

η = sobrepotencial

$$j = Fk^0 [O]^{1-\alpha} [R]^\alpha \left(\exp[(1-\alpha)f(E - E_{eq})] - \exp[-\alpha f(E - E_{eq})] \right)$$

j_0 = Corriente de intercambio

k^0 = constante cinética de electrodo

$$j = j_0 \left(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta} \right)$$

Oxidación (rama anódica) Reducción (rama catódica)

$[k^0] = \text{cm/s}$
heterogénea

$10^{-9} \text{ cm/s} < k^0 < 1-10 \text{ cm/s}$

Synoptic table 25.6* Exchange current densities and transfer coefficients at 298 K

| Reaction | Electrode | $j_0 / (\text{A cm}^{-2})$ | α |
|--|-----------|----------------------------|----------|
| $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ | Pt | 7.9×10^{-4} | |
| | Ni | 6.3×10^{-6} | 0.58 |
| | Pb | 5.0×10^{-12} | |
| $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ | Pt | 2.5×10^{-3} | 0.58 |

Ecuación de Butler-Volmer

$$j = j_0 \left(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta} \right)$$

Oxidación
(rama anódica) Reducción
(rama catódica)

$$\alpha = 0.5$$

Coefficiente de transferencia

Ecuación de Butler-Volmer

$$\eta > 0$$

$$j = j_0 e^{(1-\alpha)f\eta}$$

Rama
Anódica

$$\eta < 0$$

$$j = -j_0 e^{-\alpha f\eta}$$

Rama
Catódica

$$\eta \sim 0 \quad (|\eta| \ll f^{-1} = 25\text{mV})$$

$$j = j_0 f \eta$$

Ambas
Ramas

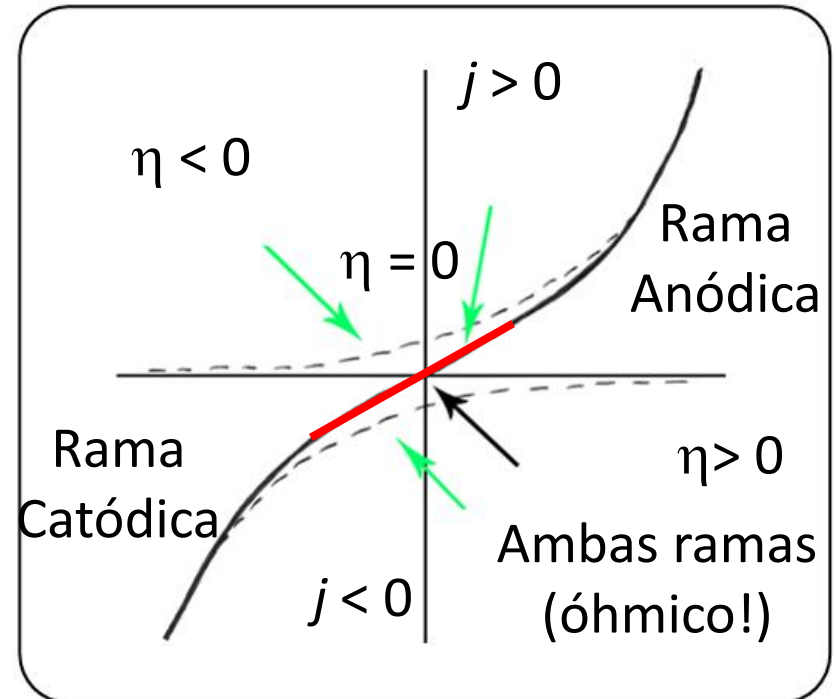


Gráfico de Tafel

Rama
Anódica

$$\eta > 0$$

$$j = j_0 e^{(1-\alpha)f\eta}$$

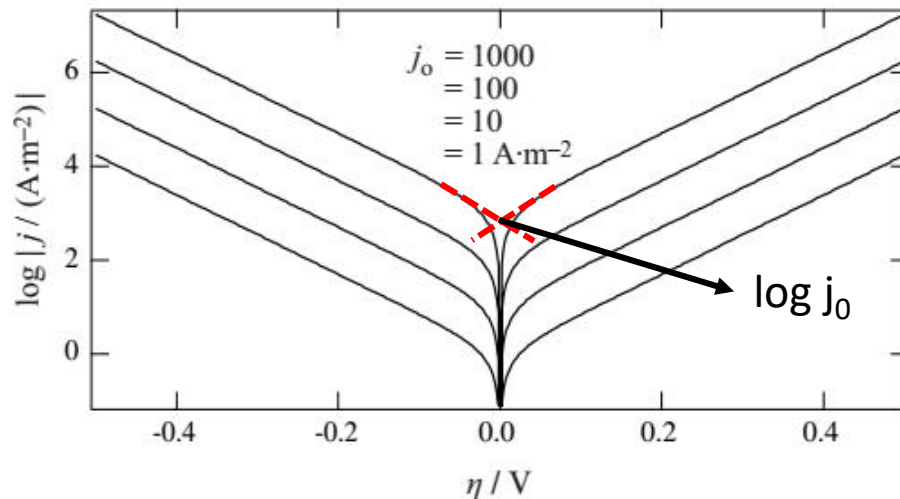
$$\ln(|j|) = \ln(j_0) + (1-\alpha)f\eta$$

Rama
Catódica

$$\eta < 0$$

$$j = -j_0 e^{-\alpha f\eta}$$

$$\ln(|j|) = \ln(j_0) - \alpha f\eta$$



Intersección:

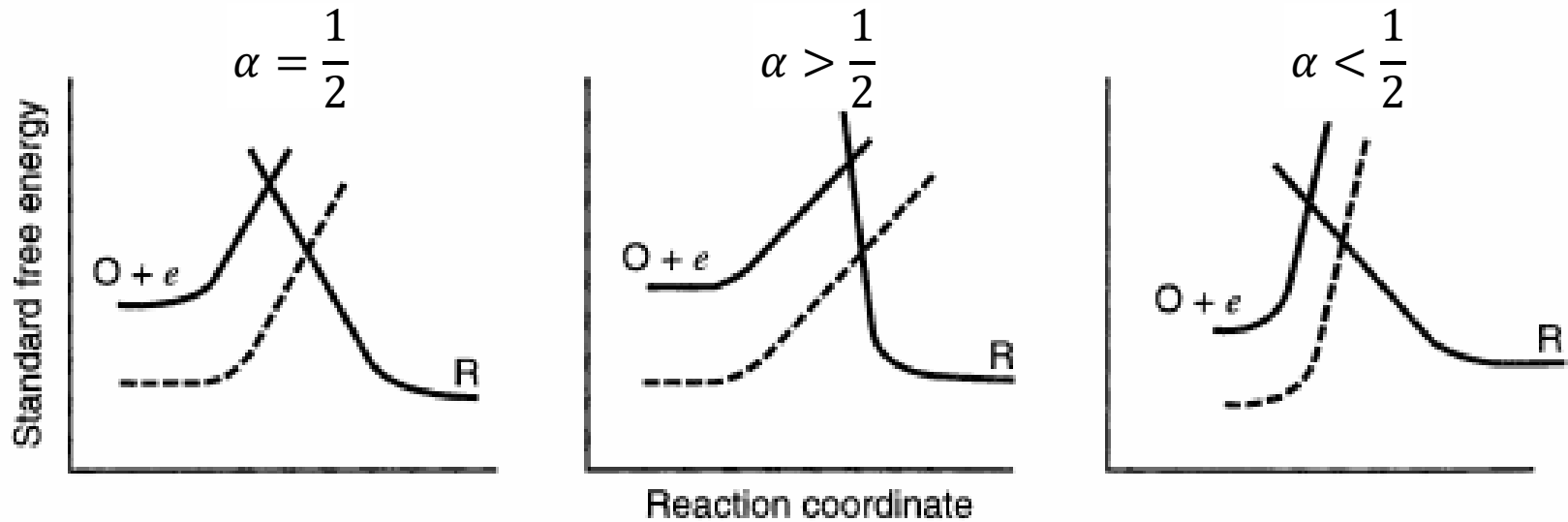
$$\ln(j_0) - \alpha f\eta = \ln(j_0) + (1-\alpha)f\eta$$

$$\Rightarrow \eta = 0 \text{ y } \ln(|j|) = \ln(j_0)$$

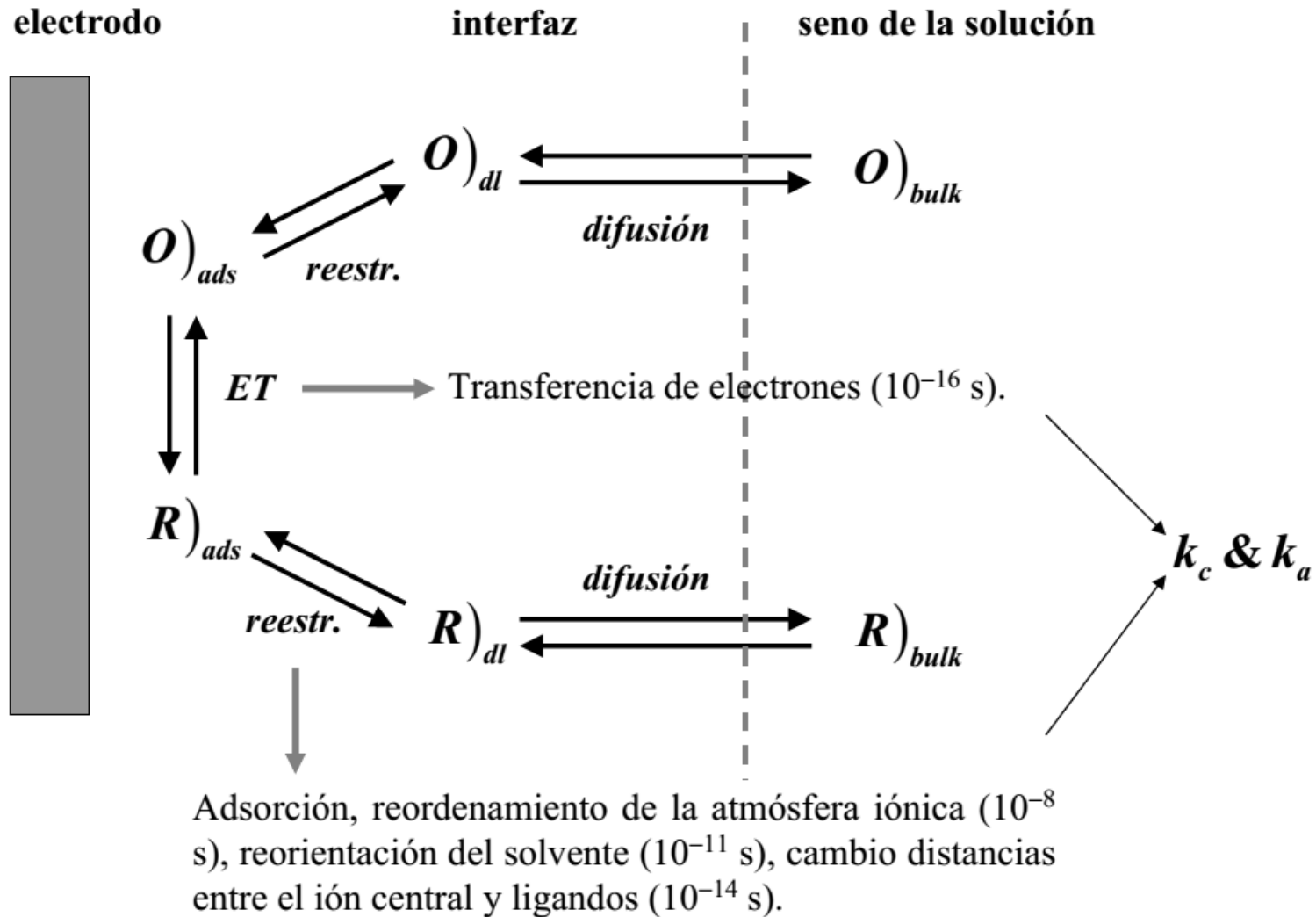
Fig. 7.8 Tafel plots ($n=1$, $\alpha=0.5$, $T=298\text{K}$). The extrapolated values for $\log|j_0|$ are respectively 3, 2, 1 and 0.

Ver hoja de cálculo

Coeficiente de transferencia α



Transporte de masa - cinética



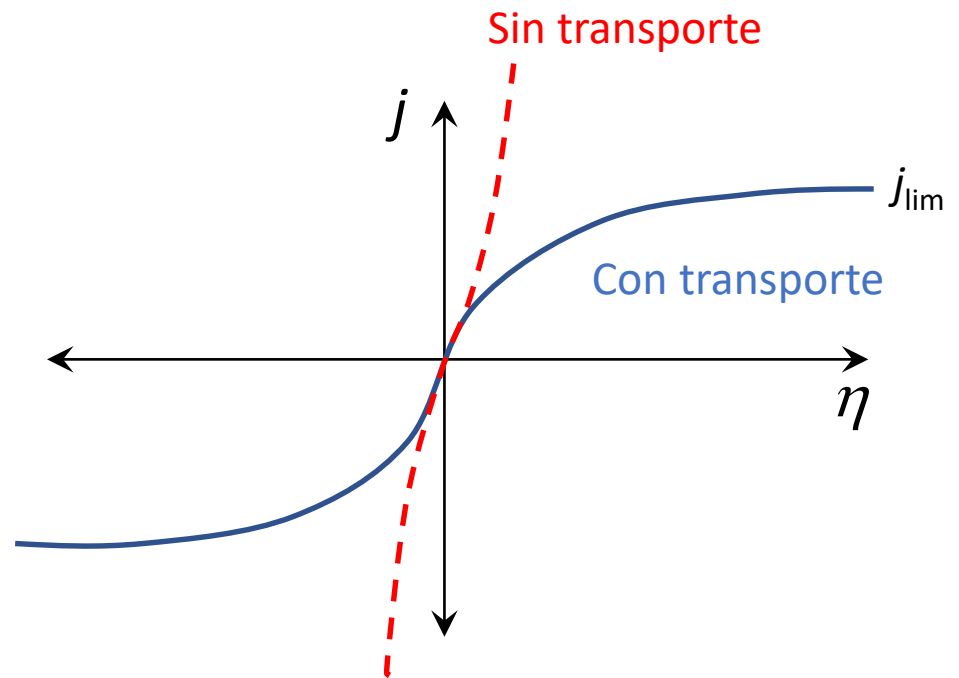
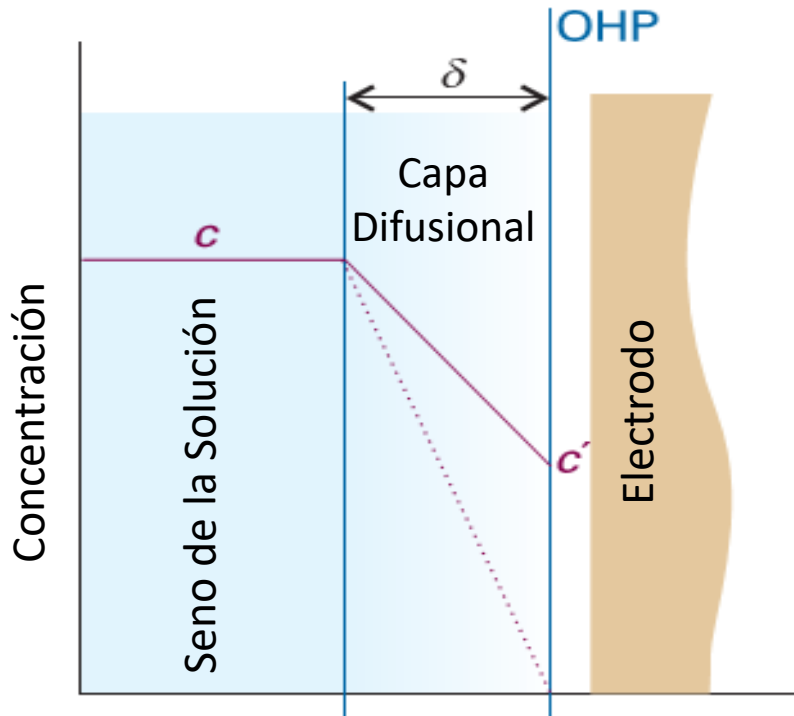
Transporte de masa - cinética

$$J = -D \frac{\partial c}{\partial x}$$

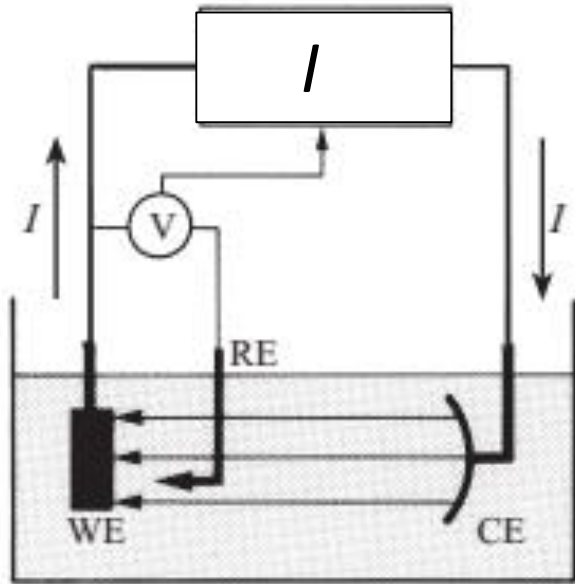
$$J = -D \frac{c - c'}{\delta}$$

$$j = zFJ = zFD \frac{c - c'}{\delta}$$

$$j_{lim} = zFJ_{lim} = zFD \frac{c}{\delta}$$



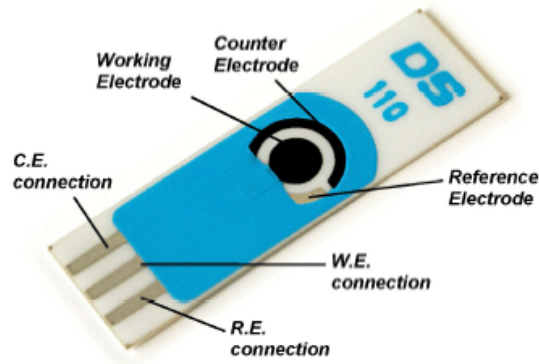
¿Cómo se mide?



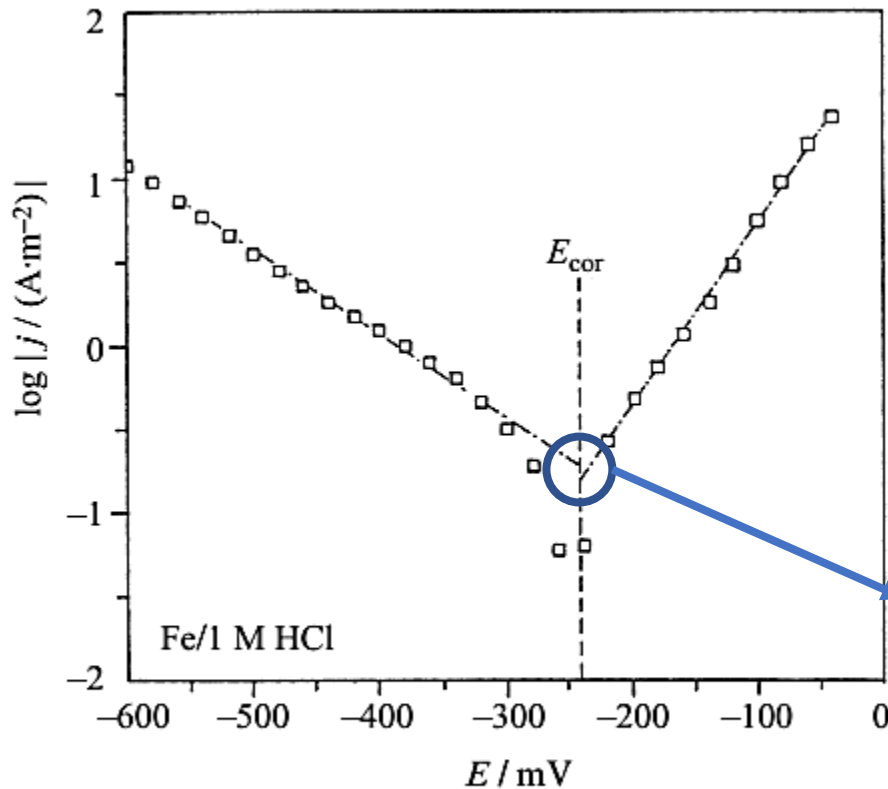
Potenciostato



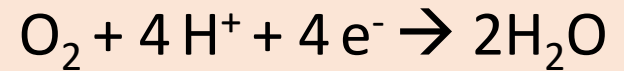
- Electrodo de trabajo:
Pt, Au, Pd, C, ITO, TiO₂
- Electrodo de referencia:
Ag/AgCl, Hg₂Cl₂/Hg,
ENH
- Contraelectrodo: Pt



Corrosión



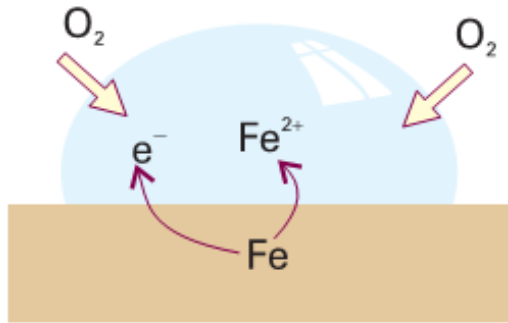
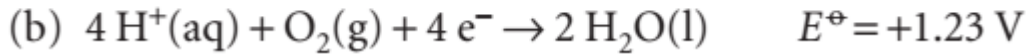
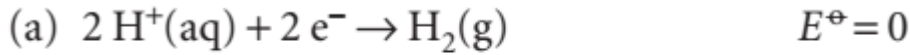
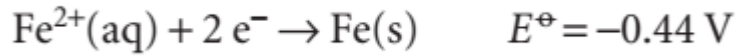
Oxidación y reducción: procesos diferentes



da idea de velocidad de corrosión!!!
(ej. cemento reforzado)

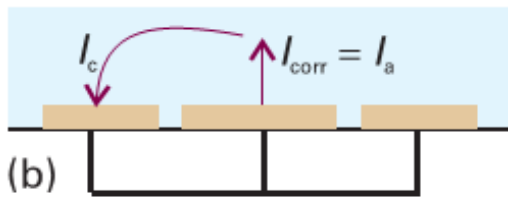
Fig. 7.9 Tafel curves for the corrosion of iron [D. Landolt, *Traité des Matériaux*, Vol.12, *Corrosion et Chimie de surface des métaux* PPUR, 3rd ed. 2003].

Corrosión



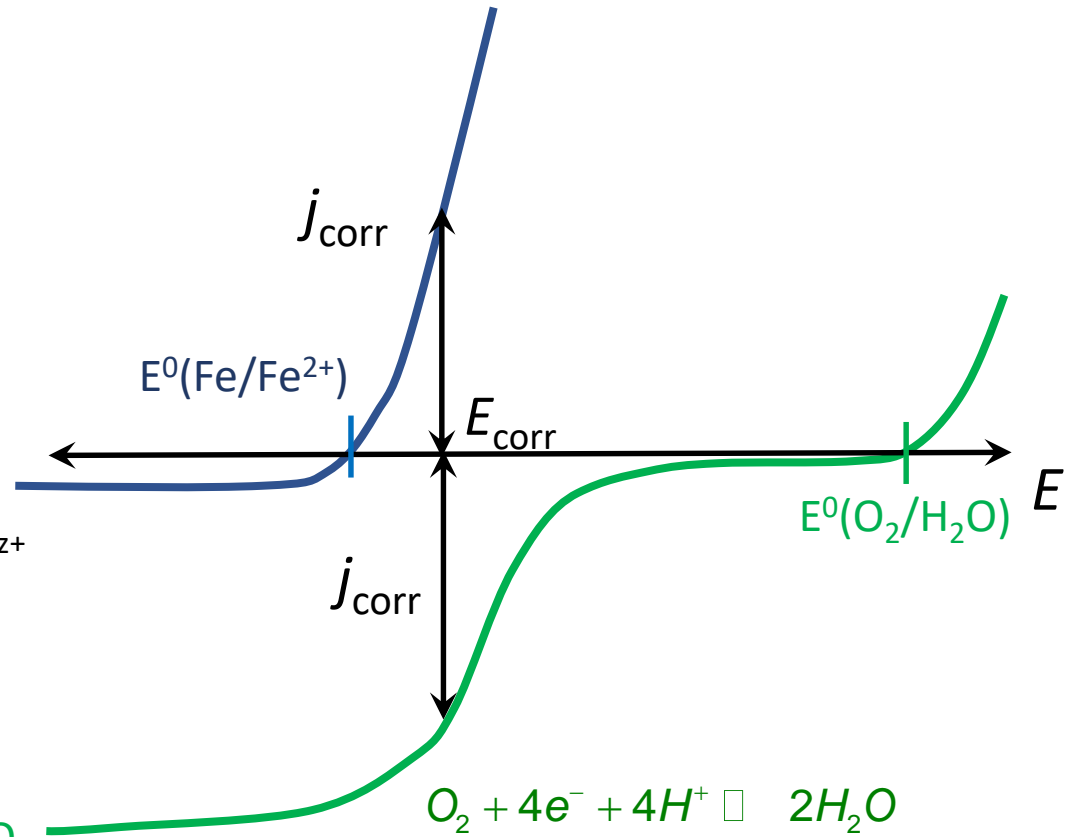
(a)

limita dif. $\text{M}^{\text{z}+}$

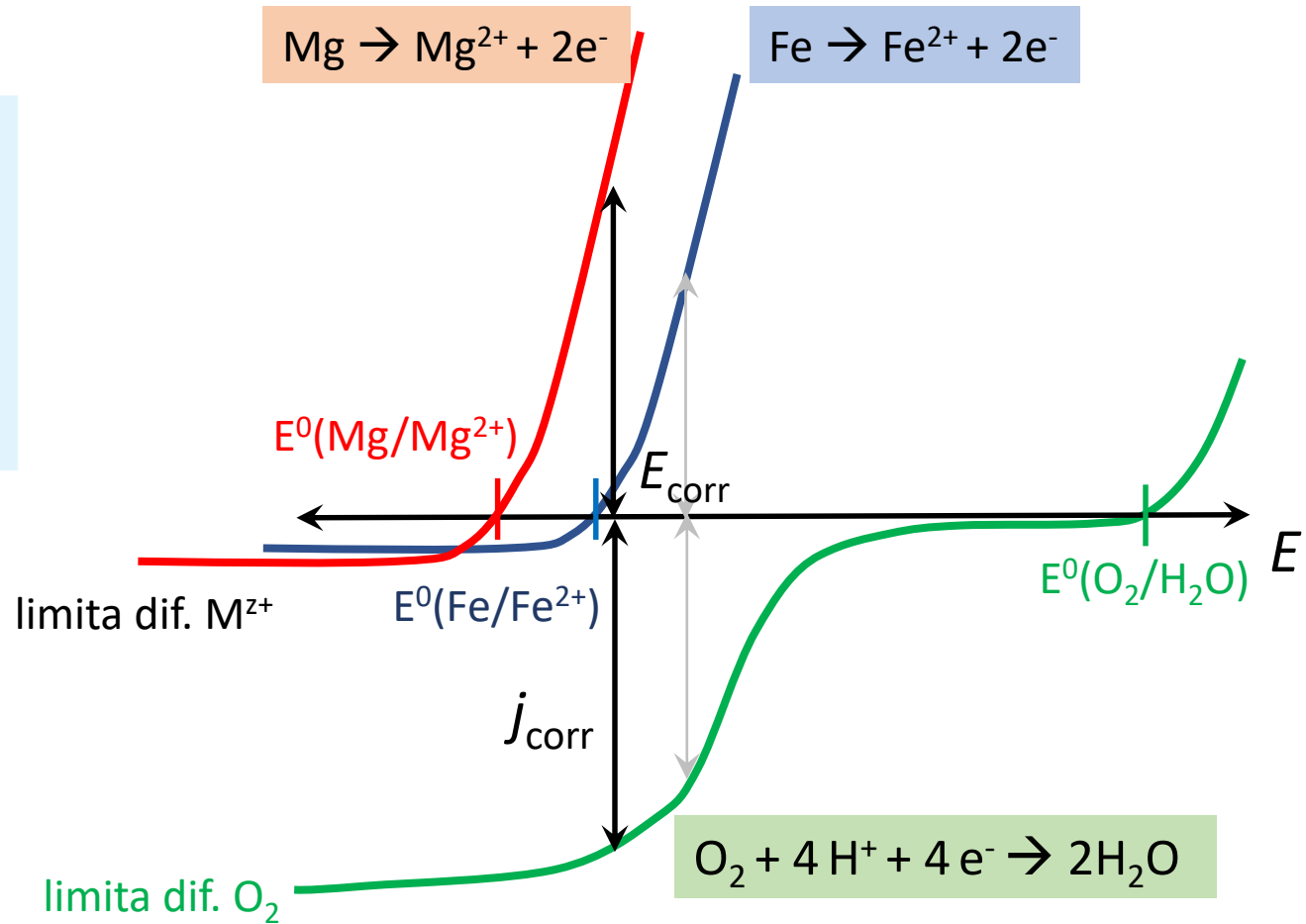
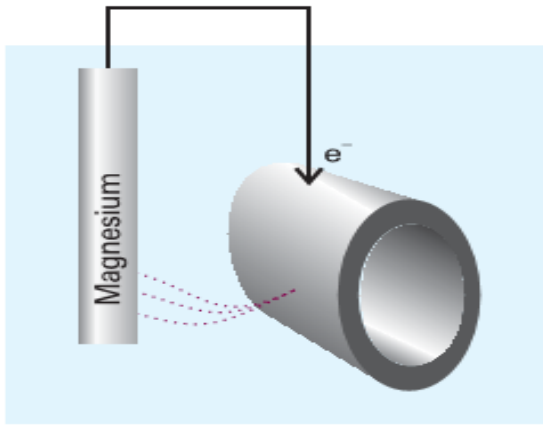


(b)

limita dif. O_2



Corrosión – protección catódica

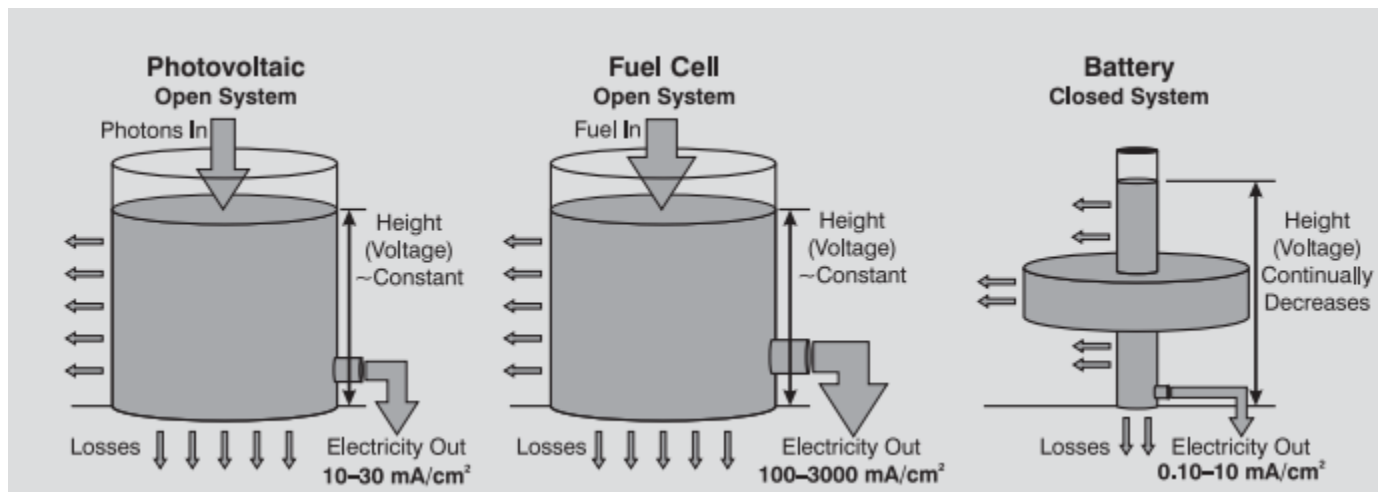
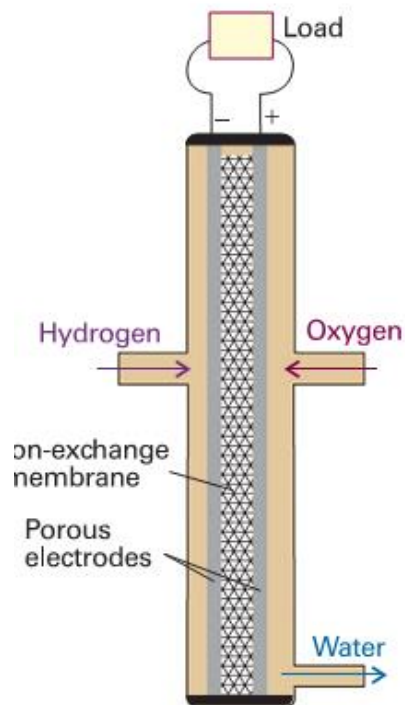


Celdas de combustible



$$j_0 = 10^{-10} \text{ A cm}^{-2}$$

$$j_0 = 8 \cdot 10^{-4} \text{ A cm}^{-2}$$



Enzimas – Cinética de electrodo

