ABC of Electrochemistry series

Electrochemical Testing Techniques
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Synopsis:

- Electrochemical Testing Classification
- Electrode Process Theory
  - Charge Transfer Controlled Process
  - Mass Transfer Controlled Process
- Voltammetry
  1. Potential Step
  2. Linear-Sweep Voltammetry
  3. Cyclic Voltammetry
  4. Anodic Stripping
  5. Differential Pulse Voltammetry
  6. Square-Wave Voltammetry
- Application
Electrochemical Testing Techniques - Classification
Electrochemical Testing Techniques – Traditional Tests

- Traditional Techniques
  - DC Techniques
  - Controlled Potential
  - Controlled Current
  - AC Impedence
  - AC Voltammetry
- Transient Techniques
- Convection Techniques
  - AC Techniques
  - RDE & RRDE
  - Flow Techniques
Classification – Transient DC Techniques

- Cyclic
- Linear Sweep
- Potential Step
- Square Wave
- Diff Pulse
- Anodic Stipping

Voltammetry
Non-Traditional Techniques

- ECMS
- In-Situ Raman
- In-Situ FTIR
- Photo Electrochemistry (chronoAbsorptometry)
- Sono Electrochemistry
- Neuro Electrochemistry
- Micro-Electrodes
Theory – A General Pathway
Electrode Process Theory

1. Double layer
2. Faradaic Process – Electron Transfer
3. Non-Faradaic Process – Electron / Non-Electron Transfer (Eg. LJP, Adsorption)
4. Standard Reduction Potential
5. Anodic Process - Oxidation
6. Cathodic Process - Reduction
7. Overpotential – Driving force
8. Reversible Reaction
9. Irreversible Reaction
10. Quasi-reversible Reaction
Electrode Process – Charge Transfer Controlled Process
Charge Transfer - Theory

\[ O + e^- \xrightarrow{k_{\text{red}}} R \]
\[ R \xrightarrow{k_{\text{ox}}} O + e^- \]

\[ i_O = F A k_{\text{ox}} c_R \]
\[ i_R = -F A k_{\text{red}} c_O \]

\[ k_{\text{red,ox}} = Z \exp \left( \frac{-\Delta G_{\text{red,ox}}}{k_B T} \right) \]
Electrode Kinetics – BV Equation

- Criteria: Applicable to Charge Transfer Controlled Processes alone.

\[ i = i_o \left\{ \frac{[O]_o}{[O]_{bulk}} e^{-\frac{\alpha n F (E - E_c)}{RT}} - \frac{[R]_o}{[R]_{bulk}} e^{\frac{(1 - \alpha)n F (E - E_c)}{RT}} \right\} \]

- Limitation:
  - High overpotentials: Tafel Approximation
  - Low overpotentials: Linear Approximation
Electrode Process – Diffusion Controlled Process
Mass Transport: Diffusion & Migration - Theory

\[
\frac{i_{d,j}}{z_j FA} = D_j \frac{\partial C_j}{\partial x}
\]

\[
\frac{i_{m,j}}{z_j FA} = \frac{z_j F D_j}{RT} C_j \frac{\partial \phi}{\partial x}
\]
**Electrochemical Testing Techniques - Voltammetry**

**Note:** Make sure the counter electrode is at least twice the size of the working electrode, to prevent current limitations. Also make sure that the solution is not stirred at any time.
Voltammetry – Potential Step

**INPUT:** Voltage Step
**RESPONSE:** Current Signal (Chrono Amperometry) / Charge (Chrono coulometry)

**Important Variables:**
1. V1 and V2
2. Time
3. Concentration of reacting species
**ChronoAmperometry**

- **Cottrell Equation**
  (Linear Diffusion)

\[
i(t) = i_d(t) = \frac{nFAD_i^{1/2}C^*}{\pi^{1/2}t^{1/2}}
\]

- Application:
  - Sensors

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**ChronoCoulometry**

- Application:
  - Study of surface processes
  - Adsorption
**INPUT:** Voltage Ramp and Reverse Ramp

**RESPONSE:** Current Signal

**Important Variables:**
1. V1 and V2
2. Scan rate
3. Concentration of reacting species
4. No. of Cycles
CV – for Faradaic Process - Reversible System

\[ |E_p - E_{p/2}| = 2.20 \frac{RT}{nF} = 56.5/n \text{ mV at 25°C} \]

\[ i_p = (2.69 \times 10^5) n^{3/2} A D_O^{1/2} C_O^{*} v^{1/2} \]

\[ E_p = E_{1/2} - 1.109 \frac{RT}{nF} = 28.5/n \text{ mV at 25°C} \]
CV – for Irreversible System

\[ i_p = (2.99 \times 10^5) \alpha^{1/2} A C_O^* D_O^{1/2} v^{1/2} \]

\[ |E_p - E_{p/2}| = \frac{1.857 R T}{\alpha F} = \frac{47.7}{\alpha} \text{ mV at 25°C} \]

\[ E_p = E_0' - \frac{R T}{\alpha F} \left[ 0.780 + \ln \left( \frac{D_O^{1/2}}{k^0} \right) + \ln \left( \frac{\alpha F v}{R T} \right)^{1/2} \right] \]

CV – for Quasireversible System and Multistep – Check Bard and Faulkner
CV – for Non Faradaic Processes

\[ M_{(aq)}^{Z^+} + Ze^- \rightarrow M_{(ads)} \cdot \]

\[ V_F = k_F \left[ M^{Z^+} \right] (1 - \theta) \]

\[ V_R = k_R \theta \]

\[ \frac{\theta}{(1-\theta)} = \frac{k_F}{k_R} \left[ M^{Z^+} \right] \]

At Equilibrium:

\[ \frac{\theta}{(1-\theta)} \exp \left( A \left( \theta - \frac{1}{2} \right) \right) = K' \exp \left( \frac{-nFE}{RT} \right) \left[ M^{Z^+} \right] \]
Voltammetry – Linear Sweep

**INPUT:** Voltage Ramp
**RESPONSE:** Current Signal

**Important Variables:**
1. V1 and V2
2. Scan rate
3. Concentration of reacting species
Application

- Effect of Scan rate on CV of Ammonia Electrooxidation on PtIr:
Square Wave Voltammetry

Parameters:
\( \Delta E \)
\( E_{sw} \)
\( T \)
\( \tau \)
\( T_d \)
References

Patterns of Ionic and Molecular Adsorption at Electrodes.


Spectroelectrochemistry. The Combination of Optical and Electrochemical Techniques

Cyclic Voltammetry


Square Wave Voltammetry

Unraveling Reactions with Rotating Electrodes.

Electrochemical Detectors in Liquid Chromatography. A Short Review of Detector Design.

Sinusoidal ac Voltammetric Methods in Electroanalytical Chemistry.

Electrochemical Impedance Spectroscopy for Better Electrochemical Measurements.
Thank You