# Electrochemically irreversible processes

***Rate ET < Rate MT***

$$Ox + ne^- \xrightarrow{k_{Red}} Red$$

**Surface concentration boundary condition**

$$\frac{i}{nFA} = D_{Ox}\left[\frac{\partial C_{Ox}(x,t)}{\partial x}\right]_{x=0} = k_{Red}C_{Ox}(0,t)$$

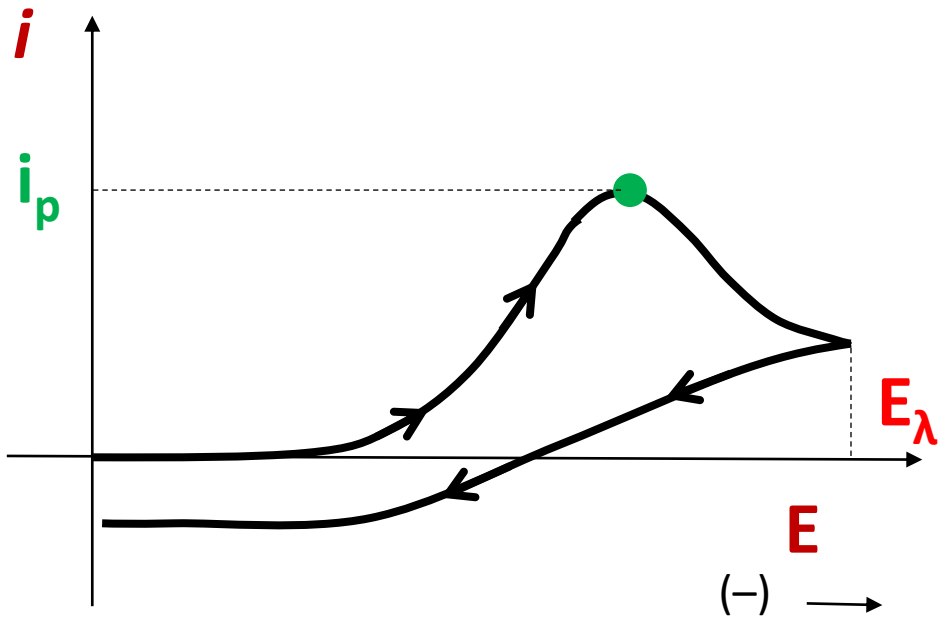
$$k_{Red} = \boldsymbol{k^0}\exp[-\boldsymbol{\alpha}\frac{nF}{RT}(\boldsymbol{E(t)} - E^{0'})] \qquad \boldsymbol{E(t) = E_i - vt}$$

*General condition for LSV sweep potential*

$$k_{Red}C_{Ox}(0,t) = \boldsymbol{k^0}\exp\left[-\boldsymbol{\alpha}\frac{nF}{RT}\left(\boldsymbol{E_i} - E^{0'}\right)\right]\exp\left[\boldsymbol{\alpha}\frac{nF}{RT}\boldsymbol{vt}\right]C_{Ox}(0,t)$$

*Numerical solution of an integral equation ….*

# Electrochemically irreversible processes: peak current




*At T = 25°C*

$$i_p = (2.99 \cdot 10^5) n (\alpha \cdot n_\alpha)^{1/2} A D_{Ox}^{1/2} C_{Ox}^{*} v^{1/2}$$

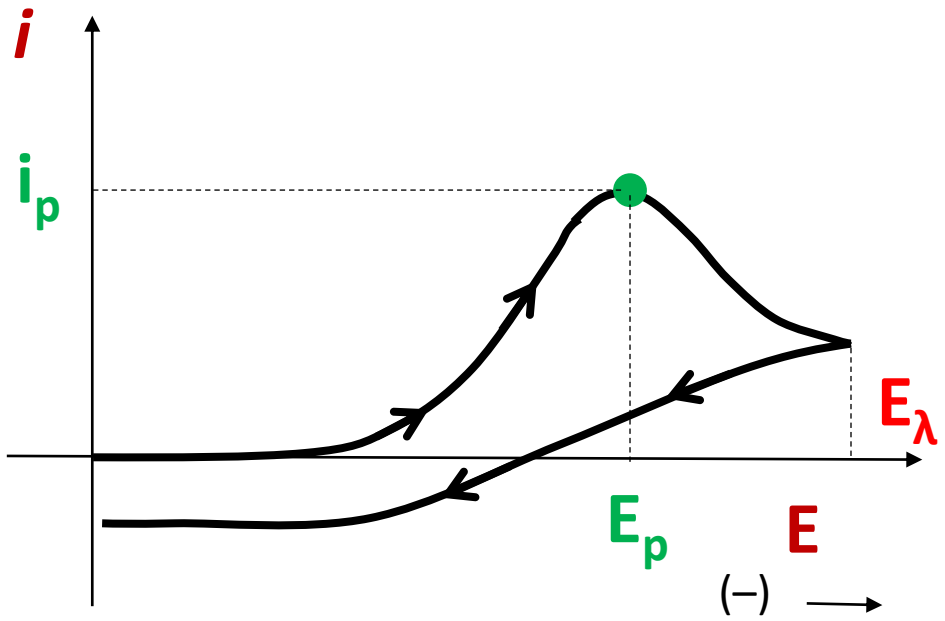
***Total** number of electrons exchanged per molecule of Ox*

*number of electrons exchanged in the **slowest step** (RDS) ($n_\alpha \leq n$)*

For an EC irreversible process, $i_p$ **depends on** $\sqrt{\alpha}$
$(0 < \alpha \leq 1)$

- under equivalent conditions, the **height of an irreversible peak is lower than that of an EC reversible peak**
- $i_{p,c} / v^{1/2}$ is constant with the scan rate ($v$)
- Current ratio $i_{p,a} / i_{p,c}$ **not defined**

# Electrochemically irreversible processes: potential




*Peak potential*

$$E_p = E^{0\prime} - \frac{RT}{\alpha n_\alpha F}\left[0.78 + ln\left(\frac{D_{Ox}^{1/2}}{k^0}\right) + ln\left(\frac{\alpha n_\alpha F v}{RT}\right)^{1/2}\right]$$

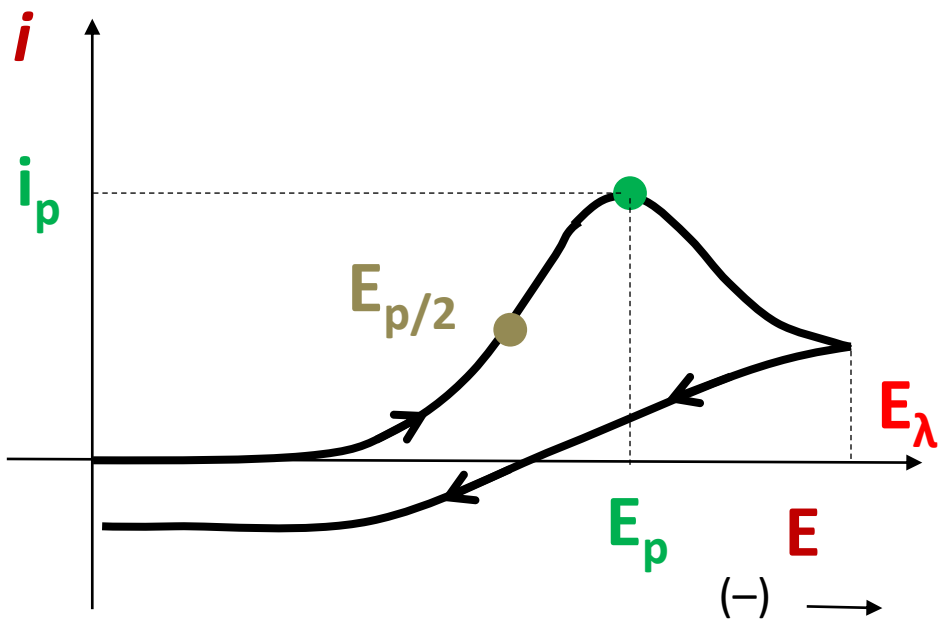
- $E_p$ is dependent on **transfer coefficient (α)** and **scan rate (*v*)**
- $E_{p,c}$ **shifts cathodically with the scan rate (*v*)**

*(T = 25°C)* $\sim \frac{30\ mV}{\alpha n_\alpha}$ $E_{p,c}$ *shift for 10-fold increase of* ***v***

***Diagnostic criterion for EC irreversible process***

- $E_{p,c}$ **occurs at significantly more negative potential compared to $E^{0\prime}$** (activation η due to slow ET rate, dependent on $k^0$)
- Since usually **$E^{0\prime}$** is not known for an EC irreversible process, $E_p$ *is typically reported at a given scan rate*
- To fully characterize an EC irreversible process, knowledge of either the thermodynamic parameter **$E^{0\prime}$** or the kinetic parameters (**α**, $k^0$) is required

# Electrochemically irreversible processes: potential




*Peak width*

$$\left|E_p - E_{p/2}\right| = \frac{1.857\ RT}{\alpha n_\alpha F} = \frac{47.7\ mV}{\alpha n_\alpha} \qquad (T = 25°C)$$

- This equation is commonly used to **calculate $\alpha n_\alpha$** (for n = 1, it gives the $\alpha$ value)

- EC irreversible peaks are typically broader compared to EC reversible ones
- i-E relationships for *multistep irreversible processes* are generally described by complex equations
- Simulation softwares are often useful to characterize an EC irreversible process

# Electrochemically quasi-reversible processes

$$Ox + ne^- \underset{k_{Ox}}{\overset{k_{Red}}{\rightleftharpoons}} Red$$

**Surface concentration boundary condition**

$$\frac{i}{nFA} = D_{Ox}\left[\frac{\partial C_{Ox}(x,t)}{\partial x}\right]_{x=0} = k_{Red}C_{Ox}(0,t) - k_{Ox}C_{Red}(0,t)$$

$$k_{Red} = \boldsymbol{k^0}\exp[-\boldsymbol{\alpha}\frac{nF}{RT}(\boldsymbol{E(t)} - E^{0'})]$$

$$k_{Ox} = \boldsymbol{k^0}\exp[(\boldsymbol{1-\alpha})\frac{nF}{RT}(\boldsymbol{E(t)} - E^{0'})]$$

$$\boldsymbol{E(t) = E_i - vt}$$

*General condition for LSV sweep potential*

- ET rate of the forward process ($k_{Red}$) has the same order of magnitude as the MT rate
- ET rate of the backward process ($k_{Ox}$) is not negligible
- **Apparent reversible/irreversible behaviour depending on the scan rate**
- More complex mathematical treatment

# Electrochemically quasi-reversible processes

The shape of the quasi-reversible voltammograms and their parameters ($i_p$, $E_p$, $E_{p/2}$) are functions of the **transfer coefficient (α)** and a **parameter Λ**:

$$\Lambda = \frac{k^0}{\left(D_{Ox}^{1-\alpha} D_{Red}^{\alpha} \frac{nF}{RT} v\right)^{1/2}} = \frac{k^0}{\left(D \frac{nF}{RT} v\right)^{1/2}}$$

*if* $D_{Ox} = D_{Red} = D$

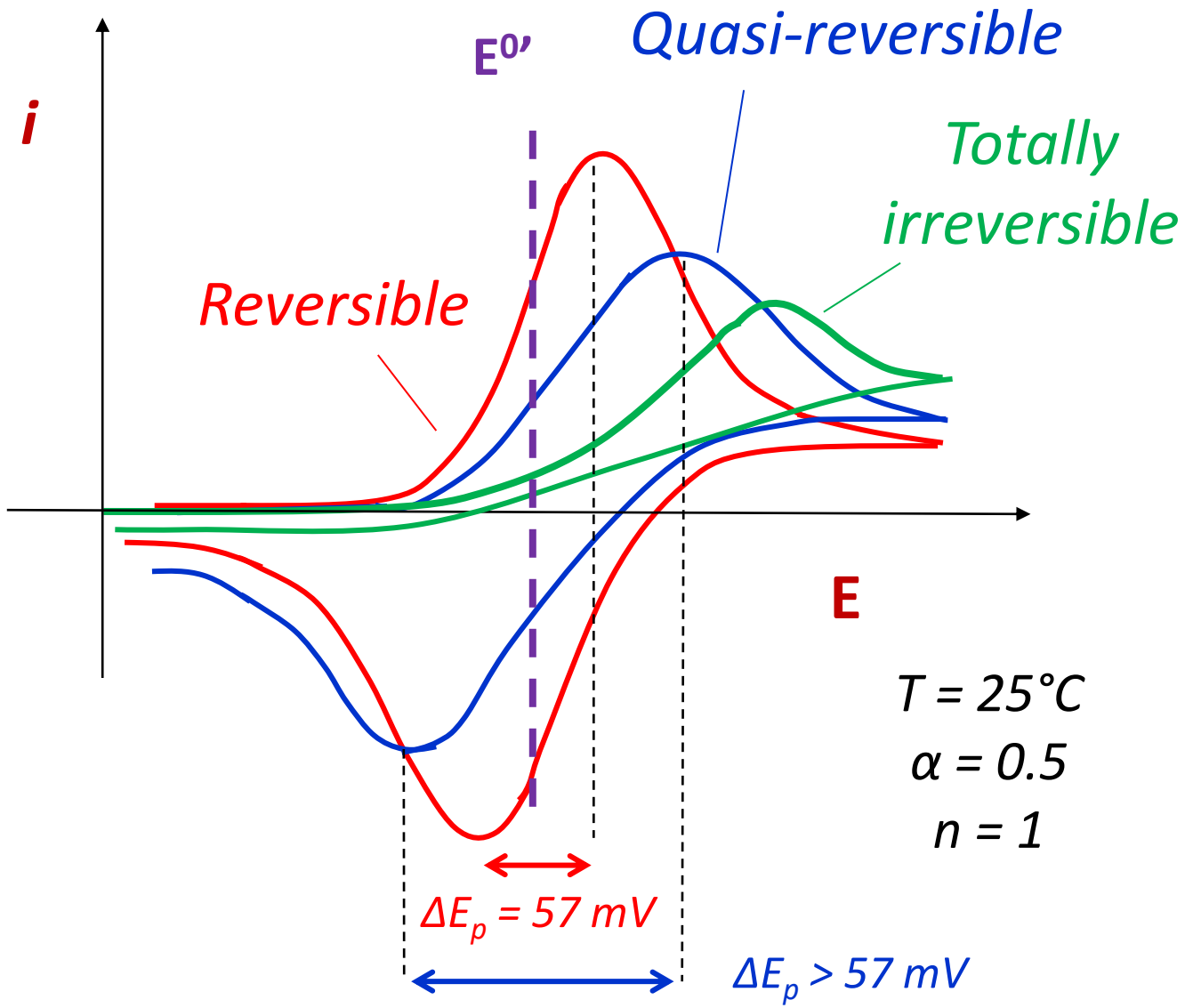
**Large Λ** ⇒ ***Reversible (nernstian)***

**Intermediate Λ** ⇒ ***Quasi-Reversible***

**Small Λ** ⇒ ***Totally Irreversible***

- At **low scan rates**, a quasi-reversible wave may become **reversible**
- At **high scan rates**, a quasi-reversible wave appears as **irreversible**

# Electrochemically quasi-reversible processes: current




- $i_{p,c}$ is not proportional to $v^{1/2}$ for a quasi-reversible wave
- $i_{p,a} / i_{p,c} = 1$ only if $\alpha = 0.5$
- $i_{p,a} \neq i_{p,c}$ if $\alpha \neq 0.5$ *(non-symmetrical voltammogram)*

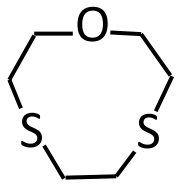
# Electrochemically quasi-reversible processes: potential

- $E_{p,c}$ **shifts cathodically with the scan rate**
- $E^{0'}$ can be approximately obtained as the average value between $E_{p,c}$ and $E_{p,a}$ only if $0.3 < \alpha < 0.7$ (mutual compensation of the potential shifts of $E_{p,c}$ and $E_{p,a}$ in opposite directions, due to kinetic effects)
- $\Delta E_p > (57/n)$ mV (at 25°C) even in the low scan rate regime, being the deviation larger by increasing the potential sweep rate
- $\Delta E_p$ is function of $\nu$, $k^0$ and $\alpha$
- **ohmic drop effect on distorsion of CV shape is similar to the effect due to heterogeneous kinetic limitations** (careful $R_u$ compensation!!!)

# Chemical meaning of electrochemical reversibility

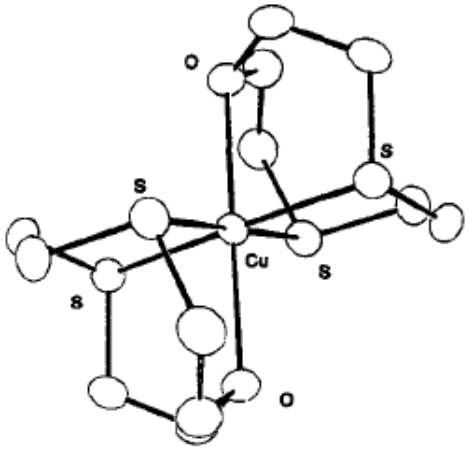
- In line with Marcus theory, geometrical reorganization accompanying ET is a crucial factor affecting the ET activation barrier
- **Electrochemical reversibility** is associated to **negligible structural reorganization** occurring upon the redox process (e.g. Ferrocene/ferrocenium couple)
- **Electrochemical quasi-reversibility** is related to **non-negligible structural changes** accompanying ET
- The **$\Delta E_p$ deviation** from the canonical 57/n mV value (at 25°C) can be used as an indicator to evaluate the extent of structural reorganization
- Redox processes characterized by a large ET activation barrier are often accompanied by severe structural reorganization or even fragmentation original molecular frame (EC irreversible)

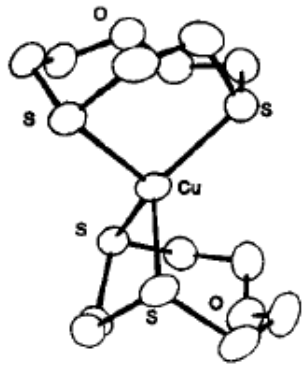
# Chemical meaning of electrochemical reversibility




= $9S_2O$

$\Delta E_p$ ($Cu^{II/I}$) = 114 mV (v = 0.1 V/s)



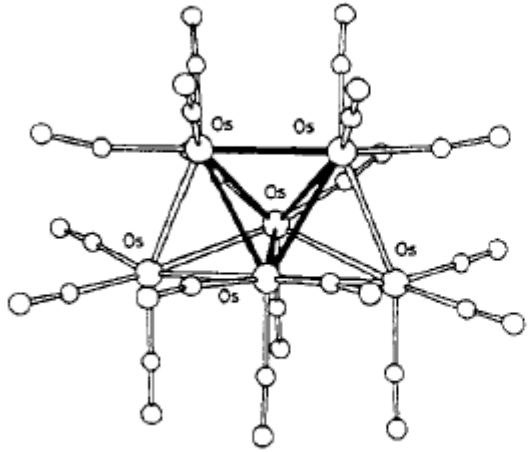

$e^-$ ⇌ $-e^-$

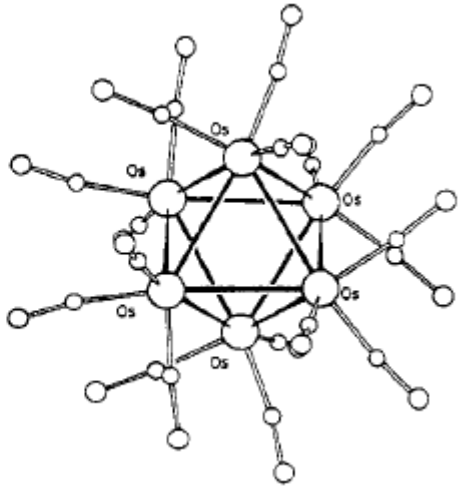
$[Cu(9S_2O)_2]^{2+}$ ⇌ $[Cu(9S_2O)_2]^{+}$

*Octahedral geometry*
*$S_4O_2$ coordination*
*($Cu^{II}$)*

*Tetrahedral geometry*
*$S_4$ coordination*
*($Cu^{I}$)*

$[Os_6(CO)_{18}]$ ⇌ ($2e^-$ / $-2e^-$) $[Os_6(CO)_{18}]^{2-}$




*Bicapped-tetrahedral geometry*

*Octahedral geometry*

$\Delta E_p$ ($[Os_6(CO)_{18}]^{0/2-}$) = 255 mV (v = 0.01 V/s)


R. C. Lucas et al, Inorg. Chem. **1997**, 36, 4508-4513
G.J. Grant et al., Inorg. Chim. Acta **2000**, 300–302


From Zanello, Nervi, Fabrizi de Biani, 2nd Ed. RSC, 2011