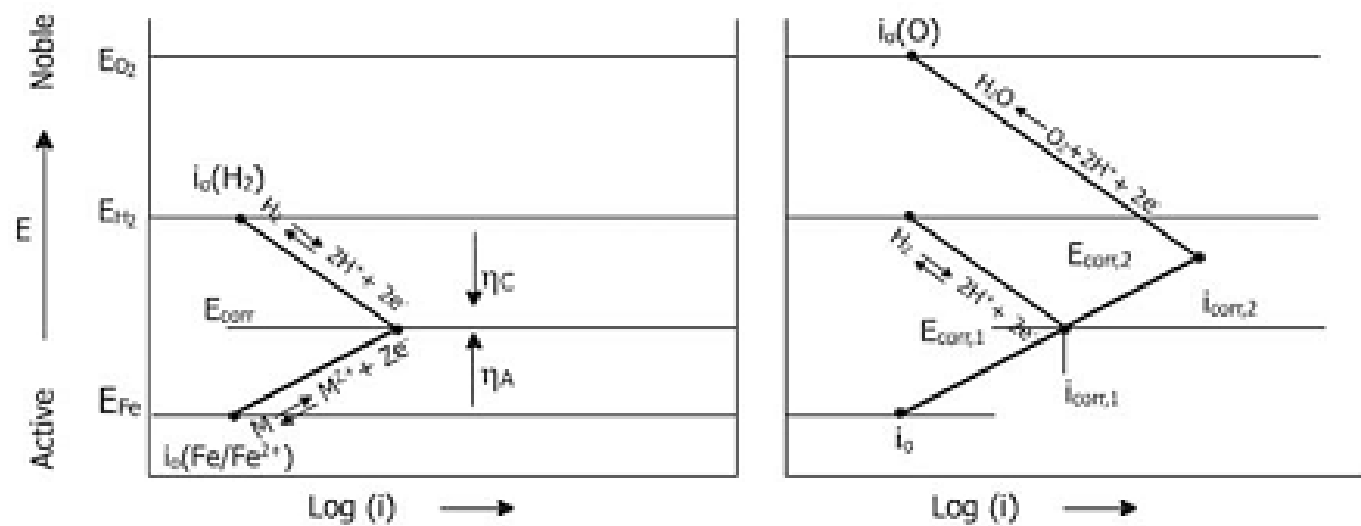
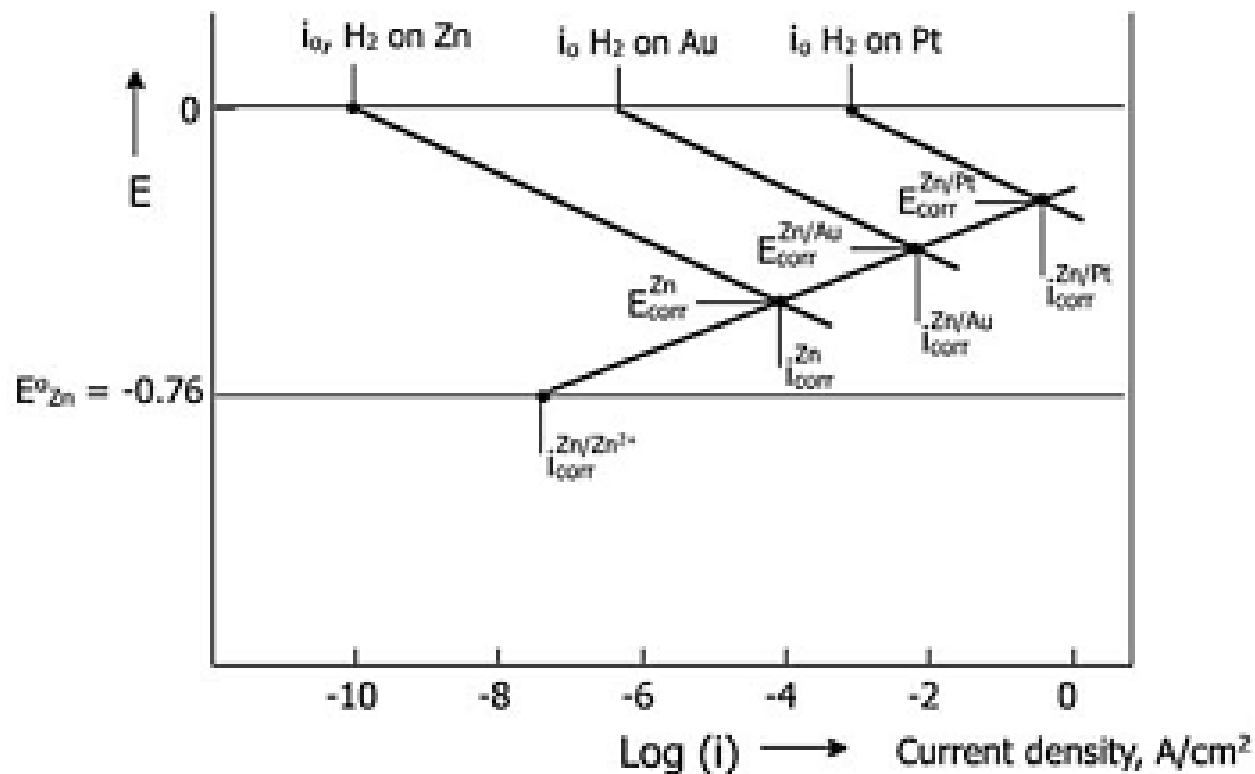




(a) Deaerated solution

(b) Aerated solution



Passivity?

**aloofness
coldness
coolness
detachment
disinterest
dispassion
disregard
dullness
emotionlessness
half-heartedness
heedlessness
indifference**

Passive or pessimistic

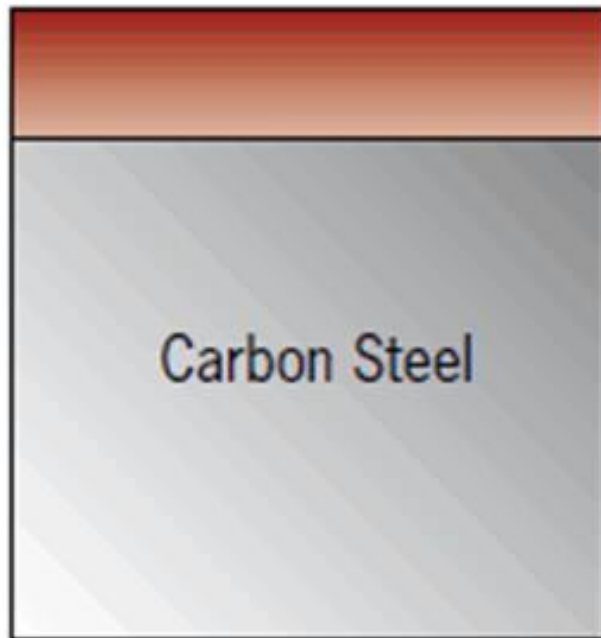
**insensibility
insensitivity
insouciance
lassitude
lethargy
listlessness
passiveness
passivity
stoicism
unconcern
unresponsiveness**



Oxygen



Rusting

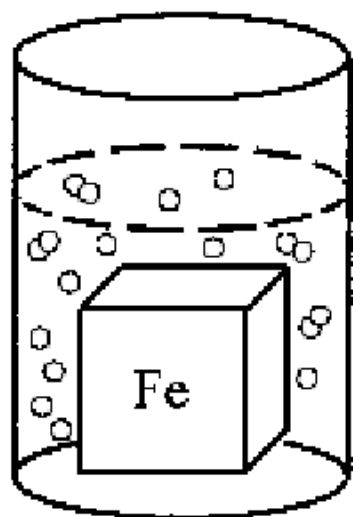


“Stain” less



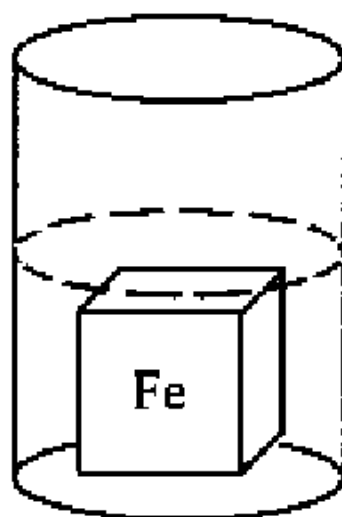
Passivity of iron in solution of HNO_3

Effect of concentrations on passivity

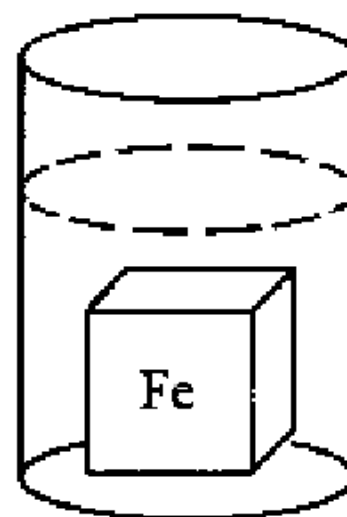


Dilute HNO_3
Violent reaction

(Active
state)



Conc. HNO_3
No reaction



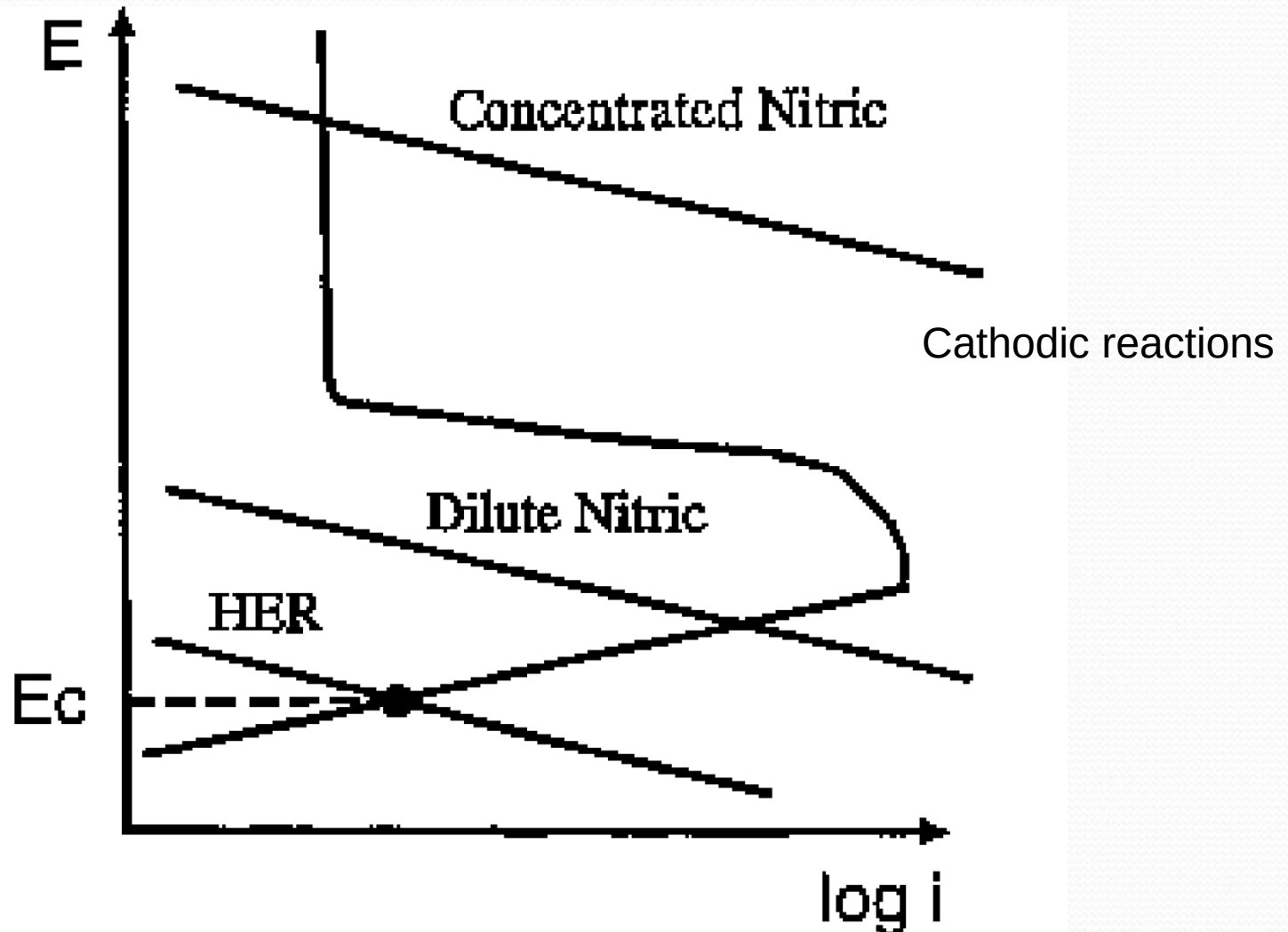
Dilute HNO_3
No reaction

(Passive
state)

Passivity?

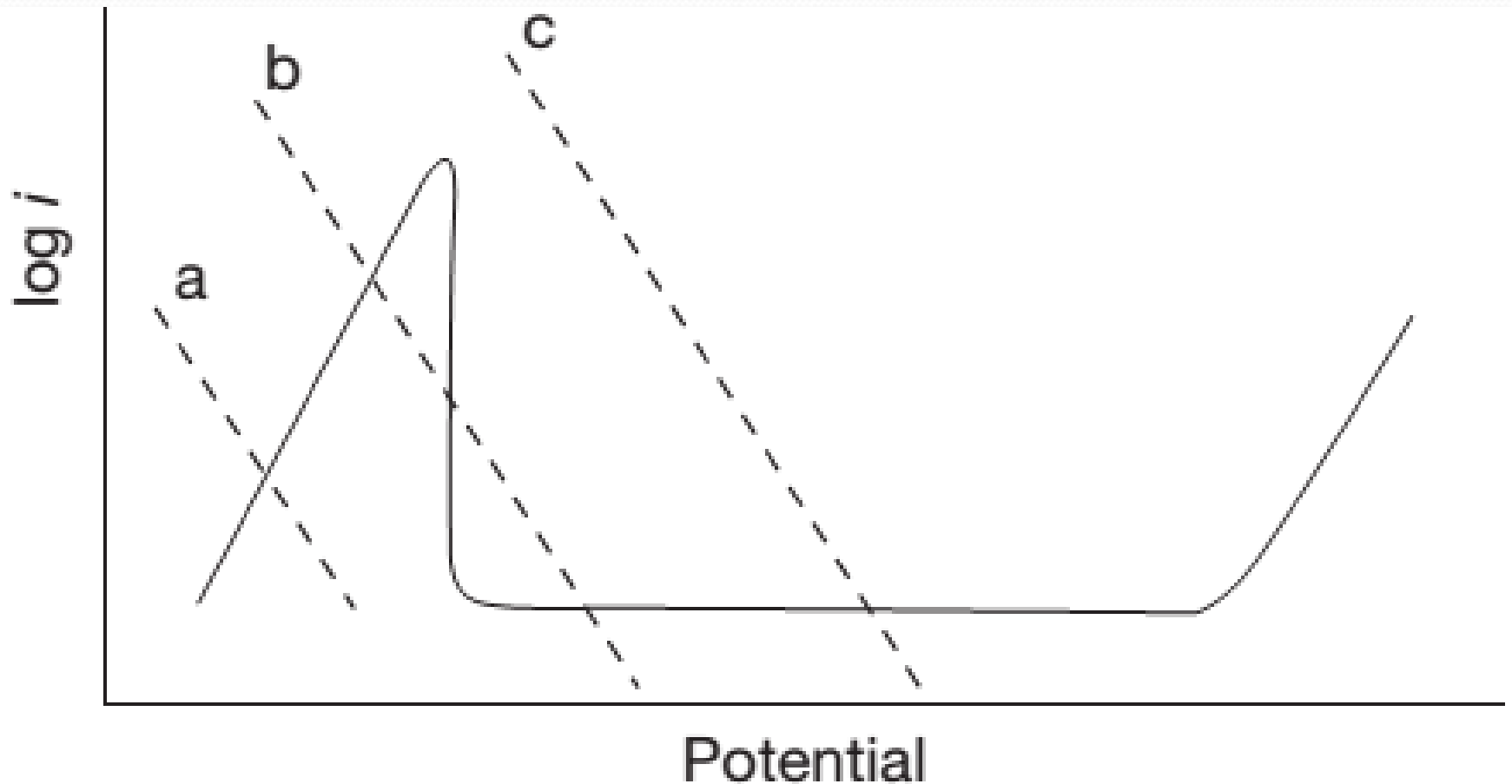
- In dilute nitric acid, Fe corrodes at a high rate?
- In concentrated nitric acid, the reaction rate slows to almost zero?
- Corrode at a high rate when surface is disturbed?

Mixed potential theory

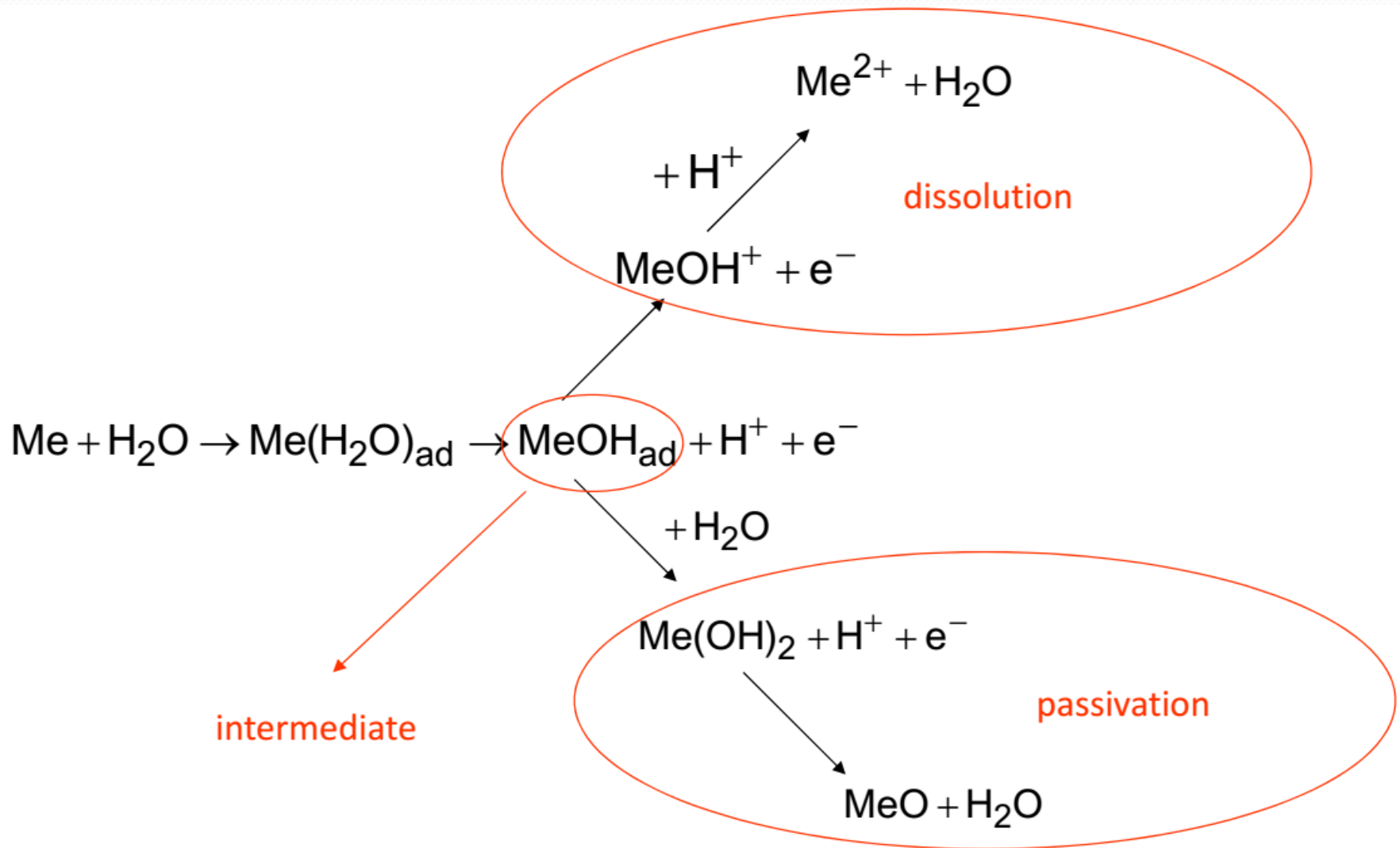


Anodic polarization curve

Effect of cathodic reactions



Passivation in aqueous solutions



Passivity by Uhlig

A metal active in the EMF series or an alloy composed of such metals is considered passive when its electrochemical behavior becomes that of an appreciably less active or noble metal.

Ex.: Cr, Ni, Ti, Zr and stainless steels.

A metal or alloy is passive if it substantially resists corrosion in an environment where thermodynamically there is a large free energy change associated with its passage from the metallic state to appropriate corrosion products

Ex. Lead in sulfuric acid and iron in inhibited pickling acid.

Pickling & passivation for stainless steel



EMF series

+V(SHE)

Electrode reaction	Standard potential at 25 °C (77 °F), V-SHE
$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	1.50
$\text{Pd}^{2+} + 2e^- \rightarrow \text{Pd}$	0.987
$\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}$	0.854
$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	0.800
$\text{Hg}_2^{2+} + 2e^- \rightarrow 2\text{Hg}$	0.789
$\text{Cu}^+ + e^- \rightarrow \text{Cu}$	0.521
$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	0.337
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0.000 (Reference)
$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.126
$\text{Sn} + 2e^- \rightarrow \text{Sn}$	-0.136
$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.250
$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$	-0.277
$\text{Tl}^+ + 2e^- \rightarrow \text{Tl}$	-0.336
$\text{In}^{3+} + 3e^- \rightarrow \text{In}$	-0.342
$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$	-0.403
$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.440

Noble

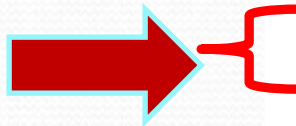
-V(SHE)

$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.763
$\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$	-1.18
$\text{Zr}^{4+} + 4e^- \rightarrow \text{Zr}$	-1.53
$\text{Ti}^{2+} + 2e^- \rightarrow \text{Ti}$	-1.63
$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.66
$\text{Hf}^{4+} + 4e^- \rightarrow \text{Hf}$	-1.70
$\text{U}^{3+} + 3e^- \rightarrow \text{U}$	-1.80
$\text{Be}^{2+} + 2e^- \rightarrow \text{Be}$	-1.85
$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.37

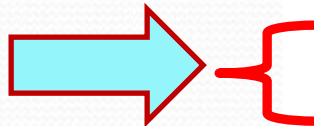
Active

Galvanic series

**Noble or
cathodic end
of series**



Platinum
Gold
Graphite
Titanium
Silver
Chlorimet 3 (62Ni-18Cr-18Mo)
Hastelloy C (62Ni-17Cr-15Mo)
18-8Mo stainless steel (passive)
18-8 stainless steel (passive)
Chromium stainless steel 11-30% Cr (passive)
Inconel (passive) (80Ni-13Cr-7Fe)
Nickel (passive)
Silver solder
Monel (70Ni-30Cu)
Cupronickels (60-90Cu, 40-10Ni)
Bronzes (Cu-Sn)
Copper
Brasses (Cu-Zn)
Chlorimet 2 (66Ni-32Mo-1Fe)
Hastelloy B (60Ni-30Mo-6Fe-1Mn)
Inconel (active)
Nickel (active)
Tin
Lead
Lead-tin solders
18-8Mo stainless steel (active)
18-8 stainless steel (active)
Ni-Resist (high-nickel cast iron)
Chromium stainless steel, 13% Cr (active)
Cast iron
Steel or iron
Aluminum alloy 2024
Cadmium
Aluminum alloy 1100
Zinc
Magnesium and magnesium alloys

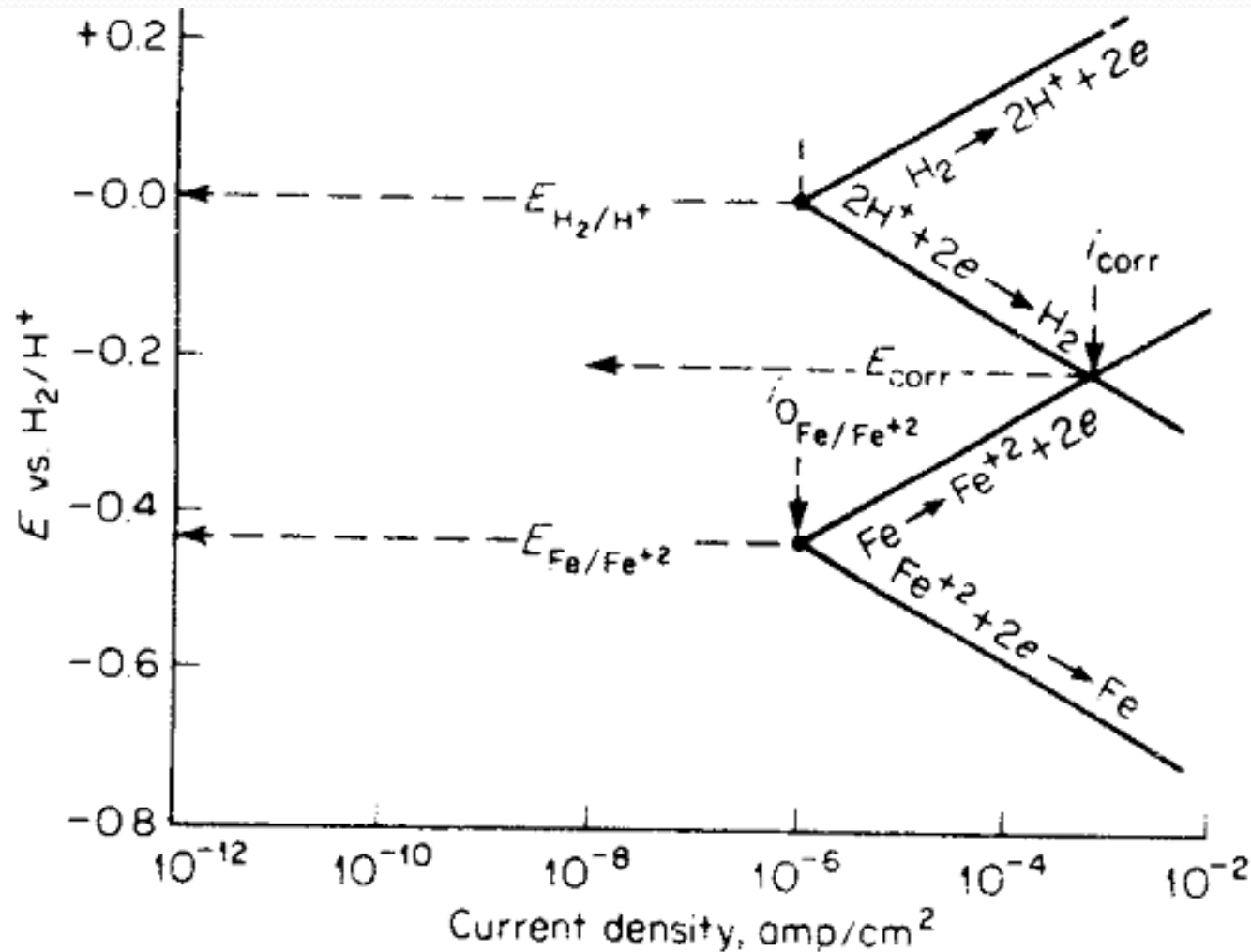


**Active or
anodic end of
series**

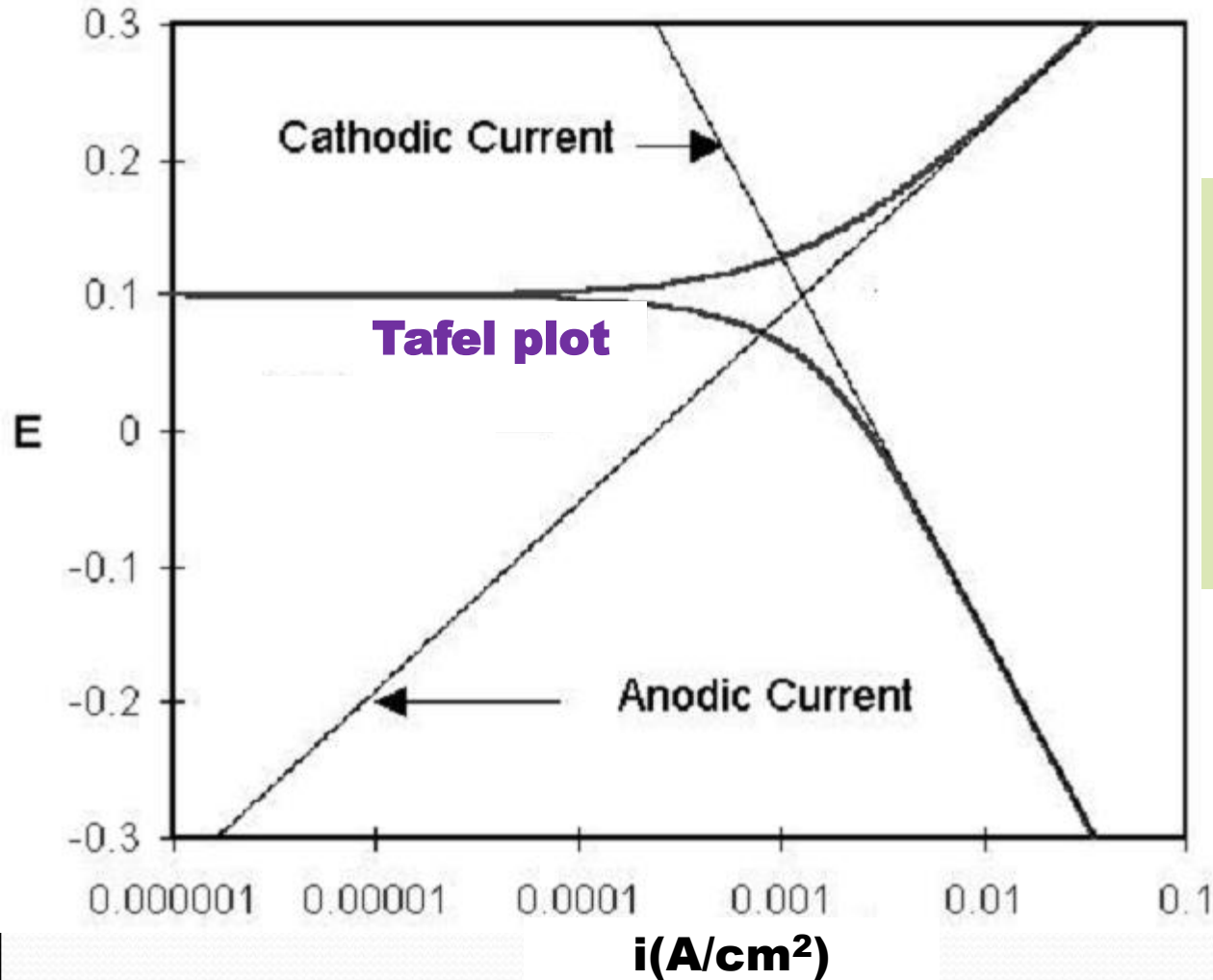
Two types of passivity :

- a) A metal is passive if it resists corrosion under anodic polarization (noble potential, low corrosion rate).**
- b) A metal is passive if it resists corrosion in spite of thermodynamic amenability to react (active potential, low corrosion rate)**

Active metal dissolution and corrosion rate



Tafel Extrapolation Technique:

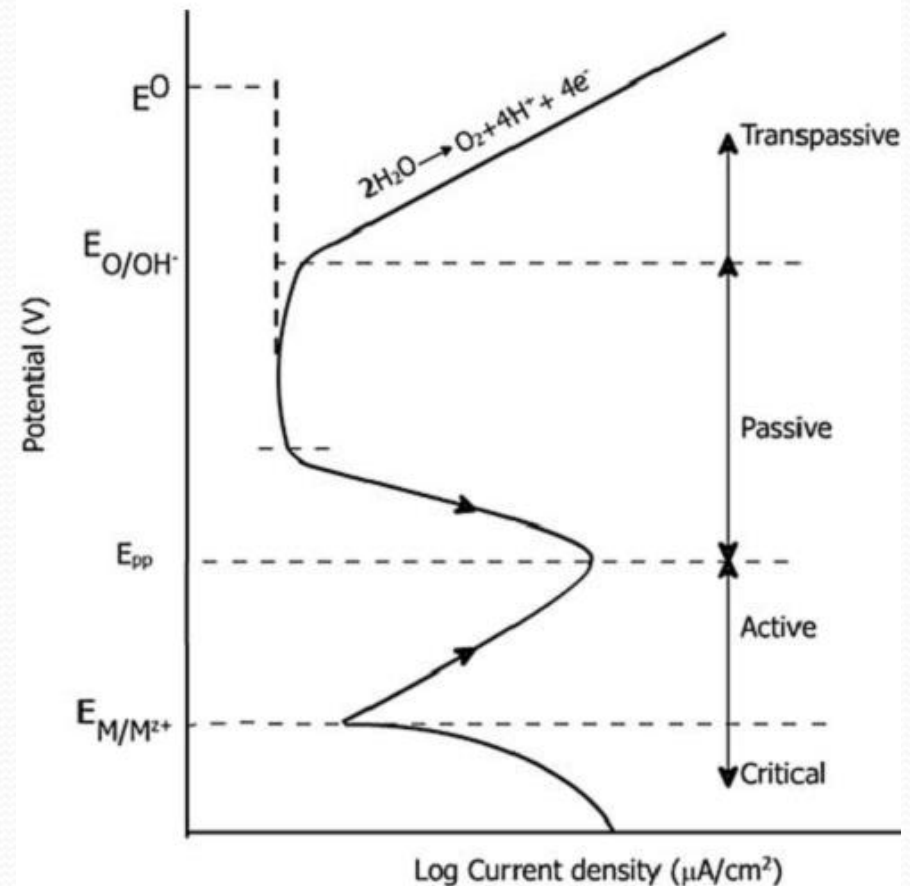
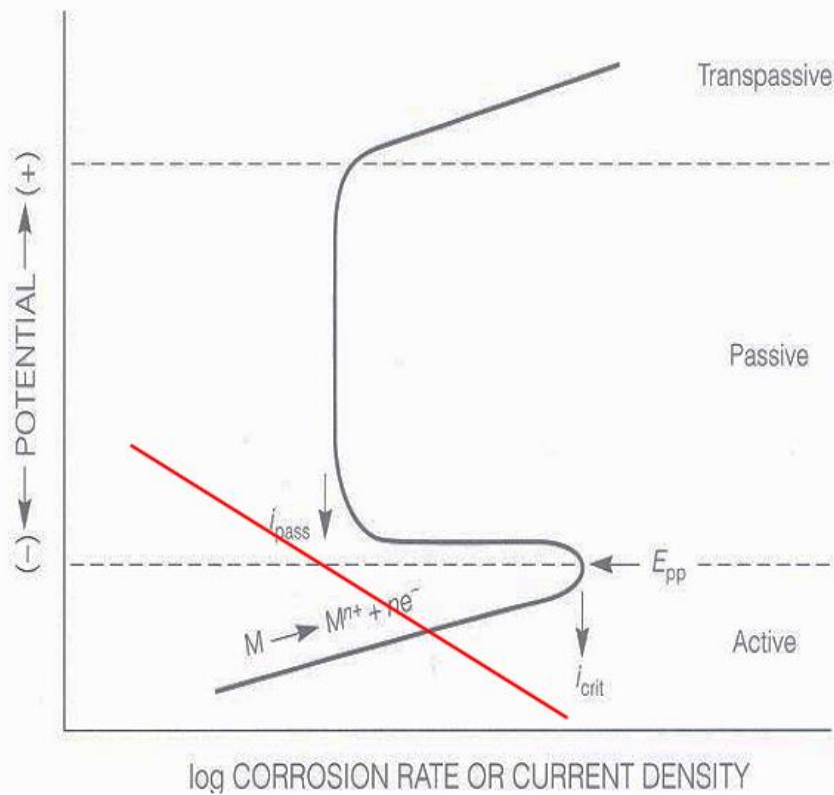


A Tafel plot for a metal specimen can be obtained by polarizing the specimen to about +300 mV anodically and -300 mV cathodically wrt reference electrode from the corrosion potential

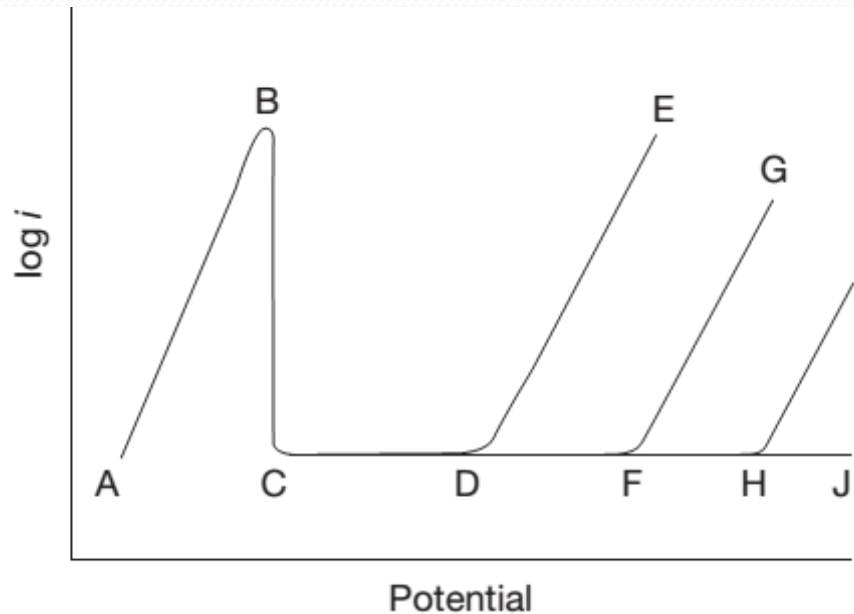
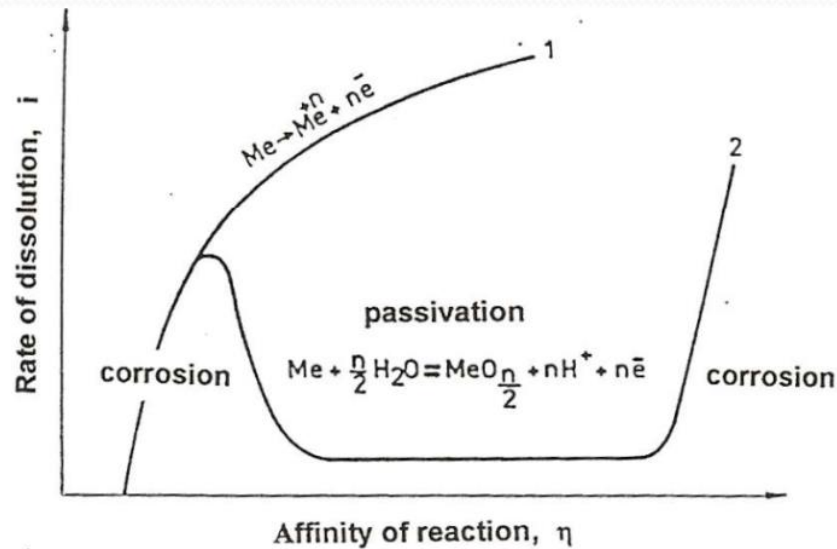
Kinetic aspects of passivation

- A metal to become passive its potential must exceed the passivation potential, a condition that can be reached in two ways:
 - **Anodic polarization (anodic passivation)**
 - **reaction with an oxidizing agent (spontaneous passivation).**

Active -passive dissolution and corrosion rate



anodic polarization curve of a metal



Kinetic aspects of passivation

- A metal to become passive its potential must exceed the passivation potential, a condition that can be reached in two ways:
 - **Anodic polarization (anodic passivation)**
 - **reaction with an oxidizing agent (spontaneous passivation).**

Metals in the passive state (passive metals) have a thin oxide layer on their surface, the passive film, which separates the metal from its environment

Metals in the active state (active metals) are film free.

Most metals and alloys that resist well against corrosion are in the passive state: stainless steel, nickel-chromium based super alloys, titanium, tantalum, aluminum, etc.

Thickness of passive films = about 1–3 nm

Exposed area of metal

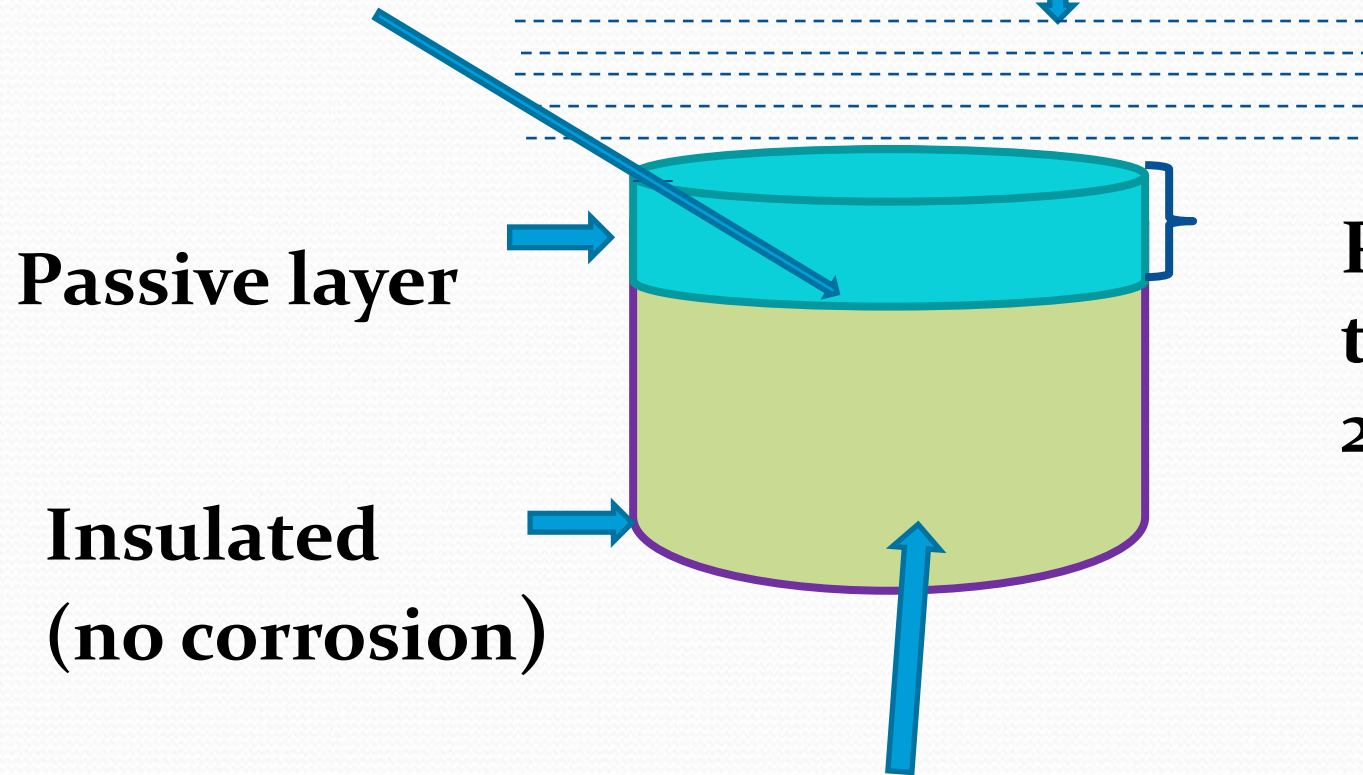
Environments (media)

Passive layer

**Passive film
thickness
2-10 nm**

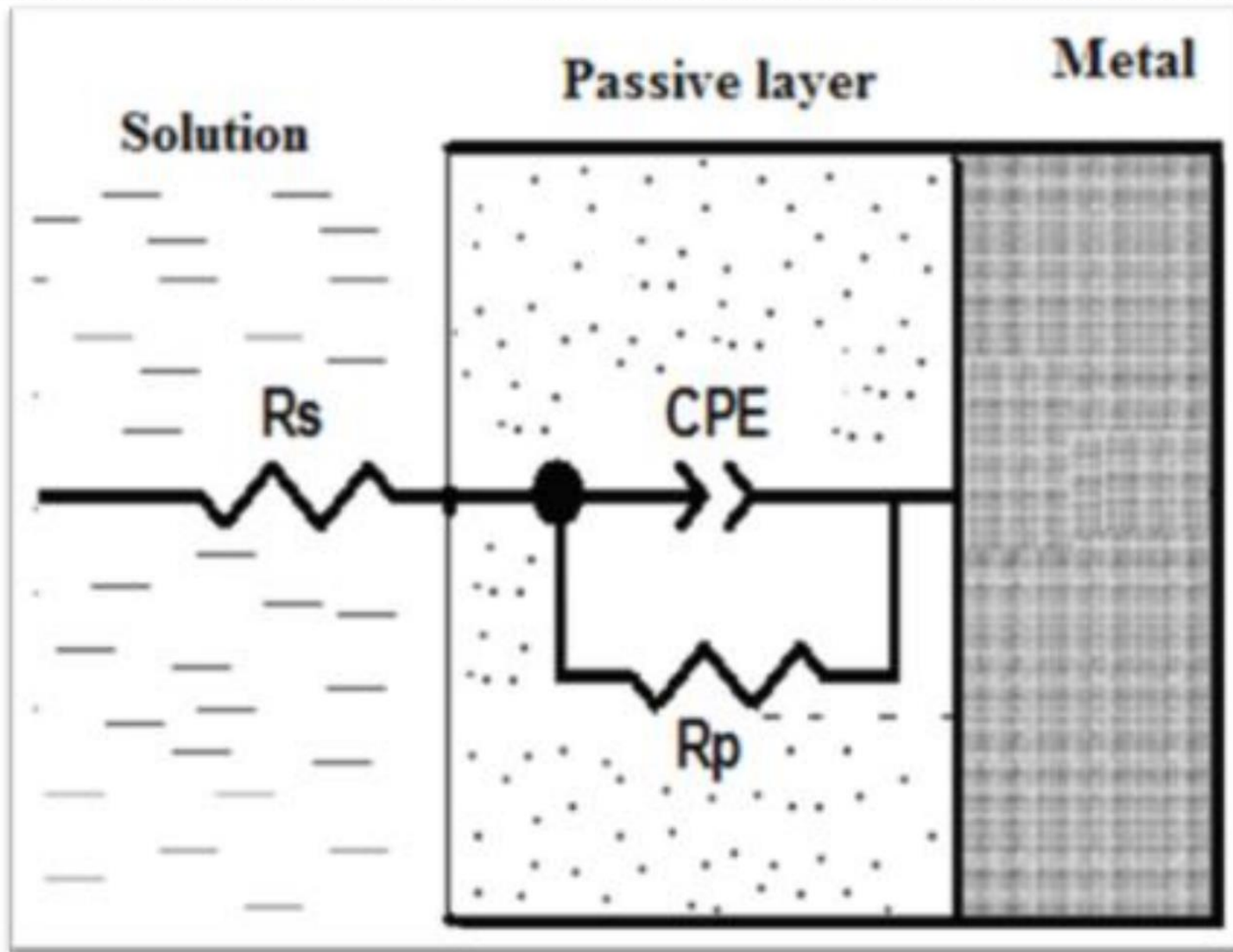
**Insulated
(no corrosion)**

Base metal



Passive film model

Passive film model

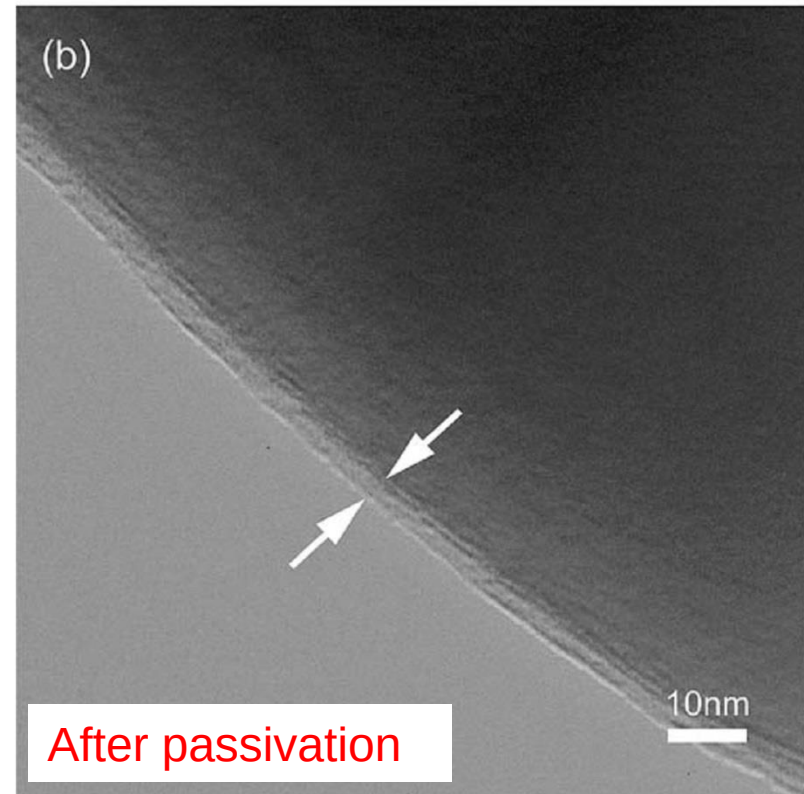
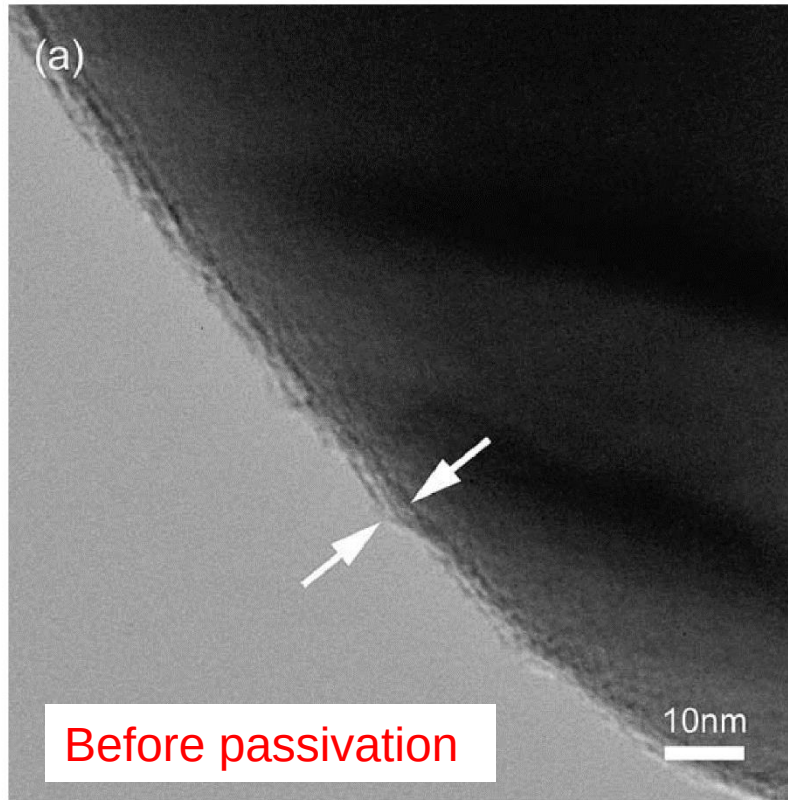


The Passivation Layer

A thin layer of oxide that forms to varying degrees (depending on the magnitude of the free energy of formation of the metallic oxide and the availability of oxygen or other species at the surface).

- This oxide layer can serve to greatly reduce the transport of corrosive species to the underlying metal's surface.
- Freshly exposed metallic surfaces will adsorb and react with oxygen present in the atmosphere almost instantaneously.

TEM bright field images of stainless steel passivated into dilute HNO_3

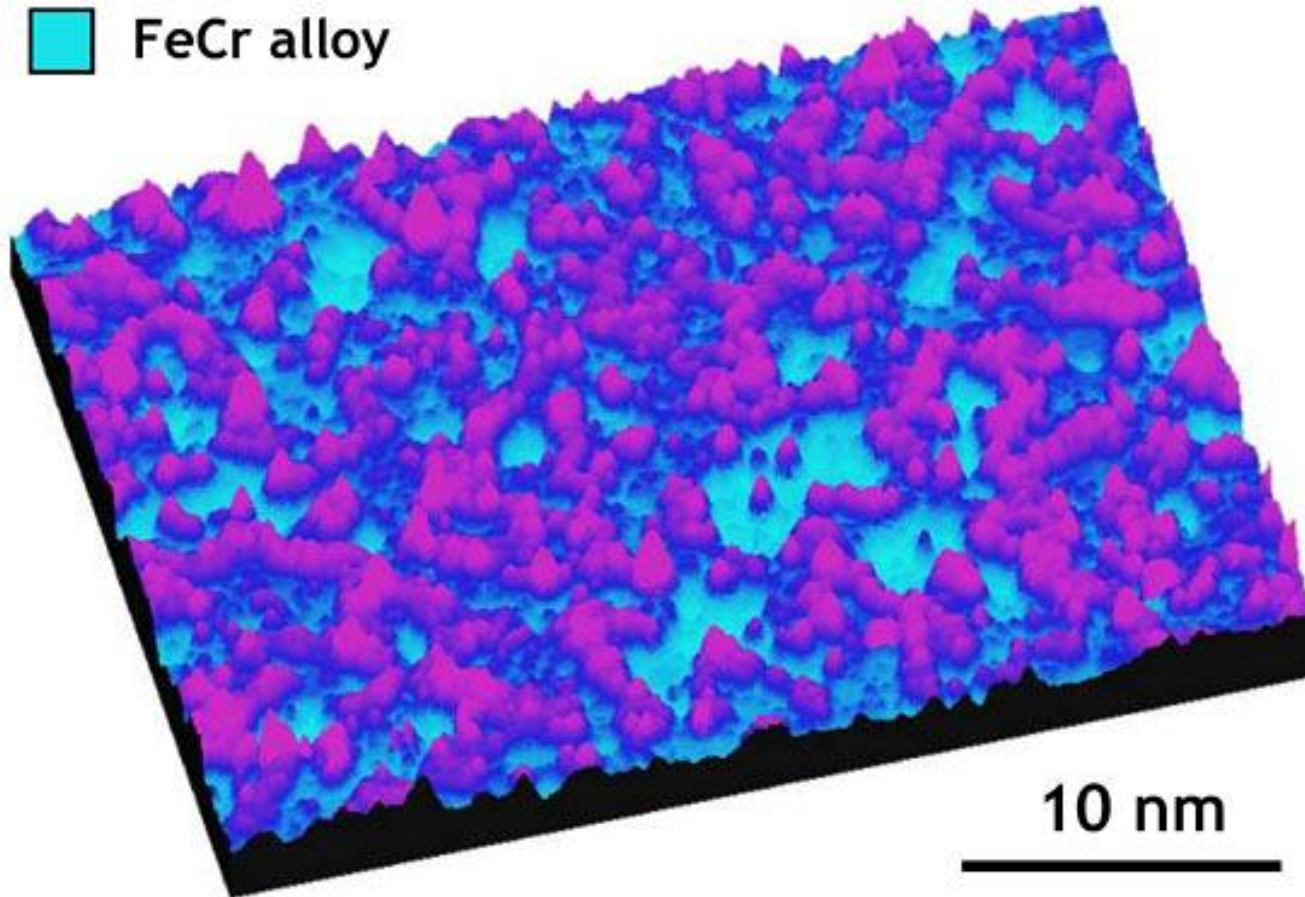


- (a) The morphology of the naturally developed surface oxide layer was blurry so that the interface between the surface oxide and matrix was not clearly observed.
- (b) Passivated surface layer exhibited smooth and uniform contrast with sharp surface layer/matrix interface.

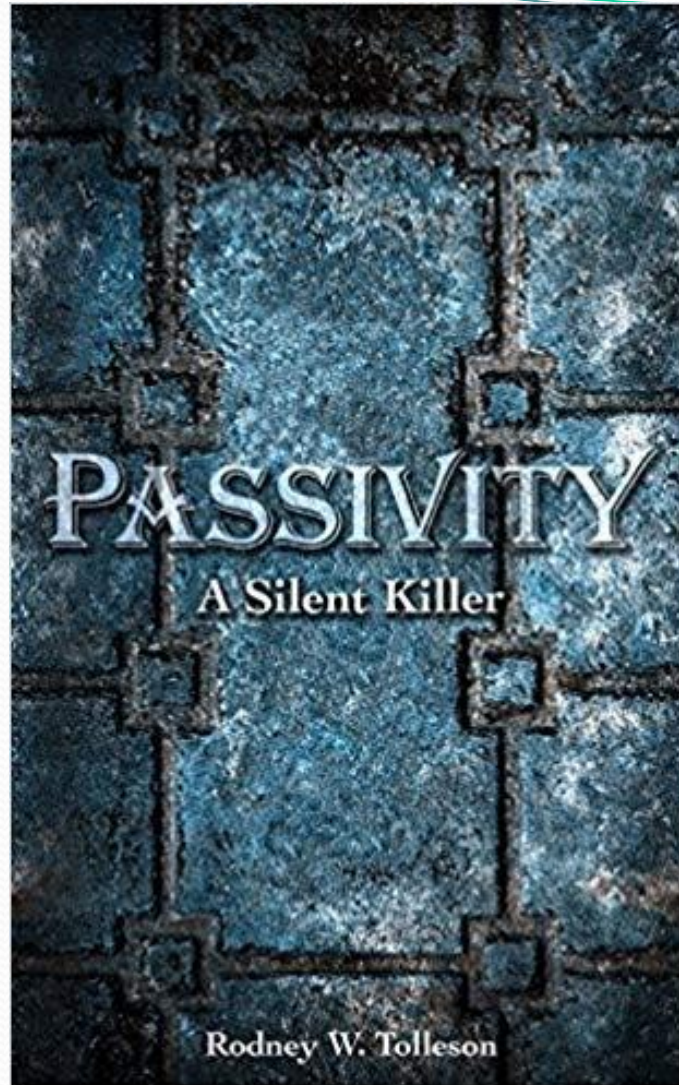
Protective oxide passive film of SS

■ Chromium oxide

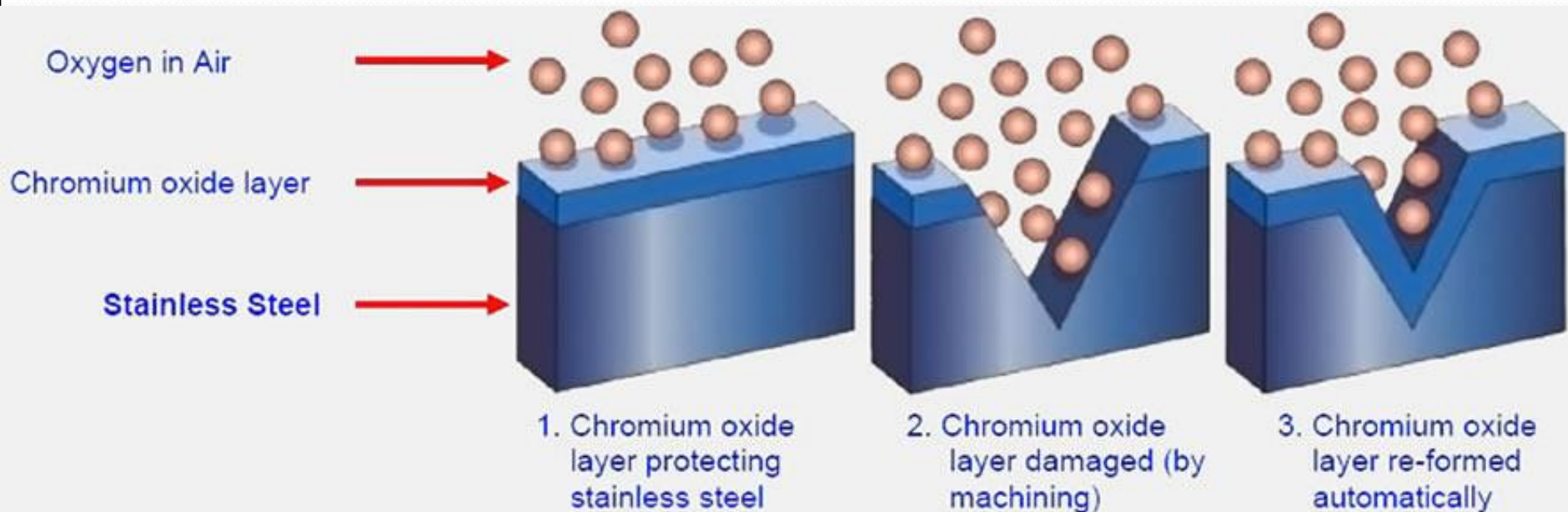
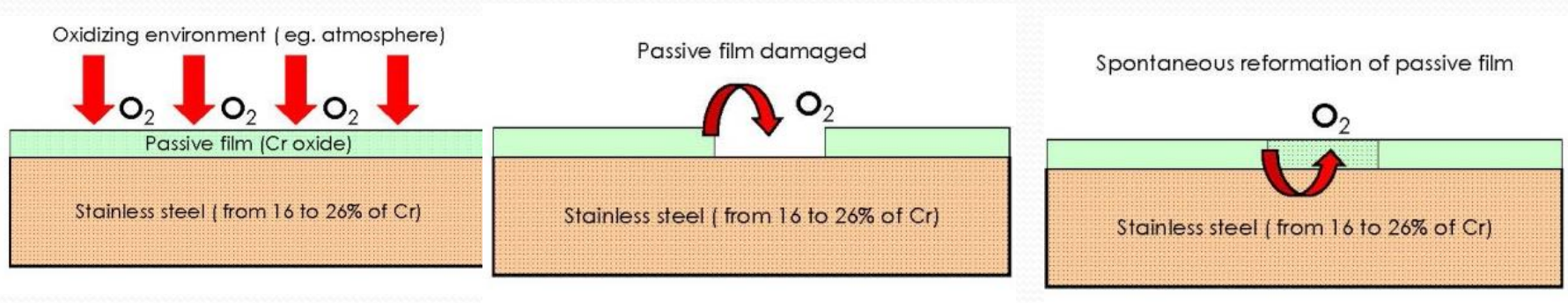
■ FeCr alloy



Scanning tunneling microscope (STM) image of protective oxide passive film on stainless steel

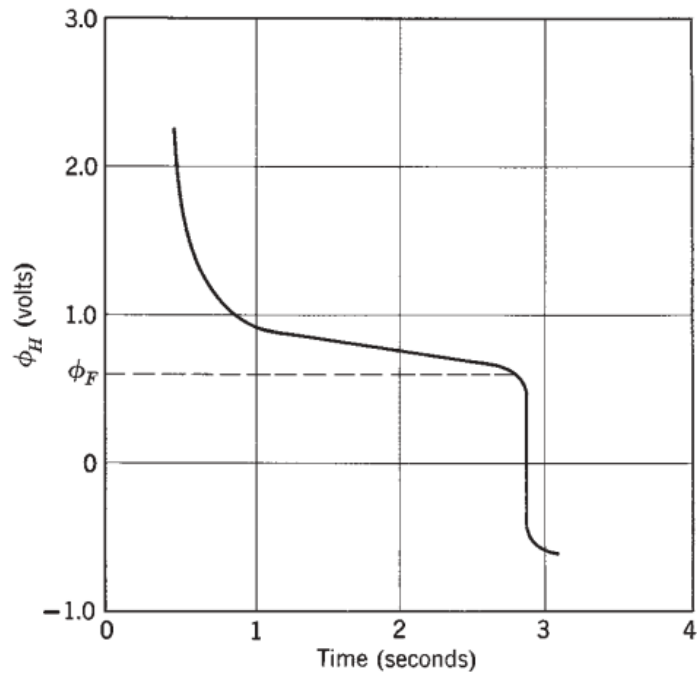


Metallic Passivity



SS passivity: Role of alloying elements

Flade potential



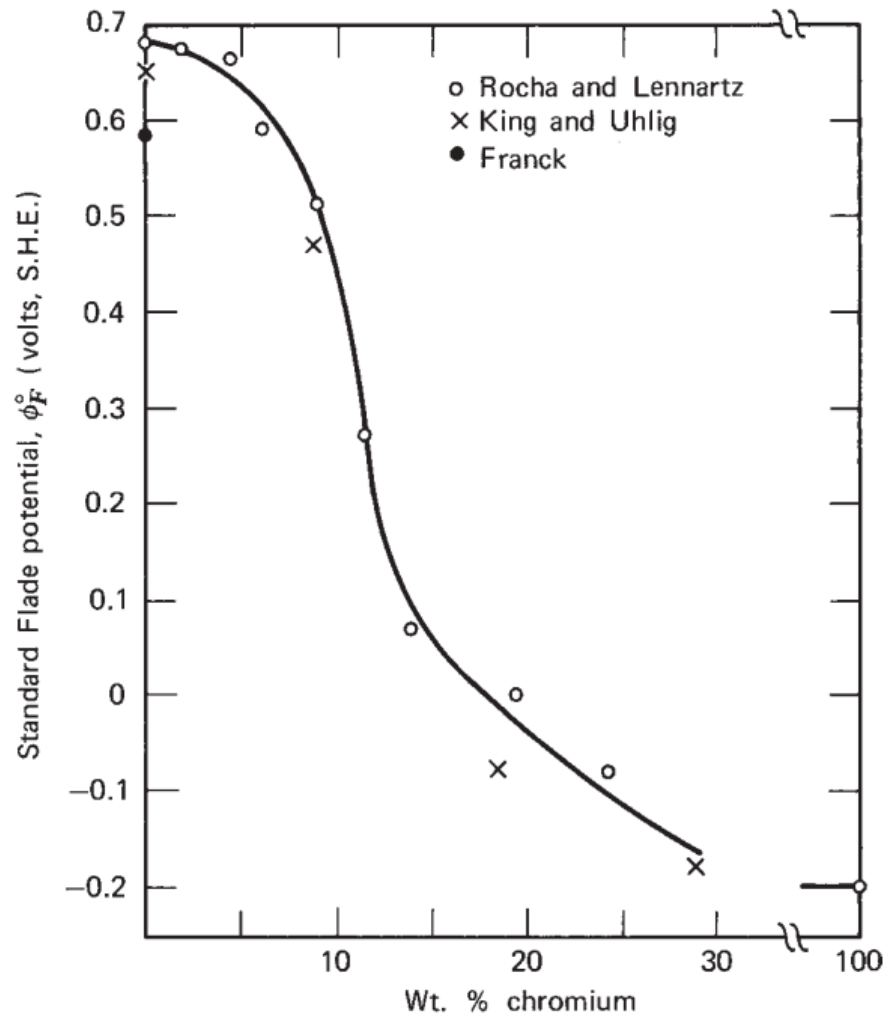
The potential at which a metal changes from a passive state to an active state

It represents the onset of full passivity on the metal surface due to film formation

Decay of passivity of iron in 1 N H_2SO_4 showing Flade potential, ϕ_H

$$\phi_F = \phi_F^\circ + \frac{0.059}{2} \log(\text{H}^+)^2 = \phi_F^\circ - 0.059\text{pH}$$

Standard Flade potentials : role of Cr



chromium-iron alloys

Active-passive metal

The anodic polarization curve for an active-passive metal consists of three regions:

1. Active region:

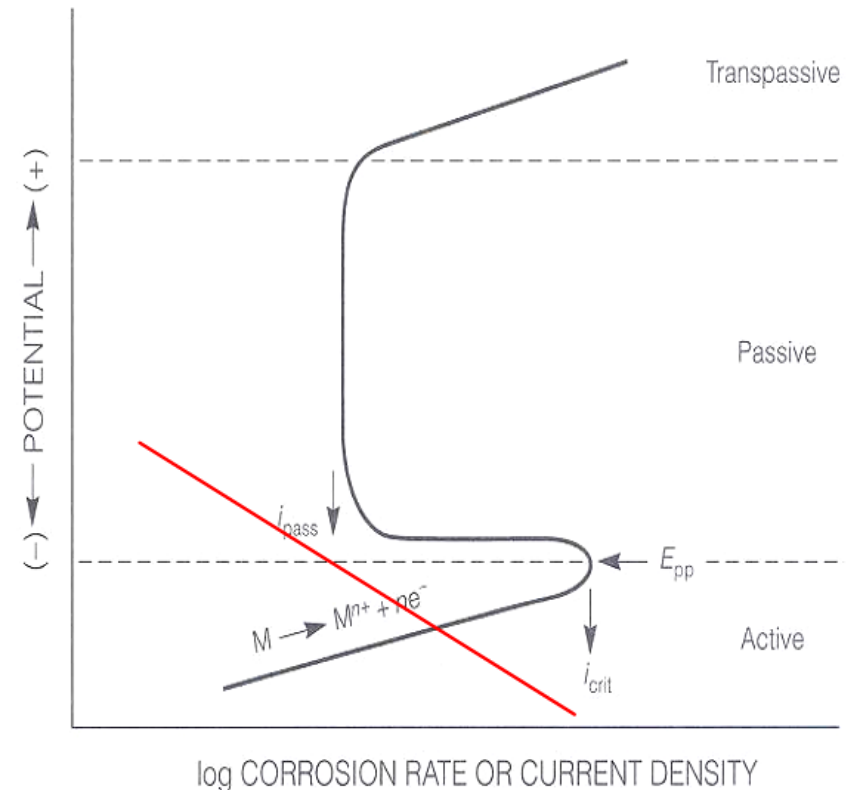
- ❖ current (i) increases with potential (E) until E_{pp} (primary passive potential)
- ❖ i_{crit} is the maximum current

2. Passive region:

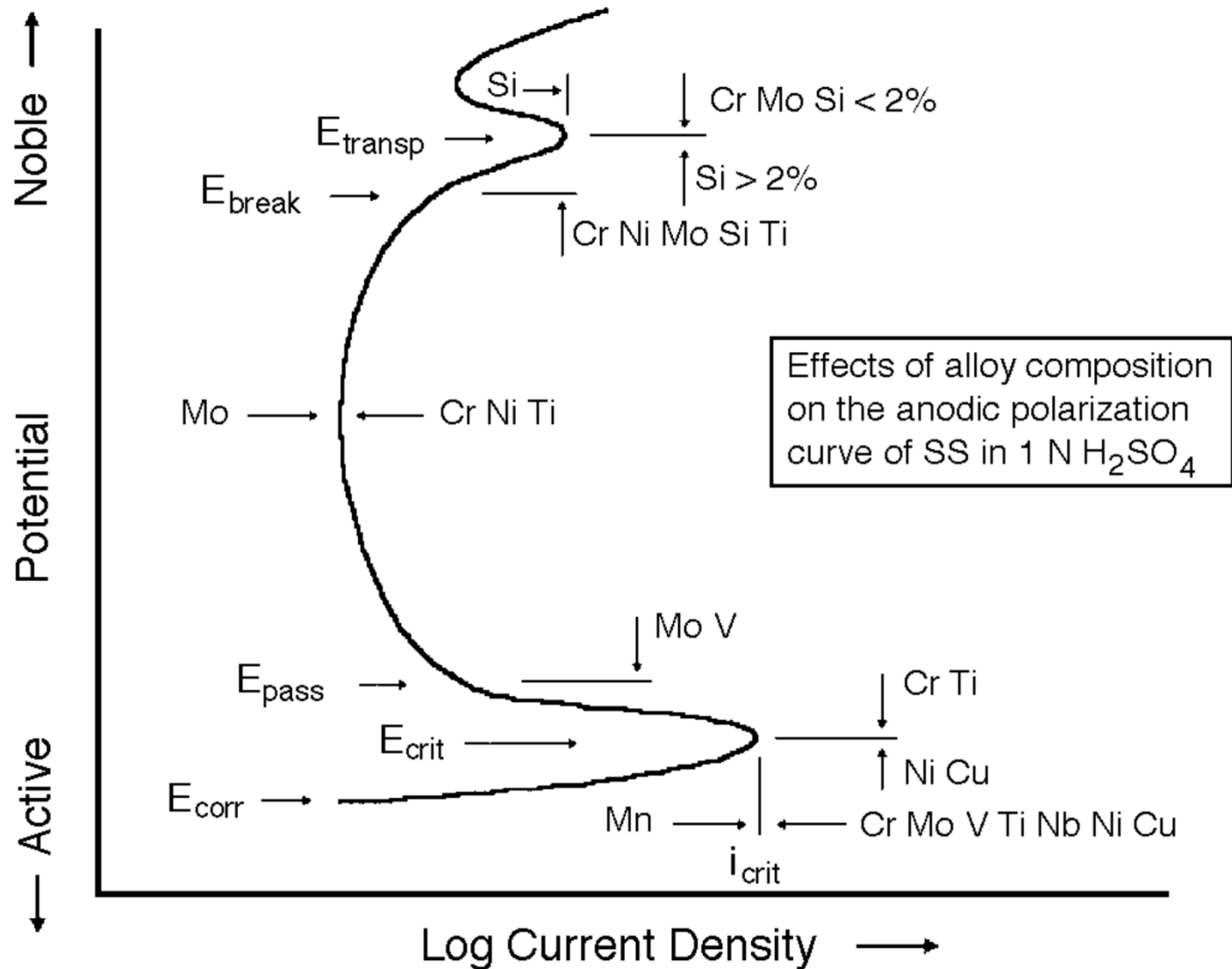
- ❖ Above E_{pp} , the passive film forms and the corrosion current density drops to i_{pass}
- ❖ I_{pass} is very small in the passive state

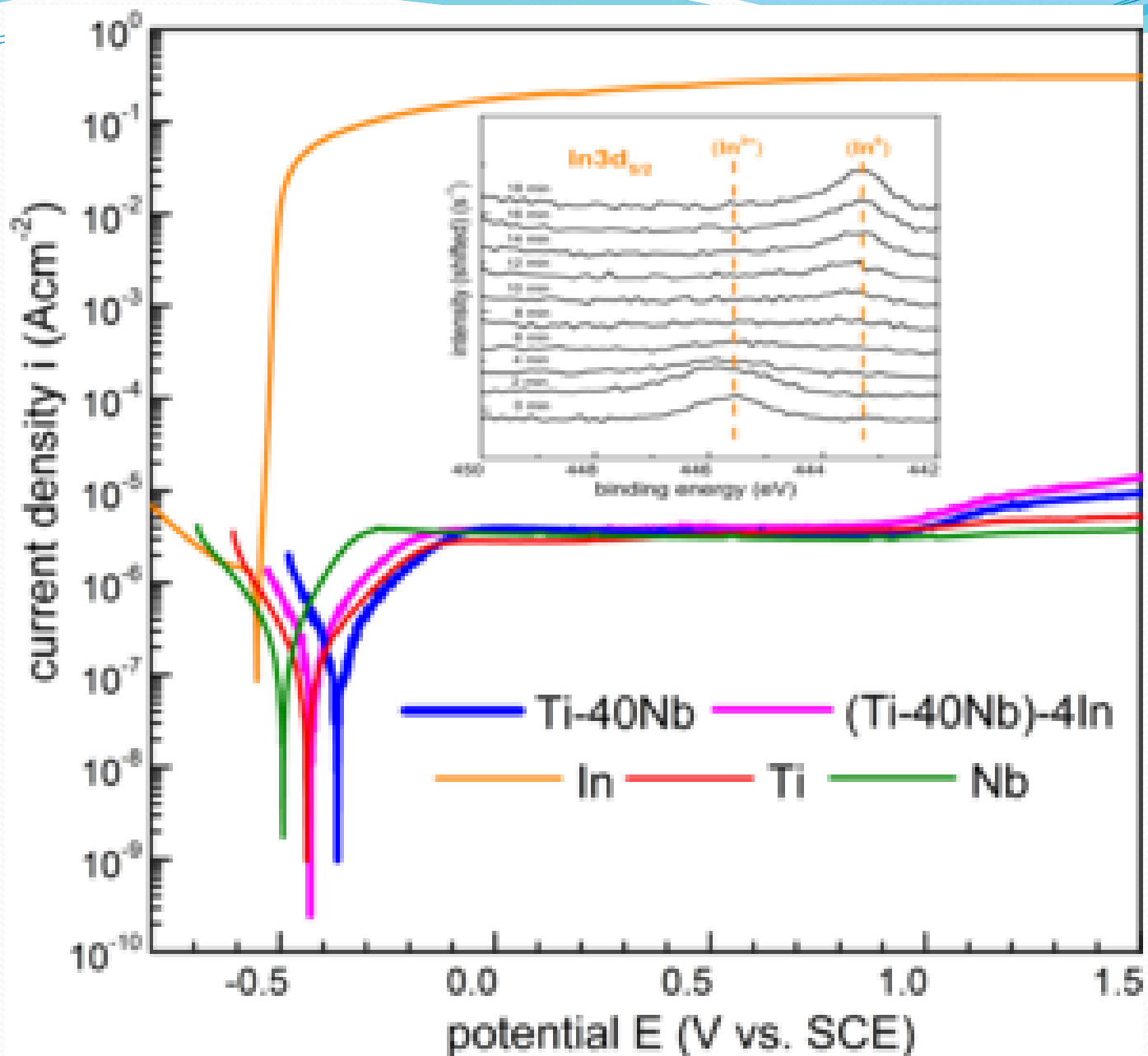
3. Transpassive region:

- ❖ the protective anodic film is damaged and may break down completely.
- ❖ i is proportional to E in the transpassive region

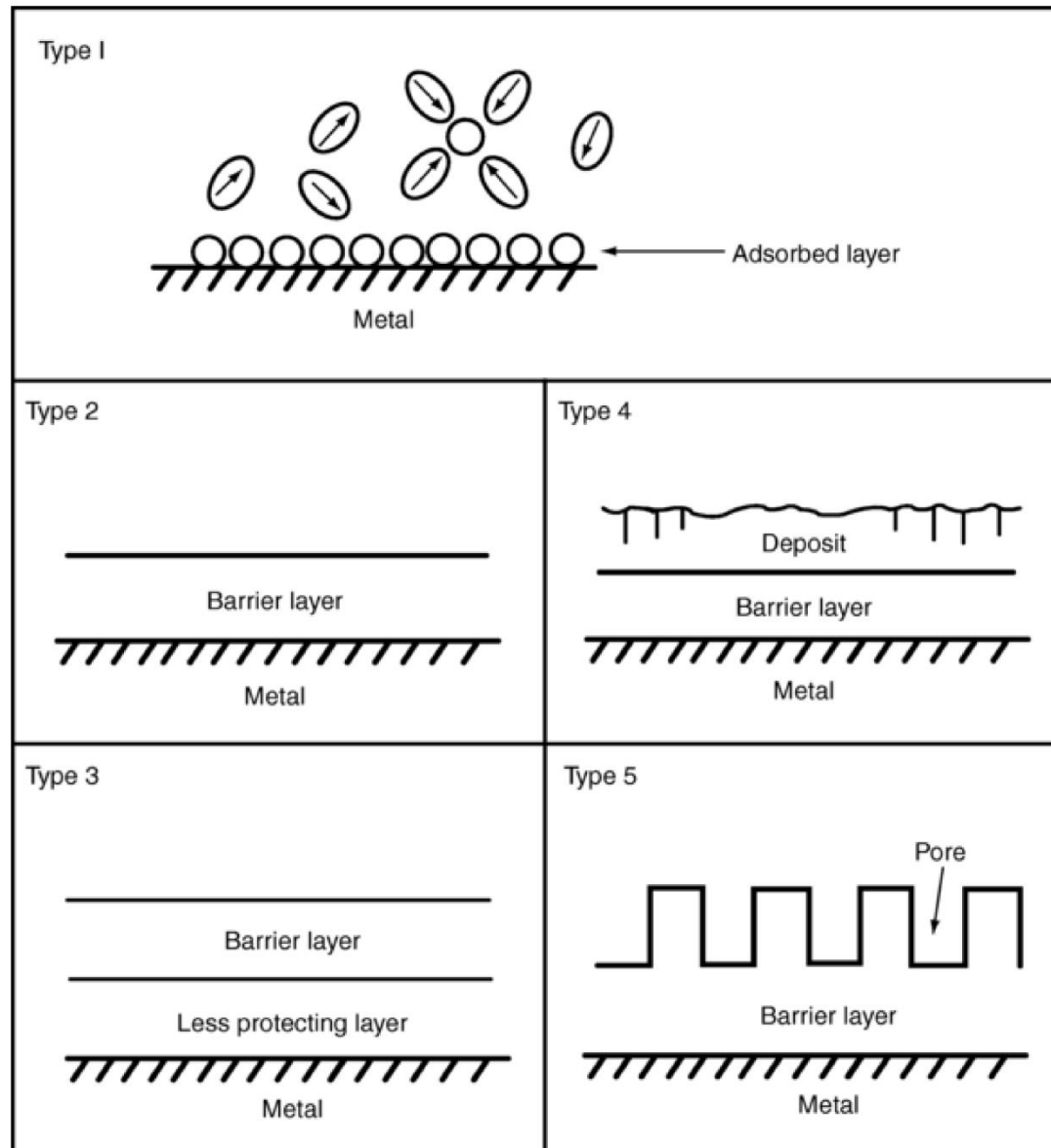


Role of alloying elements



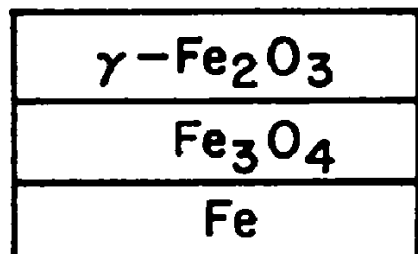


Proposed models of passive film on iron



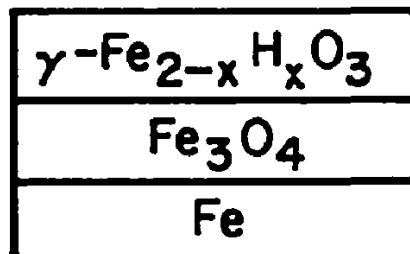
Proposed models of passive film on iron

A



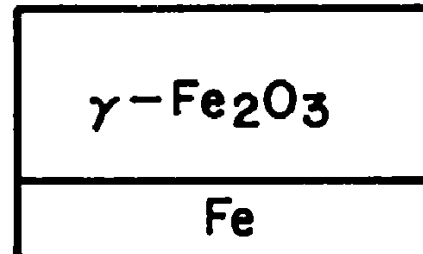
Double layer (DL)
 $\gamma\text{Fe}_2\text{O}_3\text{--}\gamma\text{Fe}_3\text{O}_4$

B



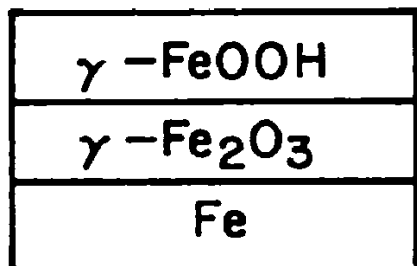
DL with Hydrogen in
 outer layer

C



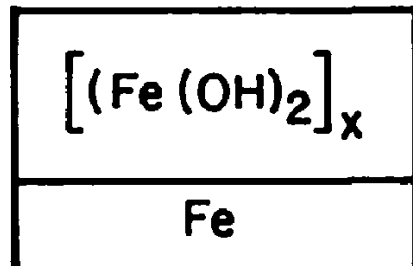
Single layer (SL)
 $\gamma\text{Fe}_2\text{O}_3$

D



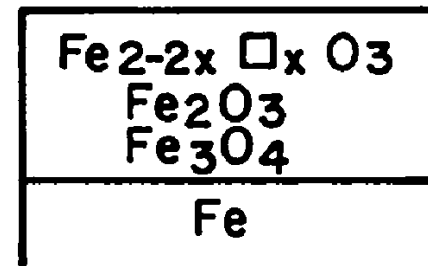
DL: $\gamma\text{FeOOH--}\gamma\text{Fe}_2\text{O}_3$

E



SL layered
 Complex $[\text{Fe}(\text{OH})_x]$

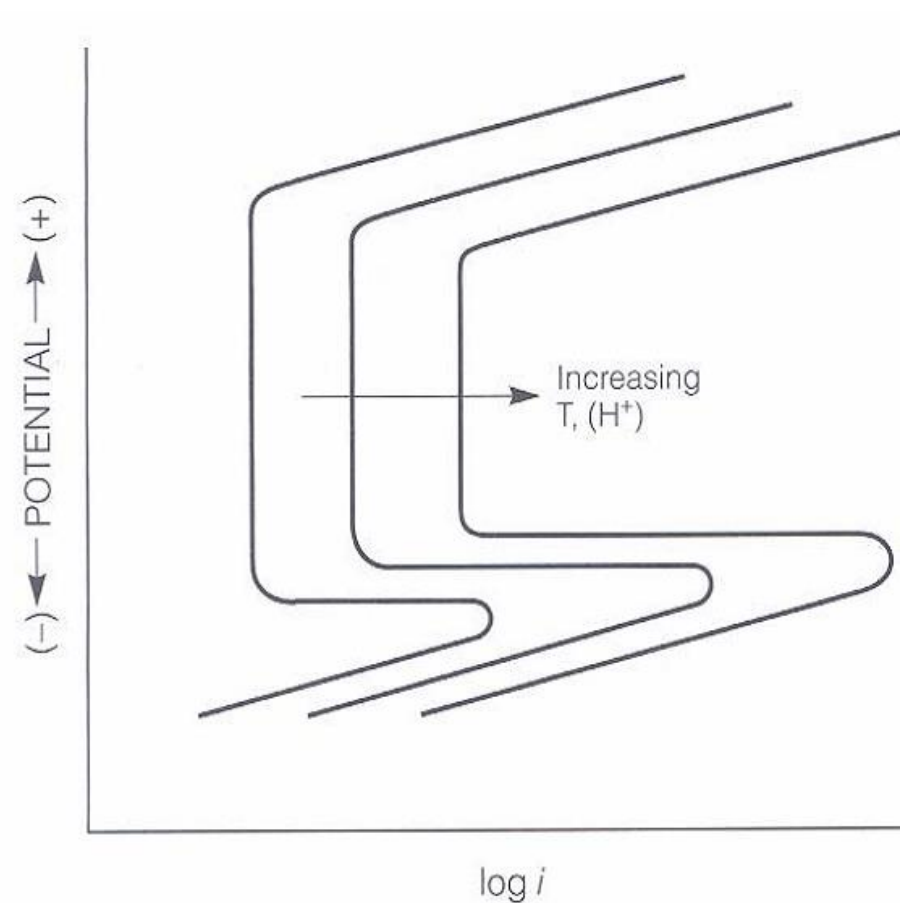
F



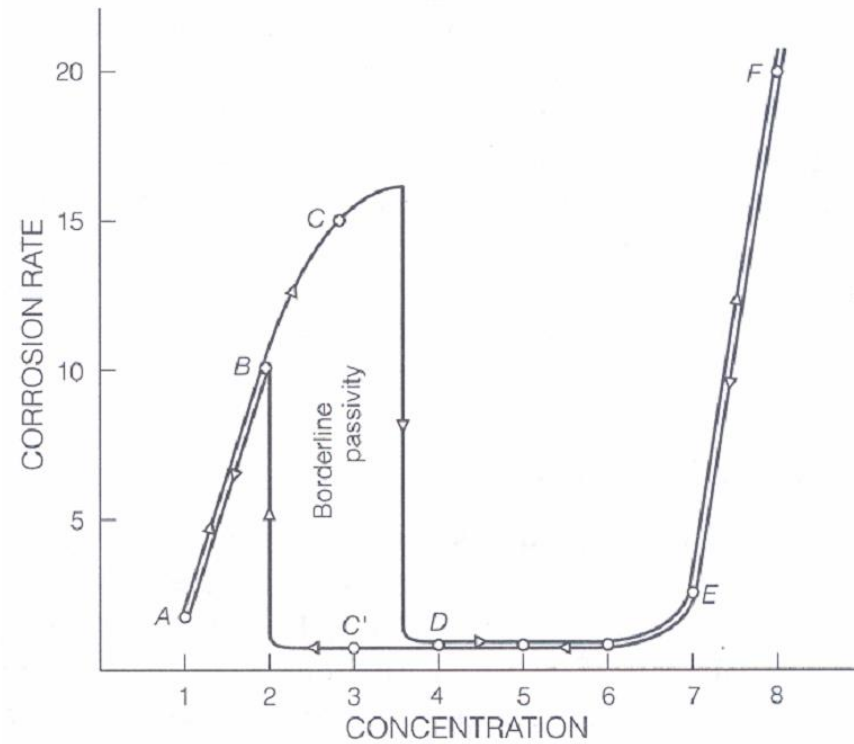
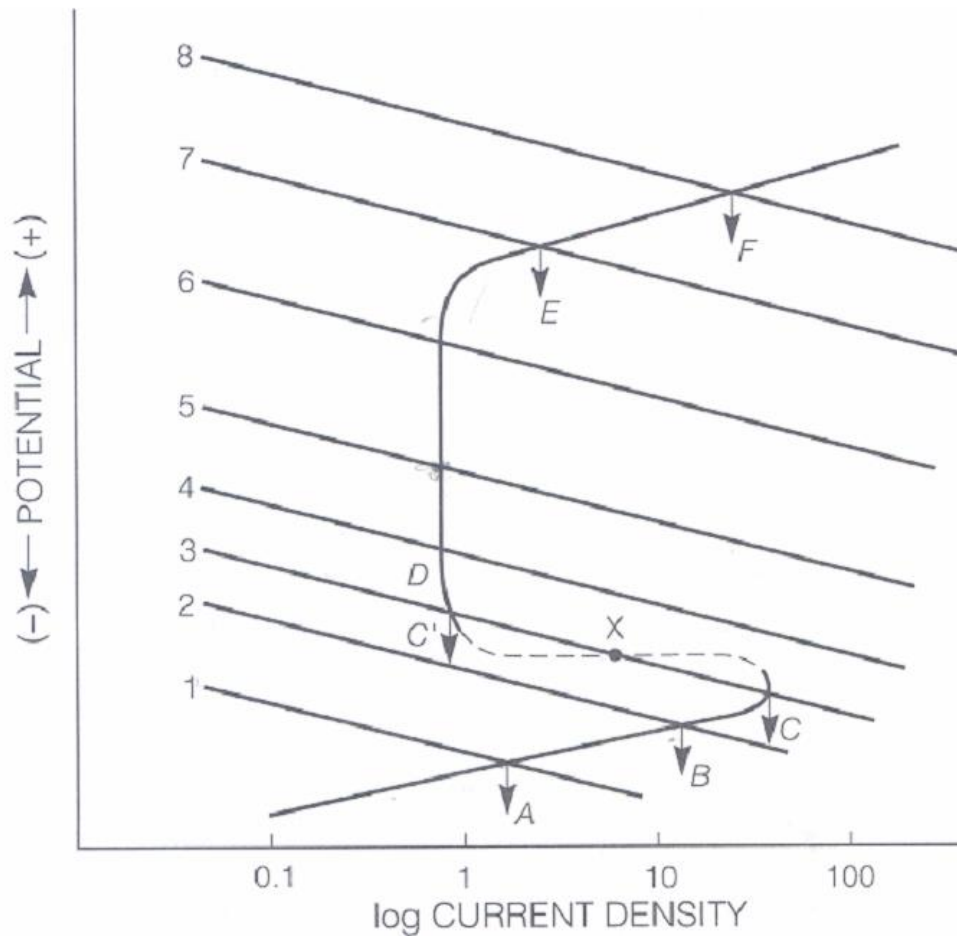
Non-stoichiometric
 cation deficient $\gamma\text{Fe}_2\text{O}_3$
 with varying numbers
 of protons

Effect of environmental conditions on Passivity

- Severe conditions of high acidity and temperature
 - decrease the passivity region
 - increase i_{pass}
 - Increase E_{pp}
 - Increase i_{crit}



Effect of oxidizer concentration



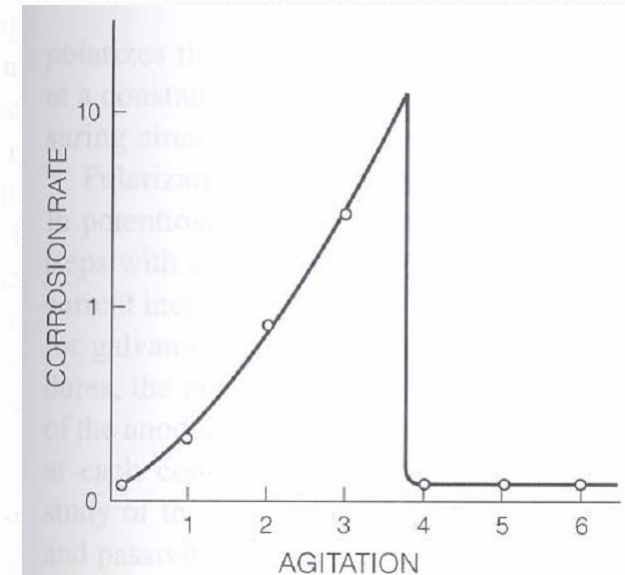
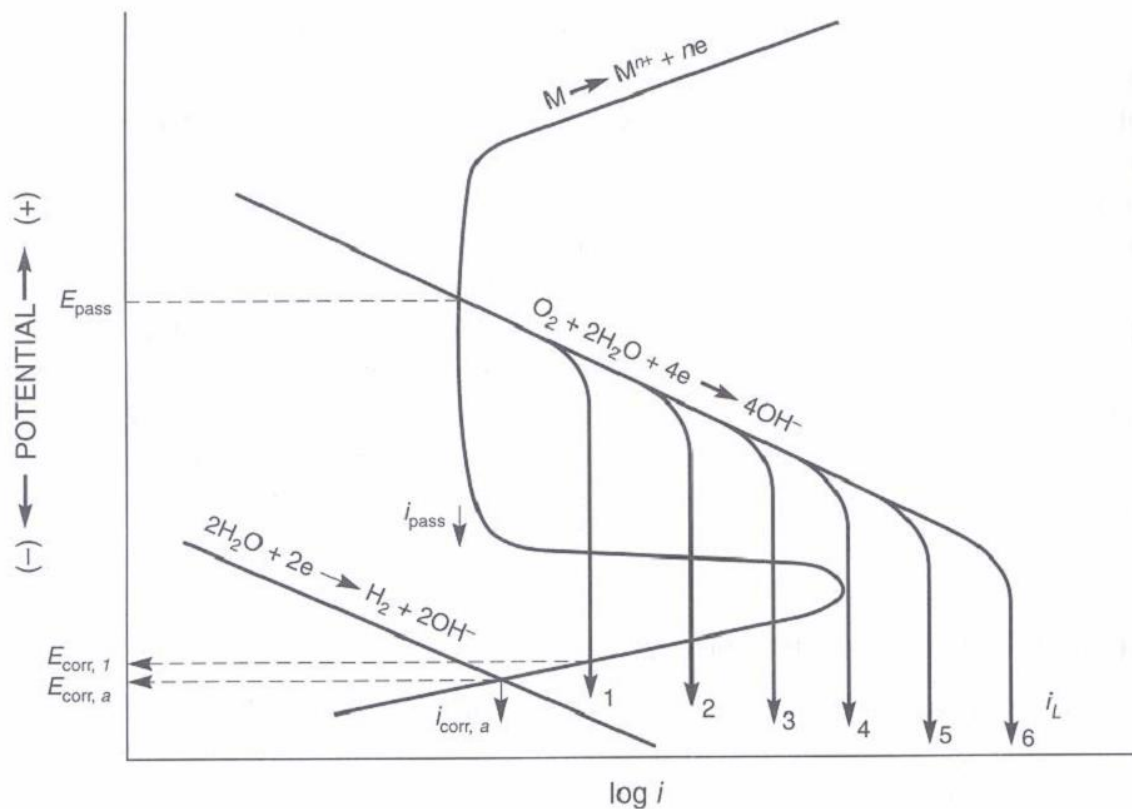
Effect of Oxidizer Concentration

- Consider different cathodic reactions from 1 to 8.
- The oxidizing power increases with increasing AF

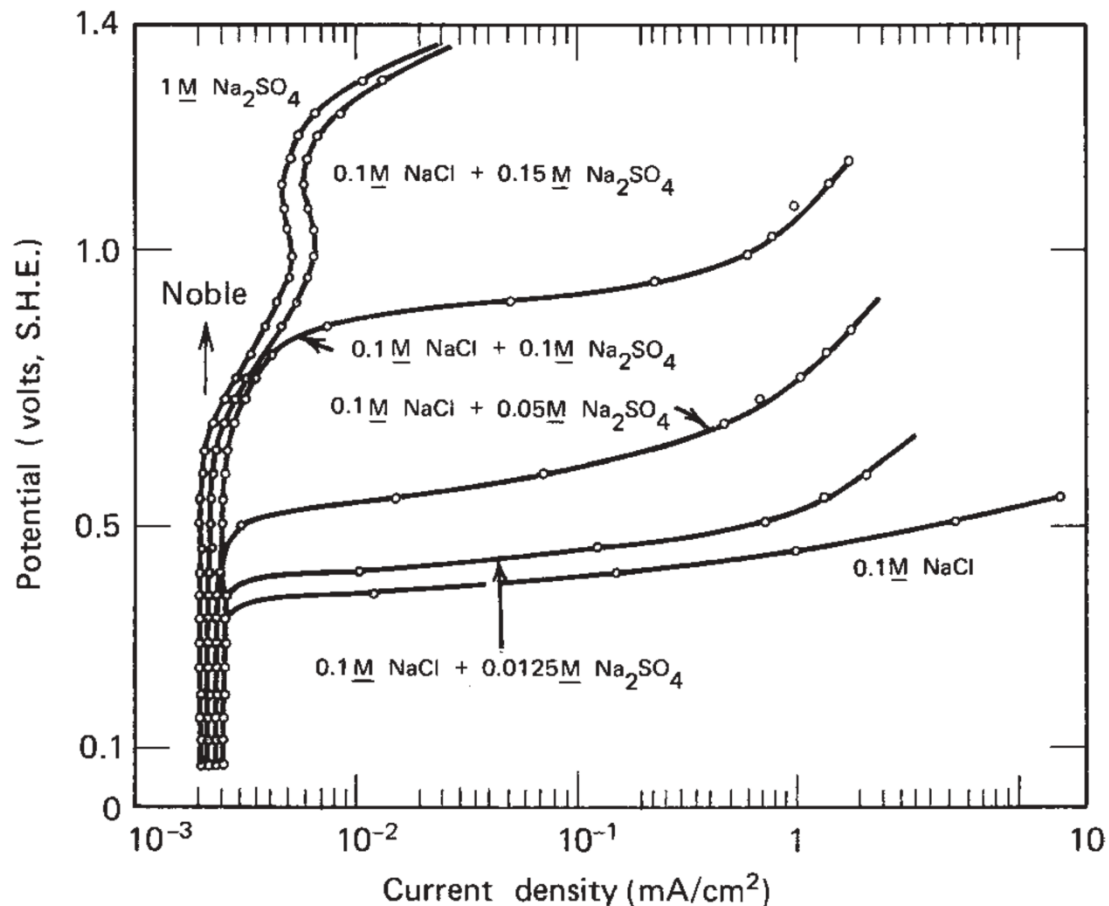
This means that the solution becomes more corrosive going from 1 to 8. As the half-cell potential of the cathodic reaction becomes more positive,

- i_{corr} :
 - increases from A to C (in the active region)
 - drops to D (in the passive region)
 - Increase from E to F (transpassive region)

Effect of solution velocity

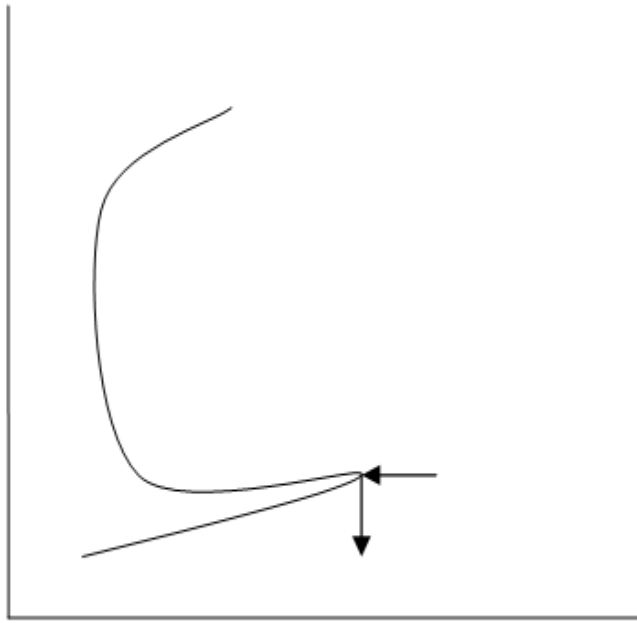


Polarization curves (SS in 0.1 M NaCl)



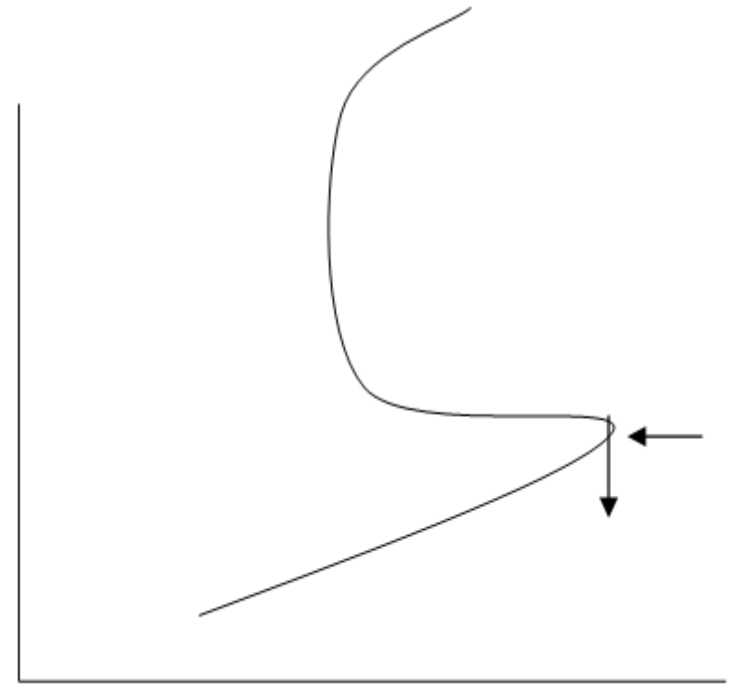
showing increasingly noble values of the critical pitting potential
with additions of Na₂SO₄

Criterion for Passivity



Excellent passivating alloy:

- Lower i_{crit}
- More active (-ve) E_{pp}
- Low i_{pass}



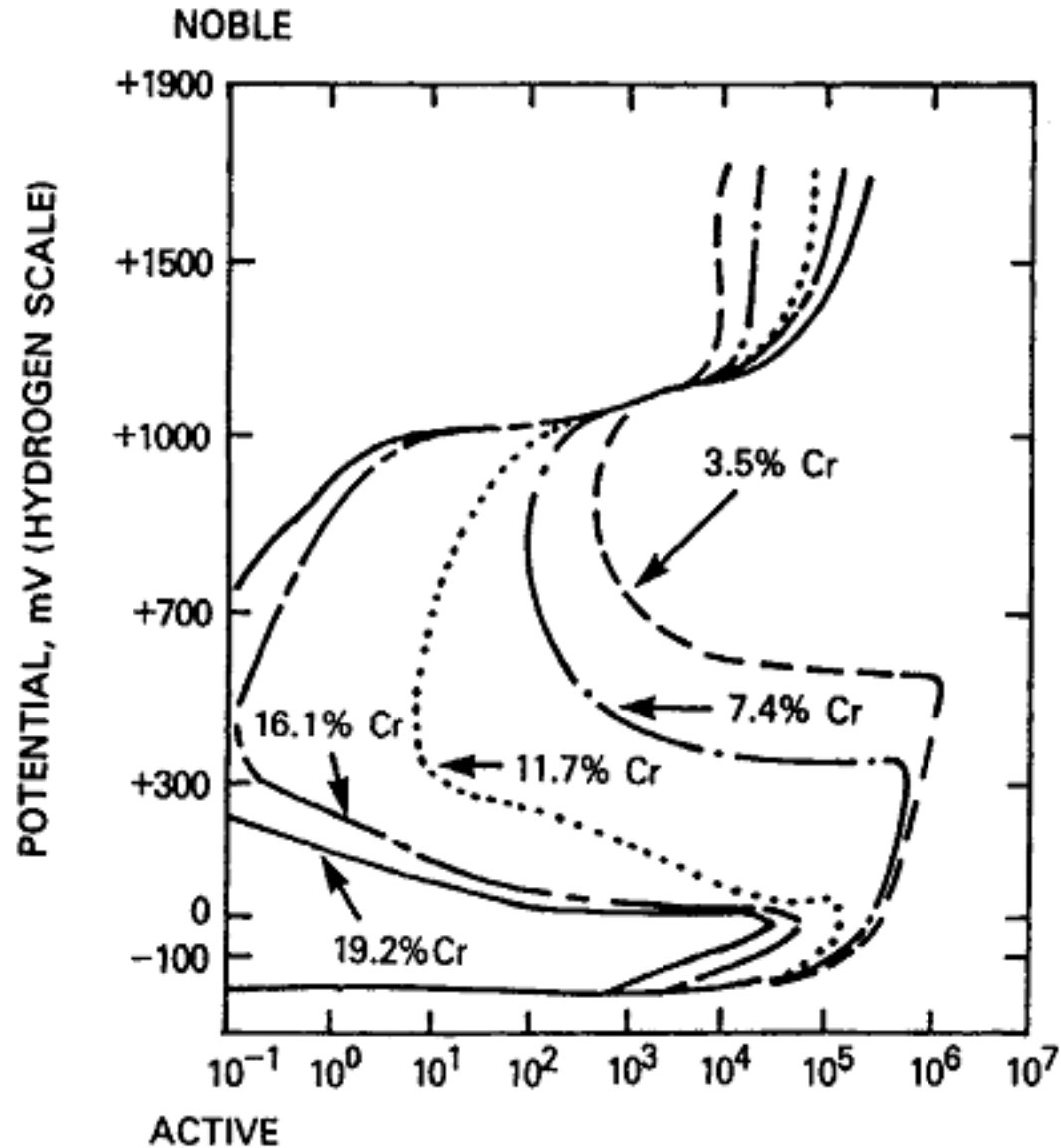
Poor passivating alloy:

- higher i_{crit}
- More anodic (+ve) E_{pp}
- high i_{pass}

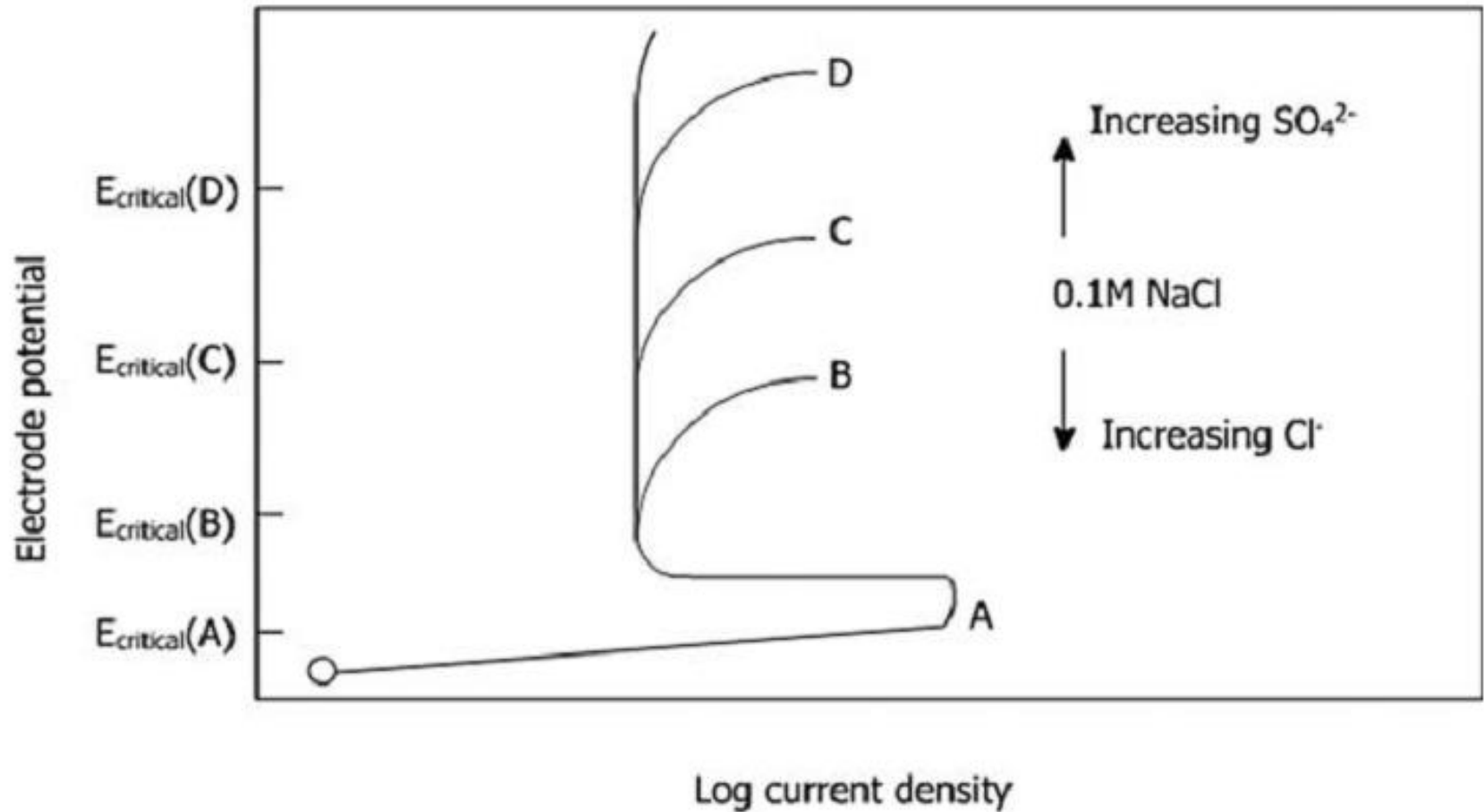
Standard free energy and standard potential of passive film formation

Oxide	$\Delta G^\circ / \text{kJ mol}^{-1}$	E° / V
Ti ₂ O ₃ (hydrated)	-1388	-1.169
Al ₂ O ₃ (Gibbsite)	-1154.9	-0.766
Ta ₂ O ₅	-1912.1	-0.753
Cr ₂ O ₃	-1058	-0.599
ZnO	-318.3	-0.420
MoO ₂	-533	-0.152
Fe ₃ O ₄ (magnetite)	-1016.5	-0.087
Fe ₂ O ₃ (hematite)	-742.2	-0.053
FeO (wustite)	-246.14	-0.041
NiO (unhydrated)	-216	0.110
MoO ₃	-668	0.075
PbO (hydrated, hexagonal)	-183.7	0.277
CrO ₃	-510	0.348
Pb ₃ O ₄	-616.2	0.431
Cu ₂ O	-148.1	0.462
CuO	-134	0.535

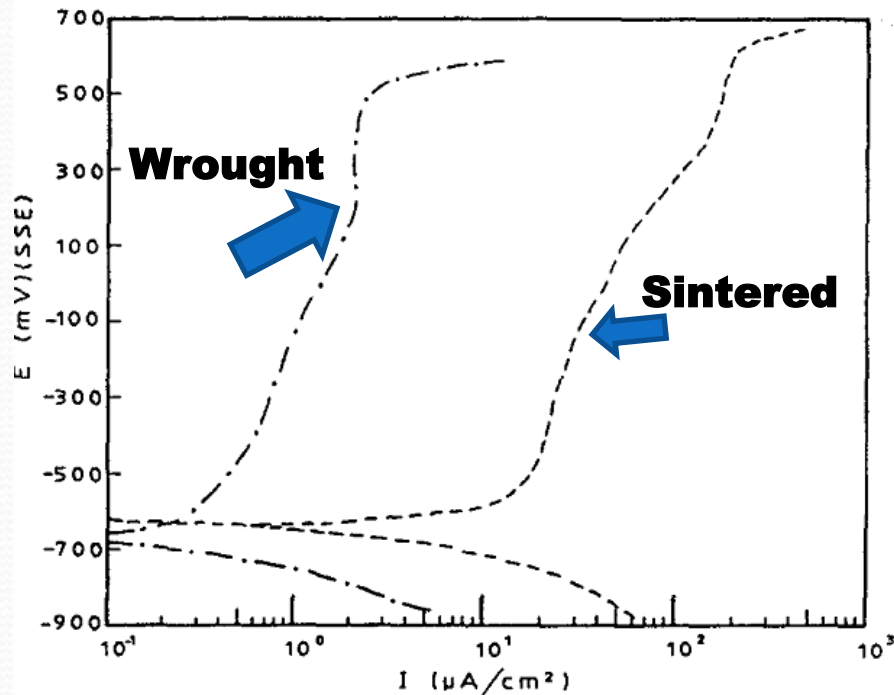
Effect of Cr content in SS



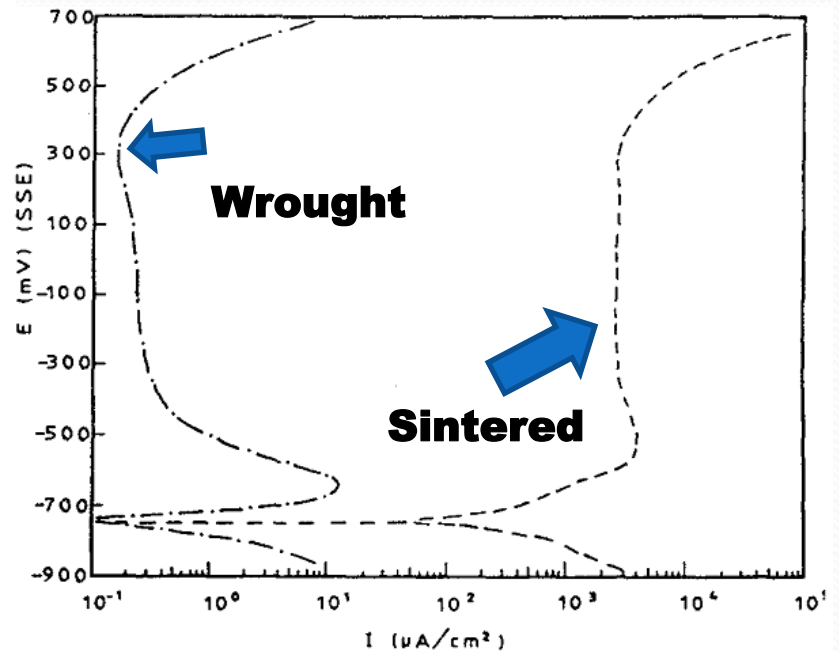
Effect of Cl^- and SO_4^{2-} on passivation of SS



Passivation of sintered and a wrought SS

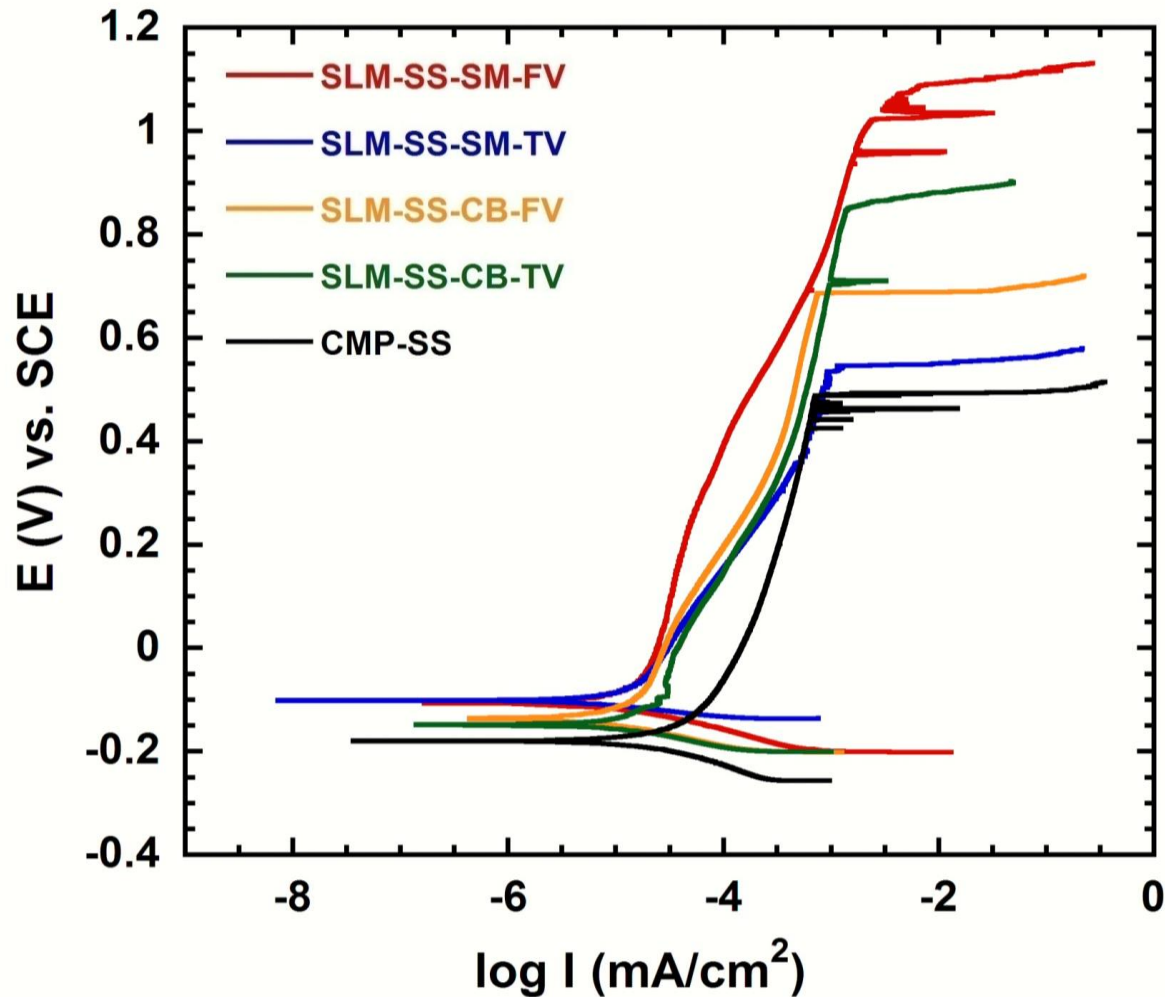


Borate buffer solution (pH- 8.7)

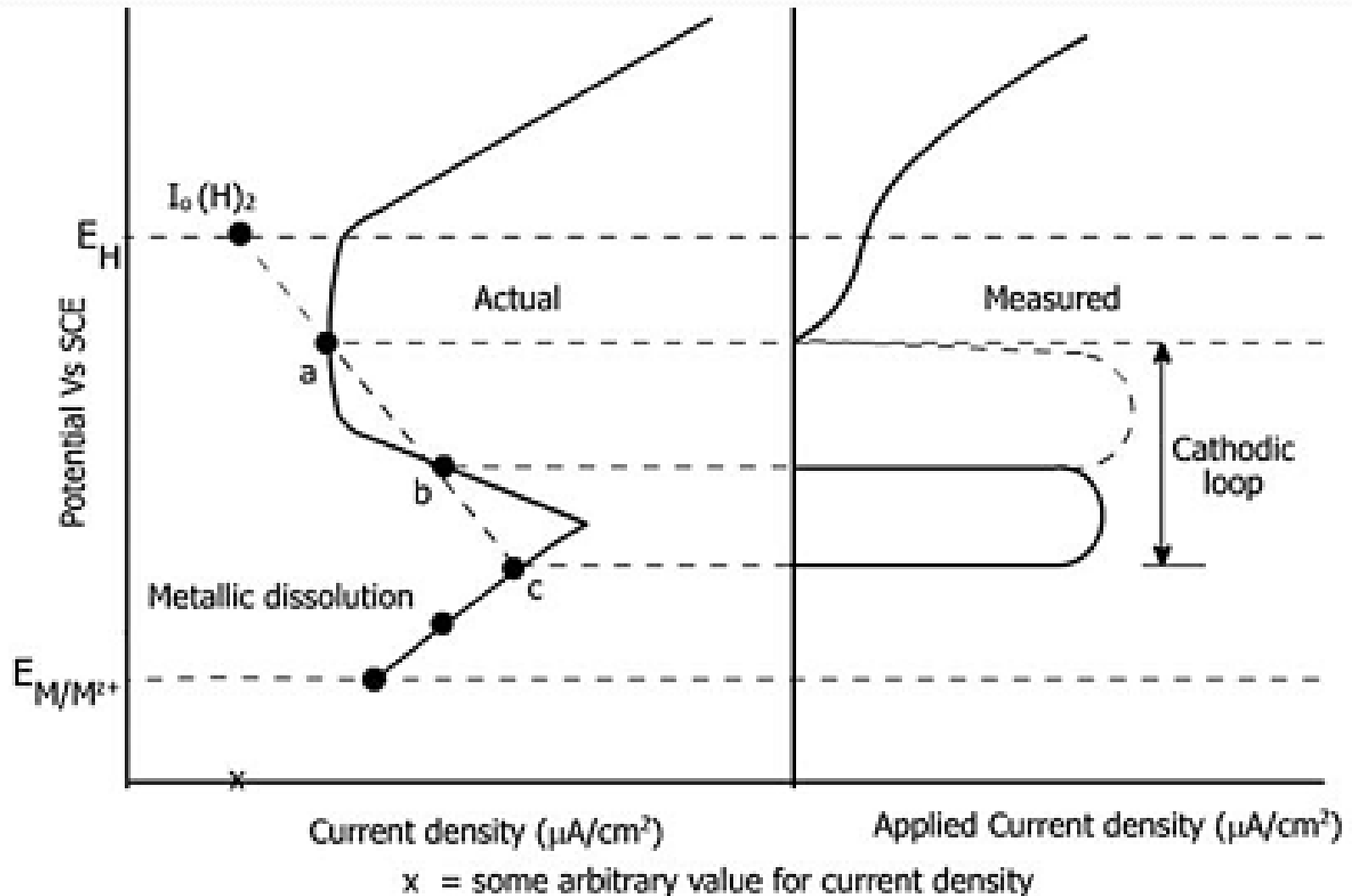


0.5 M H_2SO_4

Passivation study of SLM stainless steels



Actual and measured polarization curve



Theories of Passivation

- Passivation is a complex phenomenon and is difficult to explain completely.
- two approaches,
 - The film theory (originated by Faraday)**
 - Absorption theory (Kolotyrkin and Uhlig)**

Film Theory

- When the film is established, its ability to protect the metal depends on the degree of self-control it imposes on dissolution of the metal.

The dissolution is the combined result of three processes:

1. Entry of metal atoms into the film as cations at the metal/film interface.
2. Transport of the metal cations or of oxygen anions through the oxide.
3. Dissolution of metal cations from the film at the film/environment interface.

- At ambient temperatures, the processes are driven by the electric field across the film and so the following properties of a film commend it as a

Passivating agent:

- Stability over a wide potential range.
- Mechanical integrity.
- Low ionic conductivity.
- Good electron conductivity to reduce the potential difference across the film.
- Low solubility and slow dissolution in the prevailing aqueous Medium

Adsorption Theory

The theory recognizes that strong anodic passivation is a characteristic of alloys of metals in the transition series,

- Singly occupied or unfilled atomic orbitals offer the facility for the highly polarized water molecules and anions in immediate contact with the metal to bind to the surface metal atoms by sharing electrons, creating the passive condition that protects the metal.
- A dynamic steady state is predicted with continuous exchange of molecules between the adsorbed layer and the aqueous environment.

- Theories of alloying to promote passivating capability by optimizing the bond strength

