Lecture 3: Biomaterials Surfaces: Chemistry

Surfaces are high-energy regions of materials and thereby facilitate chemical reactions that influence performance of biomaterials.

This lecture will focus on 2 classes of surface chemistry relevant to biomaterials:

- Chemisorption on metals and oxides
- Aqueous corrosion of metals

1. Chemisorption

Strong modifications to electronic structure/ electron density of adsorbate molecule (> 0.5 eV/surface site)

Important Examples:

a) Metal Oxide Formation on Metals
   “metals just wanna be oxides” \( xM + \frac{1}{2}yO_2 \rightarrow M_xO_y \)

\( \Delta G^0 \) of oxide formation is negative for all but a few metals (e.g., Au)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta G^0 ) (joules)</th>
<th>T range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2Cr + 3/2 O_2 = Cr_2O_3 )</td>
<td>-1,120,300 + 260T</td>
<td>298-2100</td>
</tr>
<tr>
<td>( Fe + \frac{1}{2} O_2 = FeO )</td>
<td>-259,600 + 62.55T</td>
<td>298-1642</td>
</tr>
<tr>
<td>( 2Fe + 3/2 O_2 = Fe_2O_3 )</td>
<td>-810,520 + 254.0T</td>
<td>298-1460</td>
</tr>
<tr>
<td>( Ti + O_2 = TiO_2 )</td>
<td>-910,000 + 173T</td>
<td>298-2080</td>
</tr>
</tbody>
</table>

How does metal oxidation happen?

One scenario is…

**step 1:** physisorption of O$_2$; ~20-25 kJ/mol

$$1 \text{ eV/molec} = 96.5 \text{ kJ/mol}$$

$$kT_{293} \approx 0.025 \text{ eV}$$

**step 2:** molecular oxygen dissociates and reduces by chemisorption; ~600 kJ/mol

**step 3:** bond rearrangement; crystallization of oxide layer

Resultant reduction in surface energy

Compare: at 1400°C: $\gamma_{\text{δ-Fe}} = 1900 \text{ dyn/cm}$

$\gamma_{\text{FeO}} = 580 \text{ dyn/cm}$

Consider metal oxidation as 2 half reactions:

$$\text{O}_2 + ze^- \rightarrow \frac{1}{2}z \text{O}^{2-}$$

$$M \rightarrow M^{z+} + ze^-$$

Electrons and ions **must traverse the oxide layer** for rxn to proceed.

Across the oxide film, an oxidation potential, $E^0 \sim 1\text{V}$ generates an electric field:

$$\Delta G^0 = -E^0 zF$$

$F= 96,480 \text{ C/mol e}^-$

$1 \text{ J} = 1 \text{ V-C}$

**WHAT HAPPENS AS THE OXIDE CONTINUES TO GROW?**

$$E-\text{Field} \approx 1 \text{ V/nm} = 10 \text{ MV/cm}$$

Ionic species are “pulled” through oxide film!
The E-field decreases. Subsequent oxide growth occurs by thermal diffusion of $M^{z+}$ to oxide surface or $O^{2-}$ to metal/oxide interface under the concentration gradient $\Delta c$:

\[ l^2 = k_p t \]

**Requirements for Passivation:**

i) small $k_p$ (rate const)

\[ k_p = \text{const} \ D \ \Delta c \]

ii) adherent oxide

Oxide layer must not scale or spall

\[ \Rightarrow \text{minimize } \Delta V_{\text{molar}} \text{ & stress build-up} \]

\[ xM + \frac{1}{2}yO_2 \rightarrow M_xO_y \]

ex., Ti ($\text{TiO}_2$), Cr ($\text{Cr}_2\text{O}_3$), Al ($\text{Al}_2\text{O}_3$)

(Al metal not used in biomaterials applications due to toxicity)

Pilling-Bedworth ratio:

\[ PB = \frac{V_{\text{oxide(formed)}}}{V_{\text{metal(consumed)}}} = \frac{\rho_M M_{M_xO_y}}{xM \rho_{M_xO_y}} \]

Want $PB \sim 1$ ($PB > 1$) for adherance of oxide to underlying metal—in practice, this rule is marginally predictive, however.
Other Metal Oxidation Rxns by Chemisorption:

*Reaction with water:* \( xM + yH_2O \rightarrow M_{xOy} + yH_2 \)

*Reaction with CO\(_2\):* \( xM + yCO_2 \rightarrow M_{xOy} + yCO \)

IS THE FORMED METAL OXIDE SURFACE STABLE?

b) Acid/Base (Acceptor/Donor) Rxns on Oxides

i) **H\(_2\)O\(_{adsorbed}\) + O\(^2-\)\(_{lattice}\) → OH\(^-\)\(_{lattice}\) + OH\(^-\)\(_{surface}\)**

Ubiquitous! e.g., oxides of Co, Ti, Cr, Fe, etc.

H\(_2\)O cleavage with H\(^+\) transfer to surface basic O\(^2-\) site & OH\(^-\) coordination with M\(^{2+}\)

M\(^{2+}\) acts as Lewis acid (e\(^-\) pair acceptor) for oxygen lone pairs
ii) \( \text{CO}_2_{\text{adsorbed}} + \text{O}^{2-}_{\text{lattice}} \rightarrow \text{CO}_3^{2-} \) (carbonate formation)

Experimentally seen, e.g., on \( \text{TiO}_2 \) (110)

iii) w/ Hydrocarbons:

Alcohols (similar to HOH): \( \text{ROH}_{\text{adsorbed}} + \text{O}^{2-}_{\text{lattice}} \rightarrow \text{RO}^- + \text{OH}^- \)

Carboxylic Acids: \( \text{RCOOH}_{\text{adsorbed}} + \text{O}_2^-_{\text{lattice}} \rightarrow \text{RCOO}^- + \text{OH}^- \)

c) Redox (Oxidation/Reduction) Reactions on Oxides

Example

Alcohol dehydrogenation to aldehyde:

\[
\text{RCH}_2\text{OH} + 2\text{O}^{2-} \rightarrow \text{RCH} + 2\text{OH}^- + 2\text{e}^- \\
\text{alcohol is oxidized} \quad \text{electrons reduce} \\
\text{M}^{2+} \text{at surface}
\]


2. Aqueous Corrosion of Metals

In water or in vivo, even a “passive” oxide layer (terminated by bound water) becomes susceptible to corrosion.

Why?

- $M^{z+}$ diffusion will always occur
- oxide may dissolve
- damage to oxide layer

**Corrosion:** the destructive result of chemical rxn between a metal or metal alloy and its environment.

**Aqueous corrosion:** involves electronic charge transfer

i.e., an electrochemical rxn

Typically, metal surface acts as both *anode* (oxidation=loss of $e^-$) & *cathode* (reduction=consumption of $e^-$) in different regions

anodic rxn: $M \rightarrow M^{z+} + ze^-$

cathodic rxns: $O_2$ (dissolved) + $4H^+ + 4e^- \rightarrow 2H_2O$

\[
\begin{align*}
2H^+ + 2e^- & \rightarrow H_2 \text{ (g)} \\
\end{align*}
\]

\[
\begin{align*}
O_2 \text{ (dissolved)} + 2H_2O + 4e^- & \rightarrow 4OH^- \\
2H_2O + 2e^- & \rightarrow H_2 \text{ (g)} + 2OH^- \\
\end{align*}
\]

in acidic

Locally, a biological environment can be neutral, acidic or basic.
Metals in aqueous solution

Metal ions leave surface; surface becomes negatively charged.

$M^{z+}$ are attracted back toward surface, establishing a dynamic equilibrium.

The resulting *charged double layer* exhibits a characteristic $E$.

Values of $E$ measured *relative* to a reference electrode (e.g., std. $H_2$ electrode = SHE), give metric of reactivity in aqueous soln.

on M electrode:

$$M \rightarrow M^{z+} + ze^-$$

on reference electrode:

$$H_2 \rightarrow 2H^+ + 2e^-$$
emf series  (Table 5, p. 432 of text)

Standard electrode potentials $E^0$ measured at unit activity (~1 N) of $M^{z+}$ ions in soln. with SHE ref.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Potential (V)</th>
</tr>
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<tbody>
<tr>
<td>Au</td>
<td>1.43</td>
</tr>
<tr>
<td>Pt</td>
<td>1.2</td>
</tr>
<tr>
<td>Ag</td>
<td>0.79</td>
</tr>
<tr>
<td>H</td>
<td>0.0</td>
</tr>
<tr>
<td>Sn</td>
<td>-0.14</td>
</tr>
<tr>
<td>Mo</td>
<td>-0.20</td>
</tr>
<tr>
<td>Co</td>
<td>-0.28</td>
</tr>
<tr>
<td>Fe</td>
<td>-0.44</td>
</tr>
<tr>
<td>Cr</td>
<td>-0.73</td>
</tr>
<tr>
<td>Al</td>
<td>-1.33</td>
</tr>
<tr>
<td>Ti</td>
<td>-1.63</td>
</tr>
<tr>
<td>Li</td>
<td>-3.05</td>
</tr>
</tbody>
</table>

If the activity of $M^{z+}$ is less than unity, the electrical potential across the metal/solution interface is modified according to the Nernst equation:

$$E = E^0 + \frac{RT}{zF} \ln \frac{a_{\text{oxidized species}}}{a_{\text{reduced species}}}$$

Equating activity to concentration:

$$a_{\text{oxidized species}} = [M^{z+}]$$

$$a_{\text{reduced species}} = [M] = 1$$

$$E(V) = E^0 + \frac{0.059}{z} \log[M^{z+}]$$

At this potential, the system is in dynamic equilibrium, i.e., equal metal dissolution and deposition rates (the exchange current density).
**A Simple Corrosion Rule:** anything that upsets the dynamic equilibrium of the charged double layer can accelerate corrosion.

**Galvanic Corrosion:** if 2 metals in contact where \(-E_A > -E_B\) (i.e., A more neg./anodic), B becomes an \(e^-\) “sink” ⇒ accelerating corrosion of A

![Diagram of Galvanic Corrosion](image)

The ↓ in \(e^-\) from A surface allows ↑ release of A\(^{z+}\)

Can be *macroscopic* scale or *microscopic* scale effect!

**Examples:**
- Plate & screw of different alloys
- Cr-depleted region at grain boundary (due to carbide formation)
- Formation of surface oxides or sulfides that conduct \(e^-\)
- Alloys exhibiting 2 phases
- Metal grains of different orientation

**Fretting Corrosion:** accelerated corrosion from two surfaces rubbing together

- metal/metal, metal/bone, metal/oxide contacts
- wear of passive oxide film
  - localized stress ⇒ ↑ \(M^{z+}\) dissolution
  - defects (terraces, steps): less bonds ⇒ ↑ \(M^{z+}\) dissolution
- repetitive movement ⇒ continual loss of corrosion products
Pitting and Crevice Corrosion: localized attacks resulting in rapid \( M^{z+} \) release at discrete sites

- initiated at local failure of passive film
  - *pitting*: surface defect; *crevice*: region of restricted transport
- remaining surface acts as cathode
  \[ \rightarrow \text{rapid penetration at defect (oxidation = reduction)} \]
- catalyzed by presence of \( \text{Cl}^- \)
- autocatalyzed by \( \uparrow \) acidity from rxn in confined volume

Photo removed for copyright reasons.


**Ex. Stainless steels in Aqueous Soln:**

For Cr contents below 12.5 at%: FeOOH resides at surface in hydrated form: \( \text{FeO}_x(\text{OH})_y \bullet n\text{H}_2\text{O} \) (iron oxyhydroxide hydrate)

In absence of \( \text{Cl}^- \), slow dissolution:

\[ \text{FeOOH} + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 3\text{OH}^- \]
With Cl⁻ present:

\[ \text{FeOOH} + \text{Cl}^- \rightarrow \text{FeOCl} + \text{OH}^- \]
\[ \text{FeOCl} + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \text{Cl}^- + 2\text{OH}^- \]

Low solubility Fe³⁺ precipitates as Fe(OH)₃ (rust)

Breakdown of passivation layer until reaching metal:

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \]

attracts Cl⁻

\[ \text{Fe}^{2+} + 2\text{Cl}^- + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{HCl} \]

local acidity ↑ in pit or crevice

Outside pit or crevice:

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^- \]
\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]

\[ \text{Fe}^{3+} + 3(\text{OH})^- \rightarrow \text{Fe(OH)}_3 \]

precipitates, further restricting transport
Steel composition effects:

**Cr:** For Cr > 12.5 at%: surface is hydrated CrOOH (chromium oxyhydroxide), i.e., $\text{CrO}_x(\text{OH})_{3-2x} \bullet n\text{H}_2\text{O}$

- renders S.S. surface passive
- increases susceptibility to pitting/crevice corrosion ($\text{CrCl}_3$ solutions have low/negative pH!)

**Mo:** ↓ dissolution rate in pits/crevices (mechanism?)

In the corrosion of metallic implants, further considerations arise with the complexity of biological fluids.

*In vivo* environment

- pH 7.4
- $T = 37^\circ\text{C}$
- anions: $\text{Cl}^-$, $\text{PO}_3^{2-}$, $\text{HCO}_3^-$ (bicarbonate)
- cations: $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$
- proteins & other biomolecules

Influence of other ions found in vivo:

- $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$: decrease corrosion rate
  - form precipitates on metal surfaces
    
    $$\text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^- \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$
    $$\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \text{ precipitates}$$

  - $\text{O}_2$ influx restricted $\rightarrow$ inhibits cathodic reduction
Biological Factors Influencing Corrosivity:

- O$_2$ levels (↑ O$_2$ ⇒ ↑ corrosion; anodic=cathodic)
- pH variations (inflammation/infection ⇒ ↓ pH)
- Cellular activity (e.g., phagocytic cells ⇒ local ↑ in oxidant conc.)
- Protein-$M^{z+}$ binding ($M^{z+}$ carried away ⇒ ↑ $M^{z+}$ dissolution)
  e.g., cytochrome oxidase, peroxidase, catalase bind Fe$^{2+}$
- Protein adsorption (↓ O$_2$ access to surface)
- Bacterial oxidation of Fe$^{2+}$ to Fe$^{3+}$ (↑ anodic rxn/Fe$^{2+}$ dissolution)

Corrosion’s Influence on in vivo Performance:

- Immunological sensitization; e.g., Ni & Cr allergic response
- Wear debris – initiates biological cascade
  (foreign body response, bone loss)
- Loss of implant structural integrity (mechanical failure)
- Metal ion toxicity: Al, Ni, Cr, V, Co, Ti; ↑ levels in blood/organs
- Carcinogenicity (tumors at implant sites, leukemia/lymphoma correlation with CoCr implants)