

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”



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

Reaction	ΔG^0 (joules)	T range (K)
$2Cr + 3/2 O_2 = Cr_2O_3$	$-1,120,300 + 260T$	298-2100
$Fe + 1/2 O_2 = FeO$	$-259,600 + 62.55T$	298-1642
$2Fe + 3/2 O_2 = Fe_2O_3$	$-810,520 + 254.0T$	298-1460
$Ti + O_2 = TiO_2$	$-910,000 + 173T$	298-2080

from D.R. Gaskell, *Intro. To Metallurgical Thermodynamics*, McGraw-Hill, 1981

How does metal oxidation happen?

One scenario is...

step 1: physisorption of O₂; ~20-25 kJ/mol

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

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

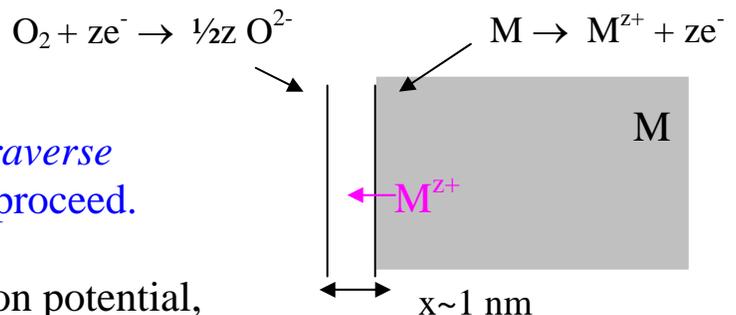
step 2: molecular oxygen dissociates and reduces by chemisorption; ~600 kJ/mol

step 3: bond rearrangement; crystallization of oxide layer

➔ *Resultant reduction in surface energy*

Compare: at 1400°C: $\gamma_{\delta\text{-Fe}} = 1900 \text{ dyn/cm}$
 $\gamma_{\text{FeO}} = 580 \text{ dyn/cm}$

Consider metal oxidation as 2 half reactions:



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:

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

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

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

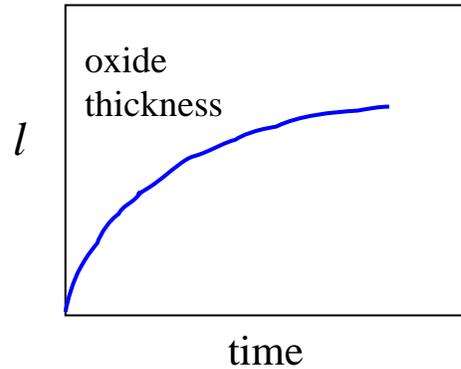
$$\text{E-Field} \approx 1 \text{ V/nm} = 10 \text{ MV/cm}$$

↪ Ionic species are “pulled” through oxide film!

WHAT HAPPENS AS THE OXIDE CONTINUES TO GROW?

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 Δc :

$$l^2 = k_p t$$



Requirements for Passivation:

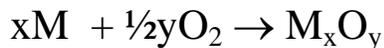
i) small k_p (rate const)

$$k_p = \text{const } D \Delta c$$

ii) adherent oxide

Oxide layer must not *scale* or *spall*

\Rightarrow minimize ΔV_{molar} & stress build-up



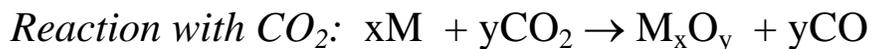
ex., Ti (TiO_2), Cr (Cr_2O_3), Al (Al_2O_3)

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

Pilling-Bedworth ratio:
$$PB = \frac{V_{\text{oxide}(\text{formed})}}{V_{\text{metal}(\text{consumed})}} = \frac{\rho_M M_{M_xO_y}}{xM_M \rho_{M_xO_y}}$$

Want PB ~ 1 (PB > 1) for adherence of oxide to underlying metal—in practice, this rule is marginally predictive, however.

Other Metal Oxidation Rxns by Chemisorption:



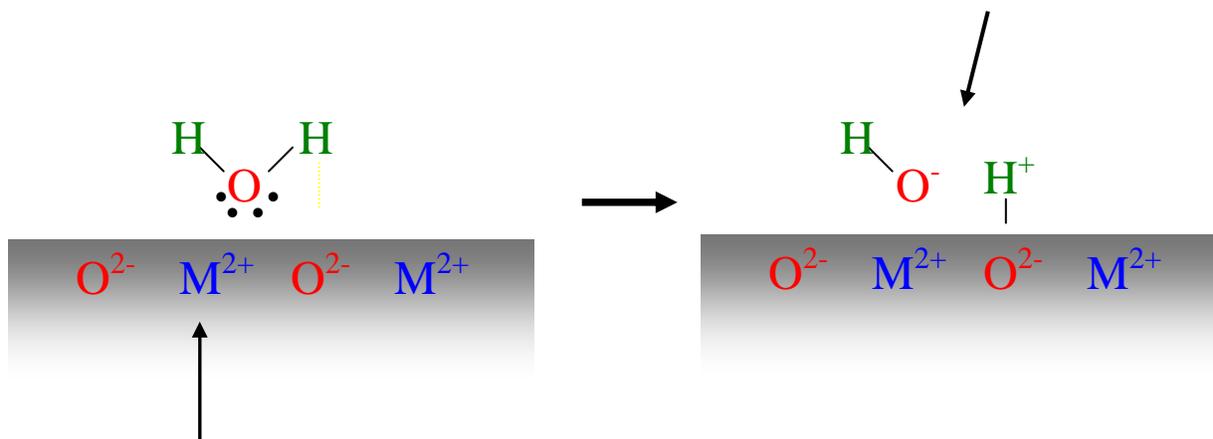
IS THE FORMED METAL OXIDE SURFACE STABLE?

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



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

H₂O cleavage with H⁺ transfer
to surface basic O²⁻ site & OH⁻
coordination with M²⁺



M²⁺ acts as Lewis acid
(e⁻ pair acceptor) for
oxygen lone pairs



Experimentally seen, e.g., on TiO_2 (110)

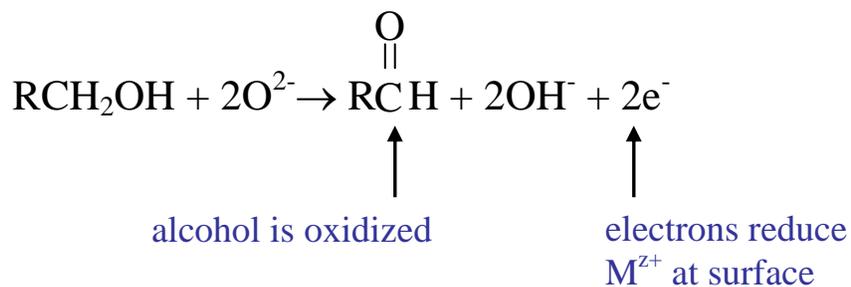
iii) w/ *Hydrocarbons*:



c) Redox (Oxidation/Reduction) Reactions on Oxides

Example

Alcohol dehydrogenation to aldehyde:



reference: V.E. Henrich and P.A. Cox, *The Surface Science of Metal Oxides*, Cambridge Univ. Press: 1994

2. Aqueous Corrosion of Metals

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

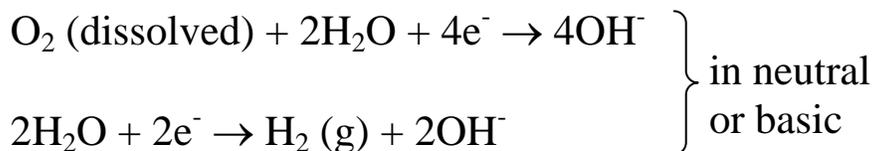
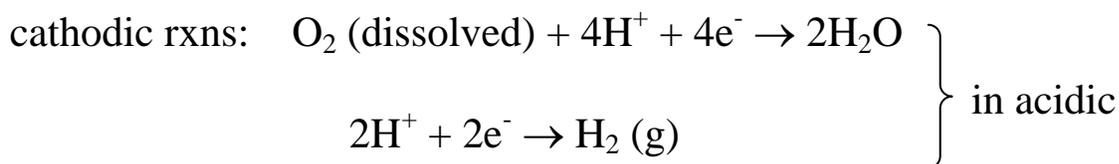
Why?

- 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.*

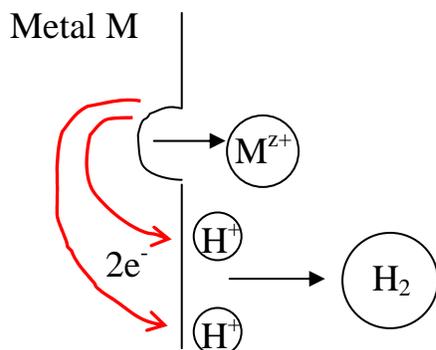
Aqueous corrosion: involves electronic charge transfer
i.e., an electrochemical rxn

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



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.

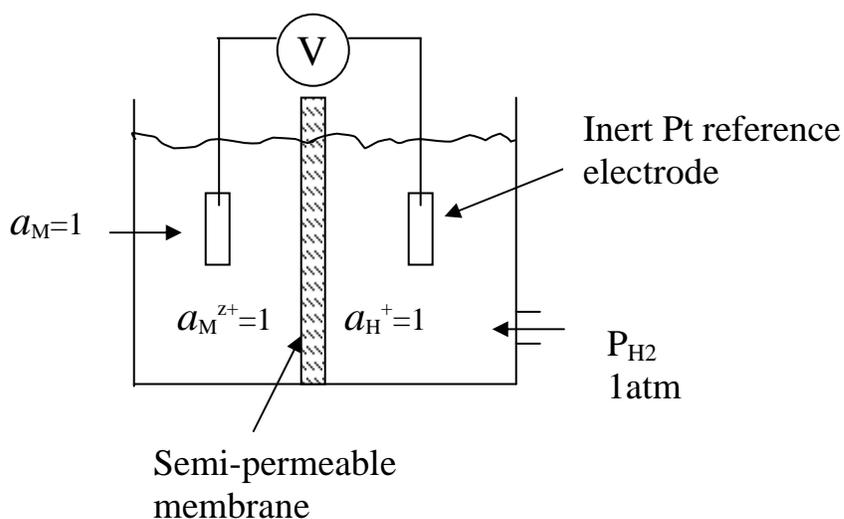
The resulting *charged double layer* exhibits a characteristic E.

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:



on reference electrode:



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.

anodic

Metal	Potential (V)
Au	1.43
Pt	1.2
Ag	0.79
H	0.0
Sn	-0.14
Mo	-0.20
Co	-0.28
Fe	-0.44
Cr	-0.73
Al	-1.33
Ti	-1.63
Li	-3.05

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:

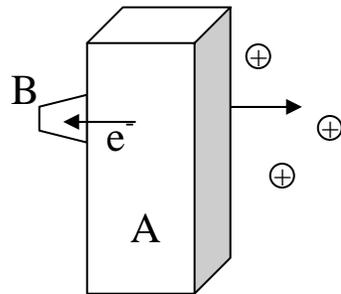
$$a_{\text{oxidized species}} = [M^{z+}] \quad a_{\text{reduced species}} = [M] = 1$$

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

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” \Rightarrow accelerating corrosion of A



The \downarrow in e^- from A surface allows \uparrow 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 $\Rightarrow \uparrow M^{z+}$ dissolution
 - defects (terraces, steps): less bonds $\Rightarrow \uparrow M^{z+}$ dissolution
- repetitive movement \Rightarrow 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
 - rapid penetration at defect (oxidation = reduction)
- catalyzed by presence of Cl^-
- autocatalyzed by \uparrow acidity from rxn in confined volume

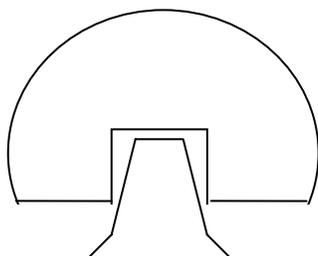


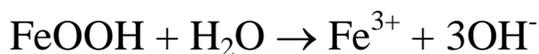
Photo removed for copyright reasons.

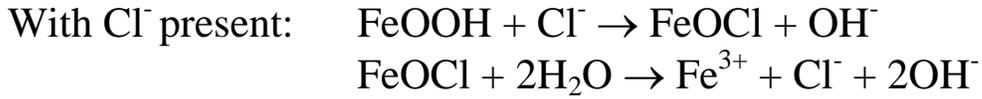
Corrosion on neck region of a femoral stem of a CoCr hip prosthesis. from J.J. Jacobs et al, "Corrosion of Metal Orthopaedic Implants", *J. Bone and Joint Surgery* **80-A**, 268 (1998).

Ex. Stainless steels in Aqueous Soln:

For Cr contents below 12.5 at%: FeOOH resides at surface in hydrated form: $FeO_x(OH)_y \cdot nH_2O$ (iron oxyhydroxide hydrate)

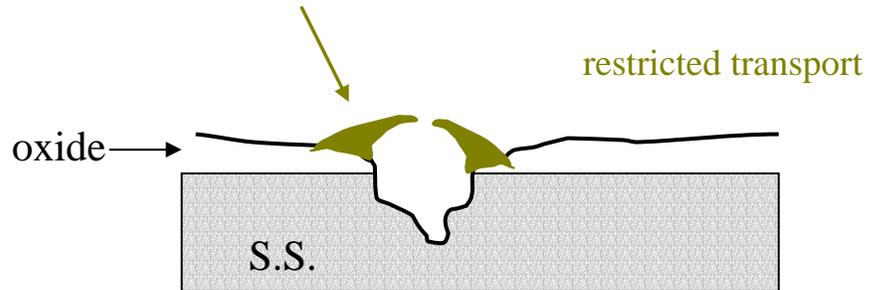
In absence of Cl^- , slow dissolution:



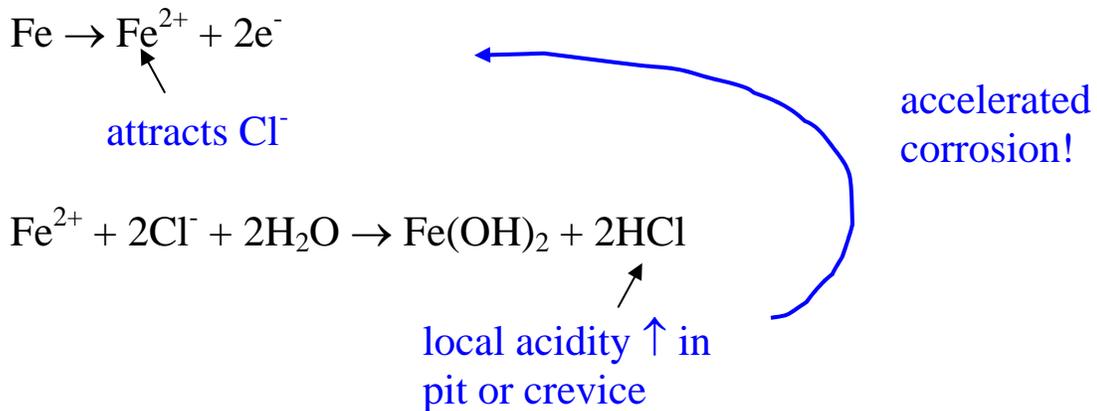


Low solubility Fe^{3+} precipitates as $\text{Fe}(\text{OH})_3$ (rust)

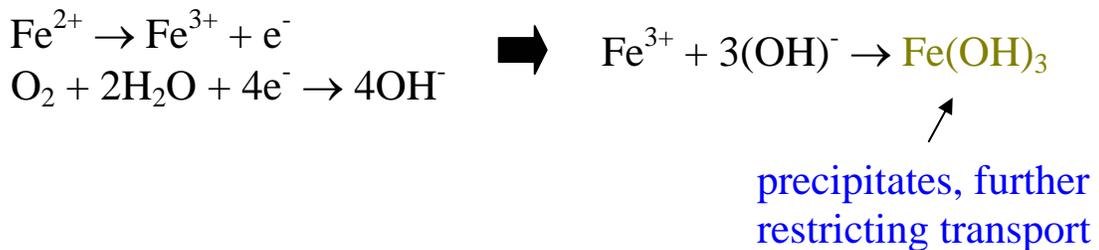
Fe_2O_3
$(\text{Fe,Cr})_2\text{O}_3$
Fe-9Cr



Breakdown of passivation layer until reaching metal:



Outside pit or crevice:



Steel composition effects:

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

- renders S.S. surface passive
- increases susceptibility to pitting/crevice corrosion (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.

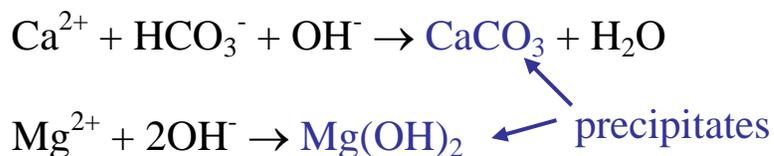
In vivo environment

- pH 7.4
- T = 37°C
- anions: Cl^- , PO_3^- , HCO_3^- (bicarbonate)
- cations: Na^+ , K^+ , Ca^{2+} , Mg^{2+}
- proteins & other biomolecules

Influence of other ions found in vivo:

Ca^{2+} and Mg^{2+} : decrease corrosion rate

- form precipitates on metal surfaces



- O_2 influx restricted → inhibits cathodic reduction

Biological Factors Influencing Corrosivity:

- O_2 levels ($\uparrow O_2 \Rightarrow \uparrow$ corrosion; anodic \equiv cathodic)
- pH variations (inflammation/infection $\Rightarrow \downarrow$ pH)
- Cellular activity (e.g., phagocytic cells \Rightarrow local \uparrow in oxidant conc.)
- Protein- M^{z+} binding (M^{z+} carried away $\Rightarrow \uparrow M^{z+}$ dissolution)
e.g., cytochrome oxidase, peroxidase, catalase bind Fe^{2+}
- Protein adsorption ($\downarrow O_2$ access to surface)
- Bacterial oxidation of Fe^{2+} to Fe^{3+} (\uparrow 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; \uparrow levels in blood/organs
- Carcinogenicity (tumors at implant sites, leukemia/lymphoma correlation with CoCr implants)