Chemical Engineering 378

Science of Materials Engineering

Lecture 30

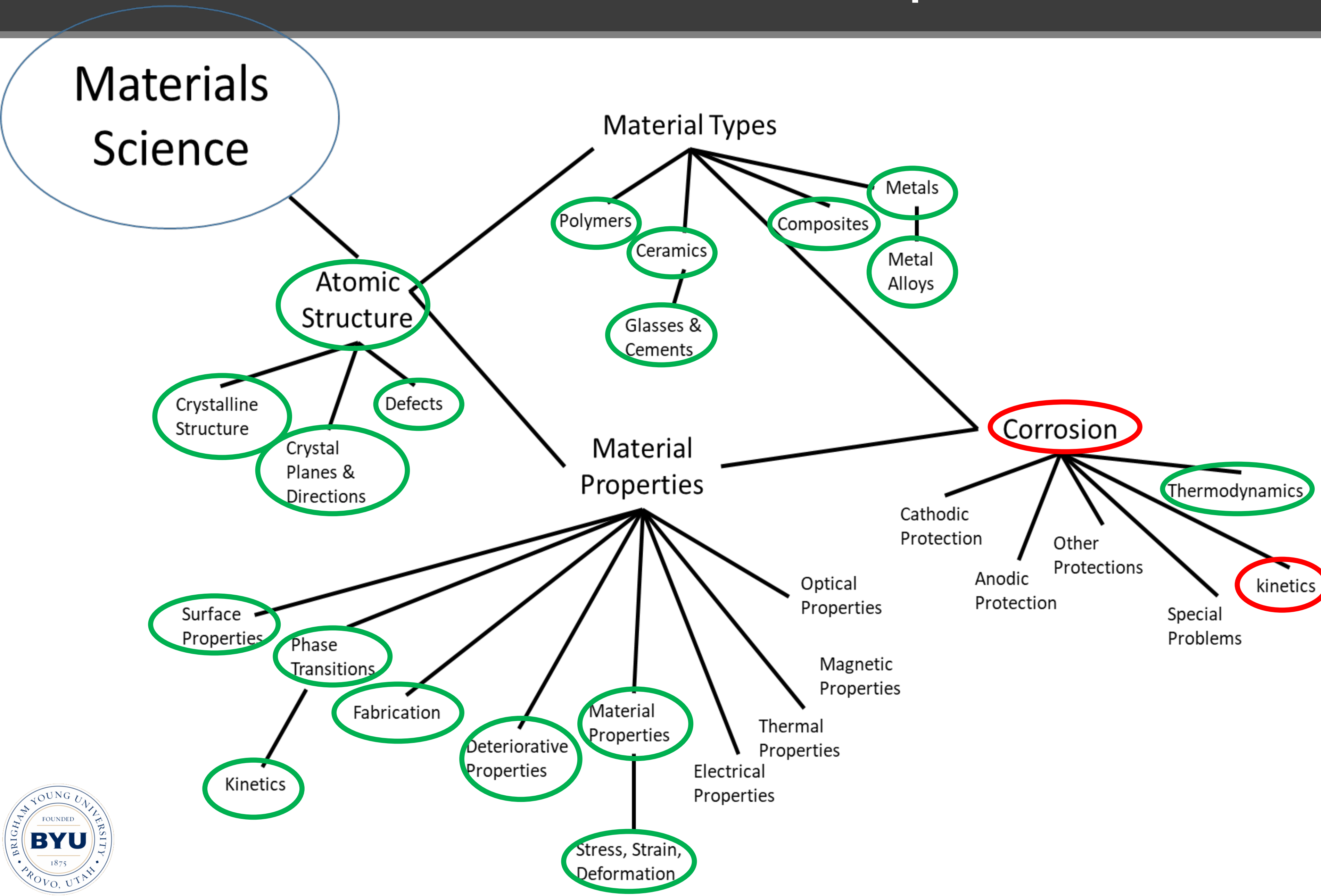
Corrosion: Kinetics

Spiritual Thought

D&C 101:16

16 Therefore, let your hearts be comforted concerning Zion; for all flesh is in mine hands; be still and know that I am God.

Materials Roadmap



Kinetics

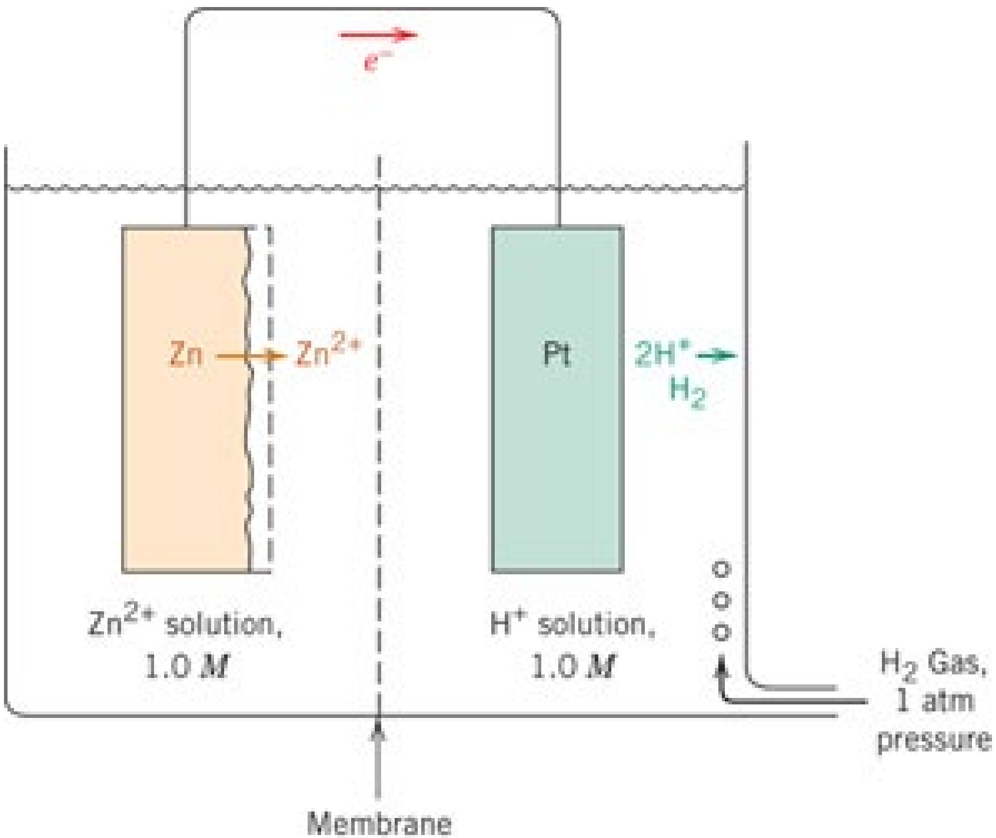
- Thermodynamics – factors that indicate spontaneity of reactions, direction, etc.
- Kinetics – how FAST things corrode
- Rate
  - Complex function of many things

$$r = \frac{i}{n\mathfrak{F}}$$

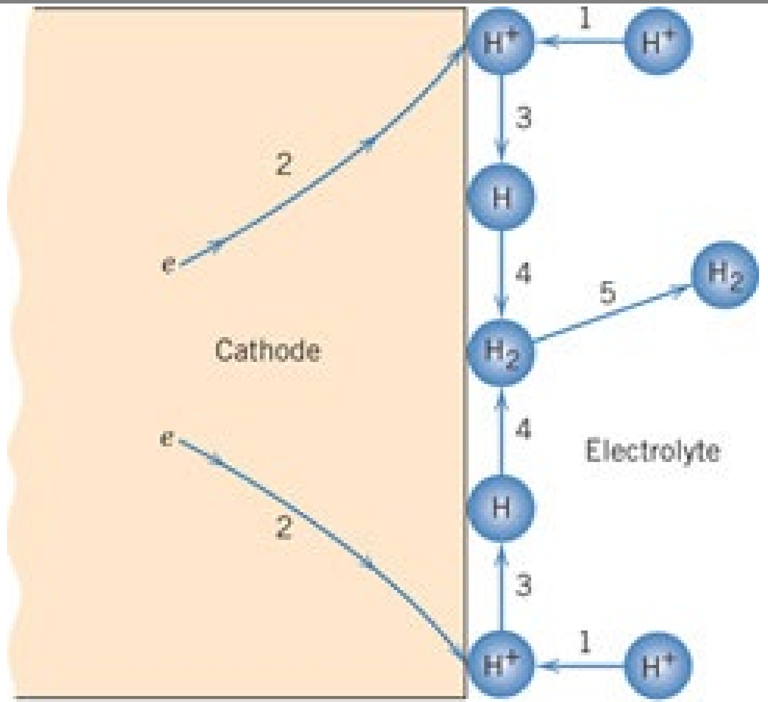
  - *i* =current density→ current per area of exposed surface
  - *Challenge: what is current density?*
    - *Following slides focus on this*

Polarization/Overpotential

- Measured (Equilibrium) value = -0.621V
- Table Value = -0.763V
- Value isn't actual value!
- Why the difference?
- Not at equilibrium
- Overpotential or overvoltage
  - $\eta = -0.621-(-0.763)$
  - $\eta = 0.142V$



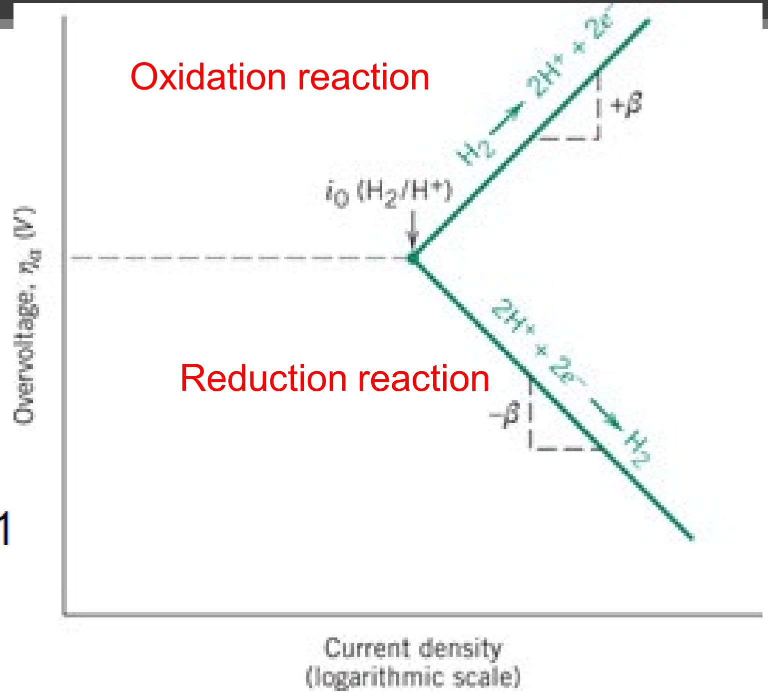
Activation Polarization



From Flinn, Richard A. and Paul K. Trojan, *Engineering Materials and Their Applications*, 4th edition, John Wiley and Sons, Inc.,1990, p. S-18, Figure 18.7.

1. Migration of hydrogen ions in solution to and adsorption onto the zinc surface
2. Motion of electrons to the interface
3. Electron transfer from the zinc to form a hydrogen atom,
$H^{+}+e^{-}\rightarrow H$, $H^{+}+e^{-}\rightarrow H$
4. Combining of two hydrogen atoms to form a molecule of hydrogen
$2H\rightarrow H\text{-}H\rightarrow H2$
5. The coalescence of many hydrogen molecules to form a bubble

Activation Polarization



$$\beta = \frac{kT}{e\alpha}$$

k = Boltzmann's constant

T = absolute temperature

e = electron charge

α = charge transfer coefficient (between 0 and 1

$$\eta_a = \pm\beta \log \frac{i}{i_0}$$

Tafel Equation
Named after German chemist Julius Tafel (1862-1918)

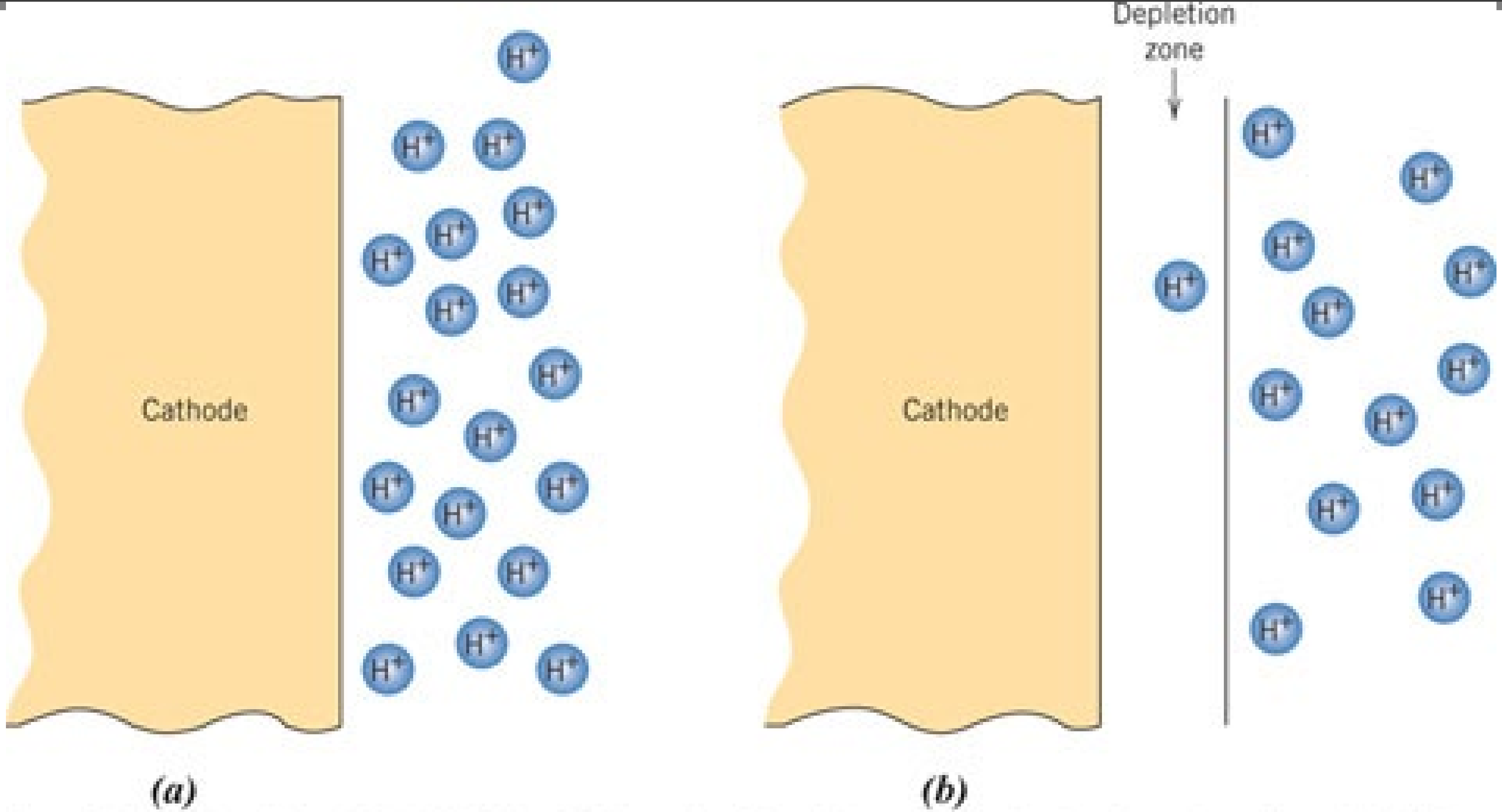
η_a = overvoltage for a half-reaction (added to the voltage for zero current)

β = constant for the particular half-reaction

i = current density

i_0 = exchange current density (back and forth during dynamic equilibrium)

Concentration Polarization

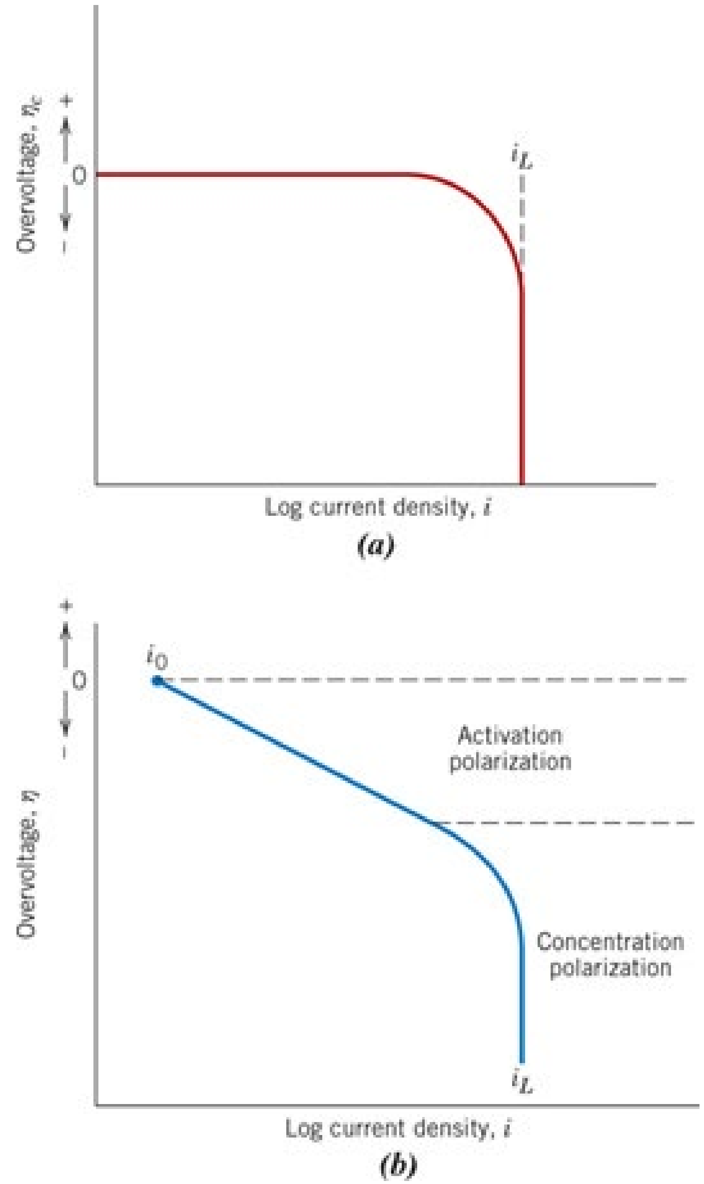


From Flinn, Richard A. and Paul K. Trojan, *Engineering Materials and Their Applications*, 4th edition, John Wiley and Sons, Inc., 1990, p. S-17, Figure 18.5.

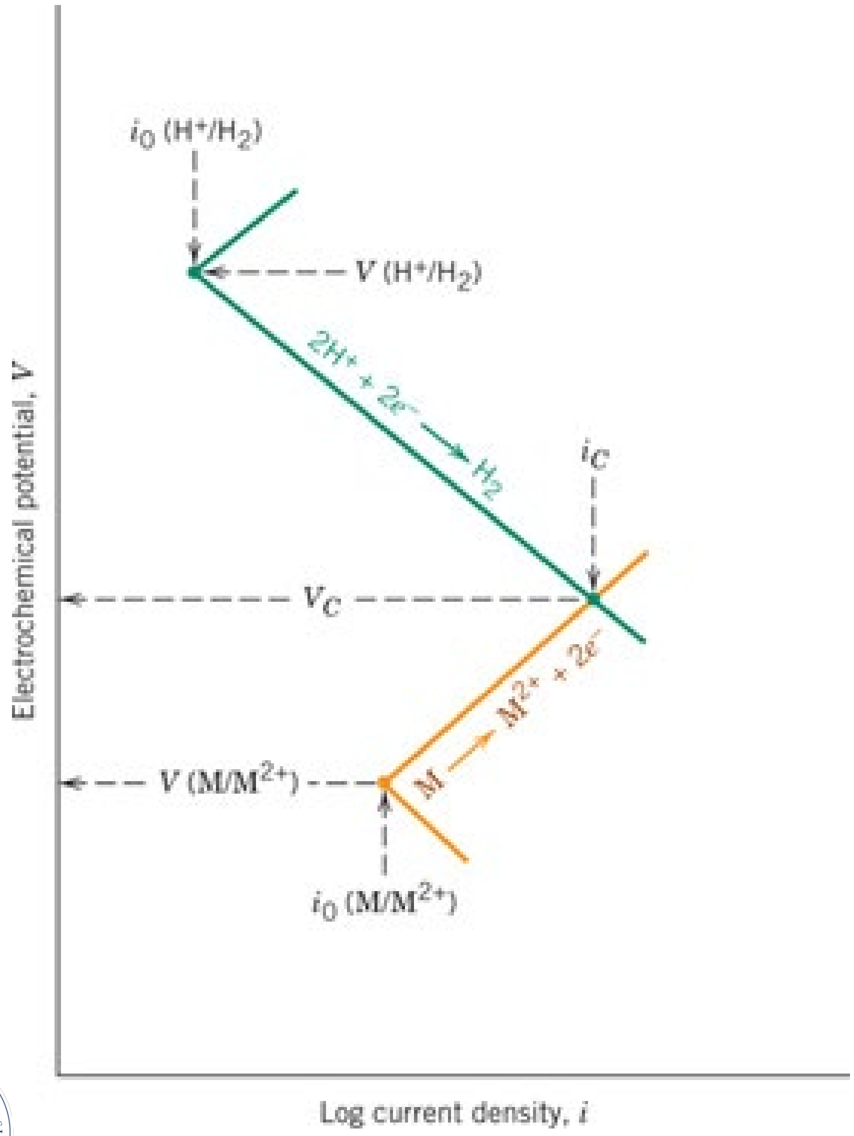
$$\eta_c = \frac{2.3RT}{n\mathfrak{F}} log\left(1 - \frac{i}{i_o}\right)$$

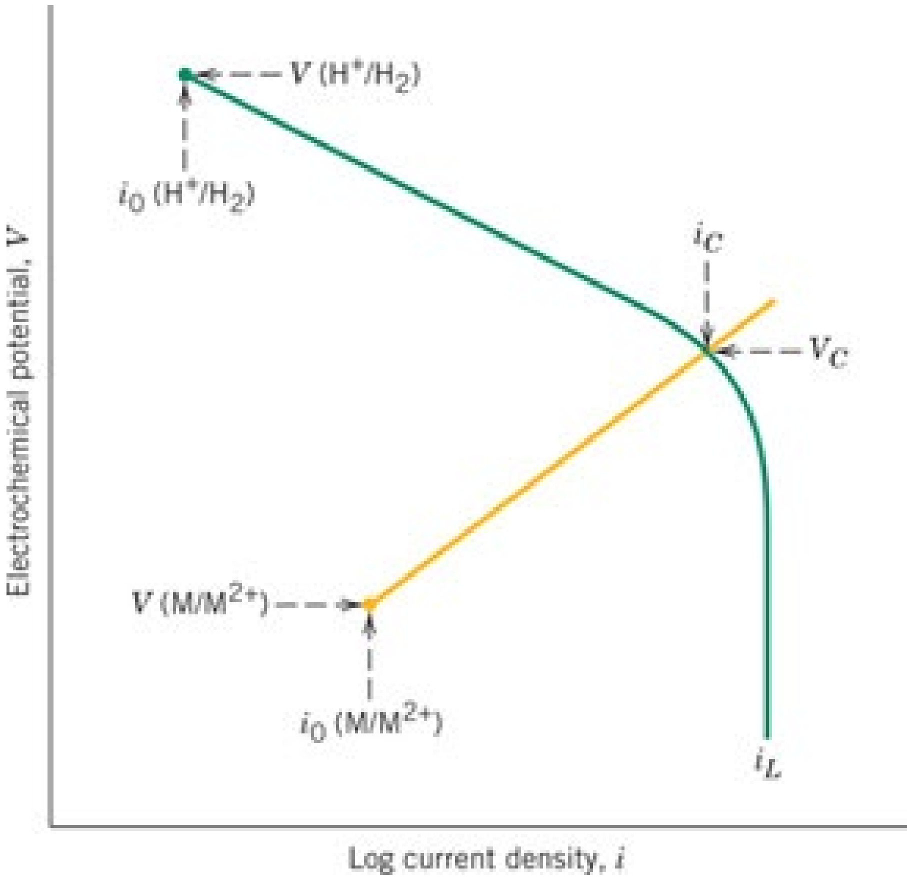
Activation and Concentration

- Concentration polarization not applied to oxidation (why?)
- Realistically reduction includes both activation and concentration
- High Current, reaction rate > mass transport rate
- Sudden drop in voltage (no ions available for reaction at interface)



Corrosion Potential and Voltage

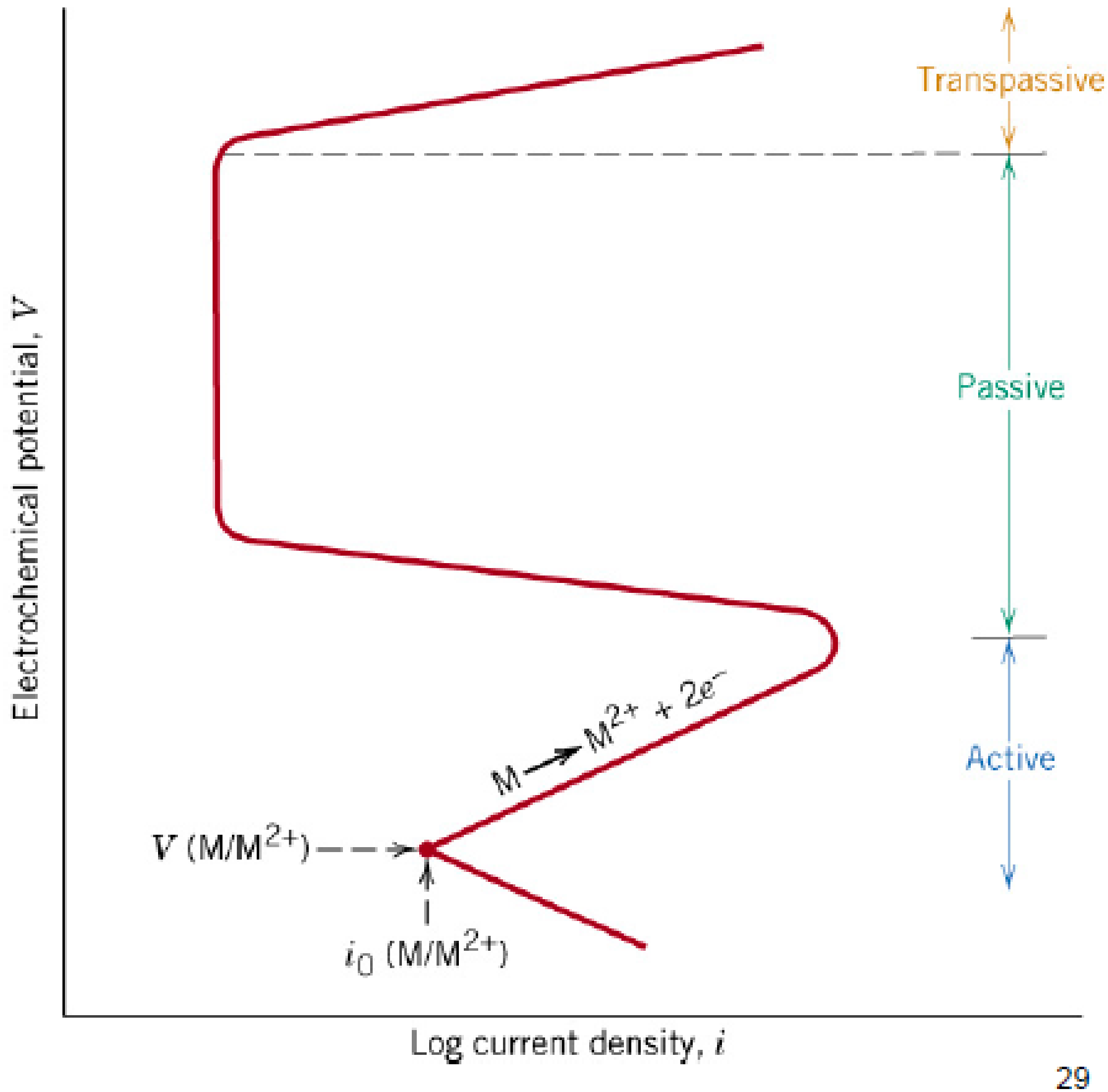




$$r_c = \frac{i_c}{n\mathfrak{F}}$$

Passivation

- Corrosion current density is greatly reduced in the passivated (inactive) state.



FORMS OF CORROSION

Forms of corrosion

- **Stress corrosion**
Corrosion at crack tips when a tensile stress is present.

- **Uniform Attack**
Oxidation & reduction reactions occur uniformly over surfaces.

- **Erosion-corrosion**
Combined chemical attack and mechanical wear (e.g., pipe elbows).

- **Selective Leaching**
Preferred corrosion of one element/constituent [e.g., Zn from brass (Cu-Zn)].

- **Pitting**
Downward propagation of small pits and holes.

Fig. 17.17, *Callister & Rethwisch 10e*. (Photograph courtesy of Rick Adler/Adler Engineering LLC of Wyoming USA)

- **Intergranular**
Corrosion along grain boundaries, often where precip. particles form.

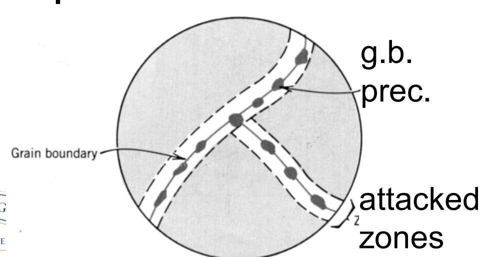


Fig. 17.18, *Callister & Rethwisch 10e*.

- **Galvanic**
Dissimilar metals are physically joined in the presence of an electrolyte. The more anodic metal corrodes.

- **Crevice** Narrow and confined spaces.

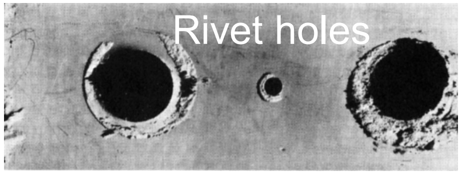


Fig. 17.15, *Callister & Rethwisch 10e*. (Courtesy LaQue Center for Corrosion Technology, Inc.)

Homework 17.19*

HW Note 17.19 On Fig 17.27, there is no line drawn yet for the anodic reaction. So to help you, draw a straight line representing the anodic reaction originating near the "V" of "Velocity" and slopes upward at about a 30° angle and intersects all of the solution velocity curves, as shown below. This will help you understand.