Spatially Resolved Local *In Operando* Techniques Visualize the Interface of Biodegradable Metals

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Abstract The degradation of biodegradable metals typically initiates locally and evolves variably, which is difficult to be captured by general experimental methods. The advancement of spatially resolved local in operando techniques enables a powerful in situ approach to study the degradation mechanism of biodegradable metals at the metal interface, especially following the evolution of interfacial pH and O_2 concentration, which are substantial factors during the metal biodegradation. The degradation behavior of biodegradable Mg, Zn, and Fe alloys are systematically characterized by spatially resolved local techniques that measure local pH, O_2 levels, and H_2 concentration at the metal interface. The local pH indicates anodic/cathodic process and formation of pH-dependent degradation products at metal interface. The local O_2/H_2 concentrations demonstrate typical cathodic reactions accompanying metal degradation, including hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR). The results reveal interfacial electrochemical processes of biodegradable Mg, Zn, and Fe alloys. Counterintuitively, ORR, a secondary cathodic process for Mg, contributes higher to the corrosion of slowly degrading ultra-high-purity Mg (16.5%) than in fast corroding commercially-pure-Mg (1.3%). The dissolution of Mg typically induces high local pH (10.4-10.6 in NaCl), which yet gets relatively low and stable (7.5-8.0) in Ca^{2+}-containing Hanks' balanced salt solution (HBSS, pH=7.4) without synthesis pH buffers at 37 °C under hydrodynamic conditions. In contrast, Zn and Fe alloys experience significant O_2 consumption and localized acidification because dissolved metal cations hydrolyze in HBSS at 37 °C. The interfacial pH variation is buffered in Ca^{2+}-containing HBSS due to Ca-P-containing precipitates. The addition of synthetic pH buffers stabilizes the interfacial pH for Zn alloys but not for Mg. The Ca-P-containing products layer protects Mg, Zn, and Fe alloys from water and oxygen in Ca^{2+}-containing HBSS, slowing ORR as the layer densify. These findings

emphasize the importance of understanding the interactions at metal-fluid interface during metal biodegradation.

Keywords Local in operando techniques; Interfacial pH; Local oxygen consumption; Local hydrogen evolution; Biodegradable metals;

Reference

[1] Cheng Wang, Ci Song, Di Mei, Linqian Wang, Wenhui Wang, Ting Wu, Darya Snihirova, Mikhail L Zheludkevich, Sviatlana V Lamaka. Low interfacial pH discloses the favorable biodegradability of several Mg alloys [J]. Corrosion Science, 2022, 197: 110059.

[2] Cheng Wang, Xiao Liu, Di Mei, Min Deng, Yufeng Zheng, Mikhail L Zheludkevich, Sviatlana V Lamaka. Local pH and oxygen concentration at the interface of Zn alloys in Tris-HCl or HEPES buffered Hanks' balanced salt solution [J]. Corrosion Science, 2022, 197: 110061.

[3] Cheng Wang, Christabelle Tonna, Di Mei, Joseph Buhagiar, Mikhail L Zheludkevich, Sviatlana V Lamaka. Biodegradation behaviour of Fe-based alloys in Hanks' Balanced Salt Solutions: Part II. The evolution of local pH and dissolved oxygen concentration at metal interface [J]. Bioactive materials, 2022, 7: 412-25.