Biodegradable Mg implants: how to improve the surface properties?

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Due to their ability to be resorbed in the human body, Mg-based implants are classified as biodegradable. To provide mechanical integrity in the body over several months, the corrosion process of an implant must be precisely controlled. Rapid implant corrosion, especially at the early stages of implantation, involves a significant risk for the patient. Plasma Electrolytic Oxidation (PEO) surface treatment has been proven an efficient method for corrosion protection of Mg alloys. We showed that PEO significantly improves the corrosion resistance of AZ31 alloy. Different post-treatments (ALD, dip-coating) further enhance corrosion resistance of the alloy as well as its biological response. They can be considered in the fabrication chain of future resorbable implants.

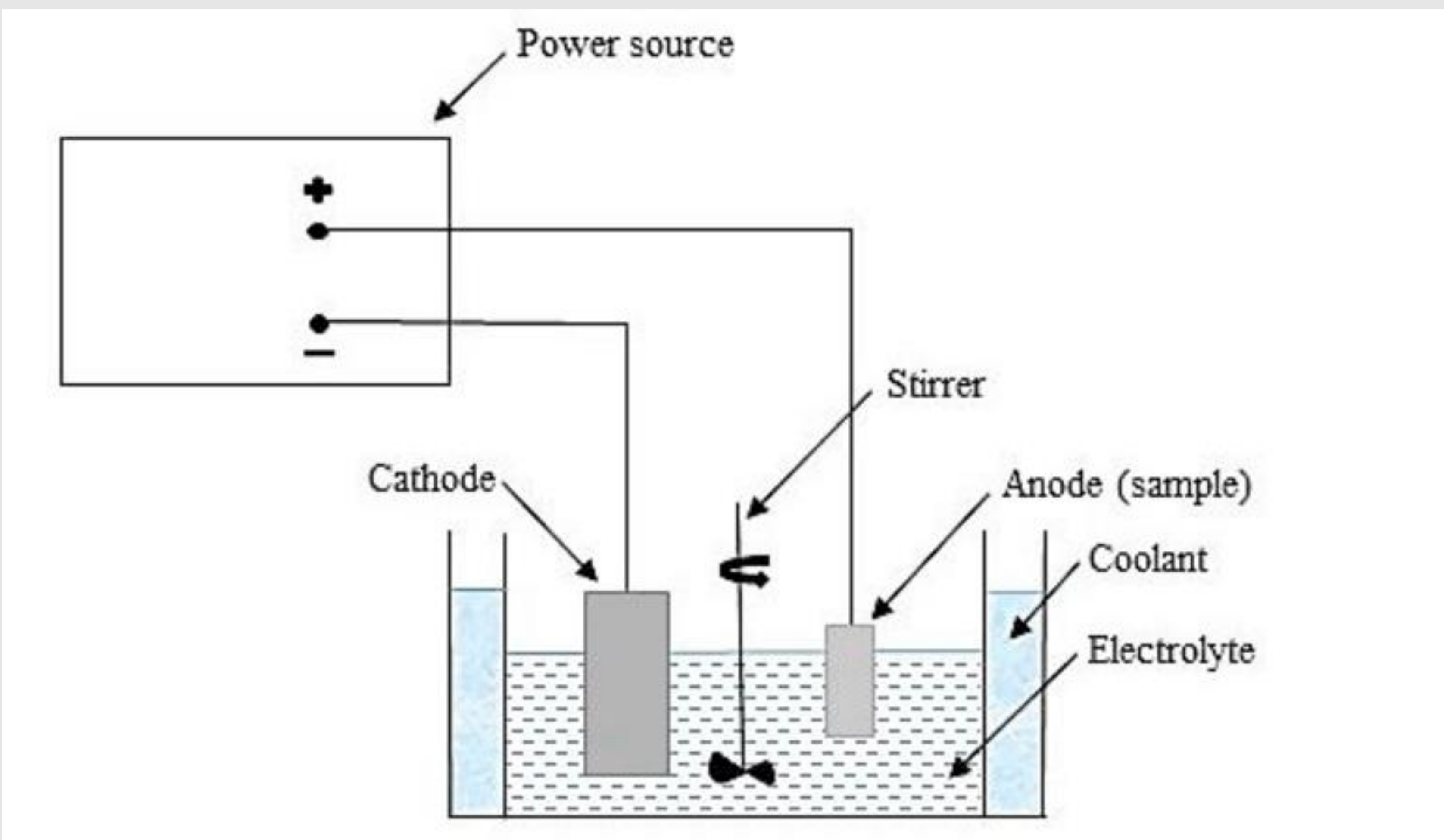
METHODS

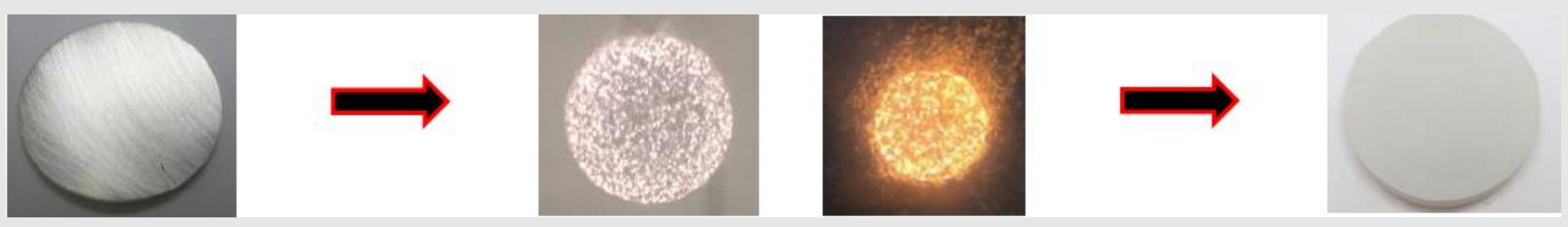
- Polished AZ31 discs (25 mm diam.) were anodized by PEO using a CIRTEM® bipolar pulsed current source (f=100 Hz; J+ varies from 30 to 70 A/dm^2, J- varies from 0 to 30 A/dm^2). Treatment time was 5 min
- The electrolyte contained 4g/l NaOH and 6.3g/l calcium glycerophosphate (pH=12.5) was used
- 2 post-treatments were performed after PEO:

1) 50nm thick TiO_2 layer was deposited by ALD
2) PLLA (poly-L-lactic acid) layer (10µm) was deposited by dip-coating

- The surface and cross-section morphology was examined by Scanning Electron Microscopy (SEM) and optical microscopy.
- Corrosion tests were performed by potentiometry. Hydrogen gas evolution was measured by immersing the samples in HCl (0.25M) solution.
- Biological assays with mouse fibroblast L929 cells were performed on the treated samples in order to assess their biocompatibility. L929 cells were grown in contact with samples extracts, degraded during 24 and 72 hours in DMEM/F12 medium supplemented with 10% FCS and 1% PenStrep. WST-8 proliferation assays were used to assess cell viability in presence and absence of the coated sample extracts. Cell viability in absence of the sample was taken as 100% viability.

PLASMA ELECTROLYTIC OXIDATION PROCESS





AZ31 polished disc | Plasma envelope & micro-arc occurrence during PEO process | PEO anodized disc

RESULTS

- PEO treatment resulted in 15 to 20 µm- thick conversion layers
- The surface of PEO-treated AZ31 samples shows typical crater-like morphology, the pore-size is influenced by the process parameters (i.e. anodic current intensity, I_+), Fig. 1
- Immersion test in simulated body fluid (SBF) shows that PEO treatment largely enhances the corrosion resistance of AZ31 (Fig. 2). However, sharp edges are more sensitive to corrosion

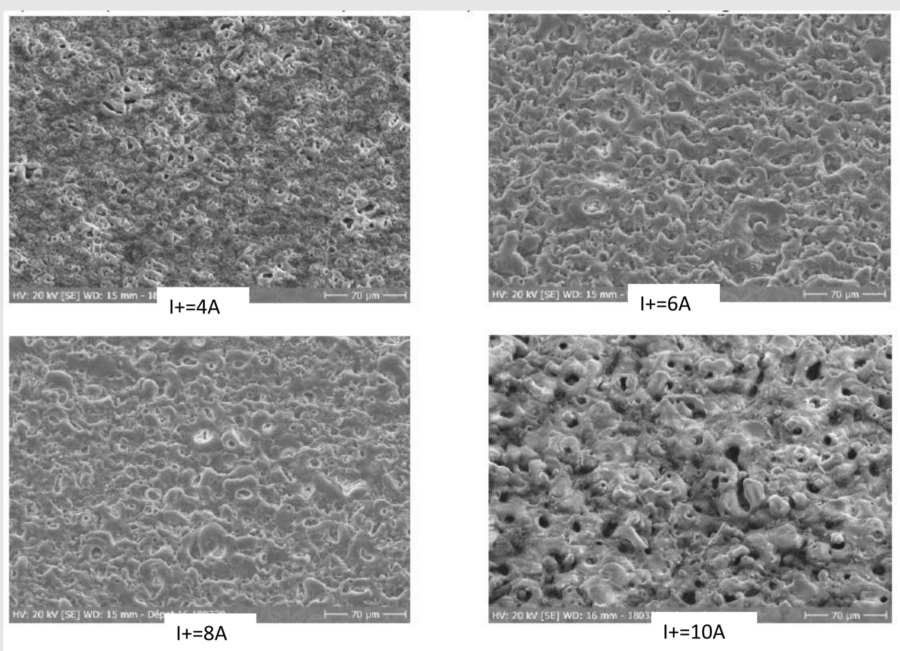


Figure 1. SEM micrographs of the surface of 4 PEO-treated AZ31 (obtained at different values of I+)

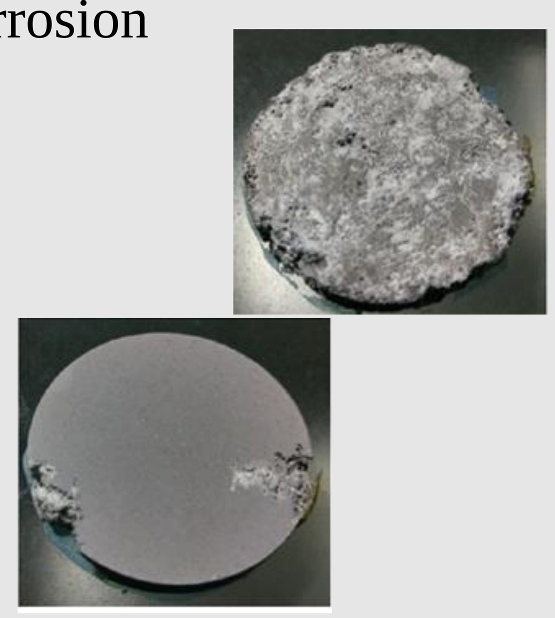


Figure 2. AZ31 untreated (top) and PEO-treated (bottom) samples immersed in SBF for 3 weeks at 37°C

- A TiO_2 50 nm-thin ALD coating homogeneously covers the surface of a PEO layer, even inside the pores (Fig. 3). ALD can be used as an efficient sealing post-treatment

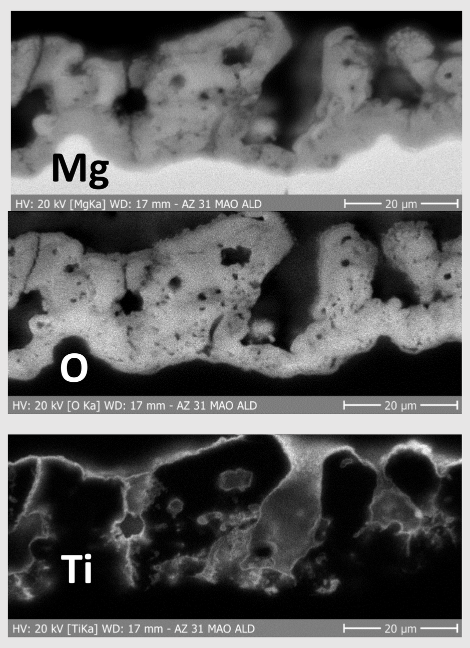


Figure 3. SEM-EDX carthography of the PEO-treated AZ31 post-treated by ALD (50 nm TiO_2)

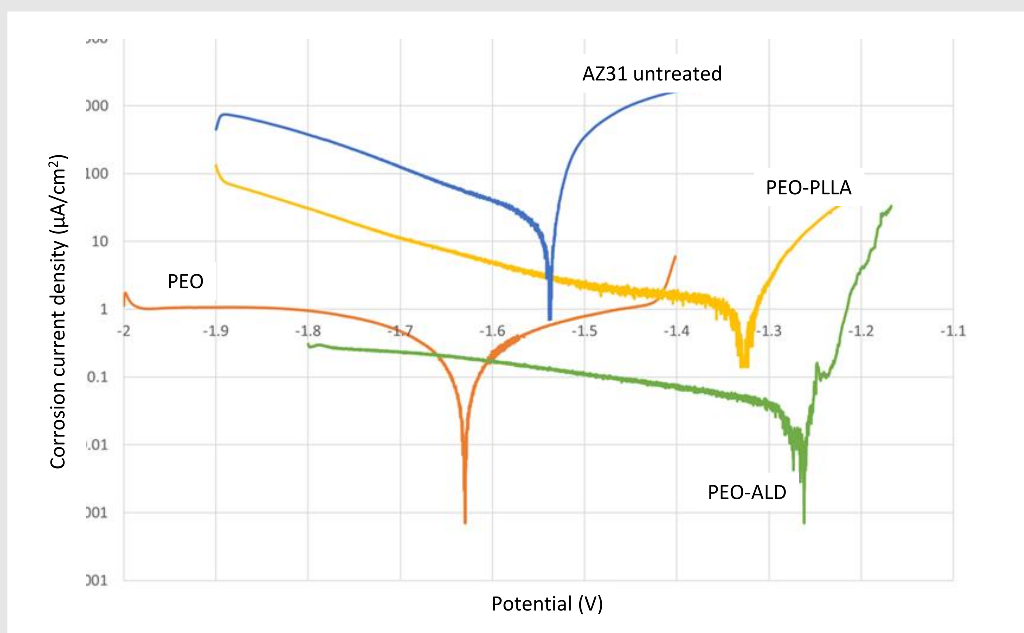


Figure 4. Potentiodynamic corrosion curves of untreated AZ31 alloy, PEO teated; PEO-treated and post-coated by ALD (50 nm TiO_2), PEO-treated and post-coated by PLLA by dip-coating

- Biological tests indicated a poor cell viability for PEO-treated AZ31. The cell viability increased significantly (> 80% vs. ref.) after ALD post-treatment (Fig. 5).

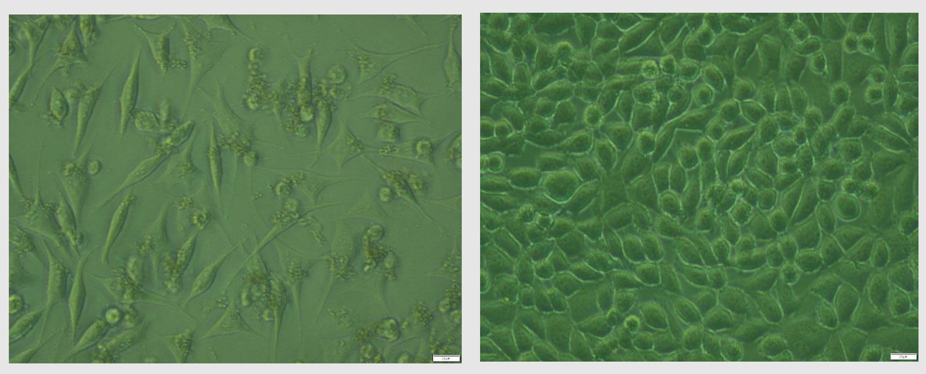


Figure 5. Optical microscopy images (200x) of L929 cells exposed during 24h to the PEO-treated AZ31 sample (left) and PEO-ALD –treated sample (right)

CONCLUSIONS

- PEO is a suitable surface treatment enhancing the corrosion resistance of Mg-based alloys. However, open pores in the PEO layer are problematic as they could be the origin of Mg^{2+} ion release from the substrate, resulting in a pH increase in the surrounded area and, thus, poor biological response.
- Post-treatments (TiO_2 by ALD, PLLA dip-coating) can further improve the corrosion resistance of the PEO-treated Mg alloys. They are necessary to obtain favorable in-vitro biological response.

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