Electrochemical Methods for Corrosion Behavior Characterization

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Introduction
- Corrosion and implant failure
- Electrochemistry and implant surfaces

Electrochemical potentiodynamic polarisation
- Macroscale characterization of Ti alloys
- Local electrochemistry by Microcapillary cell techniques

Electrochemical Impedance Spectroscopy
- Measurement principle
- Characterization of biodegradable Metallic Mg implants

Crevice and galvanic corrosion investigation
- Static and dynamic electrochemical setups
- Example of Stainless Steel and Co-Cr-Mo alloys

Conclusions
Acknowledgments

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Laboratory for Corrosion and Materials Integrity
P. Schmutz

Physico-chemistry of reactive metal surface
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Ti alloys
- Corrosion resistant
- Other problems related to fatigue or fretting

Stainless Steel Co – Cr based alloys
- Pitting corrosion
- Crevice corrosion
- Galvanic corrosion

Mg alloys
- Biodegradable

In Vitro testing of corrosion processes

Decreasing dependence on testing media

Increasing corrosion resistance

Choice of testing solution chemistry

Less relevant

P. Schmutz et al., Interface, 17(2), 35-40 (2008)
Cook S.D., et al., The in vivo performances of 250 internal fixation devices: a follow-up study. *Biomaterial, 1987, 8; p. 177*

**Crevice corrosion:**
- 90% of the plates and screws (26 months average)
Accelerate the corrosion process by using more aggressive media is an alternative but not always possible.

Electrochemical methods are a good alternative:
- Very small currents can be measured
- It allows earlier detection of on-going degradation processes
- Corrosion rates are directly linked to electrical charge flow

There is a very broad range of different information can be gained.
Surface processes and electrochemistry on implants

**Oxidation and Corrosion**

**Macroscale methods:**
- Open Circuit Potential
- Potentiodynamic polarization

**Micro- and Nanocapillaries:**
- Local measurements
- Solution analytics

**Dedicated artificial crevice setups:**
- Galvanic coupling
- Mechanical sollication

**Electrochemical Impedance Spectroscopy (EIS)**

**Dedicated artificial crevice setups:**

**Electrochemical surface modifications:**
- Anodizing
- Electropolishing

Thick anodic oxide on Mg
Principle of microcapillary cell

Full local electrochemical control for heterogeneous materials characterization

Setup designed by Dr. Thomas Suter at the Institute for Material Chemistry and Corrosion, ETH Zurich.
Localized corrosion characterization

Stainless Steel : 18Cr/10Ni

Electrochemical polarization measurements

Stainless Steel implants

- Plastically deformed and scratched areas are very susceptible to localized corrosion
Ti alloys and electrochemical Polarization

International standard
ISO 10271:2001 (Dental Implants)

Lactic acid solution (pH 2.2)
5.85 g/l NaCl + 10 g/l C₃H₆O₃

Ti grade 4 + transfer piece: Ti₆Al₇Nb

Ti and Ti alloys
- No corrosive attack under static conditions
- Some ionic release detected by ICP-MS
**EIS: Electrochemical Impedance Spectroscopy**

**Measurement at corrosion potential**

Voltage perturbation (10 mV) is applied

- The current response in function of frequency is measured

Ohm’s law gives a simple relation

\[ U = I \times R \]

When AC signal are applied, the relation is

\[ E_{ac} = I_{ac} \times Z \quad Z: \text{impedance} \]

**Simple model**

- for electrochemical Interface

\[ R_p \]

\[ R_s \]

\[ C \]

- For Mg: \( R_p = 1000 \ \text{Ohm/cm}^2 \)

- Corrosion rate \( \sim 220 \ \mu\text{m/year} \)
EIS: data representation

**Nyquist plot**

- Imaginary vs. Real component

**Bode plot**

- Frequency dependent representation
Magnesium is not only biocompatible... It is an important element in hundreds of metabolic processes. Suggested daily ratio: 350 mg/day

Mg-Y-Re alloys are preferred to AZ91/AZ71.

A defined degradation sequence during the first 3-6 months is aimed at balancing the pH of blood.
Experimental strategy: alloys and solutions

- 3 alloys with systematic variation of Y, Zn for screening experiments

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg</th>
<th>Zn</th>
<th>Y</th>
<th>RE</th>
<th>Zr</th>
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<tbody>
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<td>WE43</td>
<td>Bal.</td>
<td></td>
<td>4.0</td>
<td>3.5</td>
<td>0.5</td>
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</tbody>
</table>

- Detailed description of WE43 dissolution

Solutions considered:

- SBF 27 as base (concentration in mmol/l)

  100.0 NaCl, 4.0 KCl, 27.0 NaHCO$_3$, 1.0 MgSO$_4$ * 7H$_2$O, 2.5 CaCl$_2$ * 2H$_2$O, 1.0 KH$_2$PO$_4$, TRİS Buffer (pH 7.4)

- Matrix of solutions with combination of ionic species
Immediate immersion of WE43 in SBF 27 with and without buffer agent

- Distinction between uniform or localized corrosion
- Double layer / surface oxide dielectric properties
- Diffusion and adsorption processes can be monitored at low frequency

Frequency resolved electrochemical impedance measurements allows to characterize reaction mechanisms.

- Increased pH
- Localized attack - fast process
- Uniform corrosion - slower

EIS: a kind of spectroscopic method
Inductive effects (3) related to ionic adsorption from solution

- Adsorption and Integration of ionic species (inductive effects) can be distinguished from purely growth of hydroxides as a function of time.
Nature of corrosion products: from ZW21 to WE43

NaCl, Tris

Transition from porous non protecting to more compact corrosion products

Important influence of Yttrium

Full SBF

WE43 3000

WZ21 1000

ZW21 220

No significant changes in the nature of the corrosion products
Defective coating model (applicable to other coatings like DLC)

- % of open pores can be determined
- Initial stage of degradation can be followed as function of time

Osteosynthesis application: Thick porous Mg-hydroxides

Electrochemical Impedance Spectroscopy

- Intact coating
- Time dependant
- Solution contact to metal through pores

Corrosion rate

\[ \text{log}(Z) \text{ vs. log}(f) \]

- Inert
- Oxide
- Alloy

Implantation time

- T1
- T2
- T3
Corrosion of metallic implant materials

- Stainless steel (SS) is very susceptible to crevice corrosion problems

- Cobalt Chromium Molybdenum (CCM) is more corrosion resistant but can release "toxic" ionic species when depassivated

  **FDA concern issued February 2011**

- Titanium Aluminum Niobium alloys show very stable passivation but are prone to fatigue-corrosion problems, inducing rapid breaking of the implant.

- Besides, the intrinsic corrosion problems, dissimilar materials will add the problem of galvanic coupling
Crevice corrosion and galvanic coupling

Investigation procedure is divided into:
- Static tests
- Dynamic tests
FIB cuts: It seems that the first 50 nm above the TiAlV are more or less totally corroded away (not a crack growth)

Si interlayer is very susceptible to crevice corrosion in-vivo

101 patients DLC/PE
101 patients Al₂O₃/PE
8.5 year follow-up
50% of DLC/PE failed
Crevice corrosion and galvanic coupling

Aeration cell:

stabilize the anodic reaction in the crevice ( < 100 µm)

All the potential and the currents flowing between electrodes can be measured

Additional passive panels to increase differential aeration

Passive or grinded sample in the crevice
Electrochemical potentials of CCM and SS

Stainless Steel: Cr 17% - Ni 13% - Mo 2.5% - Mn 2% - Fe Bal
CCM: Co 66% - Cr 28% - Mo 6%

- There is a risk of galvanic incompatibility between SS and CCM especially in case of damaged surfaces

**Lactic acid solution pH2**

9 g/l NaCl, 0.4 g/l KCl, 0.5g/l CaCl₂, 0.2g/l NaHCO₃

**Ringer’s solutions pH8**
Crevice corrosion has been monitored in lactic acid condition and a significant current measured for the coupling SS-SS.

It takes 8 days for localized corrosion to take place and then the current is progressively increasing.

In Ringer’s solution, the environment is too mild to initiate an attack in a reasonable time.
CCM fully repassivates very fast at low pH (dominating influence of chromium)

SS is unable to repassivate in crevice conditions

The introduction of CCM in the combination SS-SS increase the risk of crevice corrosion for the steel
In vivo degradation of CoCrMo hip implants

Study under dynamic conditions:

According to ASTM-F75-92

Total Hip Replacement (THR) in 12 sheep; Euthanasia after 8.5 months

- S. Virtanen, A. Hogson (ETHZ)
- B. von Rechenberg, Tierspital Zürich
- S. Mischler (EPFL)

CCM (66% / 28% / 6%)

- Clinical Analysis
- Corrosion
- Wear
Dissolution processes studied by ICP-MS

Characterization methods

Static immersion

or

Online Microcapillary flow system coupled to ICP-MS Spectrometer

CCM (66% / 28% / 6%)

Extremely high dissolved ions concentration is found in the tissues next to the implant when micro-motion is present!
Macro- and microelectrochemical polarization allow to characterize the intrinsic corrosion resistance of materials in aggressive media. The method is ideal in relation with materials development (structure, defects).

Electrochemical Impedance Spectroscopy is the preferred method for a detailed investigation of complex corrosion processes at the OCP. The frequency dependent “spectroscopic information allow to track different corrosion processes (localized, uniform) occurring in parallel on surfaces and coatings.

Electrochemical crevice and galvanic coupling setups are necessary to simulate the aggressive local chemistry that is responsible for most of the implant failures.

Dynamic characterization in crevice and galvanic conditions will be the most relevant electrochemical tests in the case of Ti alloys that are highly corrosion resistant in static conditions (not shown in the webversion).

Leaching of metallic ions that can be investigated by ICP methods is a corrosion related aspect that should not be neglected.