

## 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

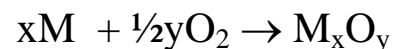
### 1. Chemisorption

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”



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

Reaction	$\Delta G^0$ (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 O<sub>2</sub>; ~20-25 kJ/mol

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

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

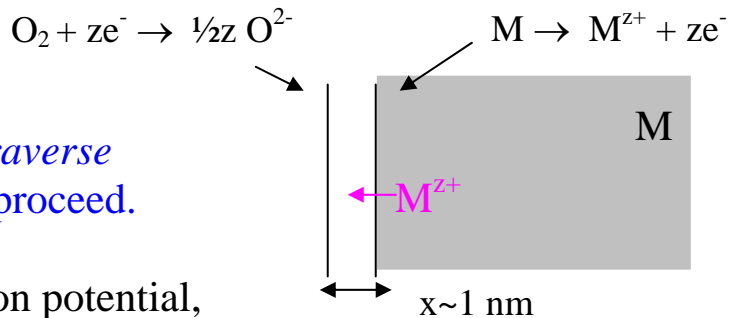
step 2: molecular oxygen dissociates and reduces by chemisorption; ~600 kJ/mol

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:

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

$F = 96,480 \text{ C/mol } e^-$   
 $1 \text{ J} = 1 \text{ V-C}$

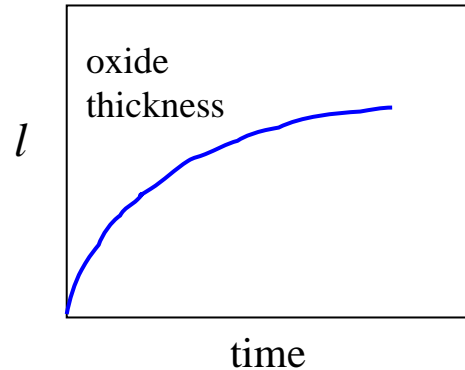
E-Field  $\approx 1 \text{ V/nm} = 10 \text{ MV/cm}$

↪ 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  $\Delta c$ :

$$l^2 = k_p t$$



*Requirements for Passivation:*

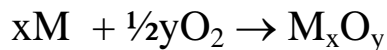
i) small  $k_p$  (rate const)

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

ii) adherent oxide

Oxide layer must not *scale* or *spall*

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



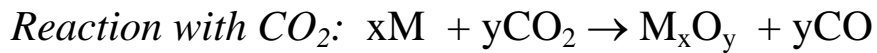
ex., Ti ( $TiO_2$ ), Cr ( $Cr_2O_3$ ), Al ( $Al_2O_3$ )

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

*Other Metal Oxidation Rxns by Chemisorption:*



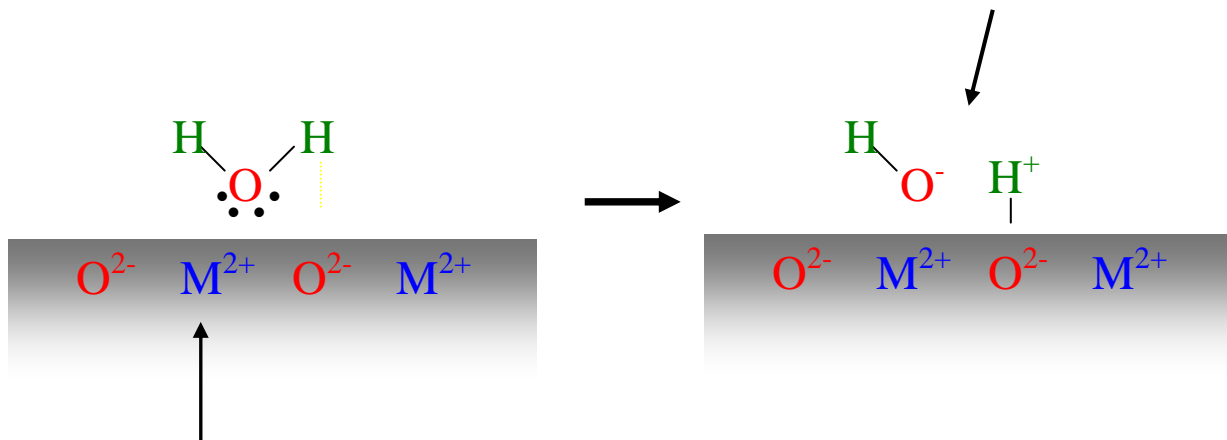
IS THE FORMED METAL OXIDE SURFACE STABLE?

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



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

H<sub>2</sub>O cleavage with H<sup>+</sup> transfer  
to surface basic O<sup>2-</sup> site & OH<sup>-</sup>  
coordination with M<sup>2+</sup>



M<sup>2+</sup> acts as Lewis acid  
(e<sup>-</sup> pair acceptor) for  
oxygen lone pairs



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

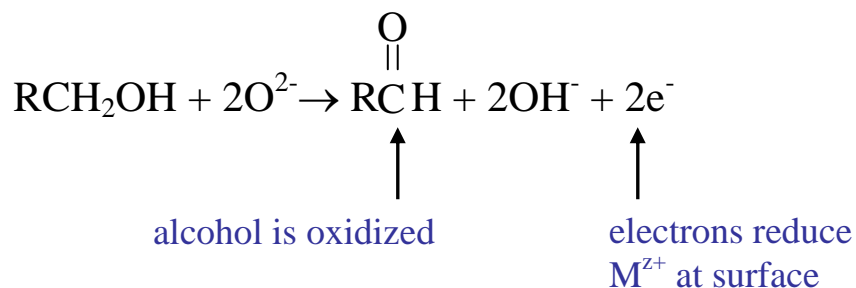
iii) *w/ Hydrocarbons:*



### 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.

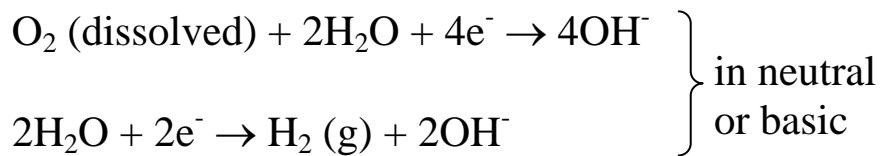
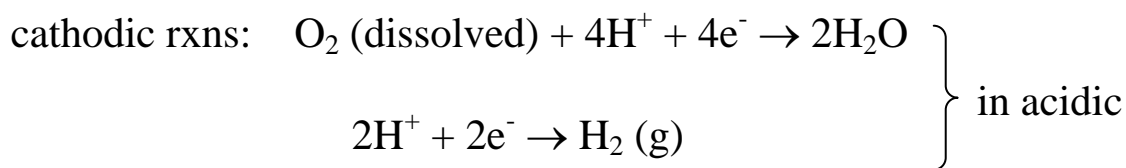
Why?

- $M^{z+}$  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.*

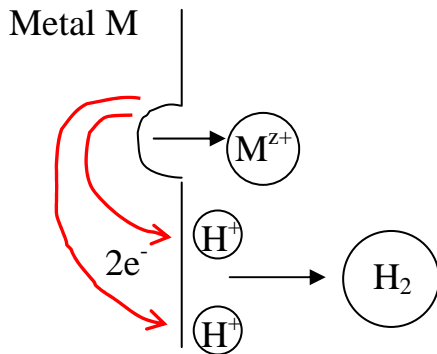
**Aqueous corrosion:** involves electronic charge transfer  
i.e., an electrochemical rxn

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.

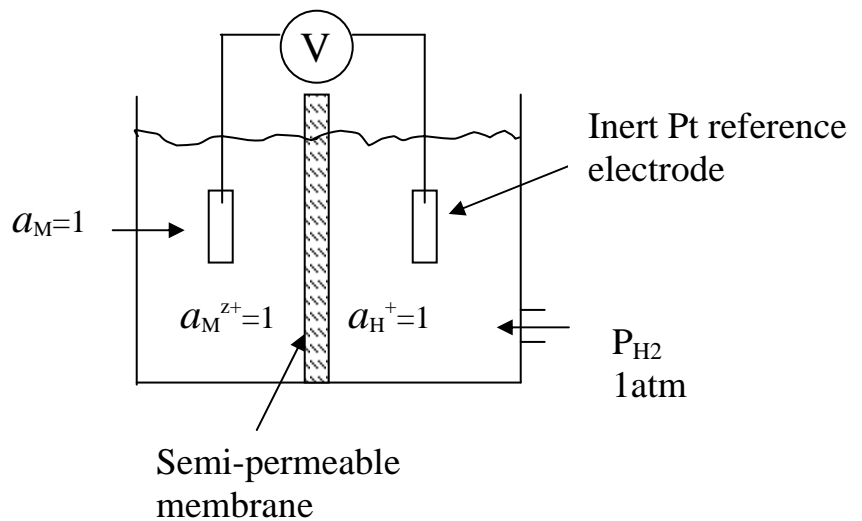
The resulting *charged double layer* exhibits a characteristic E.

Values of E measured *relative* to a reference electrode (e.g., std. H<sub>2</sub> 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 ( $\sim 1$  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:

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

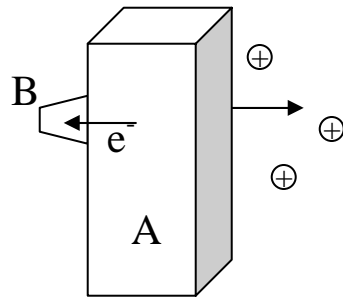
$$E(V) = E^0 + \frac{0.059}{z} \log[M^{z+}]$$

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

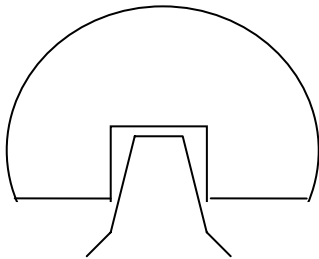


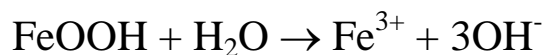
Photo removed for copyright reasons.

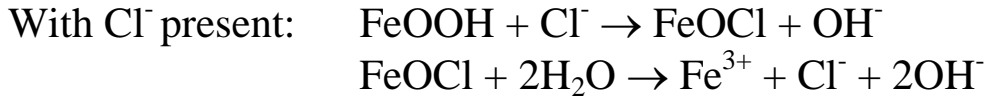
Corrosion on neck region of a femoral stem of a CoCr hip prosthesis. from J.J. Jacobs et al, "Corrosion of Metal Orthopaedic Implants", *J. Bone and Joint Surgery* **80-A**, 268 (1998).

### 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)

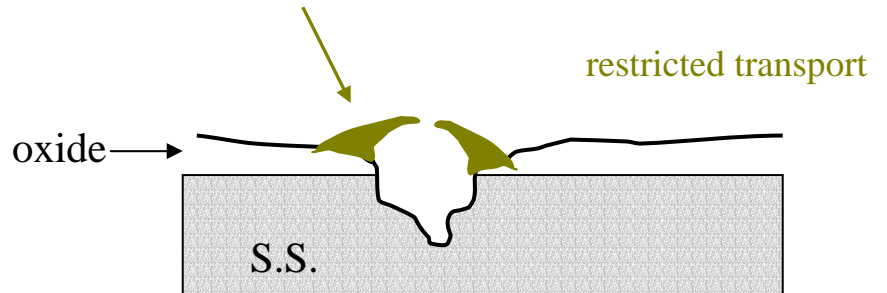
In absence of  $Cl^-$ , slow dissolution:



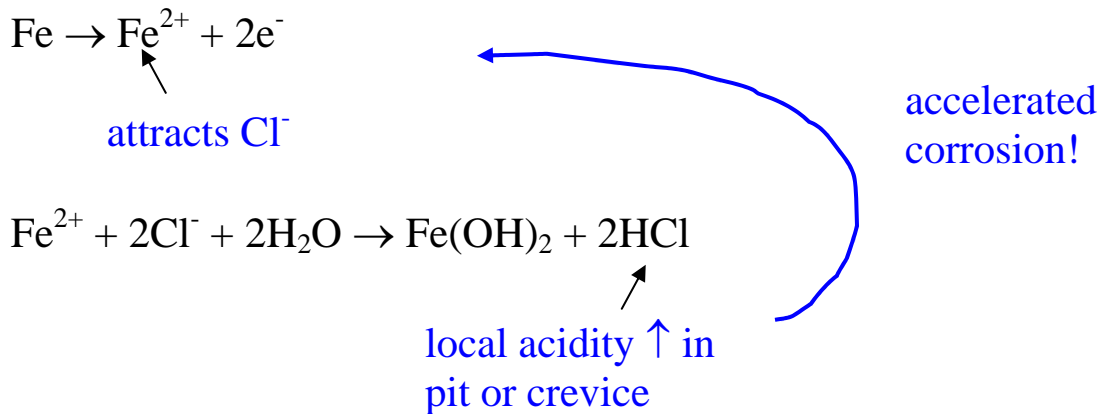


Low solubility  $\text{Fe}^{3+}$  precipitates as  $\text{Fe}(\text{OH})_3$  (rust)

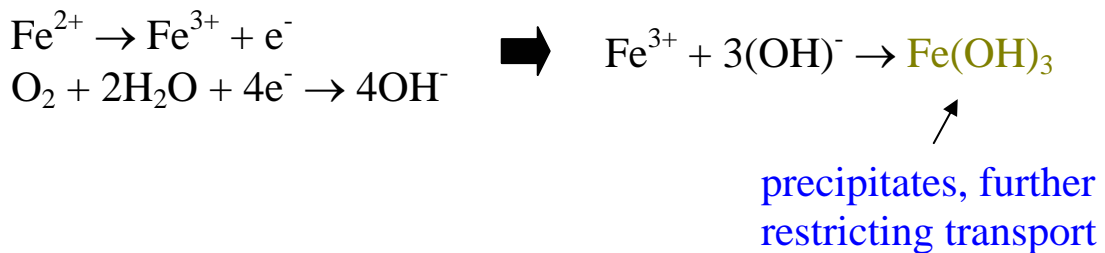
$\text{Fe}_2\text{O}_3$
$(\text{Fe,Cr})_2\text{O}_3$
Fe-9Cr



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 ( $\text{CrCl}_3$  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.

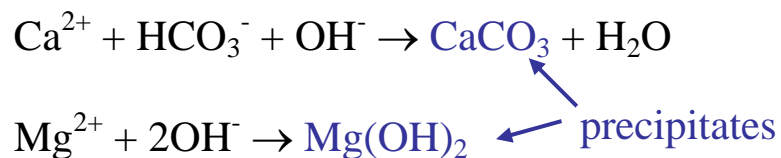
*In vivo environment*

- pH 7.4
- T = 37°C
- anions:  $\text{Cl}^-$ ,  $\text{PO}_3^-$ ,  $\text{HCO}_3^-$  (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



- $\text{O}_2$  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)