



# **Análise Instrumental III**

**(Parte C)**

**Prof. Dr. Marcos Lanza**

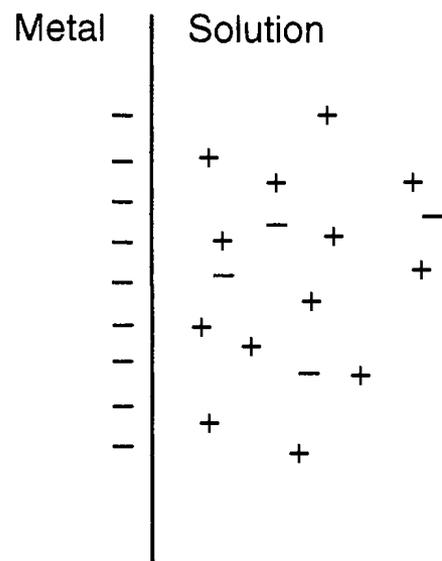
# Tópicos

- 1) Apresentação das principais técnicas eletroanalíticas utilizadas em Química Analítica;**
- 2) Fundamentos gerais de algumas técnicas eletroanalíticas: amperometria, polarografia, voltametria e técnicas relacionadas.**

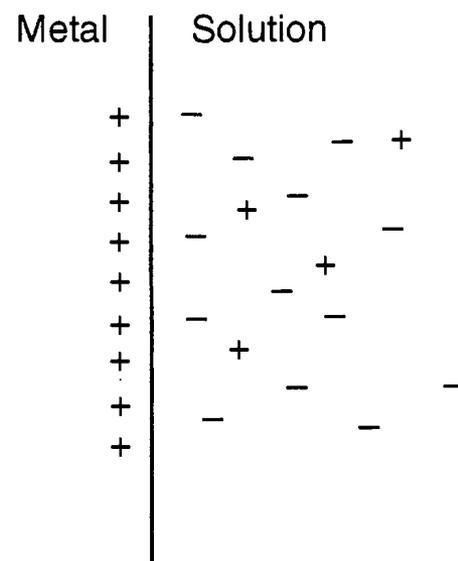
## Bibliografia

- **D. A. Skoog, F. J. Holler, T. A. Nieman, *Princípios de Análise Instrumental*. 5ª Ed. (2002).**
- **D. C. Harris, *Análise Química Quantitativa*, 6ª Ed (2005)**
- **D. A. Skoog et al, *Fundamentos de Química Analítica* (2006)**
- **Ticianelli, E. A.; Gonzalez, E. R.; *Eletroquímica*, 3ª Ed (2013)**
- **Livros e periódicos**

# A Dupla Camada Elétrica

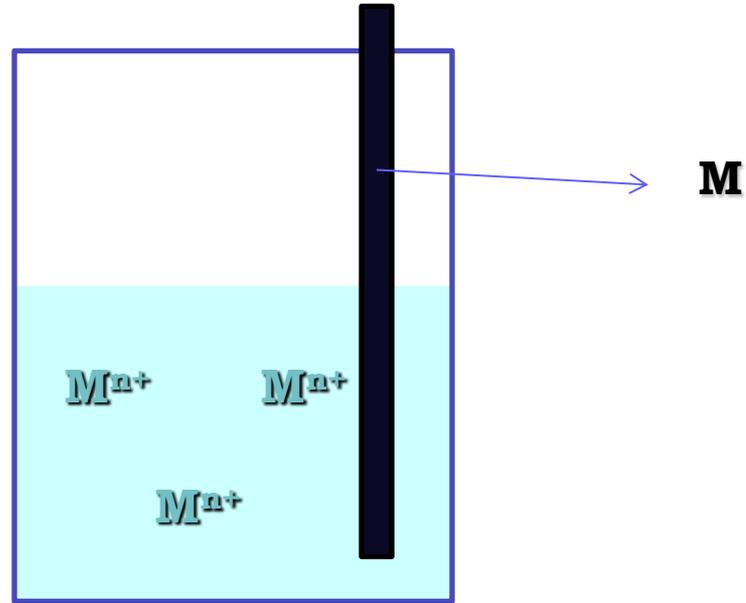


(a)



(b)

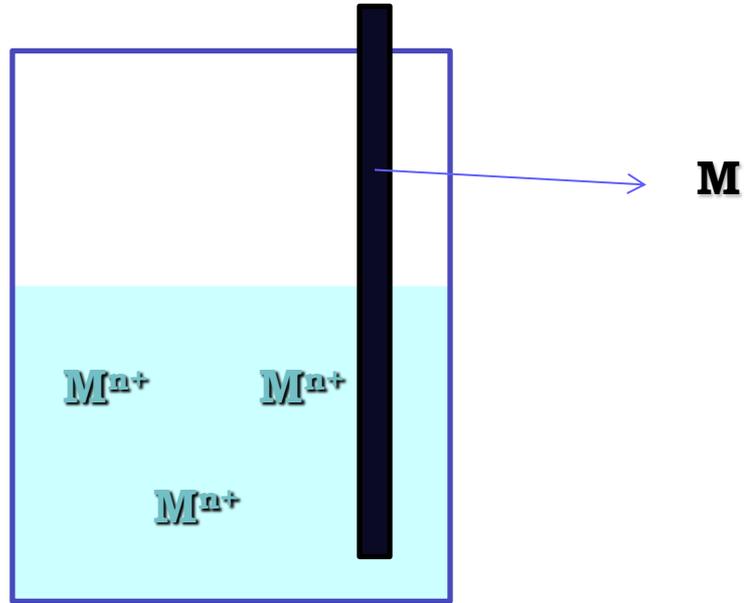
## Eletrodo:



**Processo Reversível**

**Potencial de equilíbrio:  $E_{eq}$**

## Eletrodo:

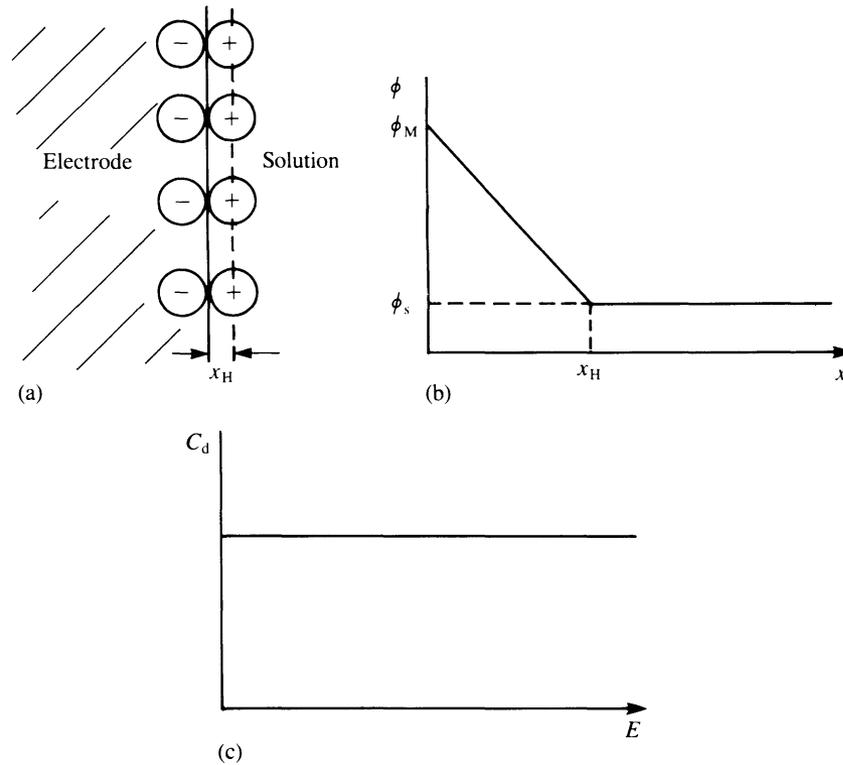


**Processo Reversível**

**Potencial de equilíbrio:  $E_{eq}$  →  $i_o$**

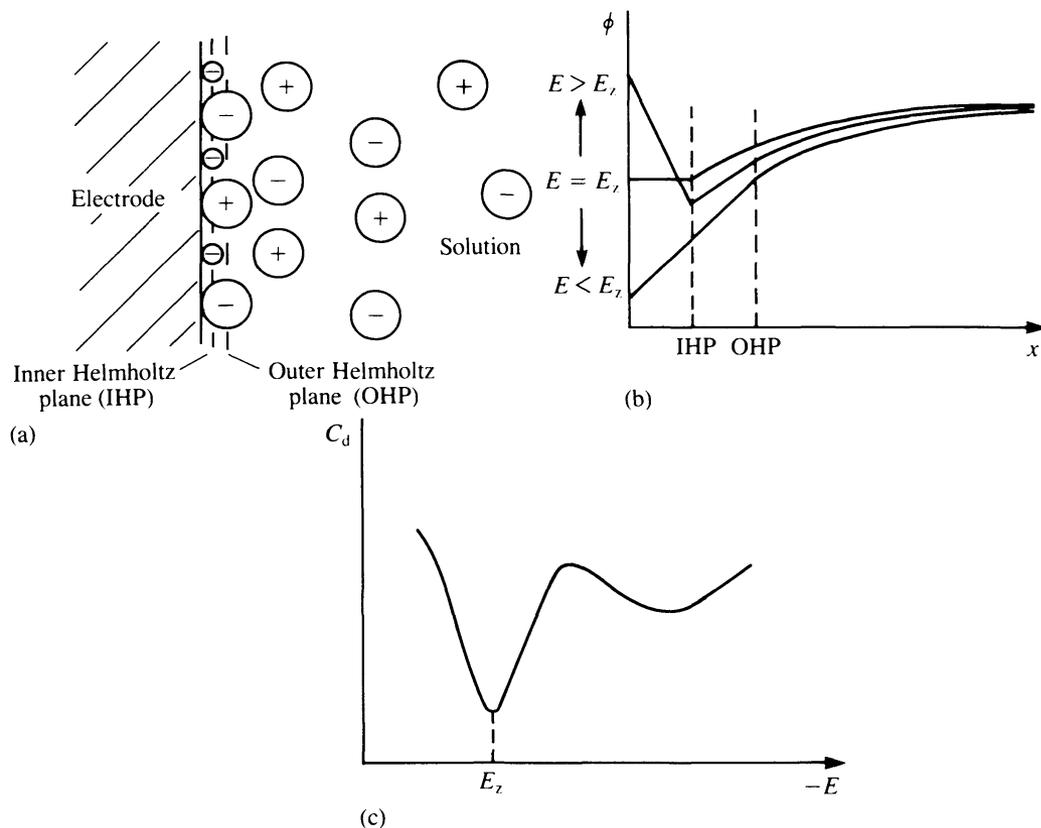
**“Corrente de troca”: não promove reação química = corrente capacitiva!**

# A Dupla Camada Elétrica



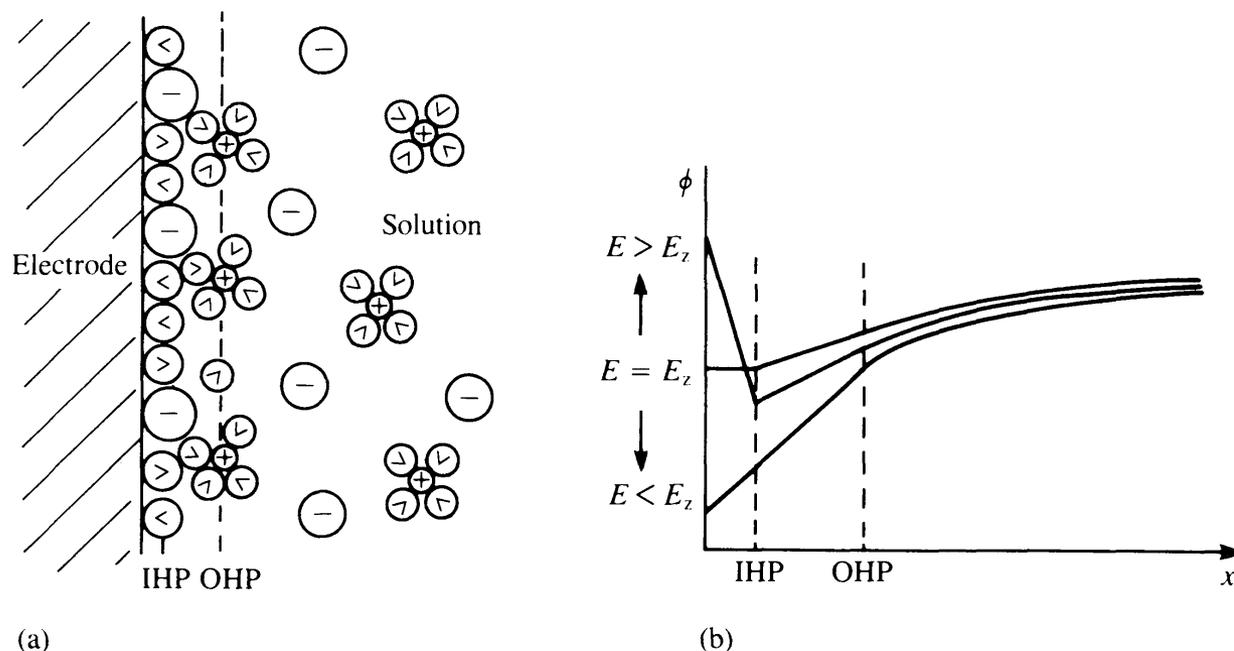
**Fig. 3.5** The Helmholtz model of the double layer. (a) Rigid arrangement of ions; (b) Variation of the electrostatic potential,  $\phi$ , with distance  $x$ , from the electrode; (c) Variation of  $C_d$  with applied potential.

# A Dupla Camada Elétrica



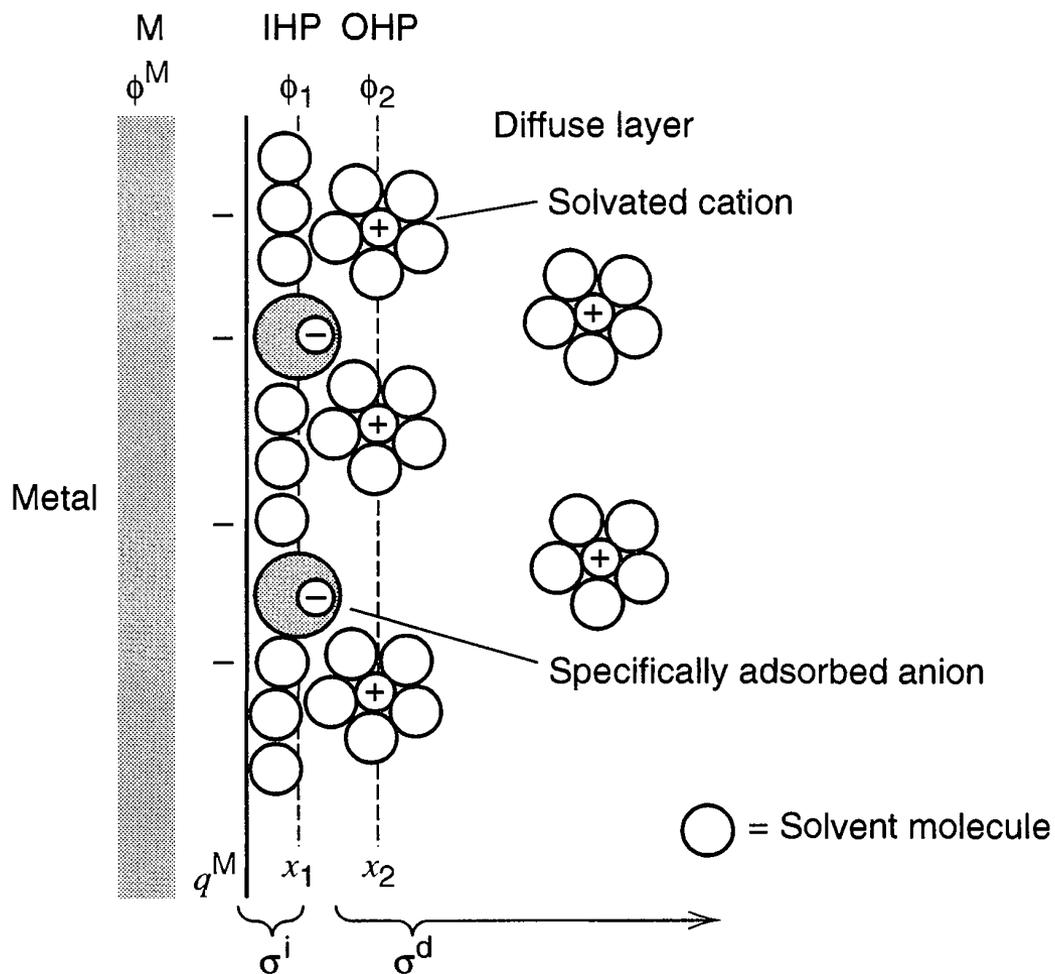
**Fig. 3.8** The Grahame model of the double layer, for the mercury electrode. (a) Arrangement of ions; (b) Variation of the electrostatic potential,  $\phi$ , with distance,  $x$ , from the electrode, according to the applied potential; (c) Variation of  $C_d$  with potential.

# A Dupla Camada Elétrica

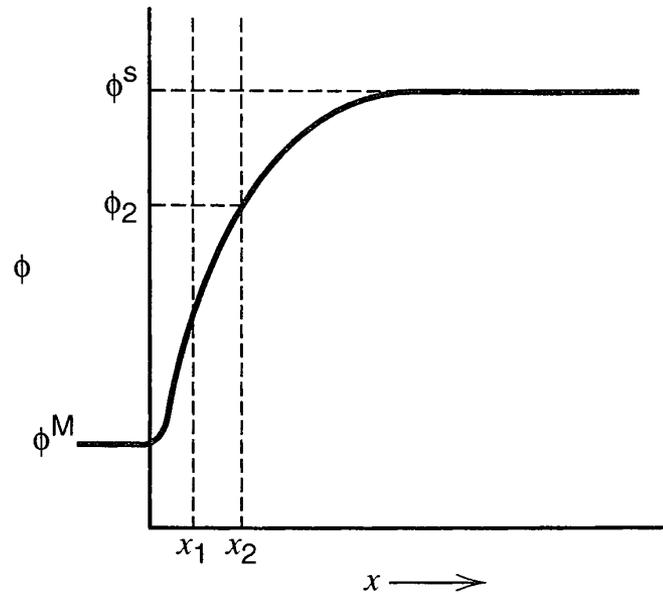
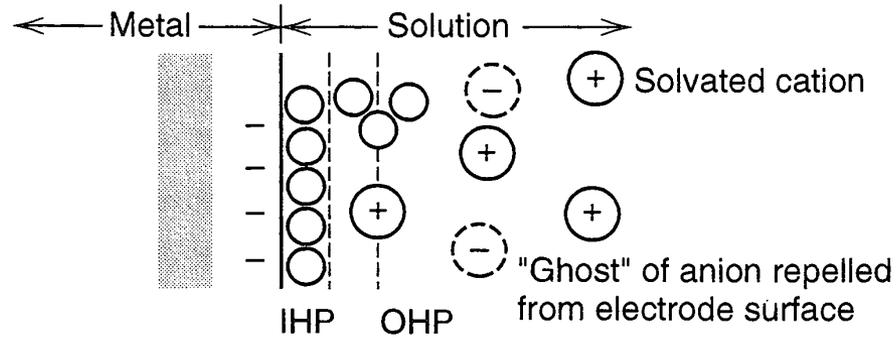


**Fig. 3.9** The model of Bockris *et al.* of the double layer. (a) Arrangement of ions and solvent molecules;  $\textcircled{+}$  represents a water molecule; (b) Variation of the electrostatic potential,  $\phi$ , with distance,  $x$ , from the electrode.

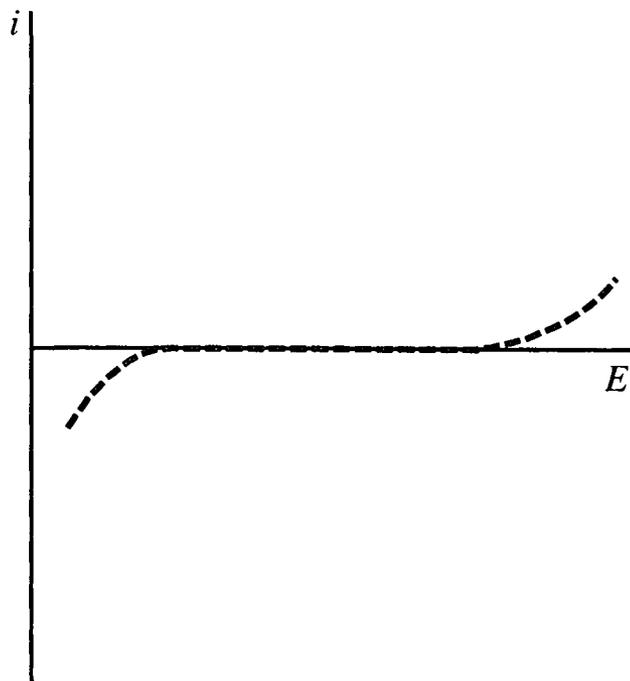
# A Dupla Camada Elétrica



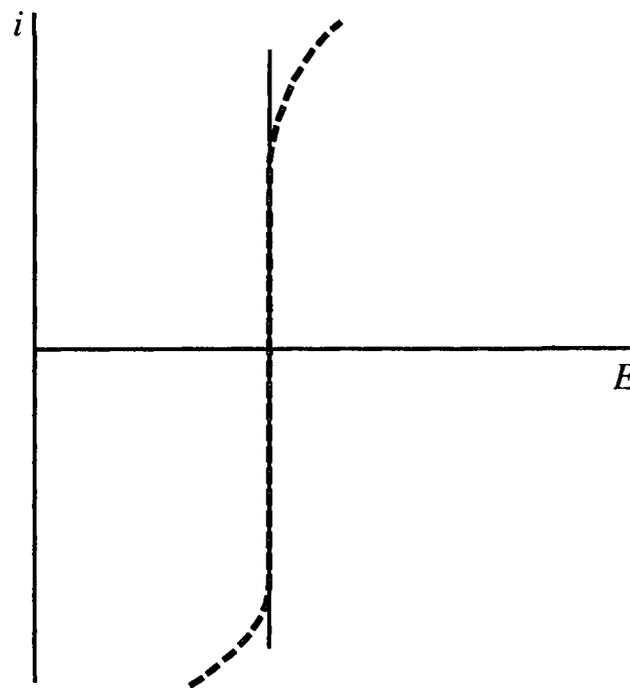
# A Dupla Camada Elétrica



# Tipos de eletrodos



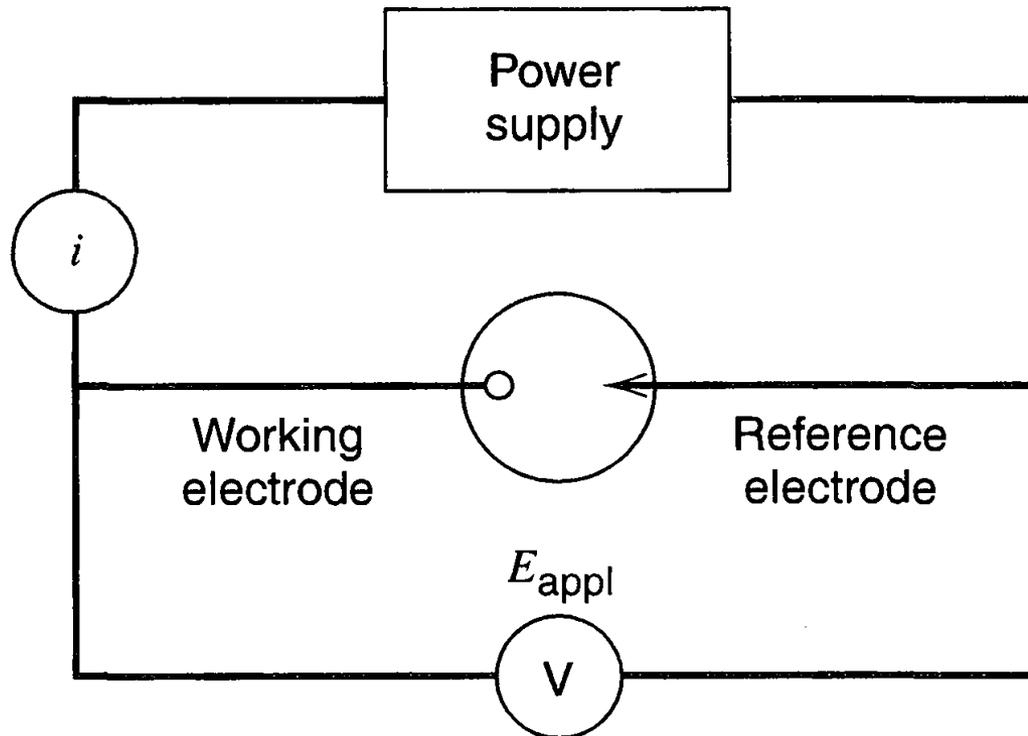
(a) Ideal polarizable electrode



(b) Ideal nonpolarizable electrode

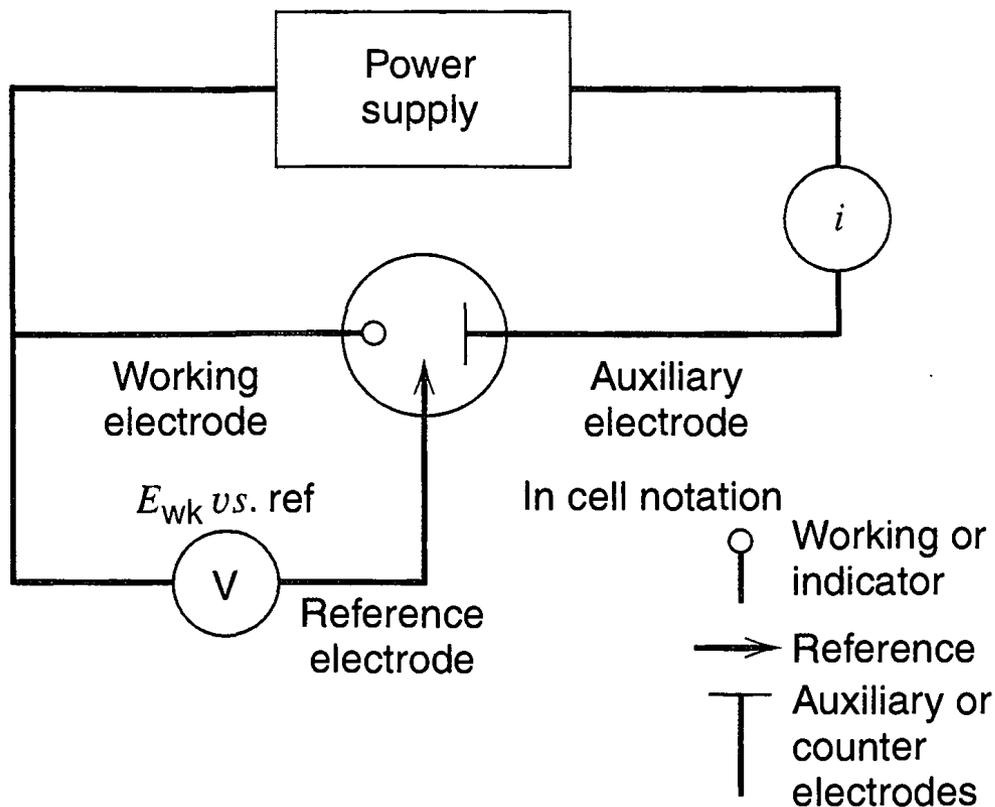
# Fonte de tensão ou Potenciostato?

## Fonte de tensão



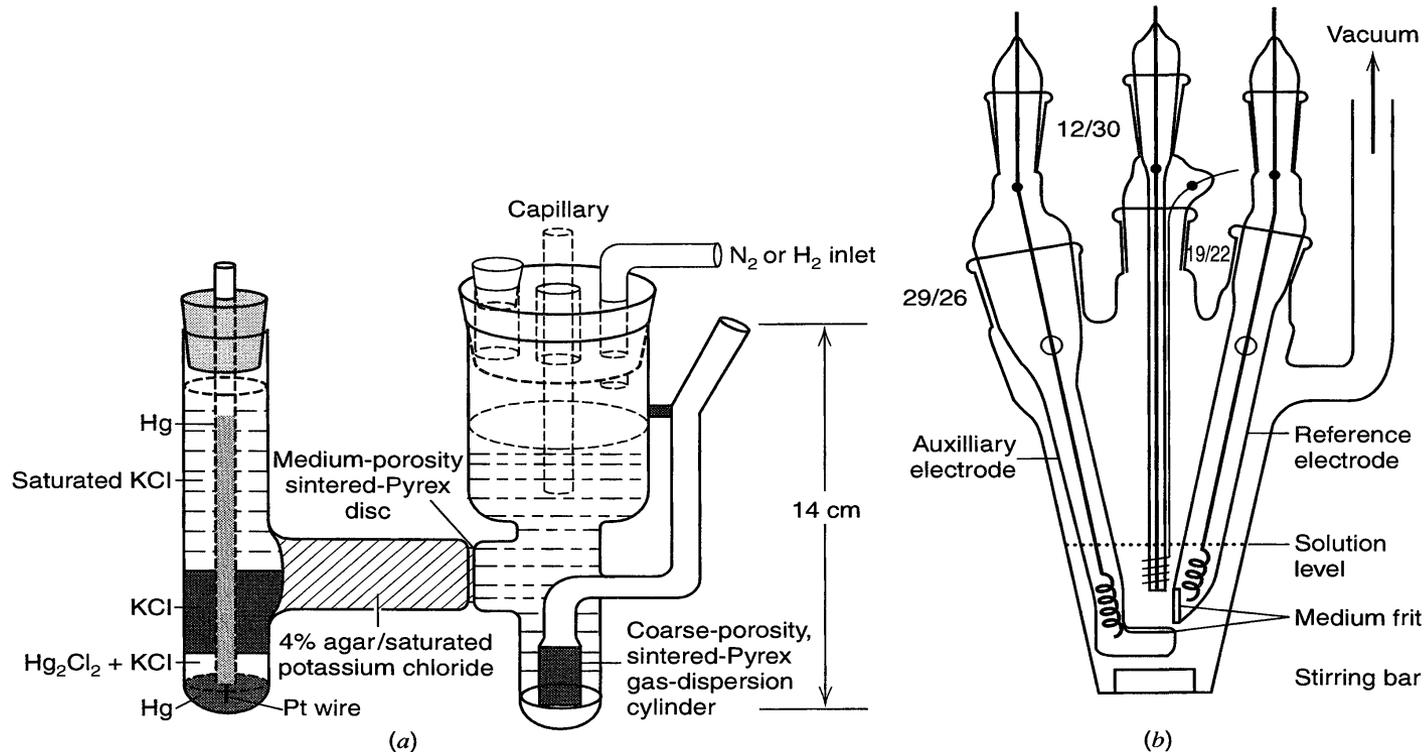
# Fonte ou Potenciostato?

## Potenciostato



# Células Eletroquímicas: 2 ou 3 eletrodos?

## Células Eletroquímicas: 1, 2 ou 3 compartimentos?



**Figure 1.3.11** Typical two- and three-electrode cells used in electrochemical experiments. (a) Two-electrode cell for polarography. The working electrode is a dropping mercury electrode (capillary) and the N<sub>2</sub> inlet tube is for deaeration of the solution. [From L. Meites, *Polarographic Techniques*, 2nd ed., Wiley-Interscience, New York, 1965, with permission.] (b) Three-electrode cell designed for studies with nonaqueous solutions at a platinum-disk working electrode, with provision for attachment to a vacuum line. [Reprinted with permission from A. Demortier and A. J. Bard, *J. Am. Chem. Soc.*, **95**, 3495 (1973). Copyright 1973, American Chemical Society.] Three-electrode cells for bulk electrolysis are shown in Figure 11.2.2.

# “Janela” de eletrodo

Reações eletroquímicas (redox) da água:

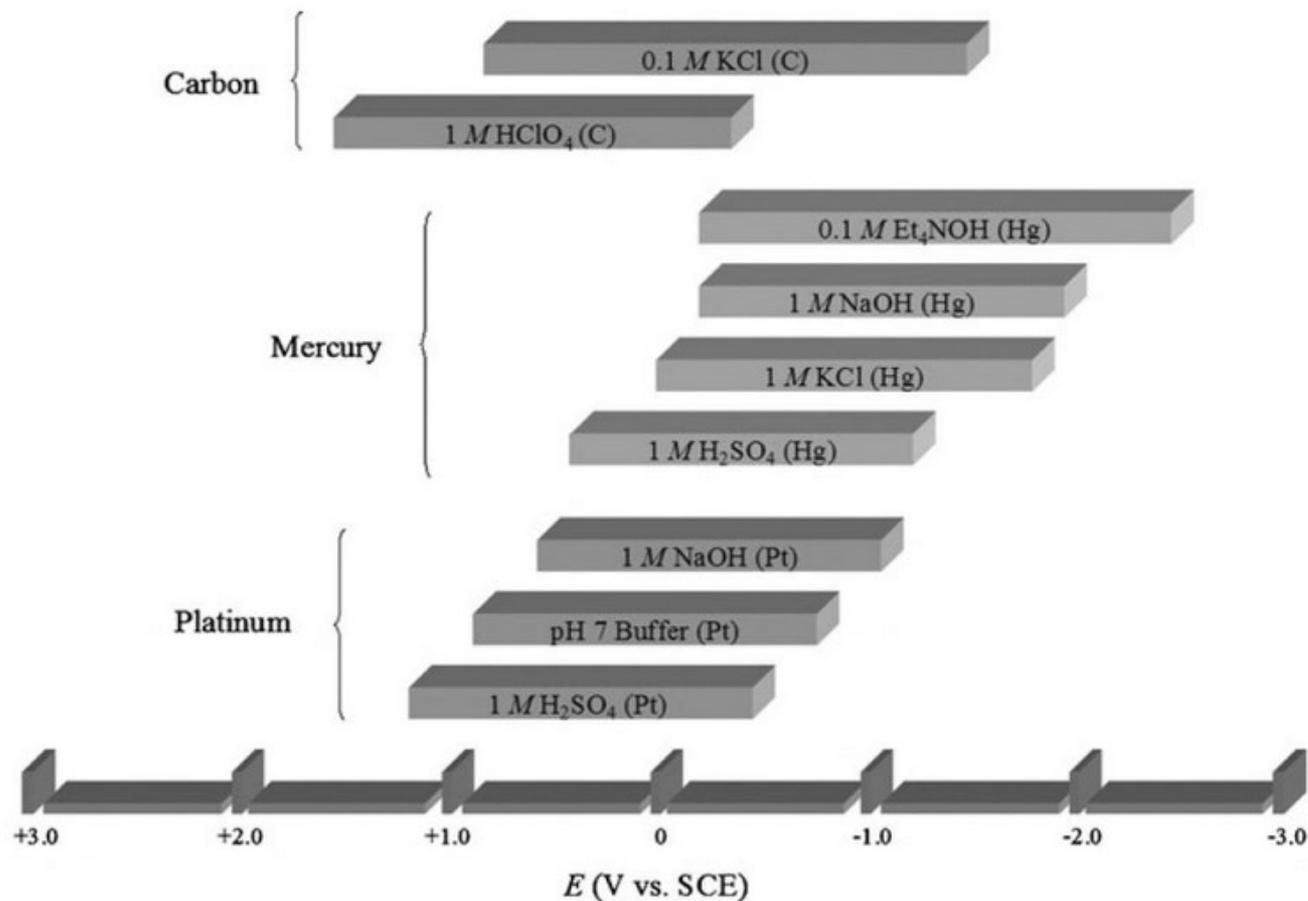
**Catodo:**



**Anodo:**

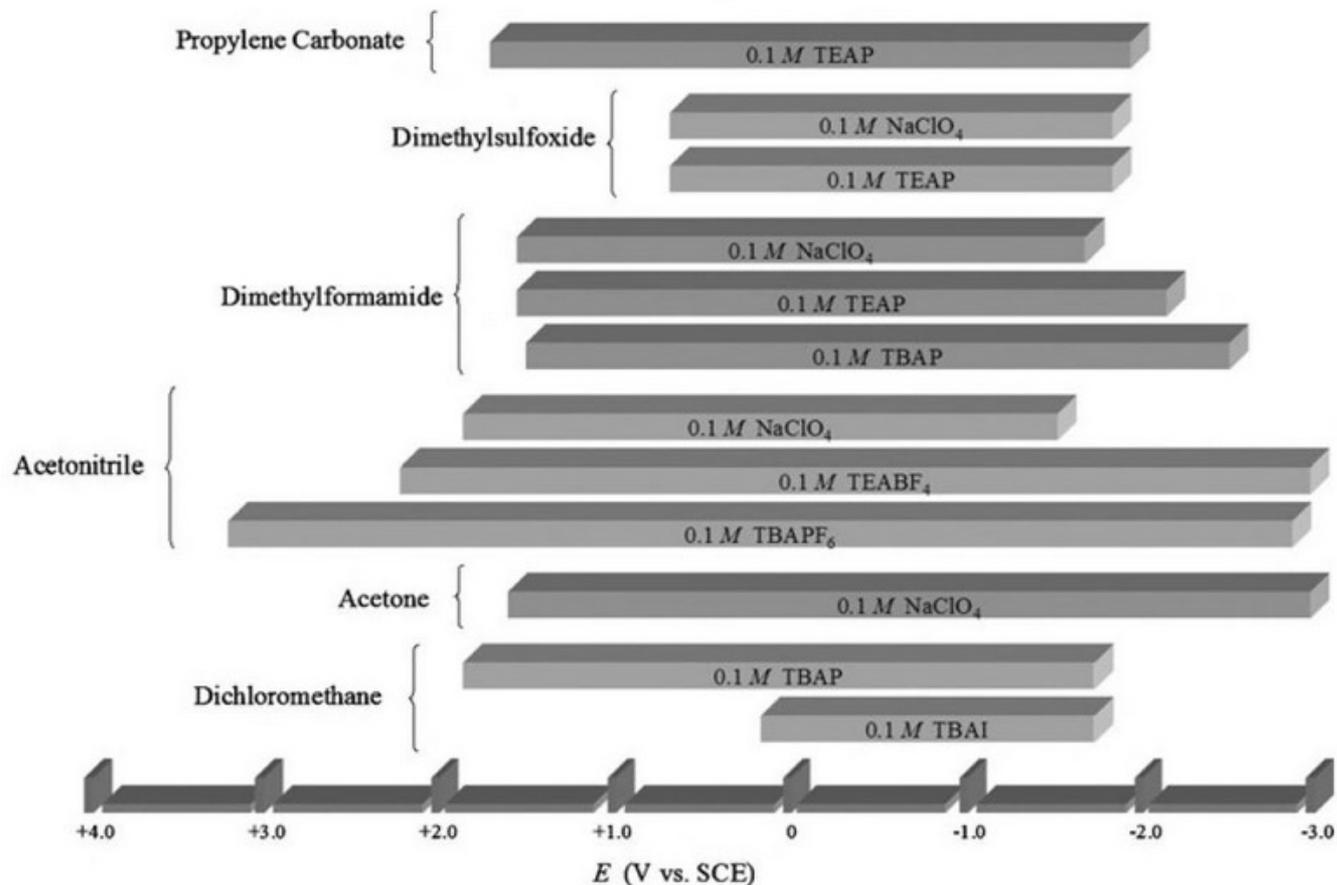


# “Janela” de eletrodo



**Figure 18.1** Estimated potential ranges in aqueous solutions at 25 °C. (for colour version: see colour section at the end of the book).

# “Janela” de eletrodo

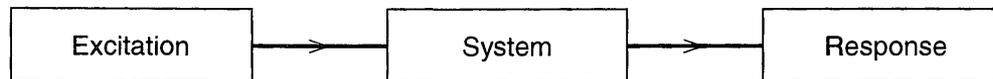


**Figure 18.2** Estimated potential ranges at Pt electrodes for non-aqueous solvent/electrolyte solutions. Data from reference (1). (for colour version: see colour section at the end of the book).

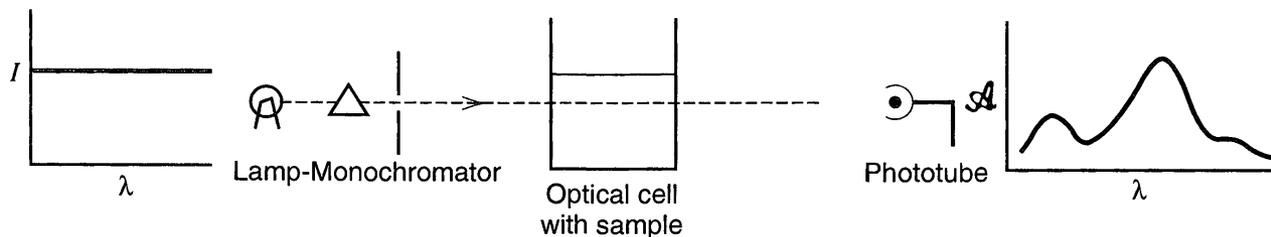
# **Cinética Química x Cinética Eletroquímica**

# Voltammetria

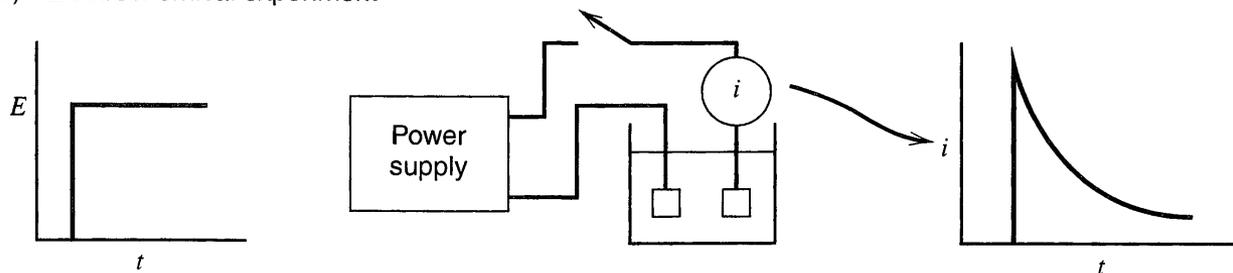
(a) General concept



(b) Spectrophotometric experiment

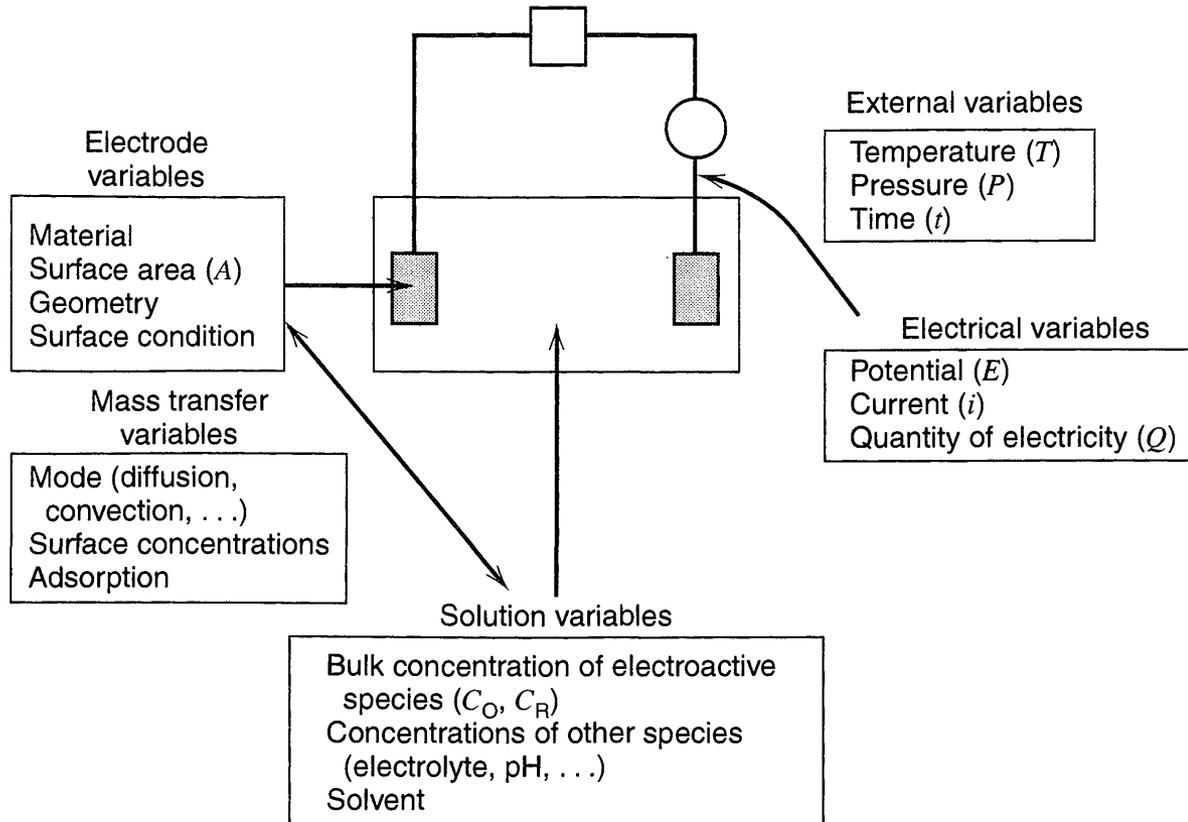


(c) Electrochemical experiment



**Figure 1.3.3** (a) General principle of studying a system by application of an excitation (or perturbation) and observation of response. (b) In a spectrophotometric experiment, the excitation is light of different wavelengths ( $\lambda$ ), and the response is the absorbance ( $\mathcal{A}$ ) curve. (c) In an electrochemical (potential step) experiment, the excitation is the application of a potential step, and the response is the observed  $i$ - $t$  curve.

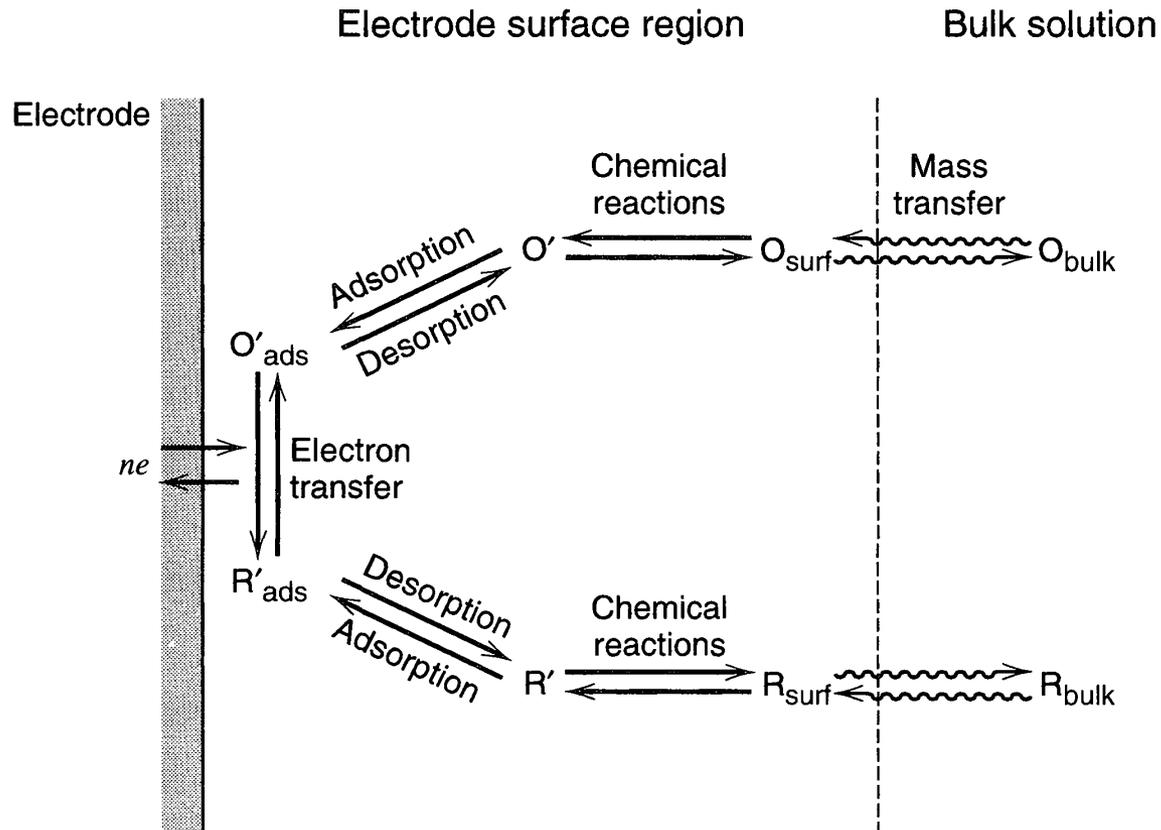
# Voltammetria



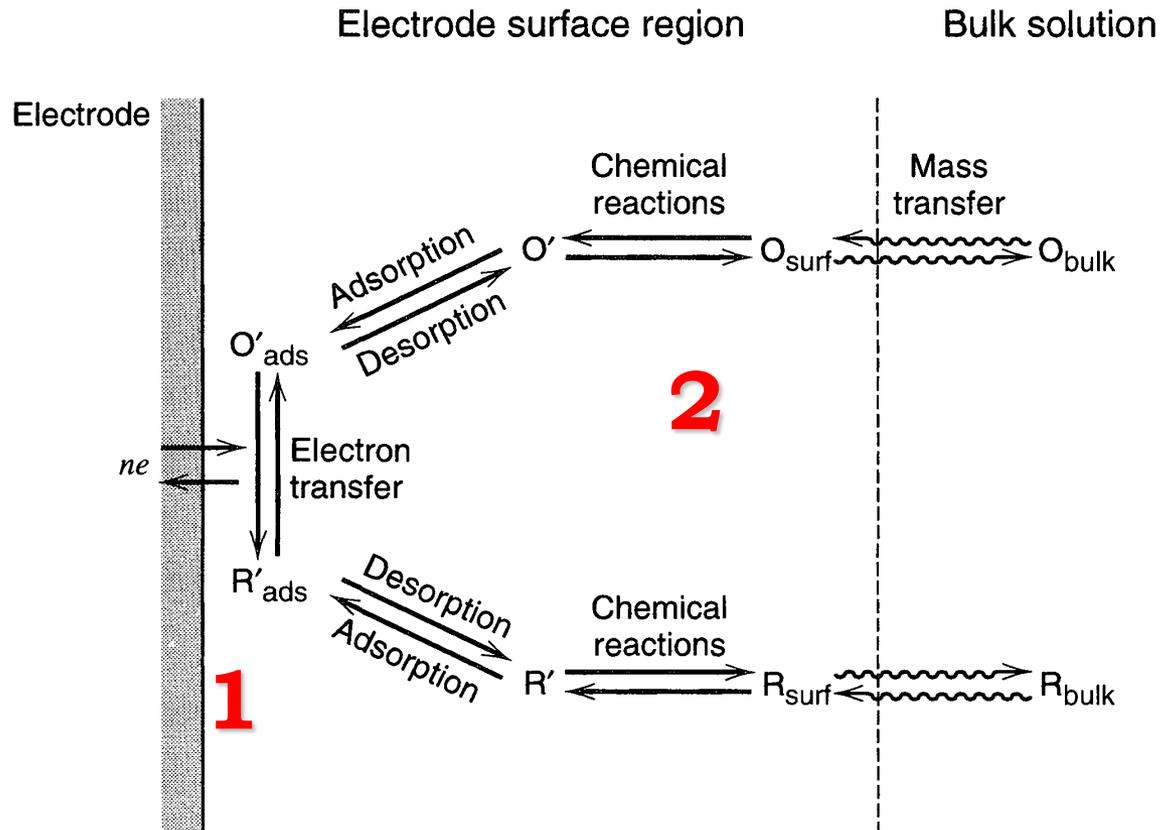
# Mecanismos de Hidrodinâmica

- 1) **Migração:** Movimento de espécies eletricamente carregadas sob a influência de um campo elétrico (um gradiente de potencial elétrico).
- 2) **Difusão:** Movimento de espécies sob a influência de um gradiente de potencial químico (ex.: concentração).
- 3) **Convecção:** Transporte de massa sob condições hidrodinâmicas. A homegeneização do meio pode ocorrer por *convecção natural* decorrente de um gradiente de concentração (ou temperatura) ou por *convecção forçada* (agitação da solução ou movimentação relativa da mesma em relação ao recipiente). A convecção é caracterizada por regiões estagnantes, de fluxo laminar ou turbulento.

# Cinética Eletroquímica



# Cinética Eletroquímica

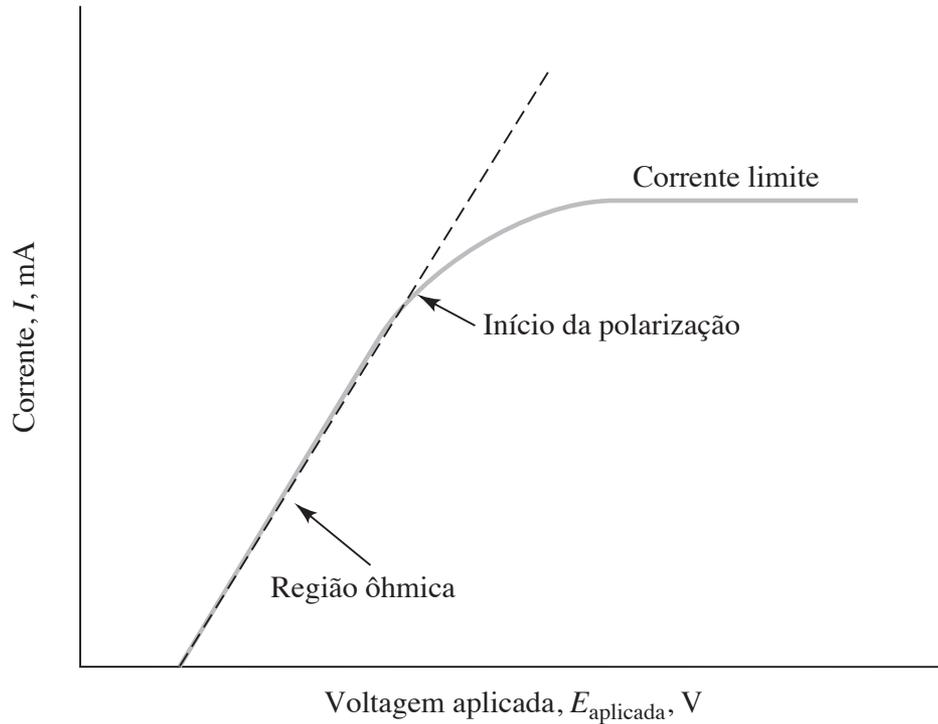


**1) Transferência de cargas**

**2) Transporte de massa (difusão)**

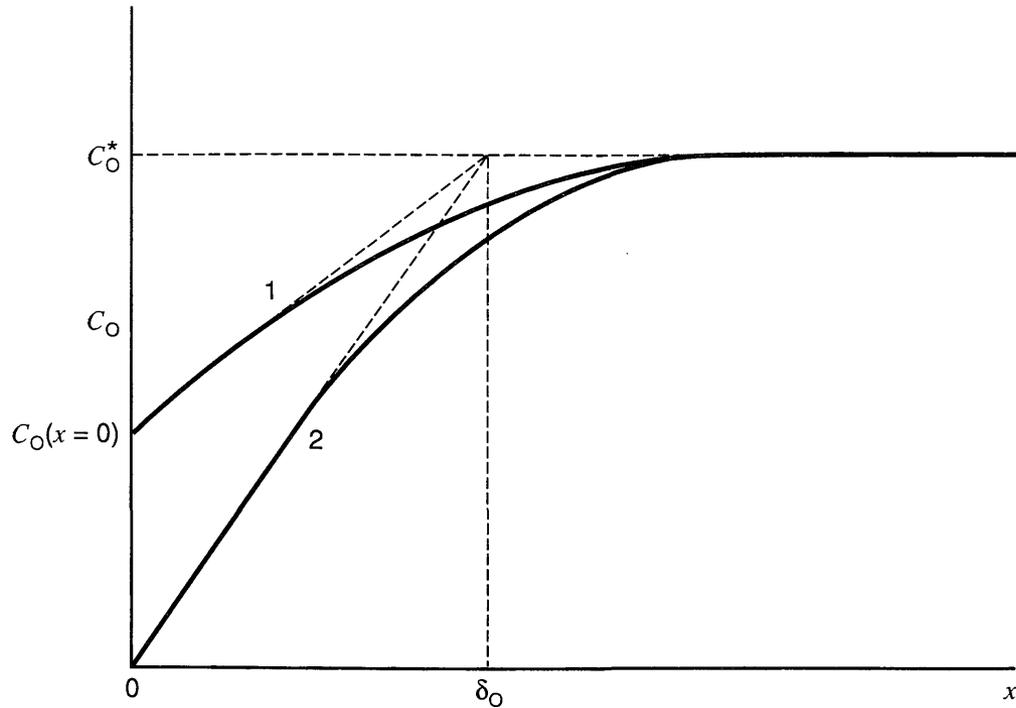


# Cinética Eletroquímica



**Figura 22-4** Curva corrente-potencial para uma eletrólise mostrando a região linear ou ôhmica, o início da polarização e o platô da corrente limite. Na região da corrente limite, diz-se que o eletrodo está completamente polarizado, uma vez que seu potencial pode variar amplamente sem afetar a corrente.

# Cinética Eletroquímica



**Figure 1.4.1** Concentration profiles (solid lines) and diffusion layer approximation (dashed lines).  $x = 0$  corresponds to the electrode surface and  $\delta_O$  is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (1) where  $C_O(x = 0)$  is about  $C_O^*/2$ , (2) where  $C_O(x = 0) \approx 0$  and  $i = i_l$ .

$$\eta = E - E_e \quad \longrightarrow \quad I = \vec{I} + \overleftarrow{I}$$

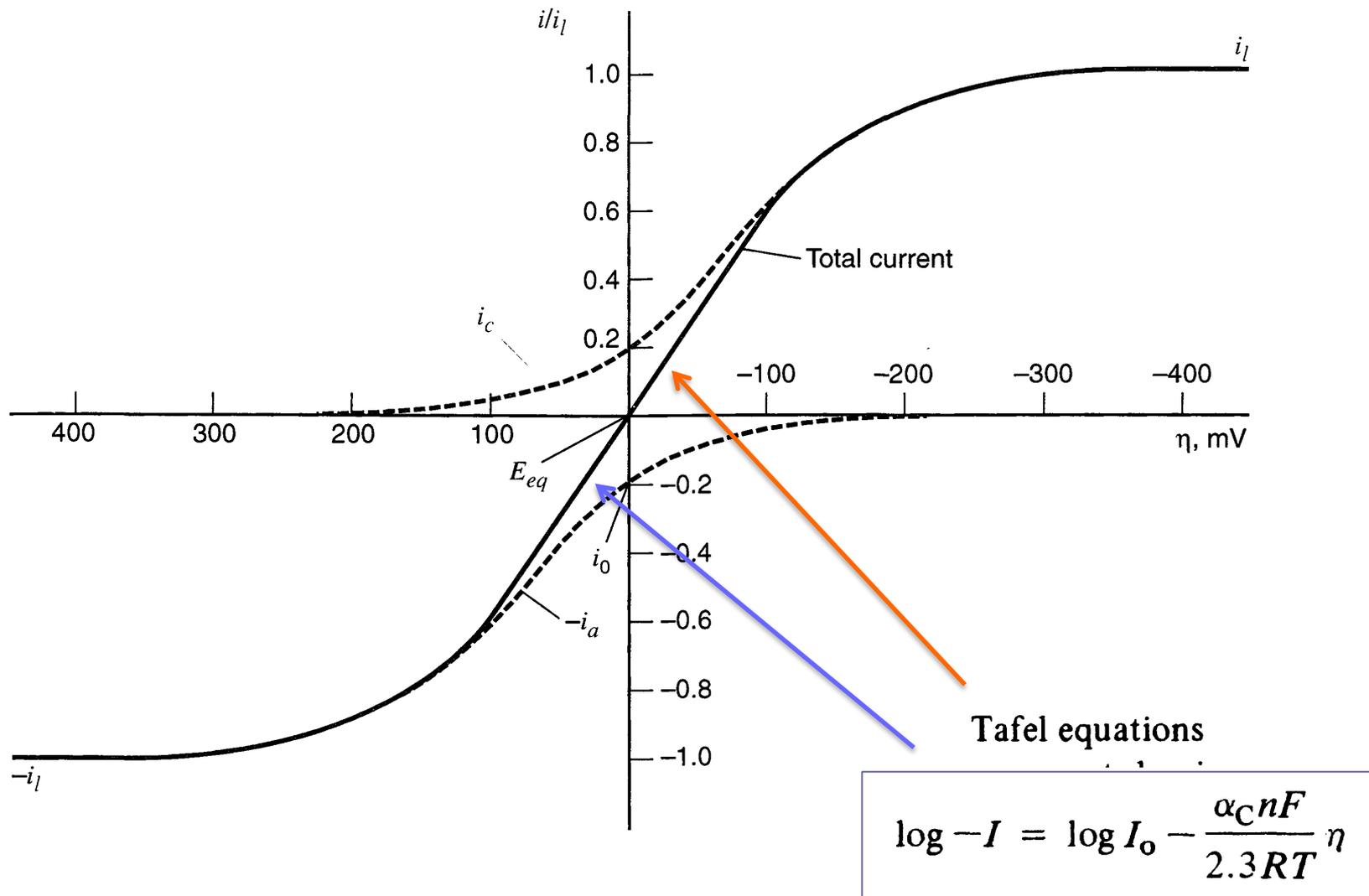
$$\vec{I} = -nF\vec{k}c_O^o \quad \text{and} \quad \overleftarrow{I} = nF\overleftarrow{k}c_R^o$$

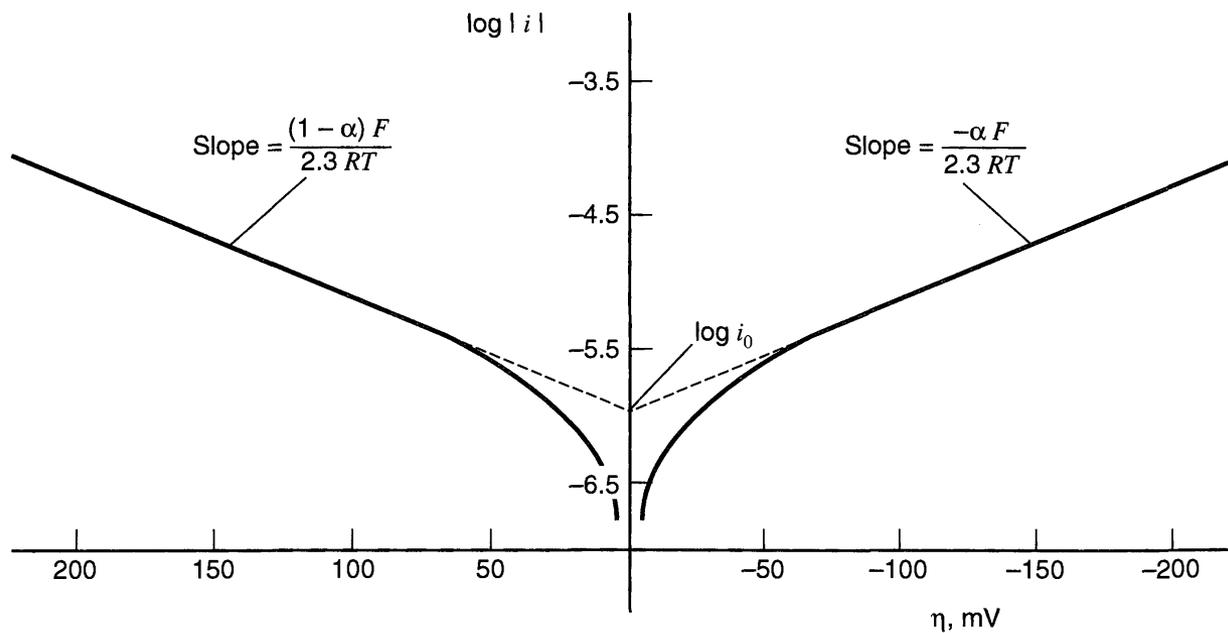
$$\vec{k} = \vec{k}_o \exp\left(-\frac{\alpha_C nF}{RT} E\right) \quad \text{and} \quad \overleftarrow{k} = \overleftarrow{k}_o \exp\left(\frac{\alpha_A nF}{RT} E\right)$$

$$I_o = -\vec{I} = \overleftarrow{I} \text{ at } \eta = 0.$$

$$I = I_o \left[ \exp\left(\frac{\alpha_A nF}{RT} \eta\right) - \exp\left(-\frac{\alpha_C nF}{RT} \eta\right) \right].$$

Butler-Volmer equation





**Figure 3.4.4** Tafel plots for anodic and cathodic branches of the current-overpotential curve for  $\text{O} + e \rightleftharpoons \text{R}$  with  $\alpha = 0.5$ ,  $T = 298 \text{ K}$ , and  $j_0 = 10^{-6} \text{ A/cm}^2$ .

# Cinética Eletroquímica

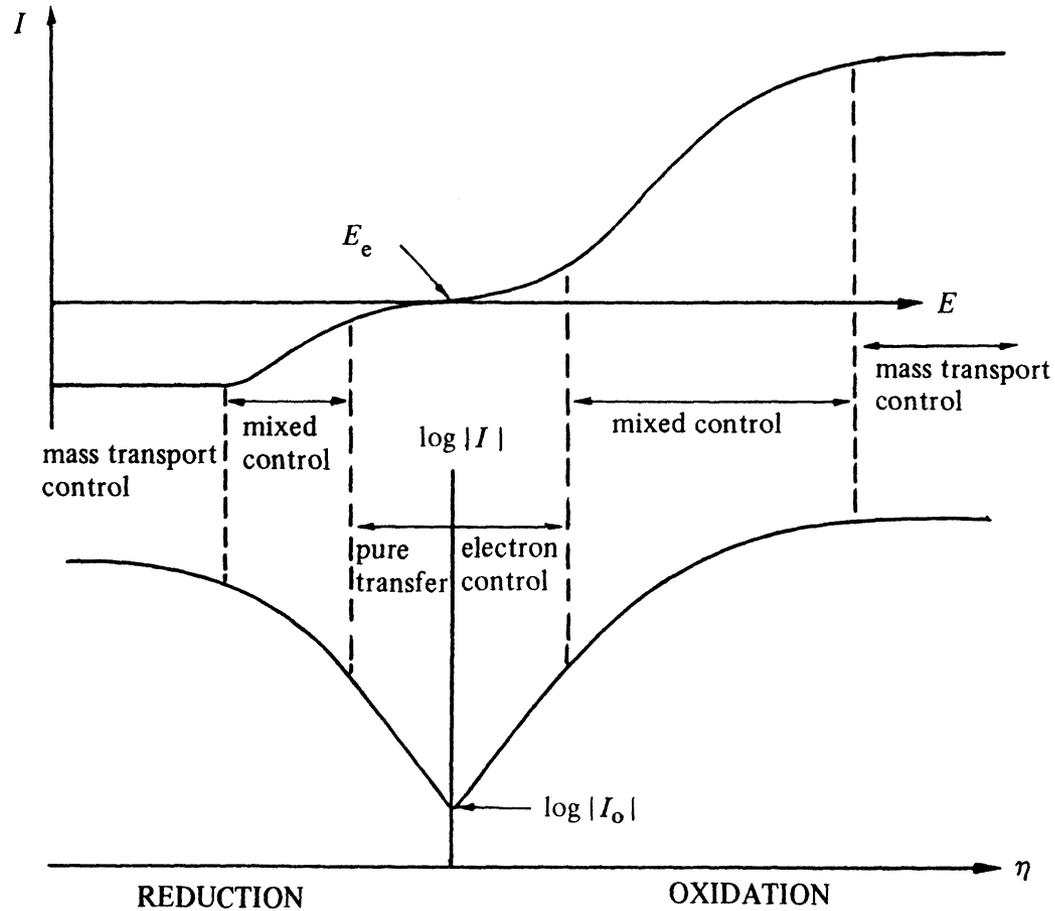
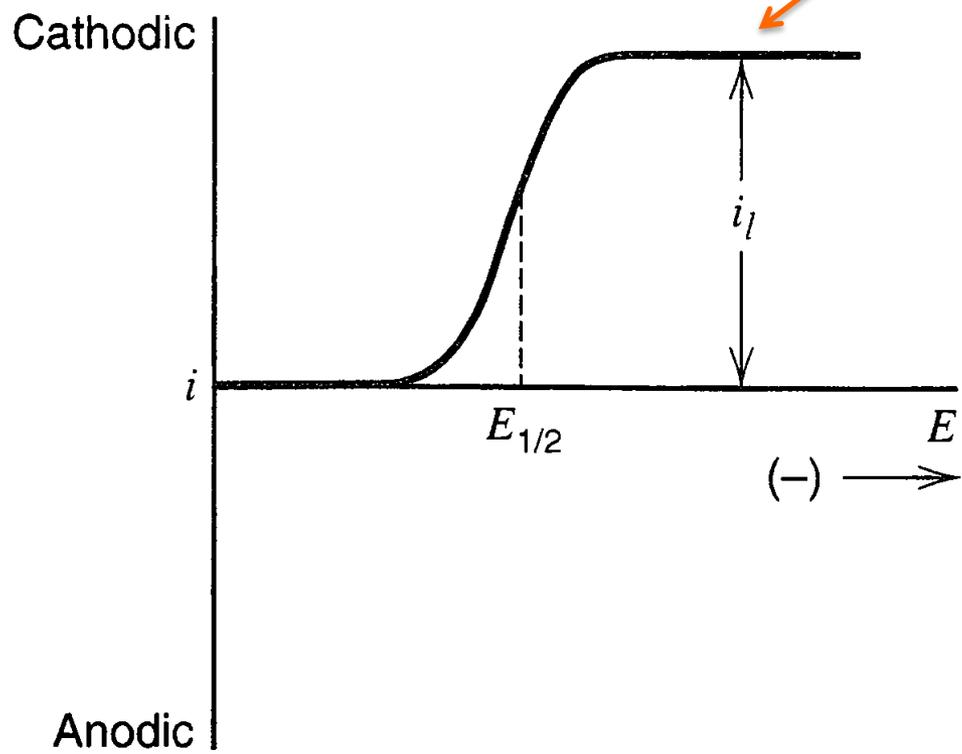


Fig. 1.12 –  $I$ - $E$  and corresponding  $\log I$ - $E$  characteristics for an irreversible electron transfer reaction. Solution as in Fig. 1.11.

$$I_L = -\frac{nFDc_O^\infty}{\delta}$$



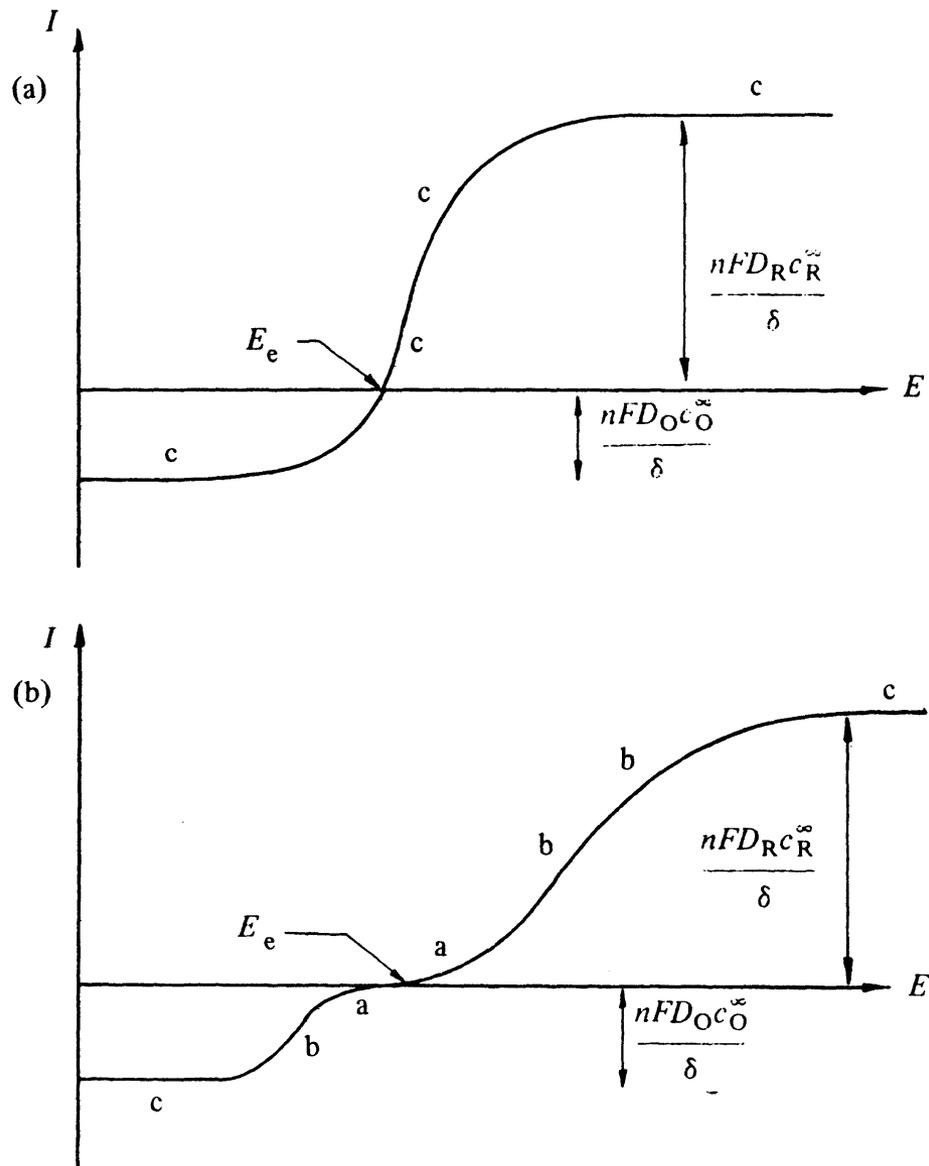
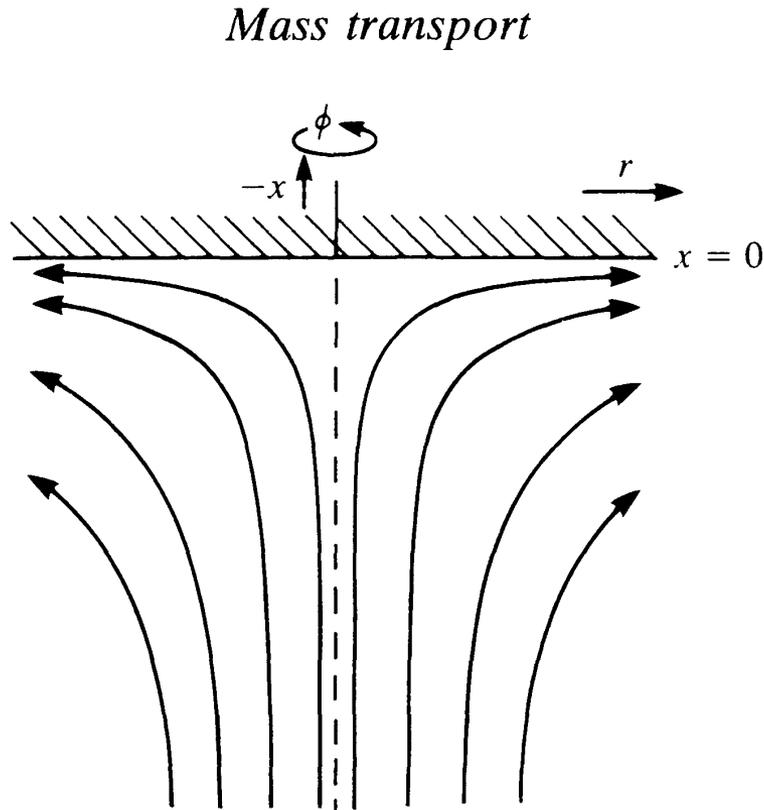


Fig. 1.11 – Complete  $I$ - $E$  curves over a wide range of overpotentials for a reaction  $O + ne^- \rightleftharpoons R$  when the solution contains  $c_R^\infty = 3c_O^\infty$ . (a) Reversible electron transfer (b) irreversible electron transfer. a: Pure electron transfer control b: mixed control c: mass transfer control.

# Cinética Eletroquímica

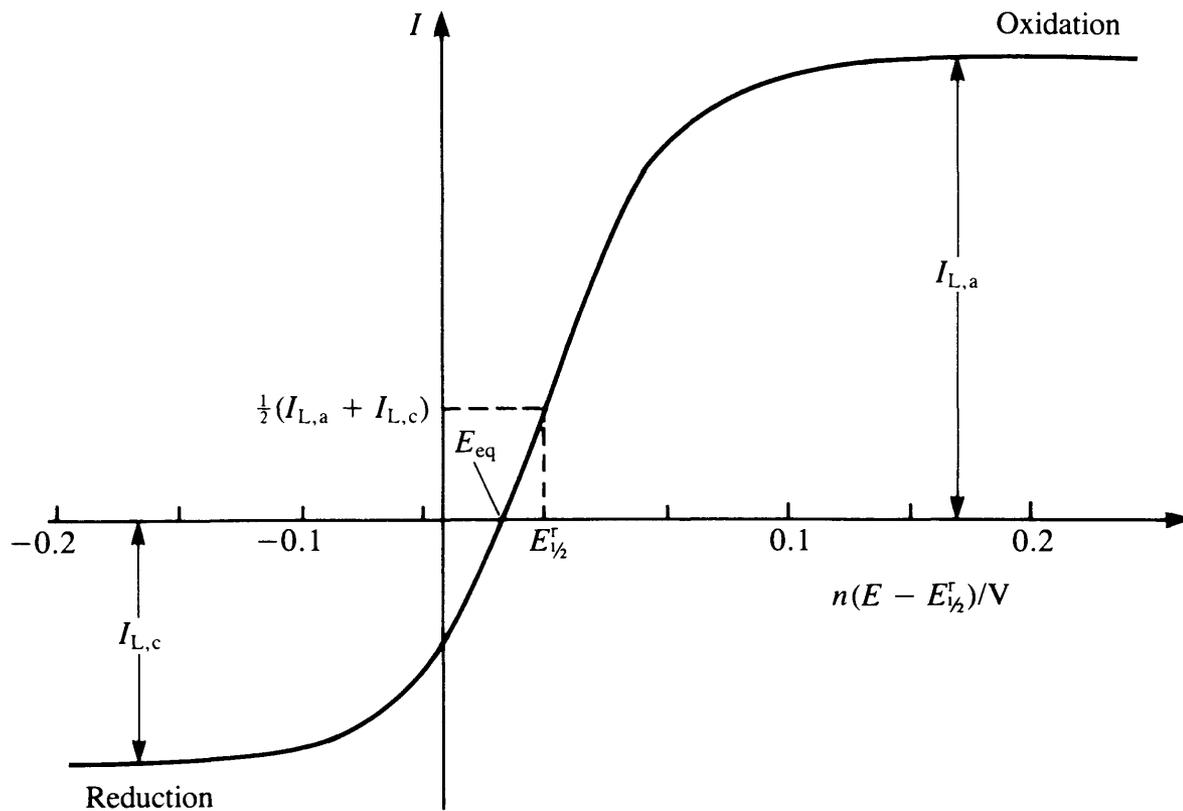


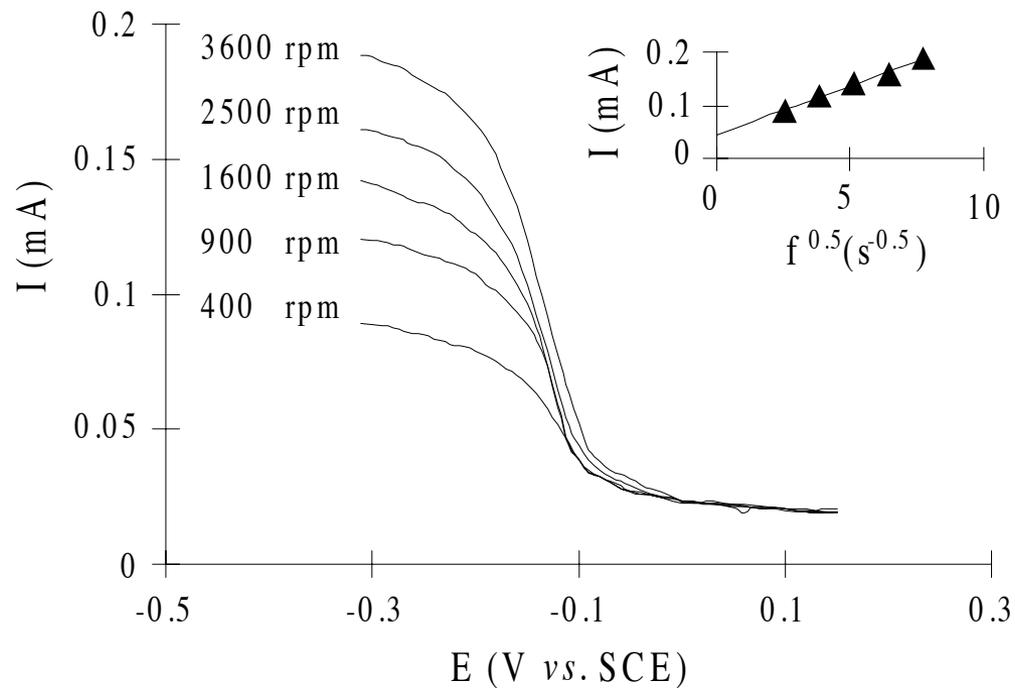
Levich equation,

$$I_L = 0.62 n F D^{2/3} \nu^{-1/6} c^\infty \omega^{1/2}$$

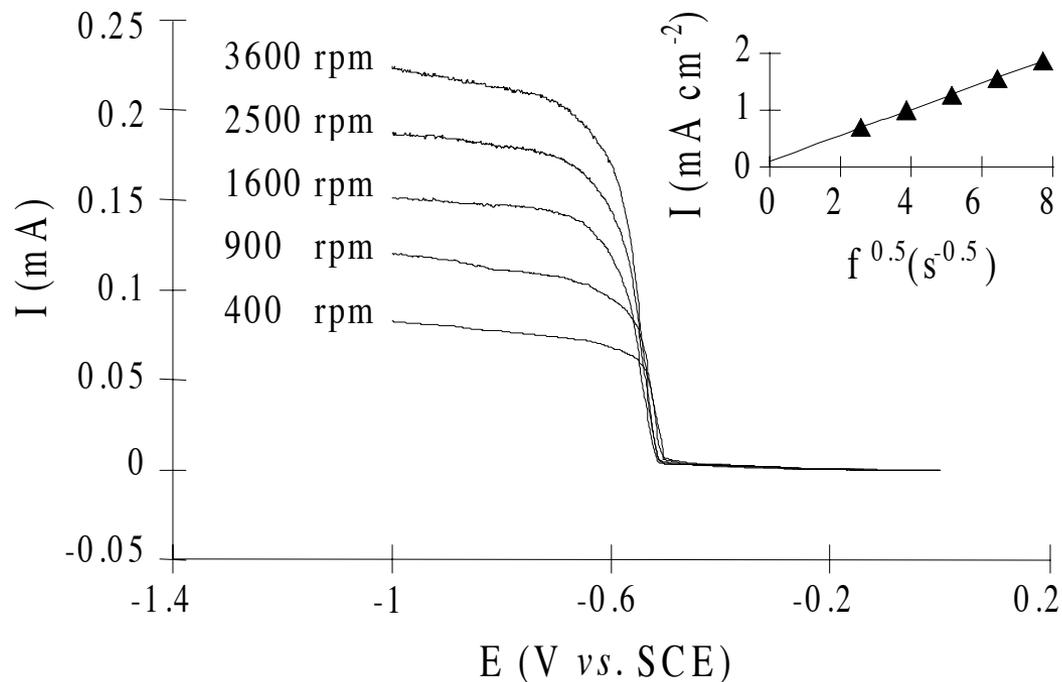
**Fig. 5.12.** Streamlines for a rotating disc.

# Cinética Eletroquímica

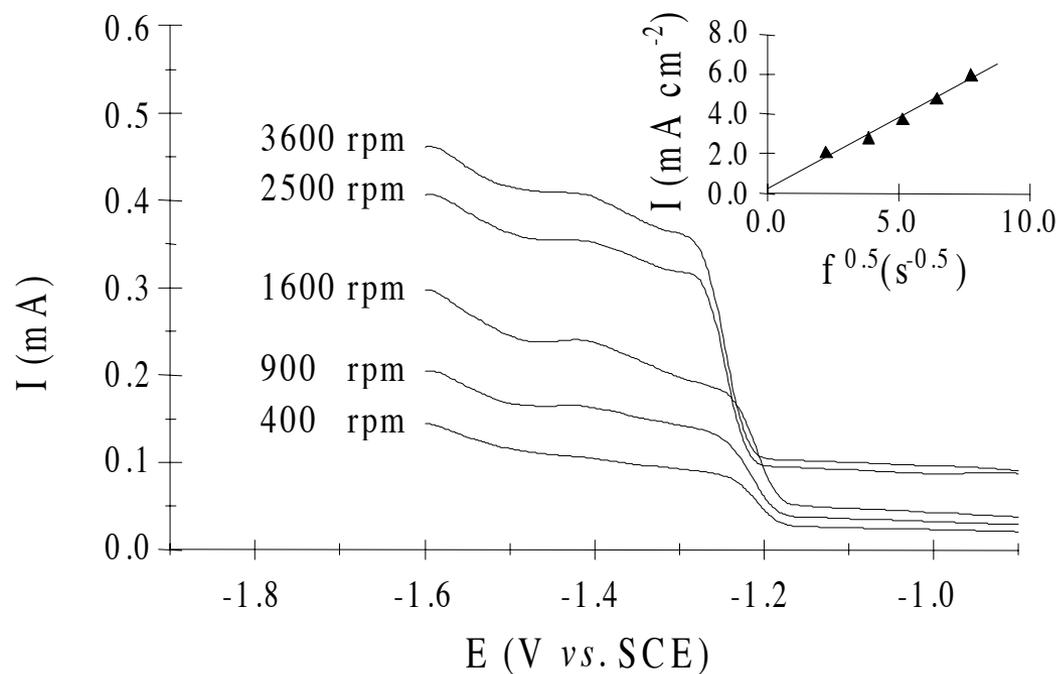




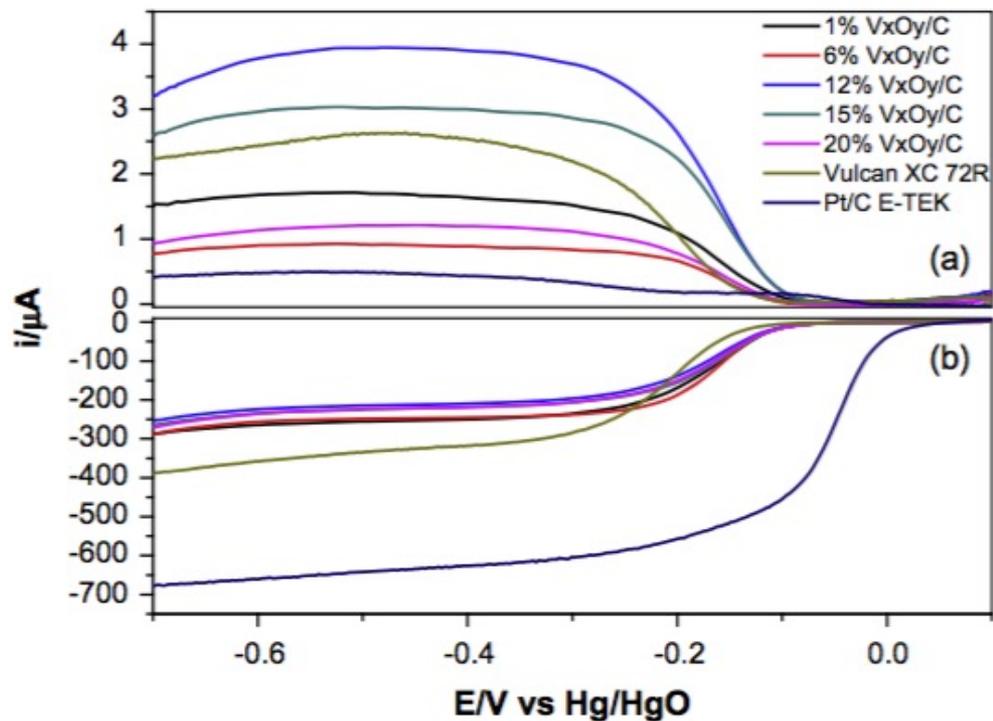
**Figure 2.** Voltammograms obtained on a glassy carbon rotating disc electrode. Solution of 50 mg/L of Cu(II). Scan rate 20 mV/s. Rotation rates as indicated in the graph. Inset: Levich plot using the limiting current values taken at the mid point of the plateaus.



**Figure 3.** Voltammograms obtained on a glassy carbon rotating disc electrode. Solution of 50 mg/L of Pb(II). Scan rate 10 mV/s. Rotation rates as indicated on the graph. Inset: Levich plot using the limiting current values taken at the mid point of the plateaus.



**Figure 4.** Voltammograms obtained on a glassy carbon rotating disc electrode. Solution of 50 mg/L of Zn(II). Scan rate 2 mV/s. Rotation rates as indicated on the graph. Inset: Levich plot using the limiting current values taken at the mid point of the plateaus.



**Fig. 4.** Steady-state polarization curves for the ORR on different proportions of vanadium oxide materials supported on carbon, Vulcan XC-72R and Pt/C E-TEK in oxygen-saturated  $1 \text{ mol L}^{-1} \text{ NaOH}$  at a scan rate of  $5 \text{ mV s}^{-1}$ . (Top) Ring current  $E_{\text{ring}} = 0.2 \text{ V}$ . (Bottom) Disk current at 1600 rpm.

# **Métodos Voltamétricos**

- 1) Determinação de corrente em função do potencial aplicado**
  - **“Voltametria”**
  
- 2) Condições de completa polarização por concentração**
  - **Mecanismo preferencial: transporte de massa do analito à superfície do eletrodo**

# **Métodos Voltamétricos**

## **(Histórico)**

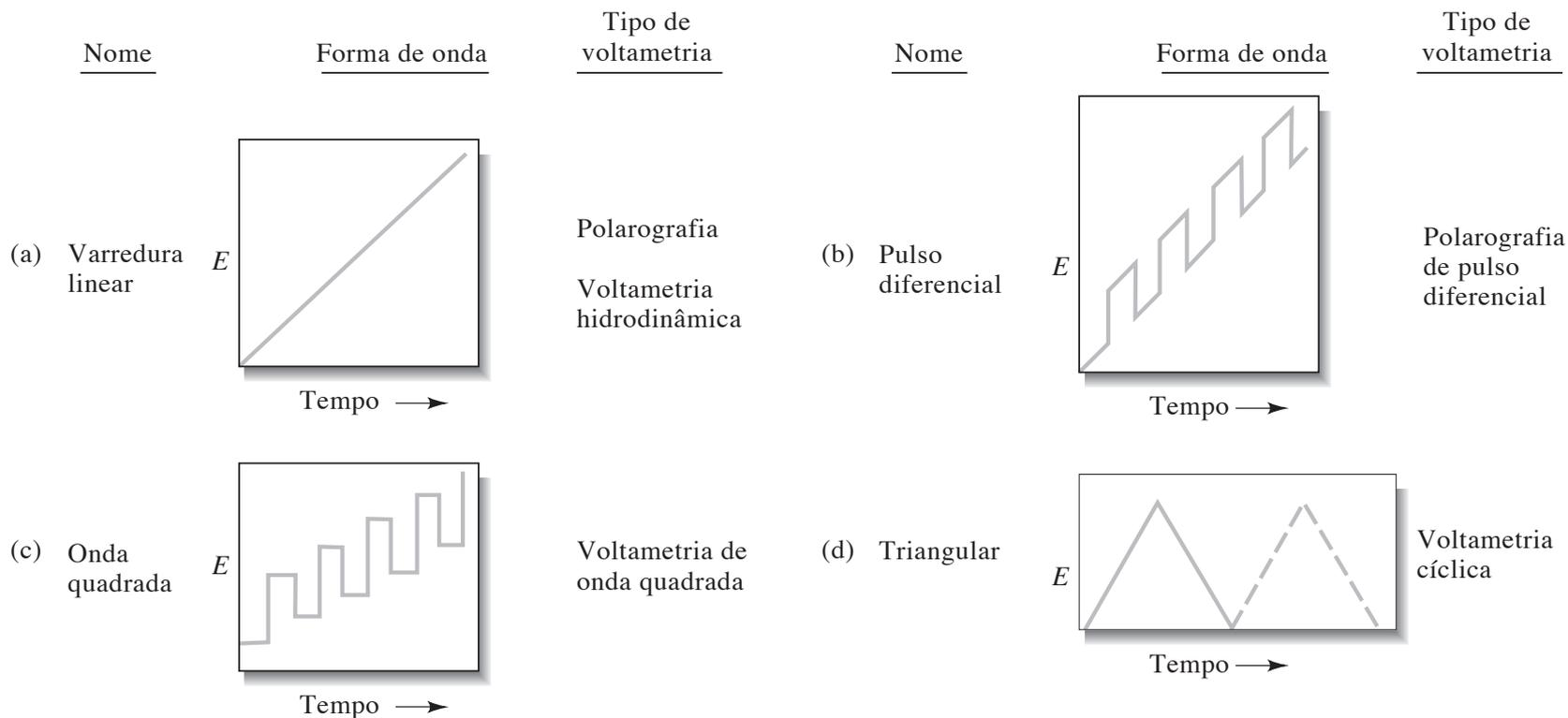
### **1) Polarografia: Voltametria usando eletrodo de gota de Hg**

- **Jaroslav Heyrovsky (~1920 / República Tcheca)**

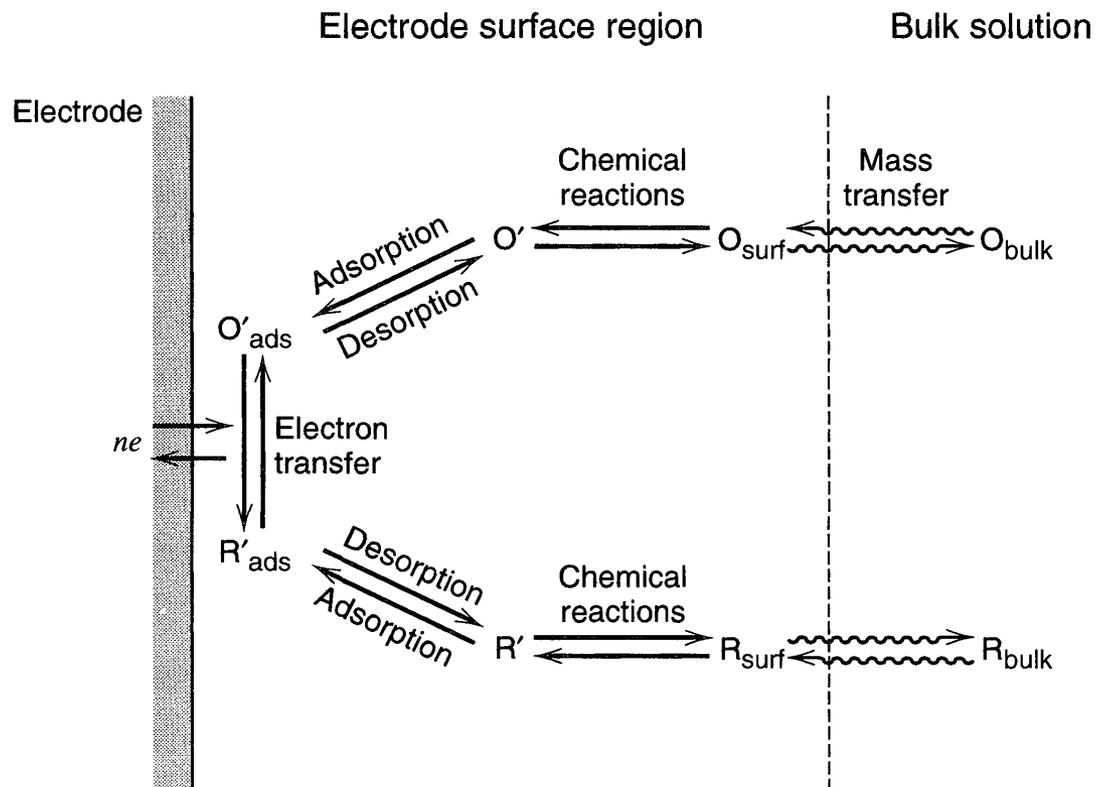
### **2) Aplicações**

- **Processos de oxidação em vários meios**
- **Processos de adsorção**
- **Mecanismos de transferência de carga**
- **Aplicações analíticas quantitativas**

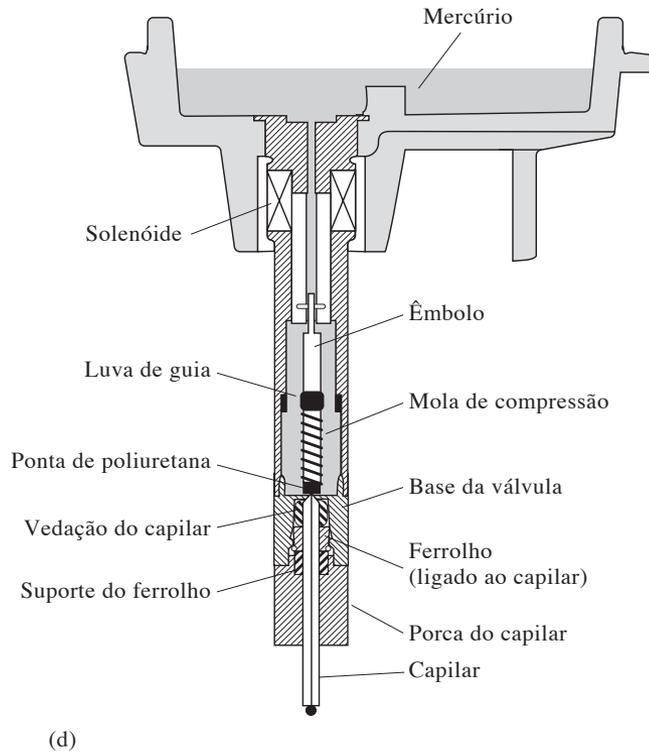
- **Sinais de excitação: funções voltagem-tempo aplicadas ao eletrodo**
- **Gráfico: “Voltamograma”**



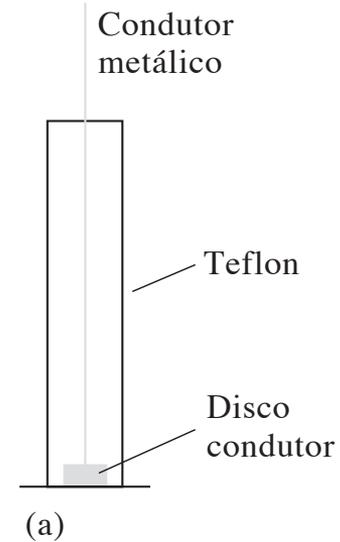
**Figura 23-1** Sinais de excitação de tensão *versus* tempos empregados na voltametria.



# Eletrodos de Hg



## Gota Estática ou Pendente (comercial)



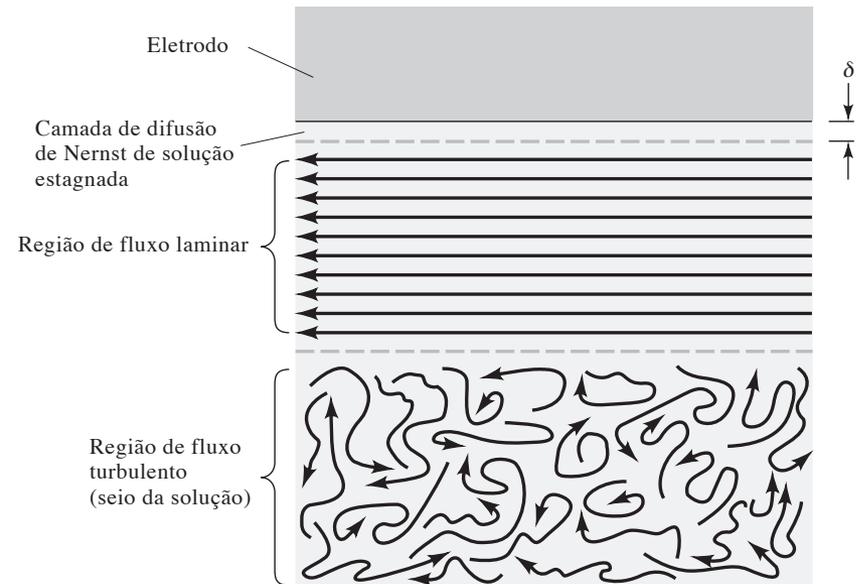
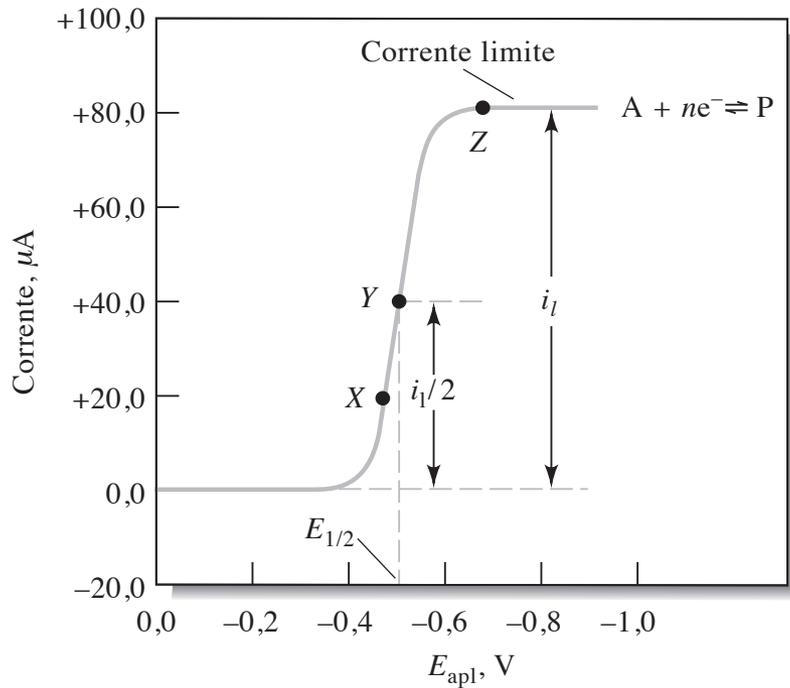
## Disco Plano

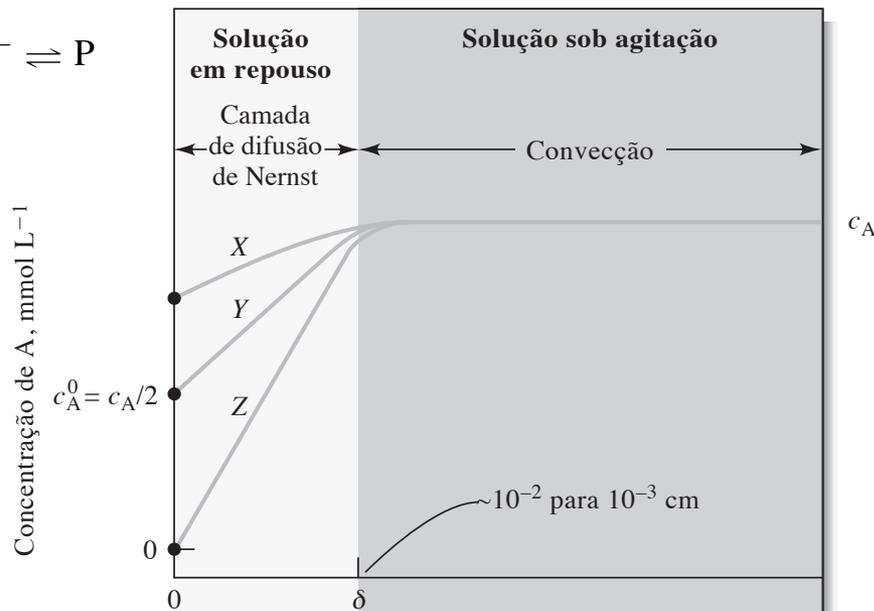
# Voltametria de Varredura Linear

## Sistema Reversível

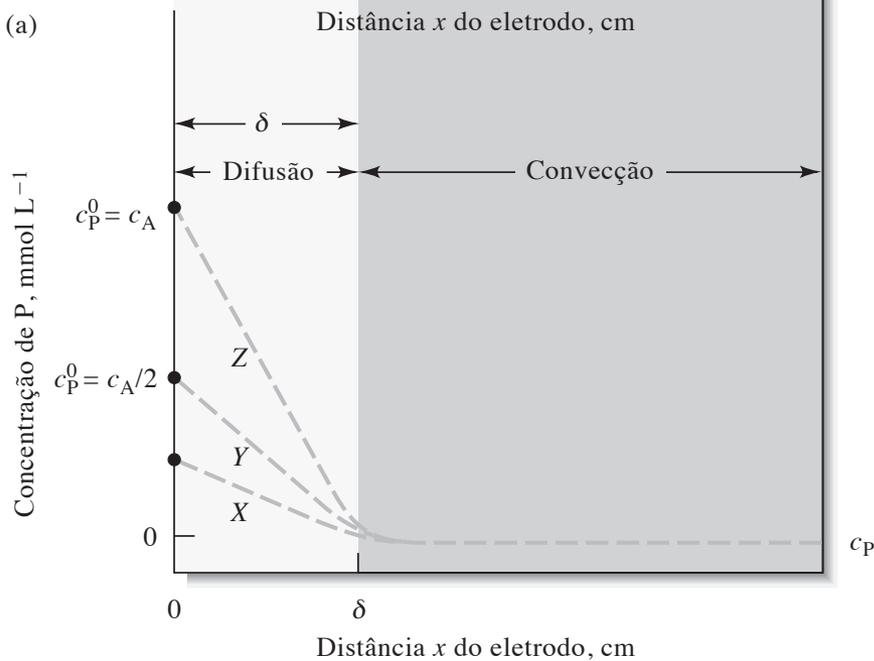


$$i_l = kc_A$$





(a)



(b)

$$i = nFAD_A \left( \frac{\partial c_A}{\partial x} \right)$$

$$i = \frac{nFAD_A}{\delta} (c_A - c_A^0) = k_A (c_A - c_A^0)$$

$$(c_A - c_A^0)/\delta \quad i_l = \frac{nFAD_A}{\delta} c_A = k_A c_A$$

**$C_A$  – Concentração de A no seio da solução**

**$C_A^0$  – Concentração de A na sup. do eletrodo**

**$\delta$  – Espessura da Camada de Difusão de Nernst**

**D – Coeficiente de Difusão de A**

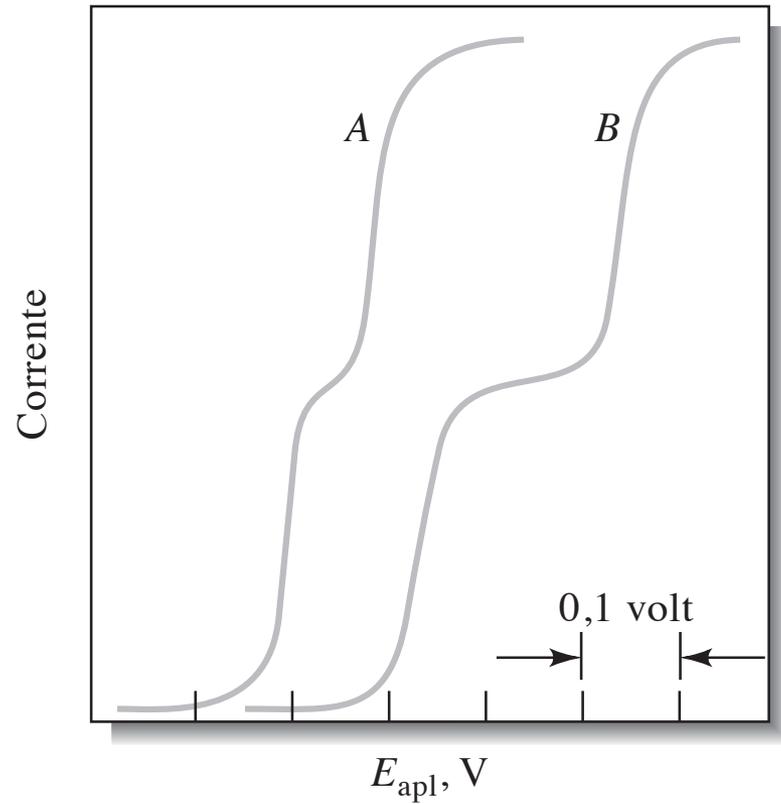
Grandeza	Unidades
$n$	mol de elétrons/mol do analito
$F$	coulomb/mol de elétrons
$A$	$\text{cm}^2$
$D_A$	$\text{cm}^2 \text{s}^{-1}$
$c_A$	mol do analito/ $\text{cm}^3$
$\delta$	cm

## Seletividade via $E_{1/2}$

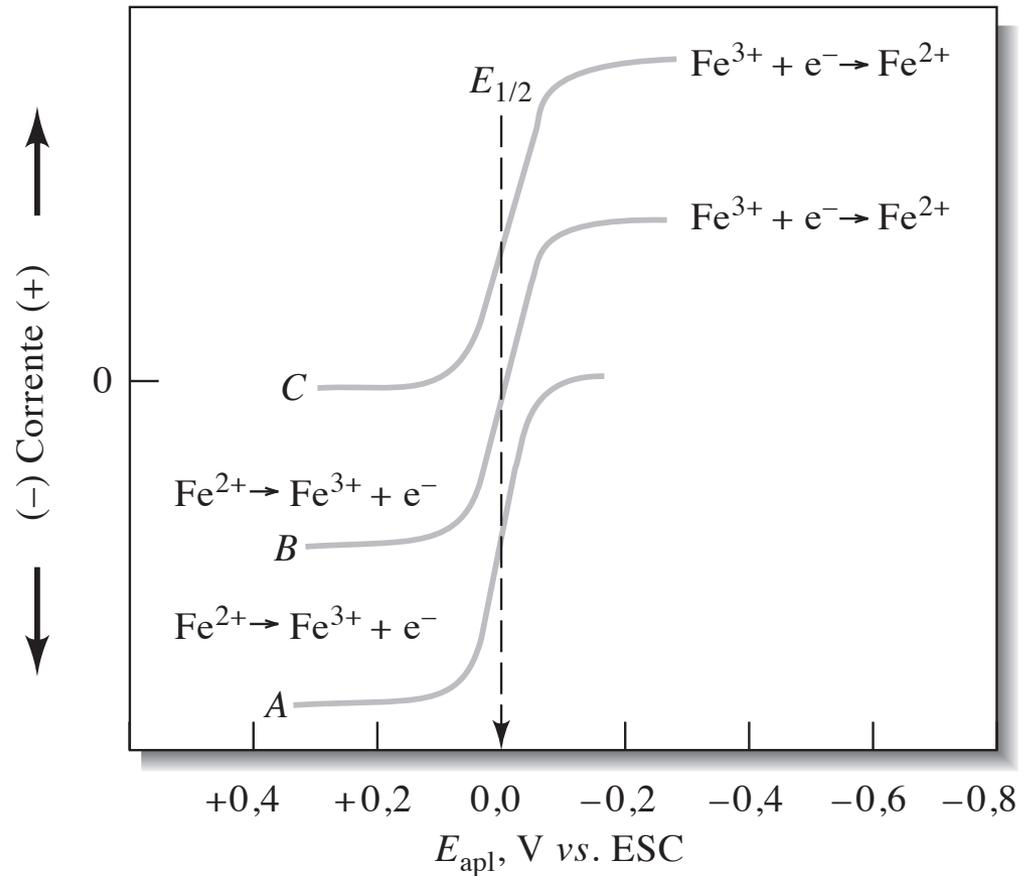
Quando:  $i = i_t / 2$

$$E_{\text{apl}} = E_{1/2} - \frac{0,0592}{n} \log \frac{i}{i_t - i}$$

$$E_{1/2} \approx E_A^0 - E_{\text{ref}}$$



## Voltamogramas mistos (catódico/anódico)



**A - Somente Fe(II)**

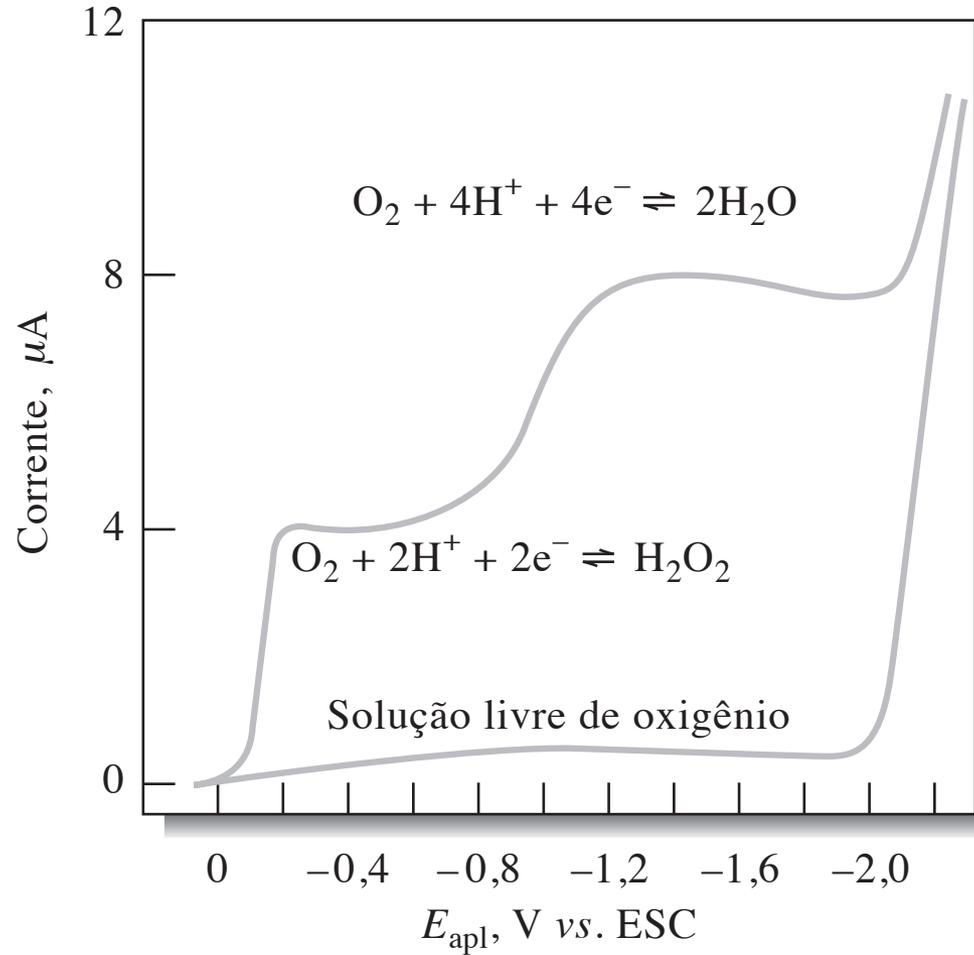
**B - Fe(II) / Fe(III)**

**C - Somente Fe(III)**

## Ondas Voltamétricas de Oxigênio



- “Purga” com  $\text{N}_2$ , Ar ou He
- “Interferência”



# Polarografia (Eletrodo Gotejante de Hg)

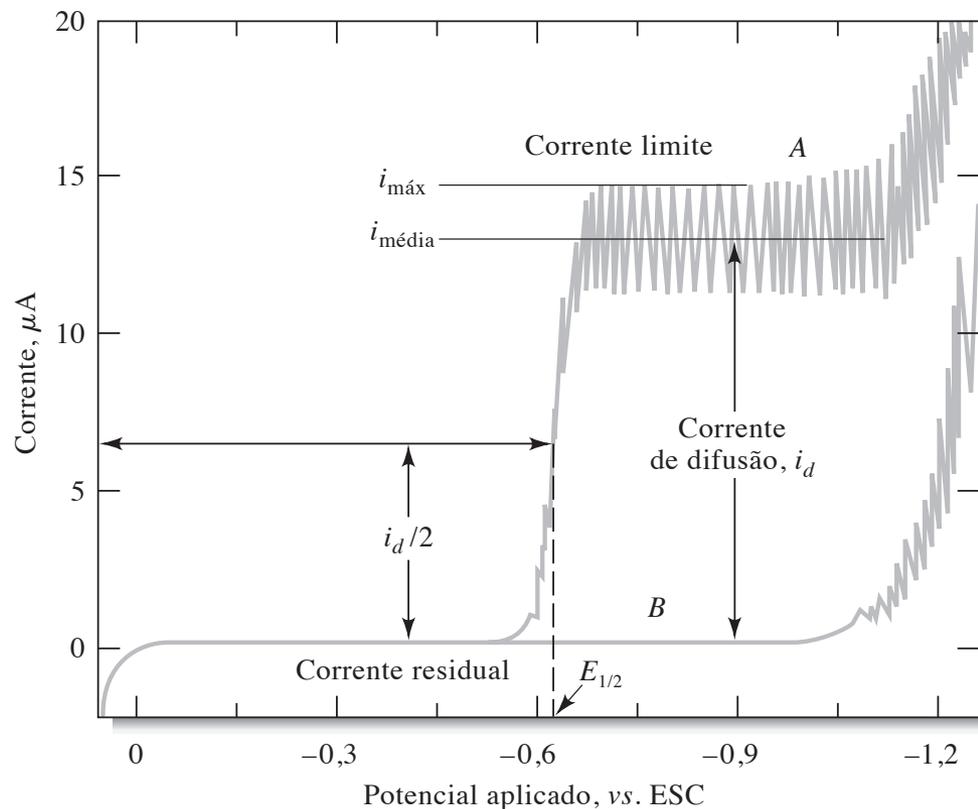


equação de Ilkovic

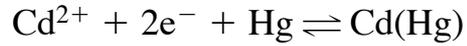
$$(i_d)_{\text{máx}} = 708 nD^{1/2}m^{2/3}t^{1/6}c$$

**t** – tempo de formação da gota (s)

**m** – velocidade do fluxo de Hg (mg/s)

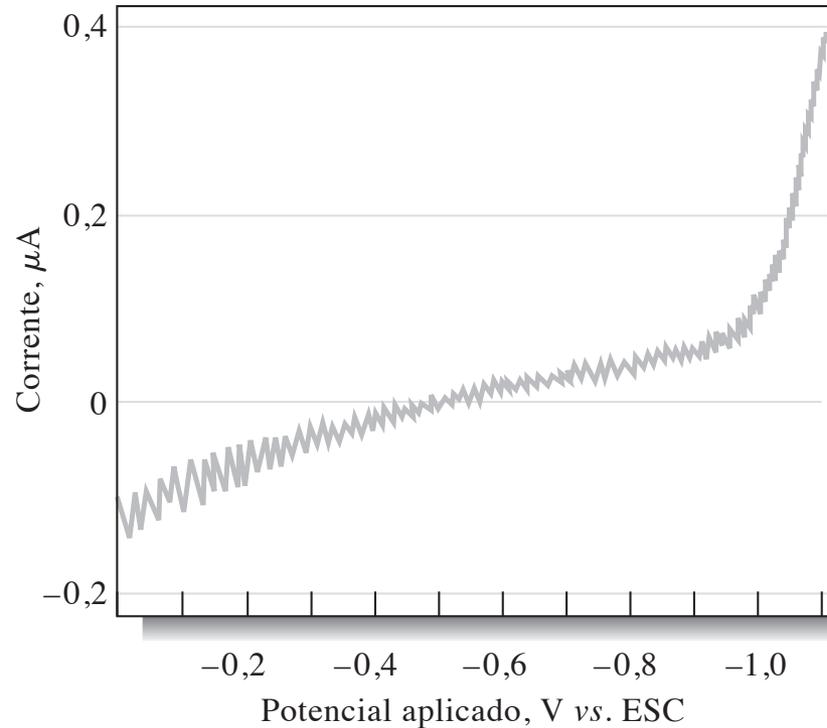


## Polarografia (Eletrodo Gotejante de Hg)



equação de Ilkovic

$$(i_d)_{\text{máx}} = 708 nD^{1/2}m^{2/3}t^{1/6}c$$



**Figura 23-17** Corrente residual para uma solução de HCl 0,1 mol L<sup>-1</sup>.

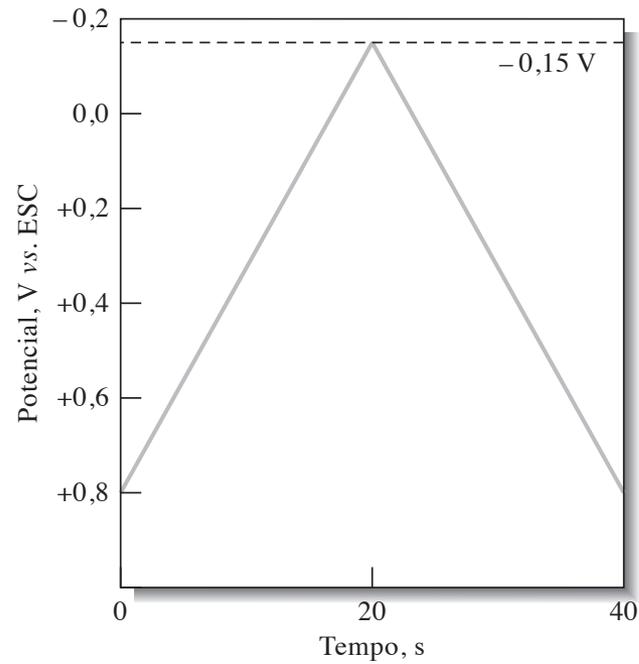
## 757 VA Computrace (Metrohm)



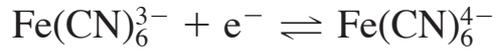
# Voltametria Cíclica

**t** – tempo de formação da gota (s)

**m** – velocidade do fluxo de Hg (mg/s)



# Voltametria Cíclica



$$\Delta E_p = |E_{pa} - E_{pc}| = 0,059/n$$

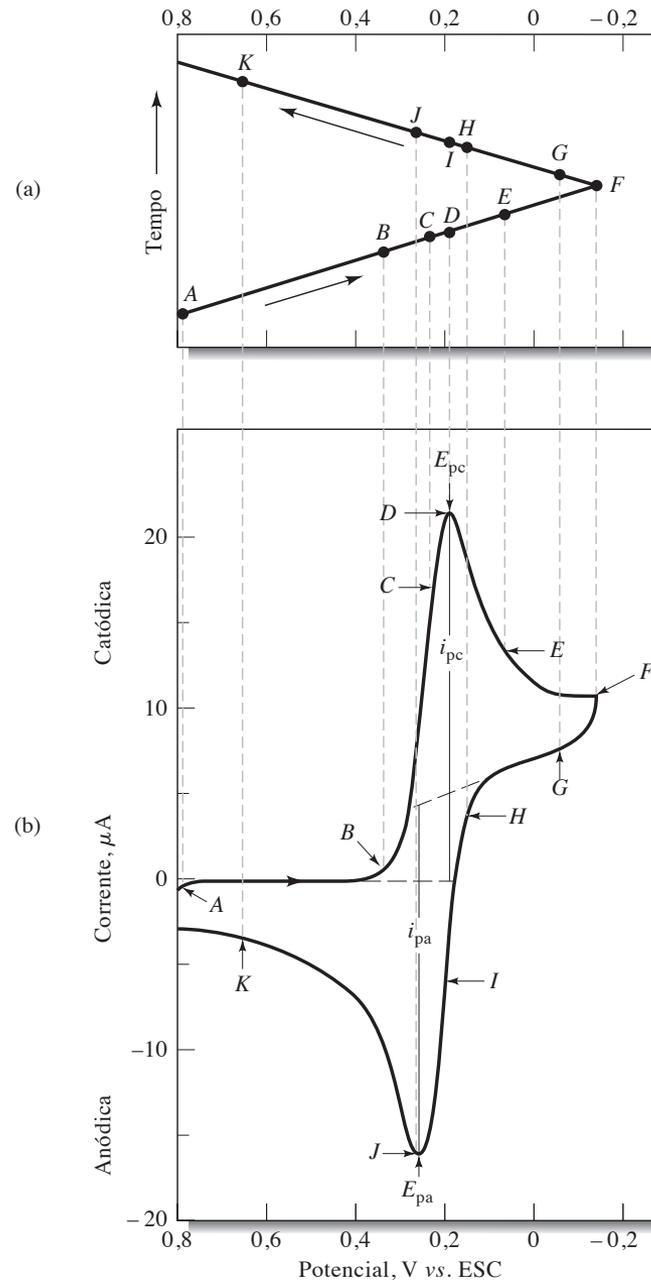
equação de Randles-Sevcik

$$i_p = 2,686 \times 10^5 n^{3/2} A c D^{1/2} \nu^{1/2}$$

$\nu$  – velocidade de varredura (V/s)

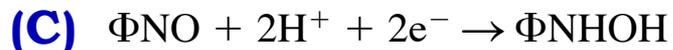
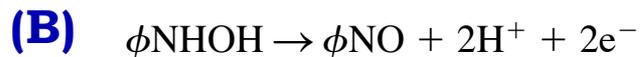
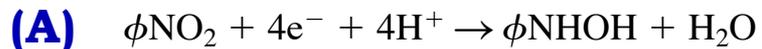
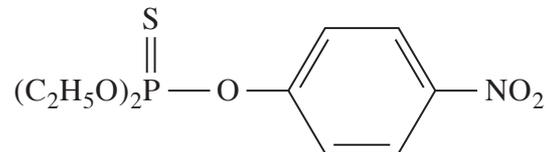
## Informações Quantitativas

- **D**
- **n**
- **c**

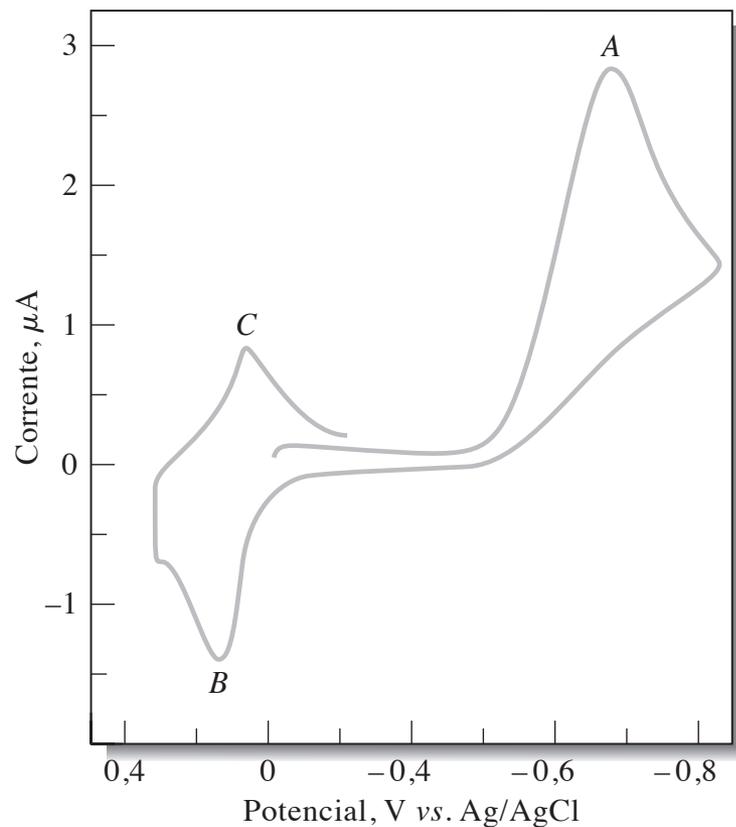


# Voltametria Cíclica

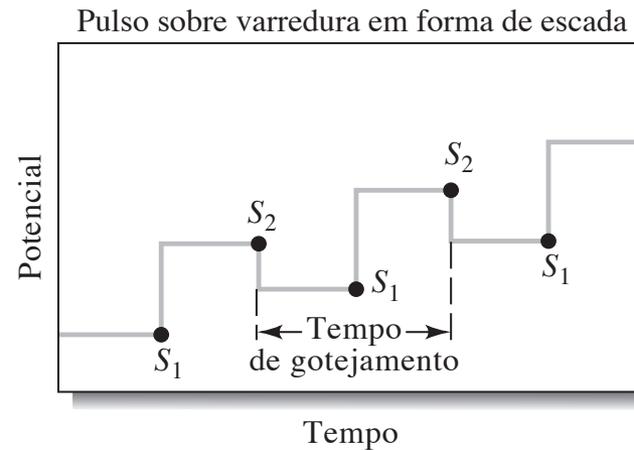
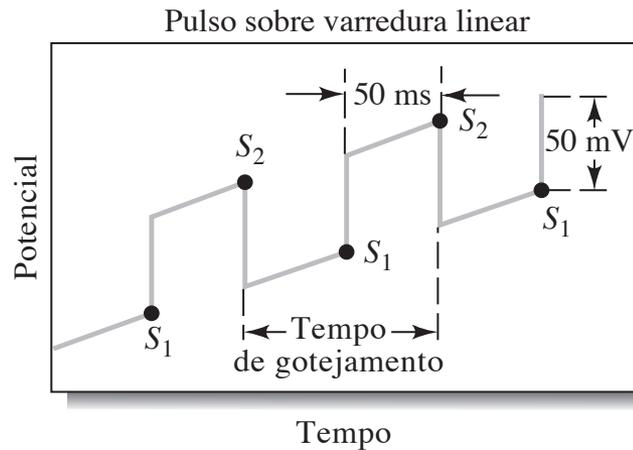
## Parathion



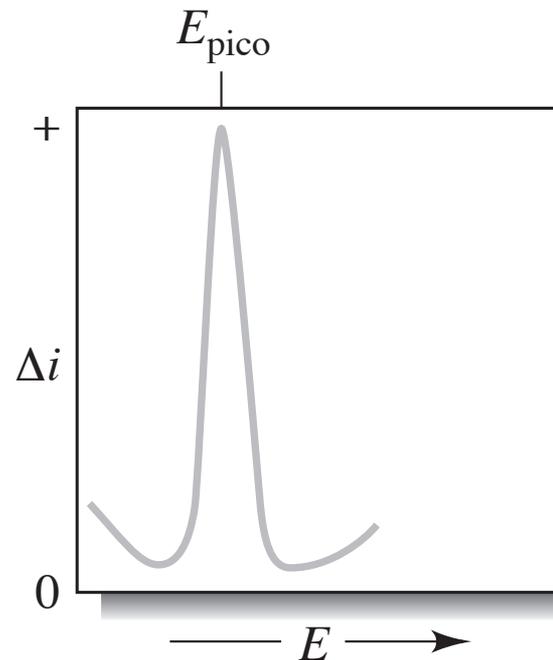
## Informações Qualitativas



# Voltametria de Pulso Diferencial



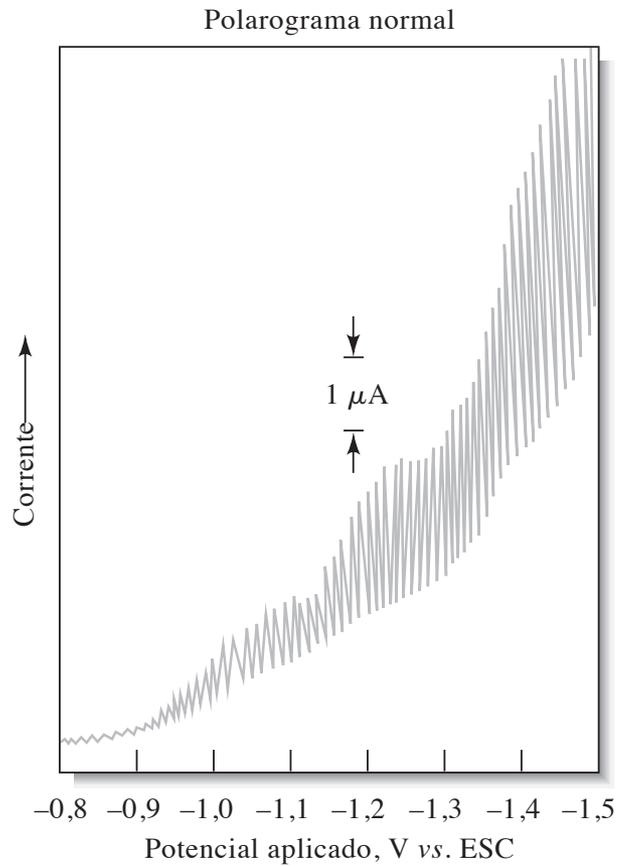
(a)



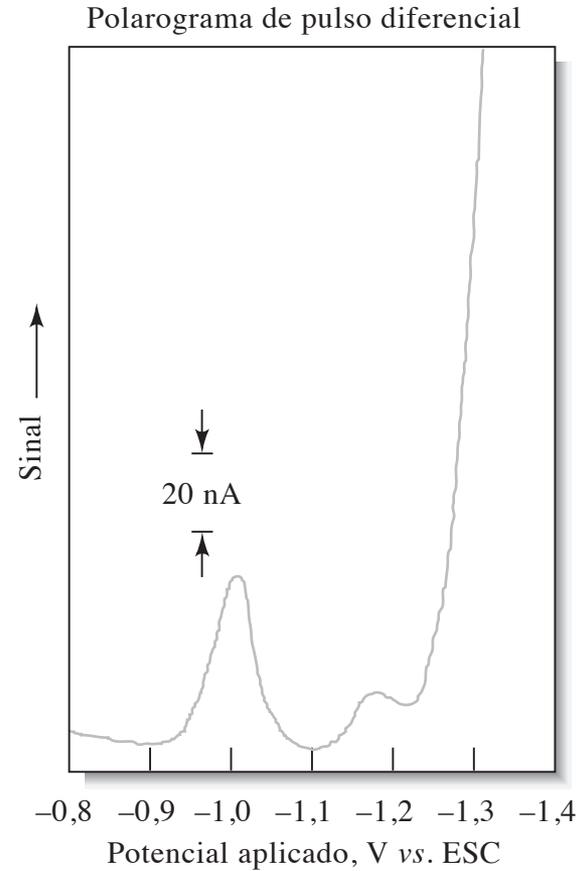
**Limites de detecção:  $10^{-7}$  a  $10^{-8}$  Mol/L**

**Informações Quantitativas**

# Voltametria de Pulso Diferencial



(b)

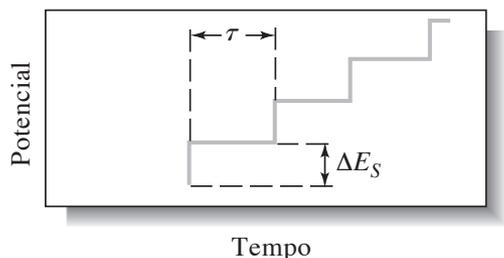


(a)

**(b) Tetraciclina.HCl 0,36 mg/L em tampão acetato 0,1 mol/L (pH= 4)**

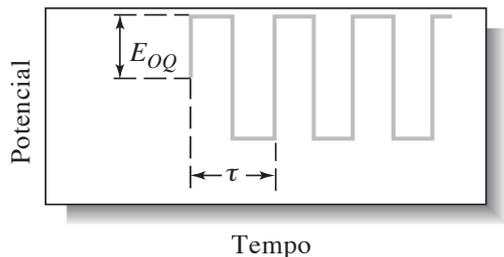
**(a) Tetraciclina.HCl 180 mg/L em tampão acetato 0,1 mol/L (pH= 4)**

# Voltametria de Onda Quadrada

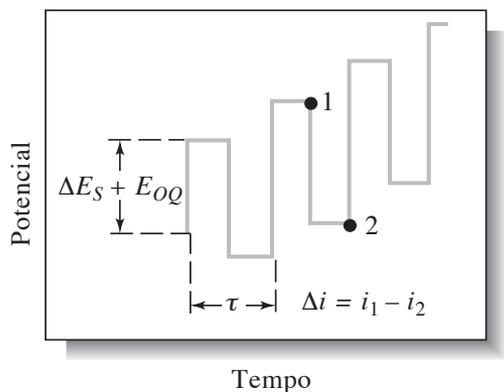


(a)

+



(b)



(c)

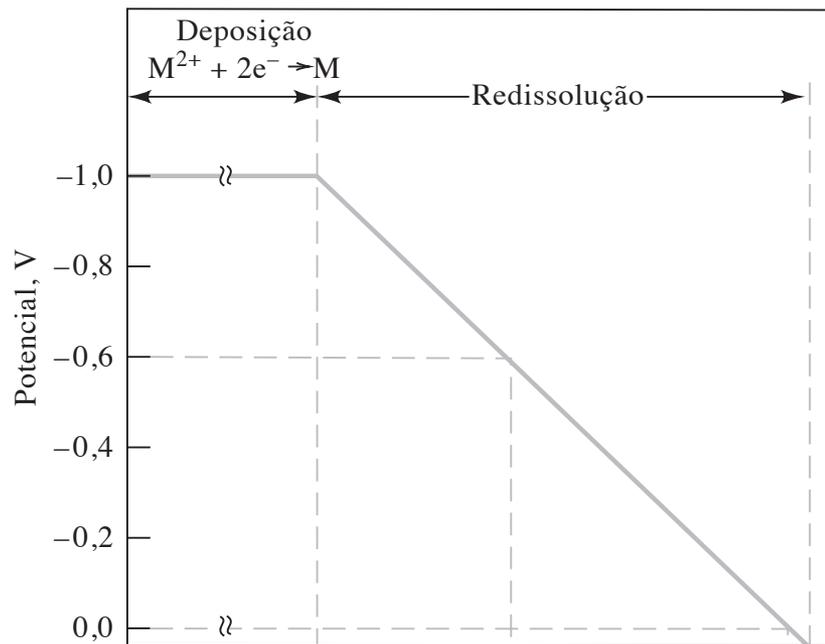
## Informações Quantitativas

- **Limites de detecção:  $10^{-7}$  a  $10^{-8}$  Mol/L**
- **Minimiza a corrente capacitiva**

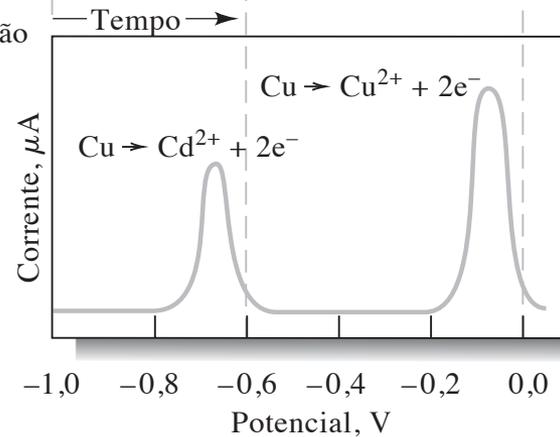
**Figura 23-21** Geração de um sinal de excitação em voltametria de onda quadrada. O sinal na forma de escada em (a) é adicionado a uma seqüência de pulsos em (b) para dar o sinal de excitação de onda quadrada mostrado em (c). A resposta de corrente  $\Delta i$  é igual a corrente no potencial 1 menos a corrente no potencial 2.

# Redissolução Anódica

**Etapa de deposição: pré-concentração**  
**(concentração de 100 a 1.000x do analito)**



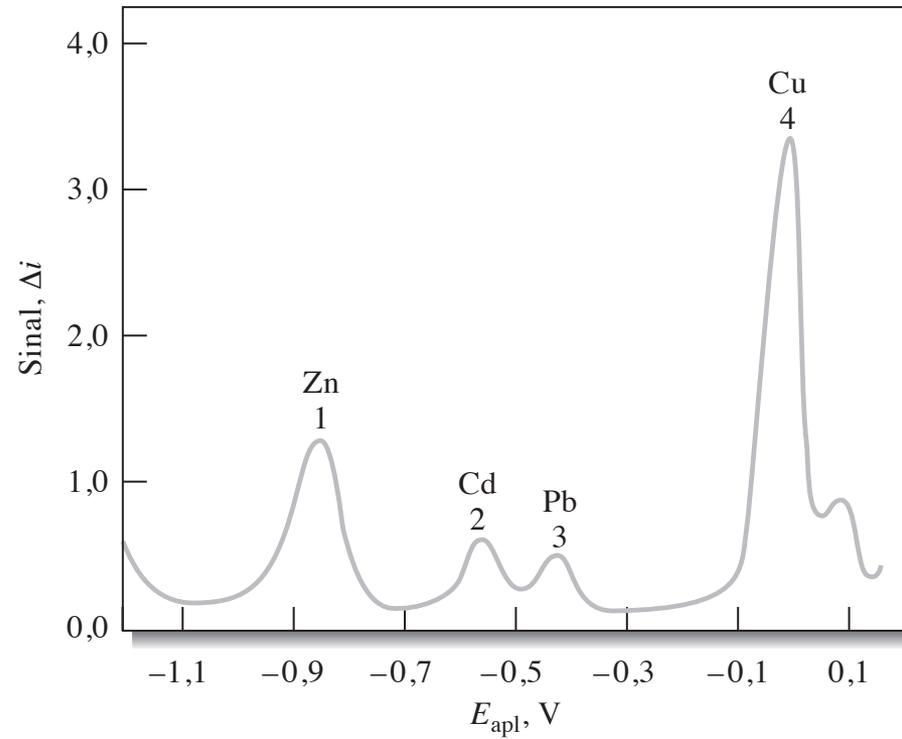
(a) Sinal de excitação



(b) Voltamograma

## Informações Quantitativas

# Redissolução Anódica



## Informações Quantitativas

# Cyclic Voltammetry Experiment

**James J. Van Benschoten, Jane Y. Lewis, and William R. Heineman**

University of Cincinnati, Cincinnati, OH 45221

**Daryl A. Roston<sup>1</sup> and Peter T. Kissinger**

Purdue University, West Lafayette, IN 47907

## Part I—Fundamentals of Cyclic Voltammetry

The  $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}/\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$  couple is known to be well-behaved both chemically and electrochemically (2). As such, it is often used as a model system in electrochemical experiments. It can be used to determine electrode areas and to diagnose problems associated with new electrochemical cell designs. In this experiment, the couple is used to clearly demonstrate some important principles of cyclic voltammetry.

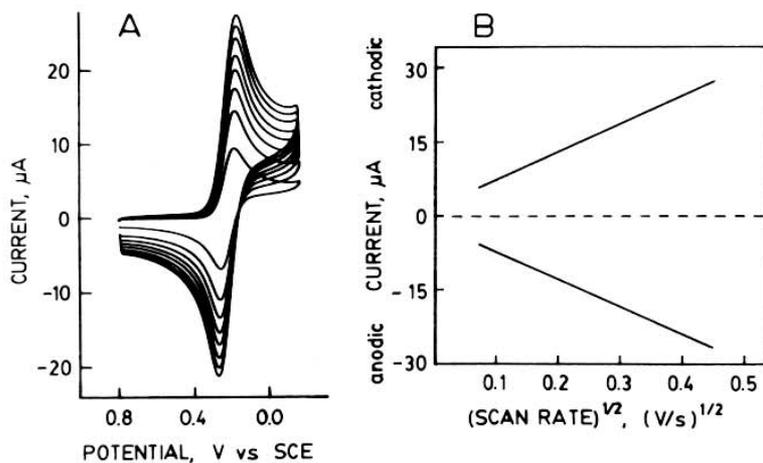


Figure 1. (A) Cyclic voltammograms of 4 mM  $K_3Fe(CN)_6$  in 1 M  $KNO_3$ . Pt electrode. Scan rate ( $\nu$ ) = 20, 50, 75, 100, 125, 150, 175, and 200 mV/s. (B) Plot of  $i_{pc}$  versus  $\nu^{1/2}$  and  $i_{pa}$  versus  $\nu^{1/2}$  from voltammograms in (A).

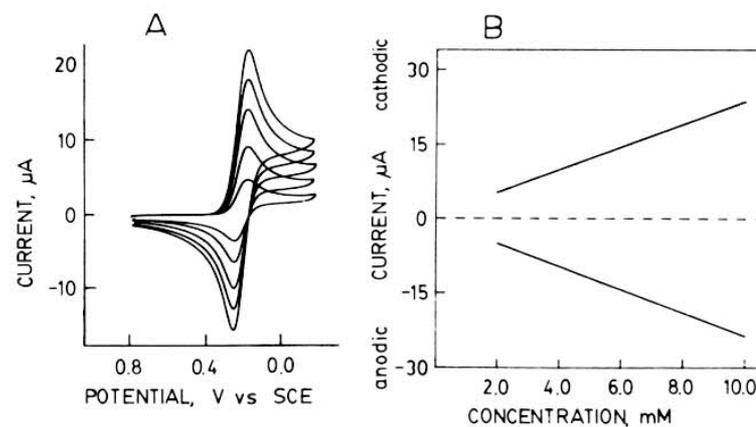


Figure 2. (A) Cyclic voltammograms of  $K_3Fe(CN)_6$  in 1 M  $KNO_3$ . Scan rate = 20 mV/s. Pt electrode. Concentration = 2, 4, 6, 8, and 10 mM. (B) Plot of  $i_{pc}$  versus concentration and  $i_{pa}$  versus concentration from voltammograms in (A).