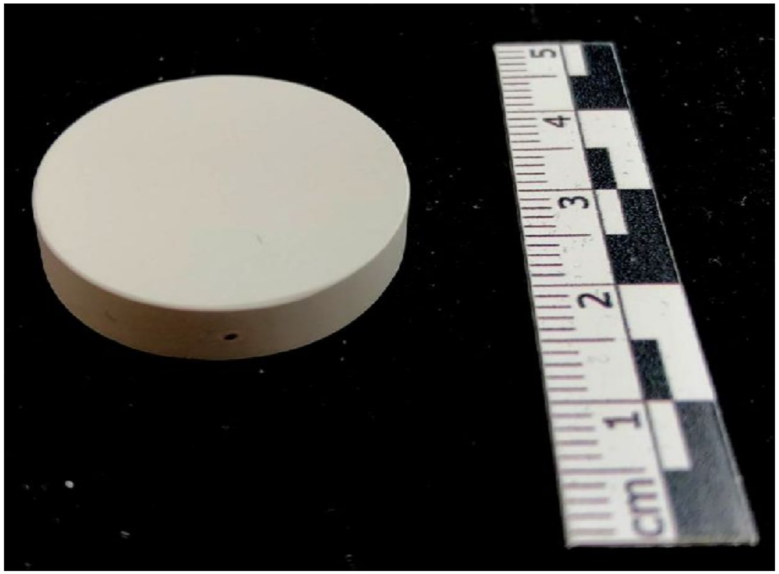


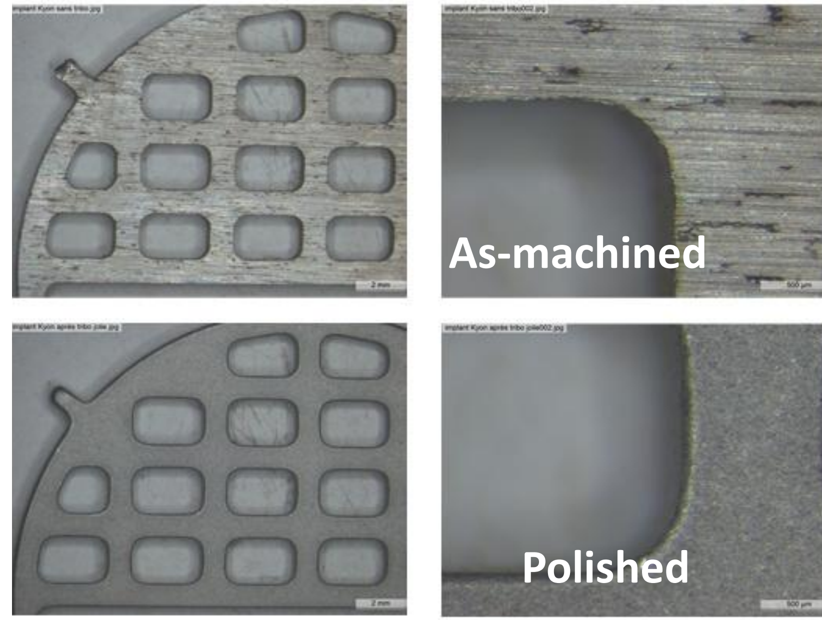
# Plasma Electrolytic Oxidation (PEO)

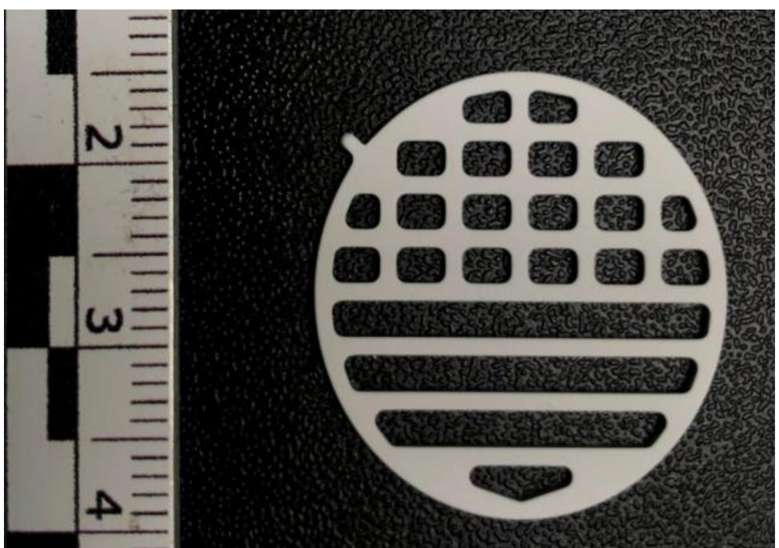
PEO is similar to conventional anodizing, but at much higher voltages (>500 V)

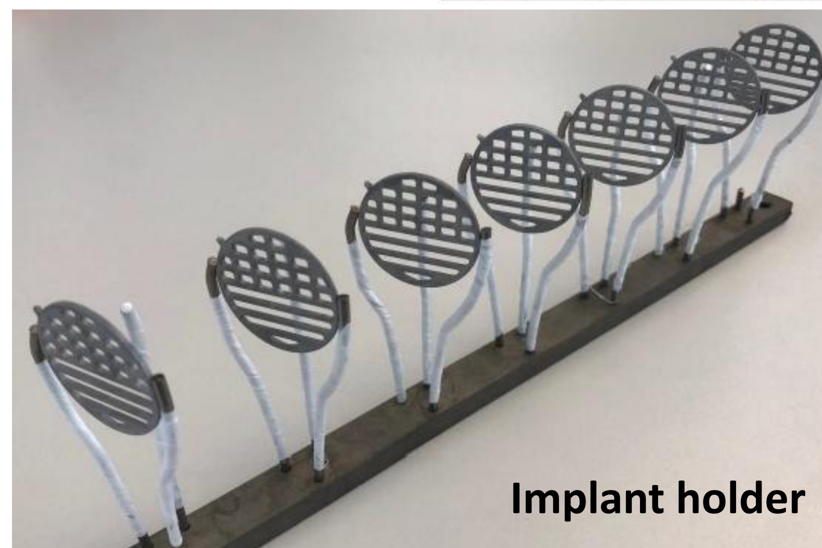
- Numerous electric arcs
- Local melting of the growing oxide layer
- Re-solidification and densification

# Test samples



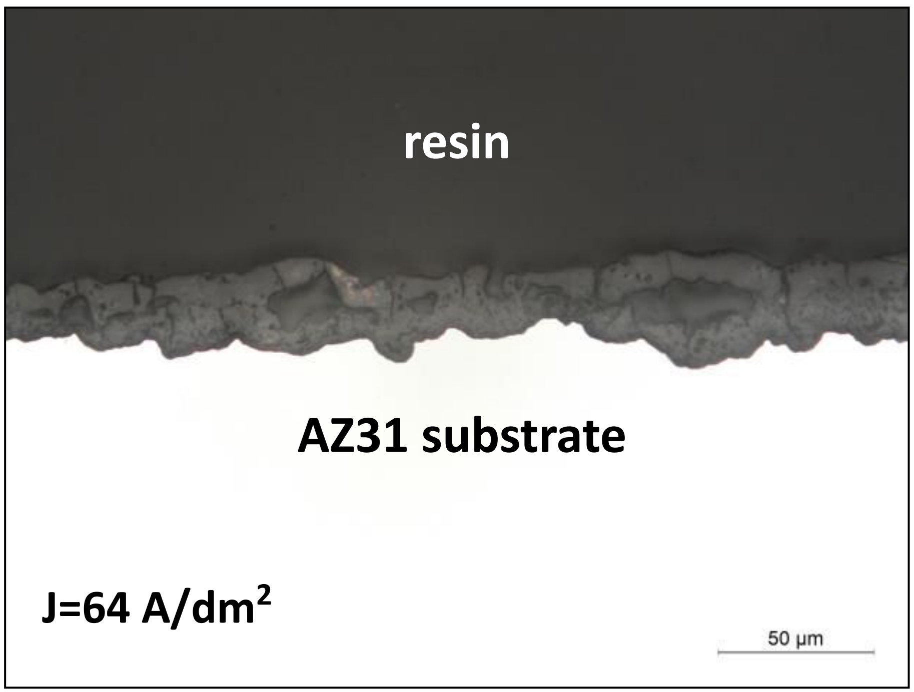



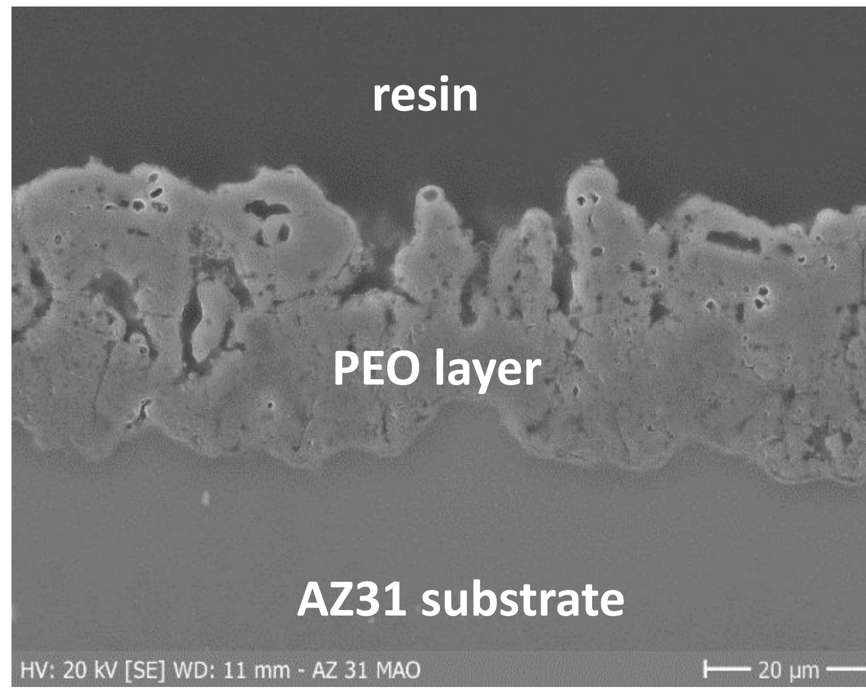



# Cross-section morphology

- High surface roughness (a few µm)
- Morphology presents internal pores
- Layer coverage is OK over 3D implant geometry (inside the holes)
- Thickness increases linearly with the current density **(J)** from **7**±2 µm at J=**24** A/dm$^2$ to **25** ±12 µm at J=**64** A/dm$^2$ (treatment time **5 min**)




*Optical Microscopy image*

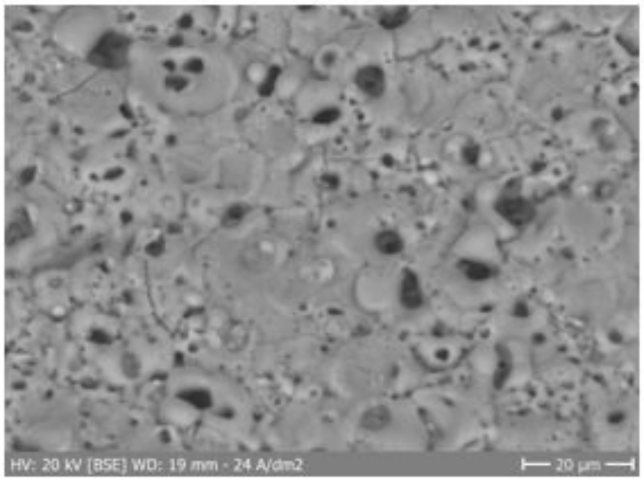



*Scanning Electron Microscopy (SEM) image*

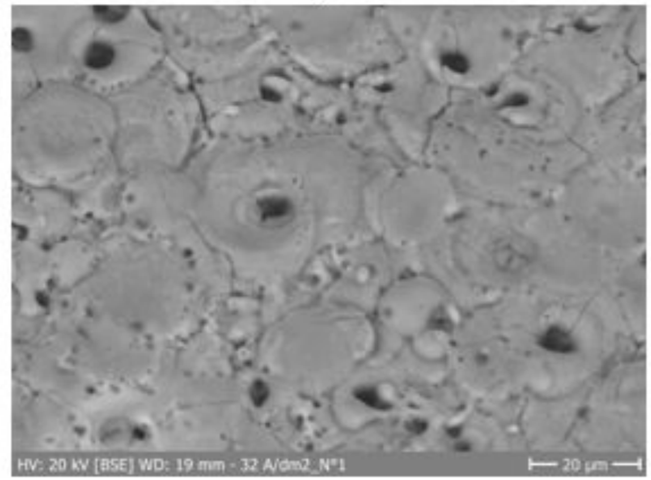
# Surface morphology

Surface morphology presents open pores. Cracks appear at higher energies

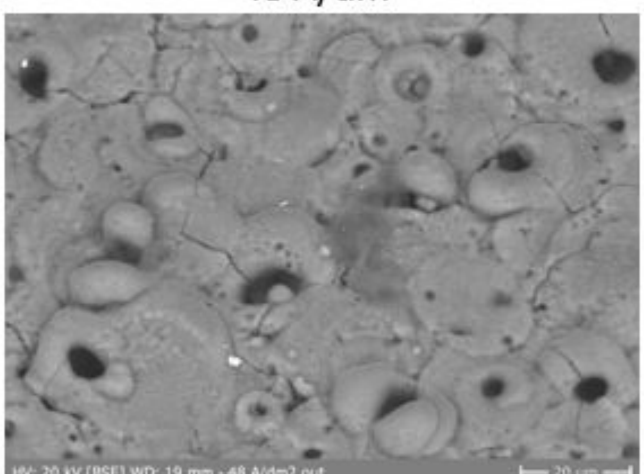
24 A/dm$^2$



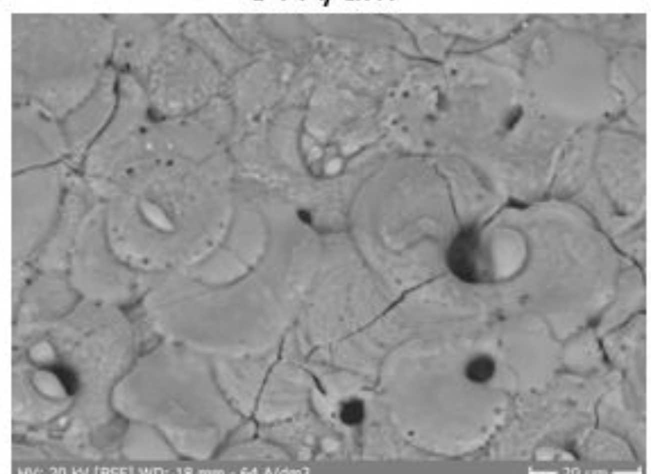

32 A/dm$^2$




48 A/dm$^2$



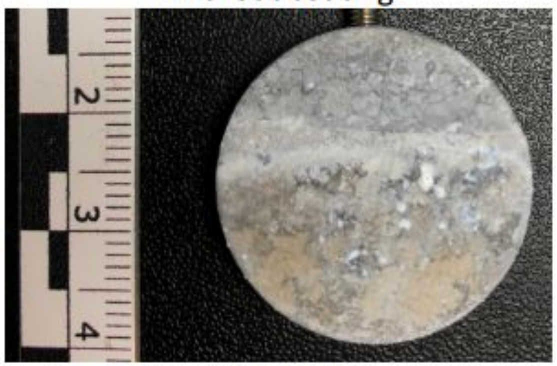

64 A/dm$^2$



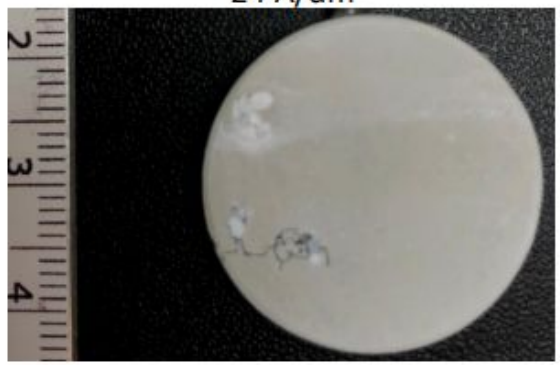
# Immersion tests of the discs

After **21 days** of immersion in Simulated Body Fluid (Ringer's solution) @37°C

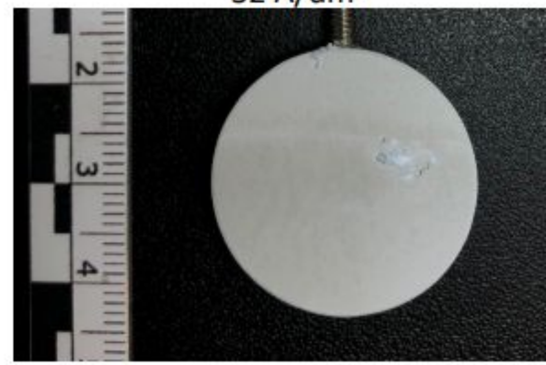
Without coating



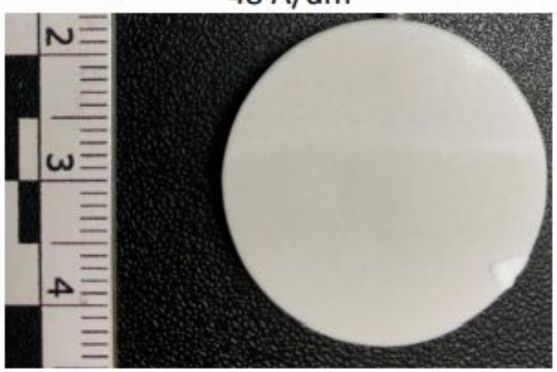
24 A/dm²



32 A/dm²



48 A/dm²



64 A/dm²

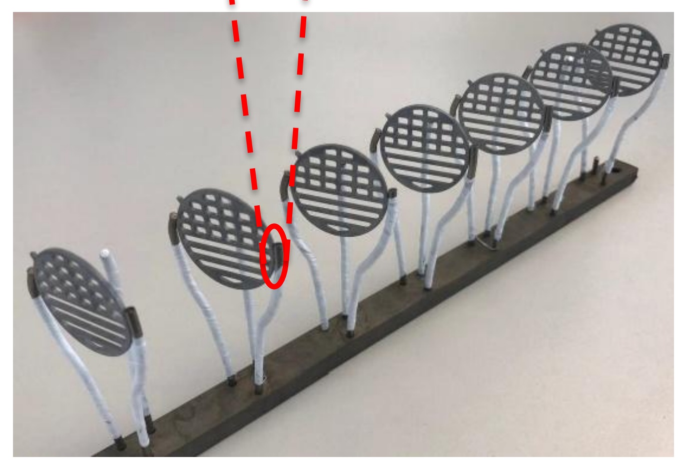
- Current density (***J***) does not have much influence on the corrosion resistance
- Corrosion spots occur randomly, esp. at edges

# Immersion tests of the implants

**7 days** **14 days** **21 days**

**PEO parameters:**

- Current density: **J=32 A/dm$^2$**
- Time: 5 min
- Layer thickness: ~10 µm

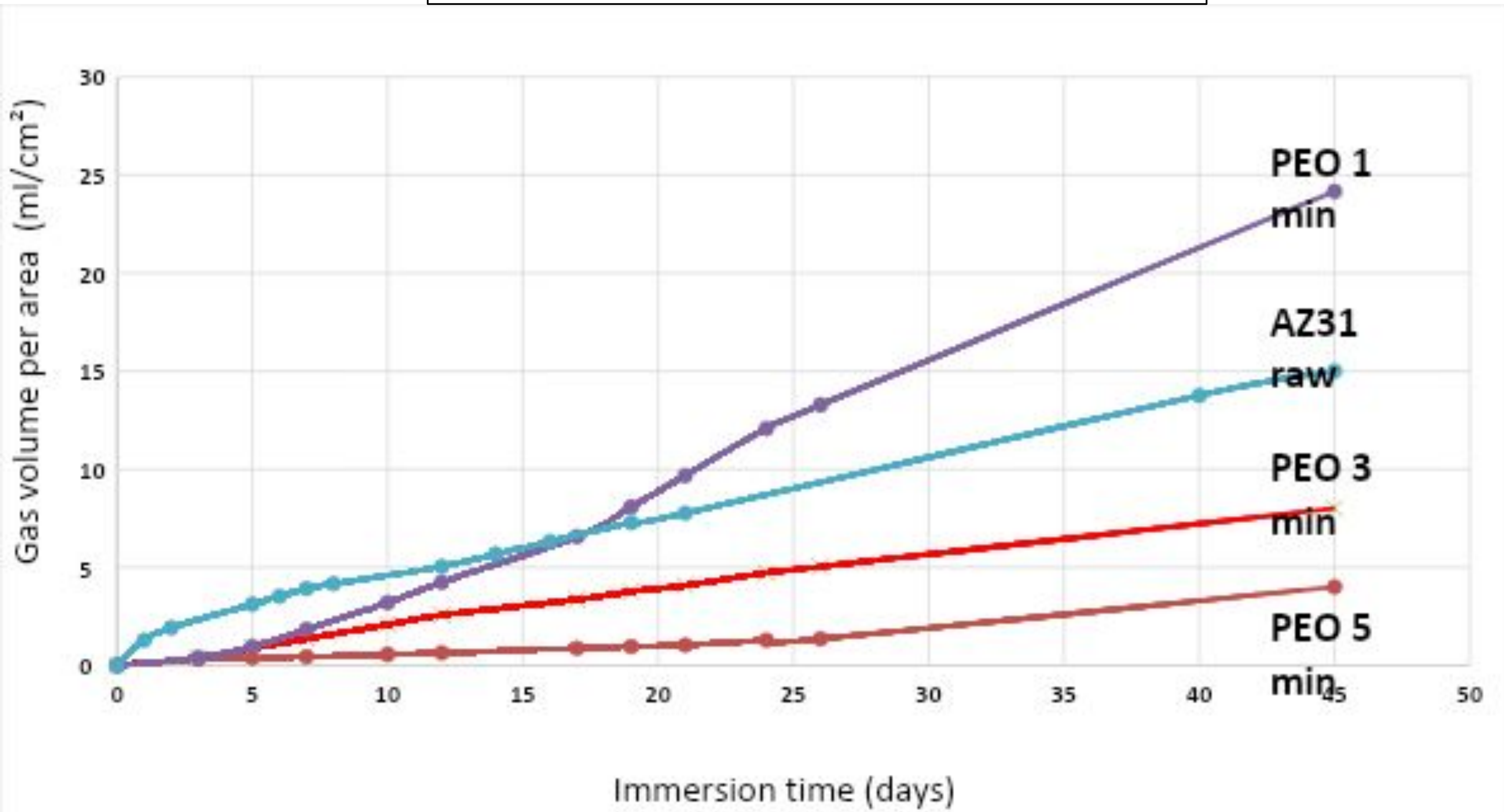


Corrosion starts at the points of contact with the sample holder

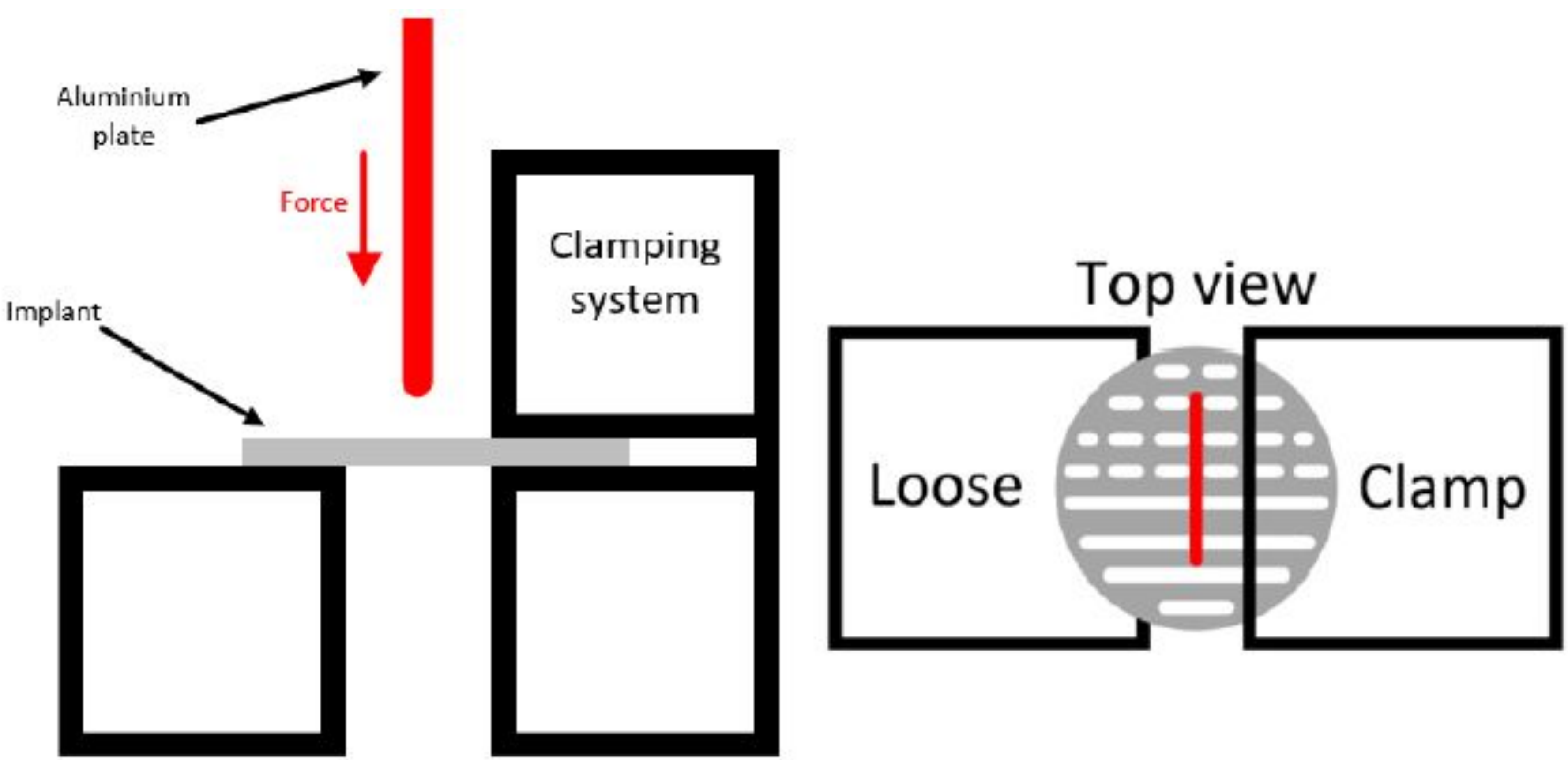
# Hydrogen gas release

**PEO parameters:**

- J=32 A/dm$^2$
- **Time: 1, 3, 5 min**
- Layer thickness: 2, 4, 10 µm

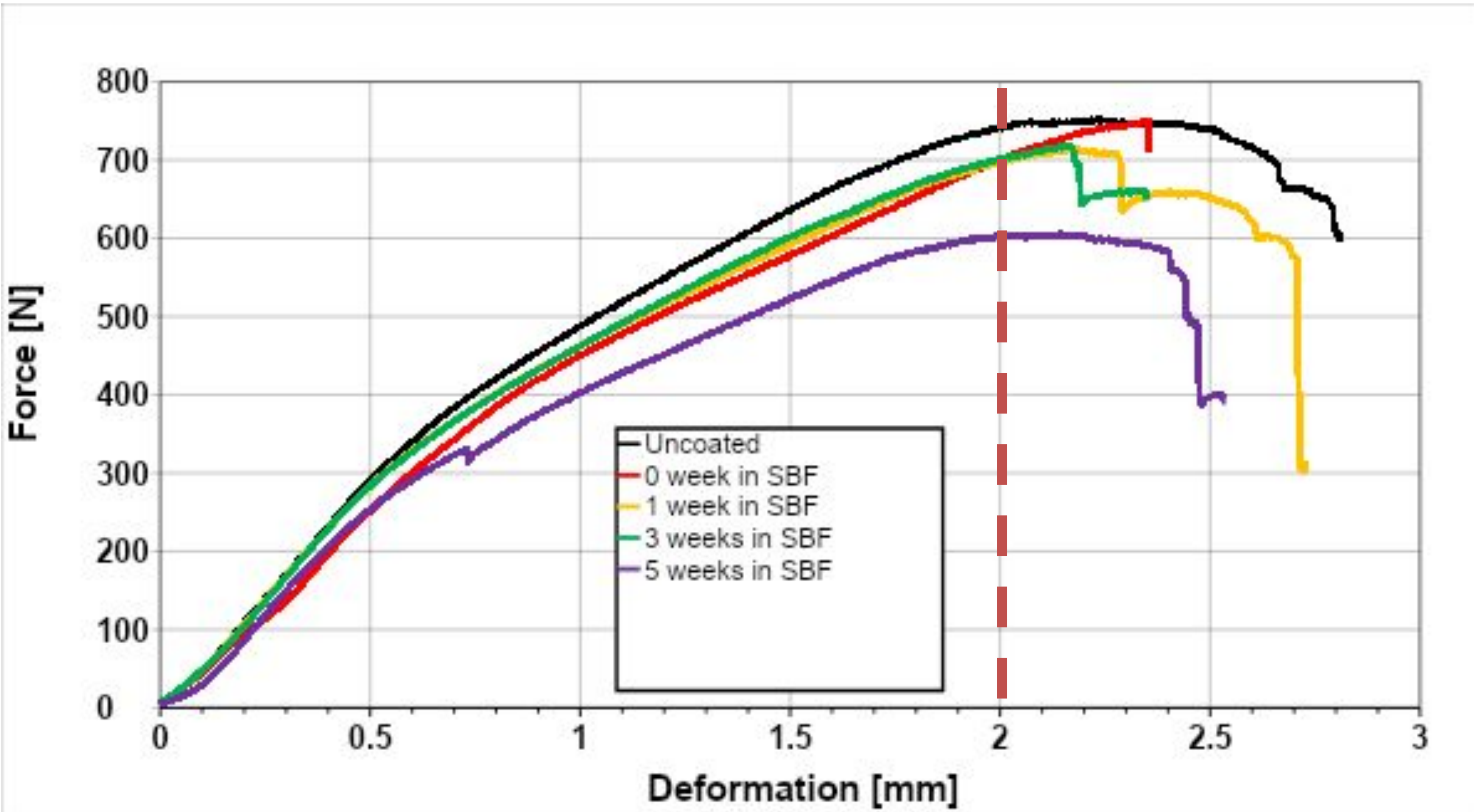


# Mechanical bending test



# Mechanical bending test results

- **No PEO :** the force (F) to bend implants 2mm **F = 740 N**
- **PEO** (5 min, J=32 A/dm$^2$) + **immersion** in SBF for **0-3 weeks** **F = 700 N**
- **PEO** + **immersion** in SBF for **5 weeks** **F = 600 N**



# Conclusions & Perspectives

- ✔ Layer thickness increases with current density (***J***) and treatment time.
- ✔ Current density (***J***) does not have much influence on the corrosion resistance. Corrosion spots occur randomly. Sharp edges and contact points with the sample holder are critical for corosion
- ✔ Gas release from the implants anodized 5 min and immersed in SBF is low and predictable (at least for 5 weeks). Treatment time allows to control the corrosion rate.
- ✔ PEO-implants immersed in SBF possess good mechanical resistance, at least up to 5 weeks
- ✔ PEO is a fast and efficient method to control corrosion rate of the AZ31 implants
- ✔ **Clinical studies are necessary to validate the use of AZ31 in veterinary implants**

# The END

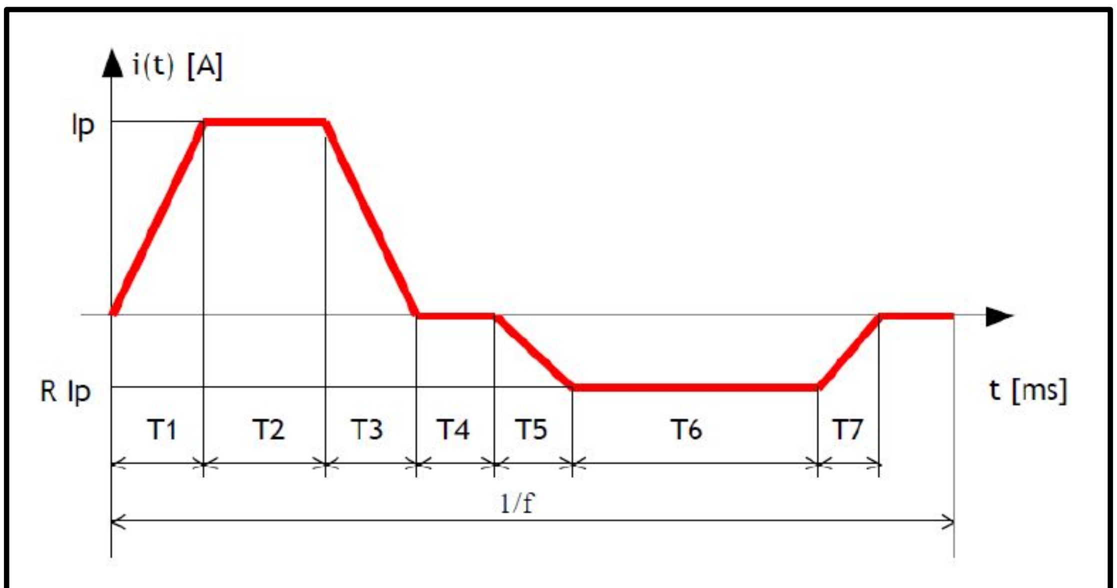
# PEO process parameters

**PEO Experiments:**

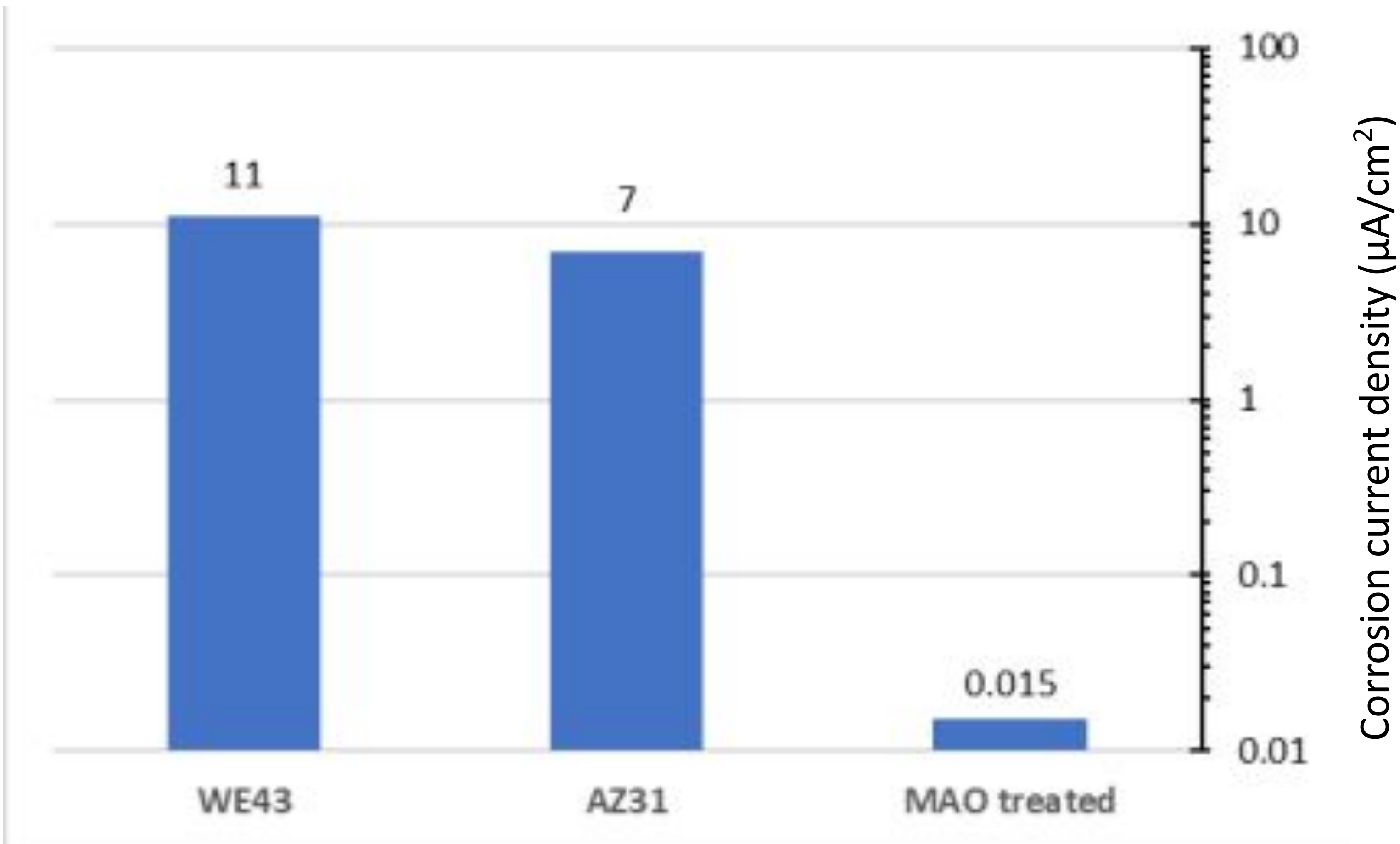
- CIRTEM® bipolar pulsed current source
  - Current density **24-64 A/dm²**
  - Maximum voltage 560 V
  - Frequency 500 Hz
  - Anode-cathode distance 18.5 cm
  - Treatment time 5 min

**Electrolyte composition:**

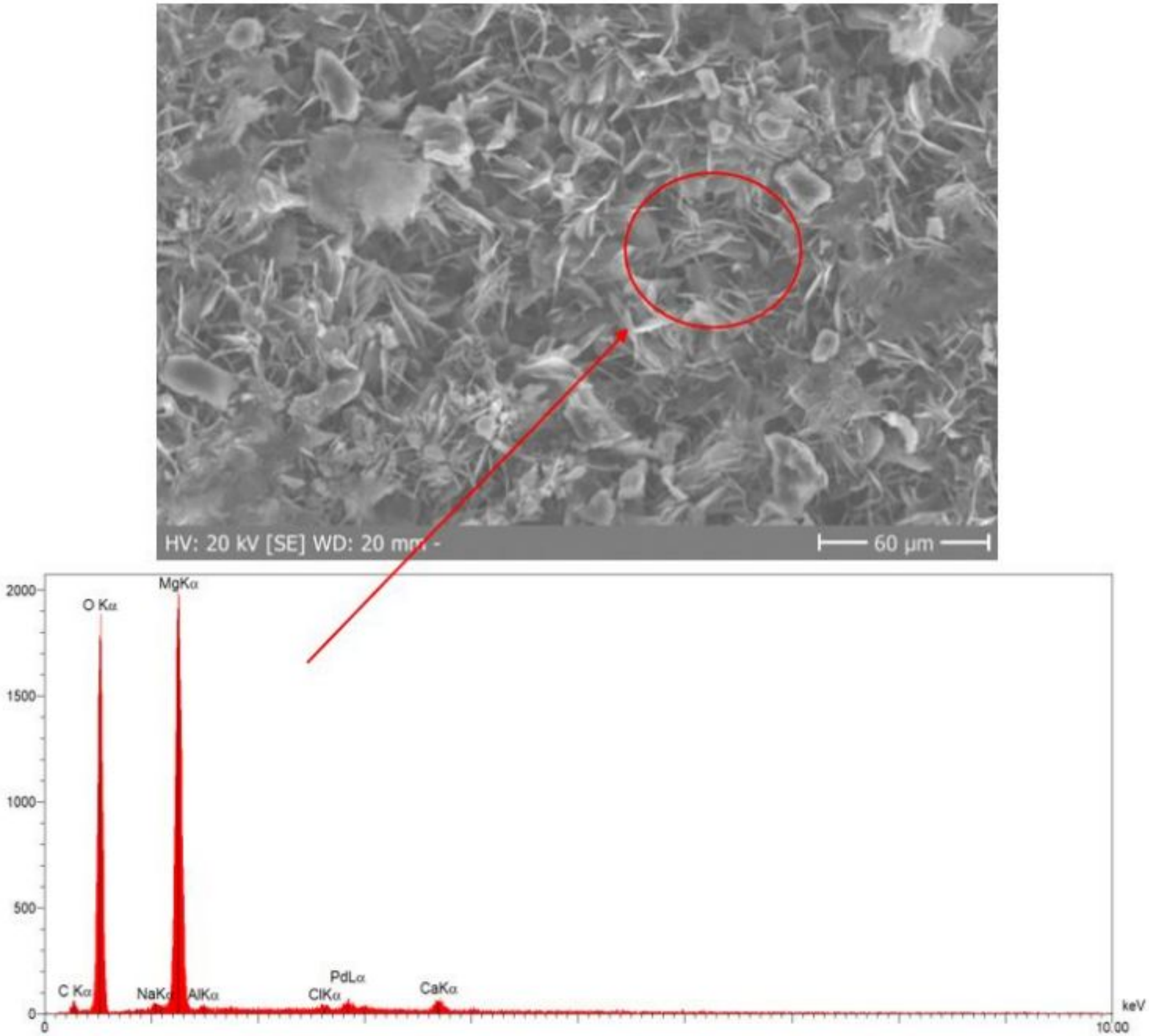
- Deionised water
- 2.8 g/l NaOH
- 7.5 ml/l of $Na_2SiO_3$
  - pH=12.5
  - Conductivity 8-13 mS/cm



# Corrosion current comparison



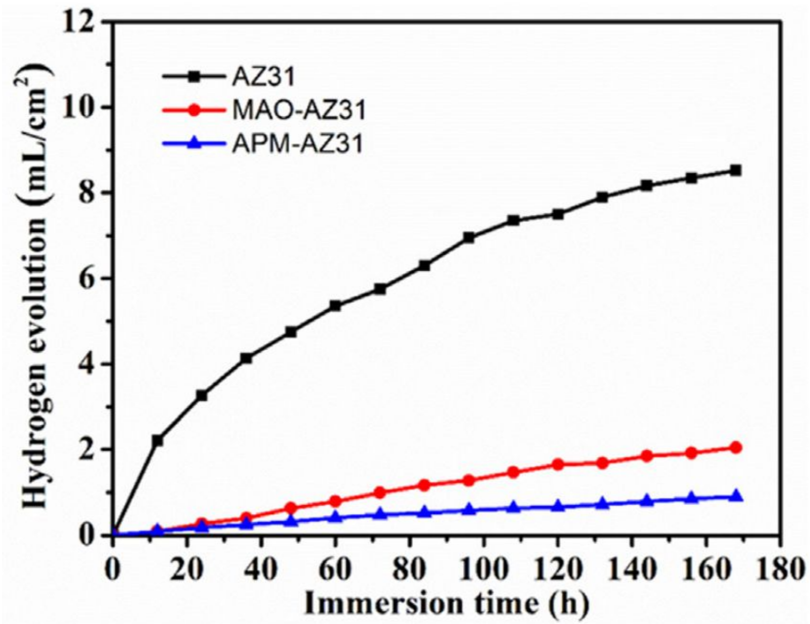
# Surface SEM-EDX analysis (after immersion in SBF)



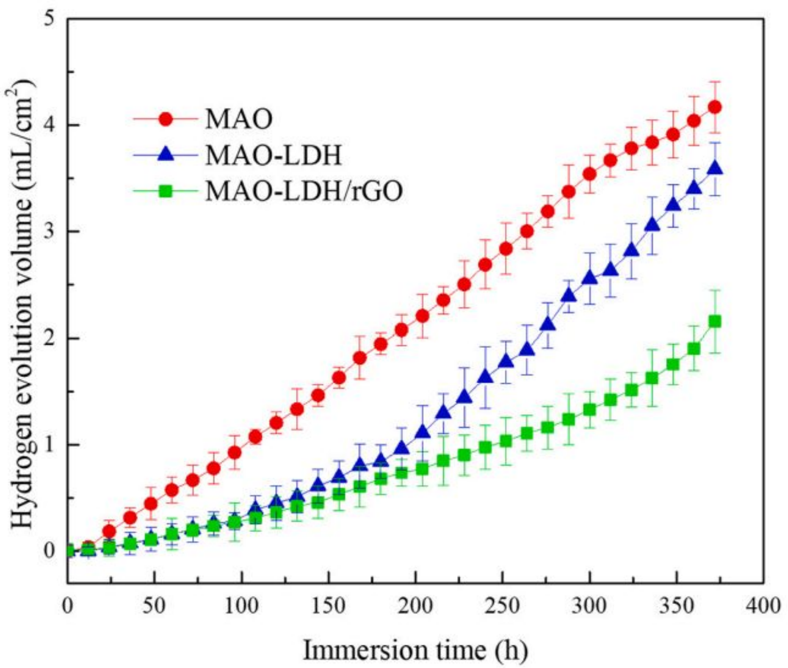
# Hydrogen gas release test

Implants immersed in SBF (Ringer's solution) @37°C up to 45 days

# Hydrogen gas release results (literature data)




Hydrogen evolution vs. immersion time for AZ31 and MAO-AZ31 (red) in PBS at 37° C.




AZ31 immersion in 3.5 wt% NaCl solution


X.Wang et al, « Enhanced anticorrosive and antibacterial performances of silver nanoparticles/ polyethyleneimine/MAO composite coating on magnesium alloys», Journal of Materials Research and Technology, Vol. 11, March–April 2021, pp 2354-2364

V. Zahedi Asl et al. « Corrosion properties and surface free energy of the Zn–Al LDH/rGO coating on MAO pretreated AZ31 magnesium alloy » Surface & Coatings Technology 426 (2021) 127764