Advanced Electrochemical Impedance Spectroscopy

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Contents

• Chapter 1. Introduction
• Chapter 2. Motivation
• Chapter 3. Impedance Measurement
• Chapter 4. Representations of Impedance Data
• Chapter 5. Development of Process Models
• Chapter 6. Constant Phase Elements
• Chapter 7. Regression Analysis
• Chapter 8. Error Structure
• Chapter 9. Kramers-Kronig Relations
• Chapter 10. Use of Measurement Models
• Chapter 11. Conclusions
• Chapter 12. Suggested Reading
• Chapter 13. Notation
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Electrochemical Impedance Spectroscopy

Chapter 1. Introduction

• How to think about impedance spectroscopy
• EIS as a generalized transfer function
• Overview of applications of EIS
• Objective and outline of course
1992 - no logo
June 6 - 11, 2010
Hotel Tivoli Carvoeiro
Carvoeiro, Algarve, Portugal
The Blind Men and the Elephant

John Godfrey Saxe

It was six men of Indostan
To learning much inclined,
Who went to see the Elephant
(Though all of them were blind),
That each by observation
Might satisfy his mind.

The First approached the Elephant,
And happening to fall
Against his broad and sturdy side,
At once began to bawl:
“God bless me! but the Elephant
Is very like a wall!” ...
Electrochemical Impedance Spectroscopy

- Electrochemical technique
  - steady-state
  - transient
  - impedance spectroscopy
- Measurement in terms of macroscopic quantities
  - total current
  - averaged potential
- Not a chemical spectroscopy
- Type of generalized transfer-function measurement
Impedance Spectroscopy

\[ Z(\omega) = \frac{\Delta \tilde{V}}{\Delta \tilde{I}} = Z_r + jZ_j \]
Impedance Spectroscopy

Applications

• Electrochemical systems
  – Corrosion
  – Electrodeposition
  – Human Skin
  – Batteries
  – Fuel Cells
• Materials

Fundamentals

• Dielectric spectroscopy
• Acoustophoretic spectroscopy
• Viscometry
• Electrohydrodynamic impedance spectroscopy
Physical Description

• Electrode-Electrolyte Interface
  – Electrical Double Layer
  – Diffusion Layer

• Electrochemical Reactions

• Electrical Circuit Analogues
Electrochemical Reactions

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]

Faradaic current density

\[ i_F = \bar{\bar{i}}_{\text{O}_2} = n_{\text{O}_2} F k_{\text{O}_2} \bar{\bar{c}}_{\text{O}_2} \exp \left\{ \frac{\alpha_{\text{O}_2} F}{RT} \left( \bar{V} - V_{\text{O}_2} \right) \right\} \]

Total current density = Faradaic + charging

\[ i = i_F + C_d \frac{dV}{dt} \]

Cell potential = electrode potential + Ohmic potential drop

\[ U = V + iR_e \]
Electrical Analogues

charging current

Ohmic Resistance

$C_{dl}$

Faradaic current

$R_e$

$R_f$
Electrical Analogue

Simple electrochemical reaction

Simple electrochemical reaction with mass transfer
Course Objectives

• Benefits and advantages of impedance spectroscopy
• Methods to improve experimental design
• Interpretation of data
  – graphical representations
  – regression
  – error analysis
  – equivalent circuits
  – process models
Contents

• Chapter 1. Introduction
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• Chapter 3. Impedance Measurement
• Chapter 4. Representations of Impedance Data
• Chapter 5. Development of Process Models
• Chapter 6. Constant Phase Elements
• Chapter 7. Regression Analysis
• Chapter 8. Error Structure
• Chapter 9. Kramers-Kronig Relations
• Chapter 10. Use of Measurement Models
• Chapter 11. Conclusions
• Chapter 12. Suggested Reading
• Chapter 13. Notation
Notation

- IUPAC Convention: \( Z' \) and \( Z'' \); \( i \)
- Present Work: \( Z_r \) and \( Z_j \); \( j \)
Advanced Electrochemical Impedance Spectroscopy

Chapter 2. Motivation

• Comparison of measurements
  – steady state
  – step transients
  – single-sine impedance

• In principle, step and single-sine perturbations yield same results

• Impedance measurements have better error structure
Steady-State Polarization Curve

Diagram of circuit with components $R_0$, $C_1$, $R_1(V)$, $C_2$, and $R_2$.

Graph showing relationship between potential $V$ and current $I$. The graph is linear, with current $I$ in mA on the y-axis and potential $V$ in V on the x-axis.
Steady-State Techniques

- Yield information on state after transient is completed
- Do not provide information on
  - system time constants
  - capacitance
- Influenced by
  - Ohmic potential drop
  - non-stationarity
  - film growth
  - coupled reactions
Transient Response to a Step in Potential

\[ I = \frac{V}{R_0 + R_1(V) + R_2} \]
Transient Response to a Step in Potential

Short times/high frequency

Current / mA

(t-t₀) / ms

Long times/low frequency

ΔV=10 mV
Transient Techniques:
potential or current steps

- Decouples phenomena
  - characteristic time constants
    - mass transfer
    - kinetics
  - capacitance
- Limited by accuracy of measurements
  - current
  - potential
  - time
- Limited by sample rate
  - <~1 kHz
**Sinusoidal Perturbation**

\[
V(t) = V_0 + \Delta V \cos(\omega t)
\]

\[
i(t) = i_0 \left\{ \exp(b_a V) - \exp(-b_c V) \right\}
\]
Sinusoidal Perturbation

-1.0 -0.5 0.0 0.5 1.0
-1.0 -0.5 0.0 0.5 1.0
1 mHz
10 kHz

(i-i_0) / max(i-i_0)
(V-V_0) / V_0

10 kHz
100 Hz
1 mHz

current potential
current potential
Lissajous Representation

\[ V(t) = \Delta V \cos(\omega t) \]

\[ I(t) = \frac{\Delta V}{|Z|} \cos(\omega t + \phi) \]

\[ |Z| = \frac{\Delta V}{\Delta I} = \frac{OA}{OB} \]

\[ \sin(\phi) = -\frac{OD}{OA} \]
Impedance Response

The graph shows the impedance response with frequency. The x-axis represents the real part of the impedance ($Z_r$) in $\Omega \text{ cm}^{-2}$, while the y-axis represents the imaginary part of the impedance ($Z_j$) in $\Omega \text{ cm}^{-2}$. The data point at 100 Hz is highlighted.
Impedance Spectroscopy

- Decouples phenomena
  - characteristic time constants
    - mass transfer
    - kinetics
  - capacitance
- Gives same type of information as DC transient.
- Improves information content and frequency range by repeated sampling.
- Takes advantage of relationship between real and imaginary impedance to check consistency.
System with Large Ohmic Resistance

- $R_0 = 10,000 \, \Omega$
- $R_1 = 1,000 \, \Omega$
- $C_1 = 10.5 \, \mu F$
  - $\tau = 0.0105 \, s$ (15 Hz)

**Impedance Spectrum**

- **Z_r, Ω**
- **Z_i, Ω**
- **Z_j, Ω**

Frequency, Hz

Impedance, Ω
Experimental Data

6 Repeated Measurements

Impedance, Ω

Frequency, Hz

Real

3% of |Z|

1% of |Z|

Imaginary
Impedance Spectroscopy vs. Step-Change Transients

• Information sought is the same
• Increased sensitivity
  – stochastic errors
  – frequency range
  – consistency check
• Better decoupling of physical phenomena
Advanced Electrochemical Impedance Spectroscopy

Chapter 3. Impedance Measurement

• Overview of techniques
  – A.C. bridge
  – Lissajous analysis
  – phase-sensitive detection (lock-in amplifier)
  – Fourier analysis

• Experimental design

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Measurement Techniques

• A.C. Bridge
• Lissajous analysis
• Phase-sensitive detection (lock-in amplifier)
• Fourier analysis
  – digital transfer function analyzer
  – fast Fourier transform

AC Bridge

- Bridge is balanced when current at D is equal to zero
  \[ Z_1Z_4 = Z_2Z_3 \]
- Time consuming
- Accurate
  \[ f \geq 10 \text{ Hz} \]
Lissajous Analysis

\[ V(t) = \Delta V \sin(\omega t) \]
\[ I(t) = \frac{\Delta V}{|Z|} \sin(\omega t + \phi) \]

Potential

\[ |Z| = \frac{\Delta V}{\Delta I} = \frac{OA}{OB} = \frac{A'A}{B'B} \]

\[ \sin(\phi) = -\frac{OD}{OA} = -\frac{D'D}{A'A} \]
**Phase Sensitive Detection**

General Signal

\[ A = A_0 \sin(\omega t + \phi_A) \]

Reference Signal

\[ S = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \left[ (2n+1)\omega t + \phi_S \right] \]

\[ AS = \frac{4A_0}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin(\omega t + \phi_A) \sin \left[ (2n+1)\omega t + \phi_S \right] \]

\[ \frac{\omega}{2\pi} \int_0^{2\pi/\omega} AS dt = \frac{2A_0}{\pi} \cos(\phi_A - \phi_S) \]

Has maximum value when

\[ \phi_A = \phi_S \]
Fourier Analysis: single-frequency input

\[ V(t) = V_0 \cos(\omega t) \]
\[ I(t) = I_0 \cos(\omega t + \phi) \]

\[ I_r(\omega) = \frac{1}{T} \int_0^T I(t) \cos(\omega t) dt \]
\[ I_j(\omega) = -\frac{1}{T} \int_0^T I(t) \sin(\omega t) dt \]
\[ V_r(\omega) = \frac{1}{T} \int_0^T V(t) \cos(\omega t) dt \]
\[ V_j(\omega) = -\frac{1}{T} \int_0^T V(t) \sin(\omega t) dt \]

\[ Z_r(\omega) = \text{Re} \left\{ \frac{V_r + jV_j}{I_r + jI_j} \right\} \]
\[ Z_j(\omega) = \text{Im} \left\{ \frac{V_r + jV_j}{I_r + jI_j} \right\} \]
Fourier Analysis: multi-frequency input

\[ Z(\omega) \]
Comparison

**single-sine input**

- Good accuracy for stationary systems
- Frequency intervals of $\Delta f/f$
  - economical use of frequencies
- Used for entire frequency domain
- Kramers-Kronig inconsistent frequencies can be deleted

**multi-sine input**

- Good accuracy for stationary systems
- Frequency intervals of $\Delta f$
  - dense sampling at high frequency required to get good resolution at low frequency
- Often paired with Phase-Sensitive-Detection ($f>10$ Hz)
- Correlation coefficient used to determine whether spectrum is inconsistent with Kramers-Kronig relations
Measurement Techniques

• A.C. bridge
  – obsolete

• Lissajous analysis
  – obsolete
  – useful to visualize impedance

• Phase-sensitive detection (lock-in amplifier)
  – inexpensive
  – accurate
  – useful at high frequencies

• Fourier analysis techniques
  – accurate
Experimental Considerations

• Frequency range
  – instrument artifacts
  – non-stationary behavior
  – capture system response

• Linearity
  – low amplitude perturbation
  – depends on polarization curve for system under study
  – determine experimentally

• Signal-to-noise ratio
Sinusoidal Perturbation

\[ V(t) = V_0 + \Delta V \cos(\omega t) \]

\[ i(t) = i_0 \exp(b_a V) \]

\[ i_c = C_0 \frac{dV}{dt} \]

\[ i_f = f(V) \]

\[ V(t) \]
Chapter 3. Impedance Measurement

Linearity

- For $f = 1$ mHz, the graphs show linear trends for different voltages.
- At $f = 10$ Hz, the graphs become more complex with non-linear behavior at higher voltages.
- At $f = 100$ Hz, the graphs exhibit oscillatory behavior, indicating non-linearity.
- At $f = 10$ kHz, the graphs form circular shapes, suggesting a more pronounced non-linear effect.

The graphs illustrate the impact of frequency on linearity, with increasing complexity as frequency increases.
Influence of Nonlinearity on Impedance

\[
\begin{align*}
Z_j & / \Omega \text{ cm}^2 \\
Z_r & / \Omega \text{ cm}^2
\end{align*}
\]
Influence of Nonlinearity on Impedance

\( \frac{Z_r}{R_t} \) vs. \( f / \text{Hz} \)

\( |Z_j| / \Omega \text{ cm}^2 \) vs. \( f / \text{Hz} \)
**Guideline for Linearity**

\[ b \Delta V \leq 0.2 \]
Influence of Ohmic Resistance

\[ b \Delta V \leq 0.2 \left( 1 + \frac{R_e}{R_i} \right) \]

\[ i_c = C_0 \frac{dV}{dt} \]

\[ i_f = f(V) \]

\[ i(t) R_e \quad \eta_s(t) \]

\[ V(t) \]
Influence of Ohmic Resistance
Overpotential as a Function of Frequency

\[ \eta_s(t) = \frac{i(t)R_e}{V(t)} \]

\[ i_c = C_0 \frac{dV}{dt} \]

\[ i_f = f(V) \]

\[ \text{Potential / V} \]

\[ \text{Potential / V} \]

\[ \eta_s / V \]

\[ \eta_s / V \]

\[ f / \text{Hz} \]

\[ 1 \text{ Hz} \]

\[ 302 \text{ Hz} \]

\[ 1.59 \text{ kHz} \]

\[ 159 \text{ kHz} \]

\[ 10 \text{ mV (b} \Delta V = 0.19) \]

\[ 100 \text{ mV (b} \Delta V = 1.9) \]
Cell Design

• Use reference electrode to isolate influence of electrodes and membranes

2-electrode

3-electrode

4-electrode

Working Electrode

Working Electrode

Working Electrode

Counterelectrode

Counterelectrode

Counterelectrode

Ref 1

Ref 2
**Current Distribution**

- Seek uniform current/potential distribution
  - simplify interpretation
  - reduce frequency dispersion
Primary Current Distribution
Modulation Technique

- **Potentiostatic**
  - standard approach
  - linearity controlled by potential

- **Galvanostatic**
  - good for nonstationary systems
    - corrosion
    - drug delivery
  - requires variable perturbation amplitude to maintain linearity

\[
i_n = i_{O_2} \left[ \exp \left( \frac{\alpha_M F}{RT} (V - V_{corr}) \right) - 1 \right]
\]

\[
i_n = i_{O_2} \left[ \left( \frac{\alpha_{Fe} F}{RT} (V - V_{corr}) \right) + \frac{1}{2} \left( \frac{\alpha_{Fe} F}{RT} (V - V_{corr}) \right)^2 + \ldots \right]
\]

\[
\Delta \tilde{I} = \Delta \tilde{V} / \left| Z(\omega) \right|
\]

\[
\Delta \tilde{V} = \Delta \tilde{I} \left| Z(\omega) \right|
\]
Experimental Strategies

- Faraday cage
- Short leads
- Good wires
- Shielded wires
- Oscilloscope
Reduce Stochastic Noise

- Current measuring range
- Integration time/cycles
  - long/short integration on some FRAs
- Delay time
- Avoid line frequency and harmonics (±5 Hz)
  - 60 Hz & 120 Hz
  - 50 Hz & 100 Hz
- Ignore first frequency measured (to avoid start-up transient)
Reduce Non-Stationary Effects

• Reduce time for measurement
  – shorter integration (fewer cycles)
    • accept more stochastic noise to get less bias error
  – fewer frequencies
    • more measured frequencies yields better parameter estimates
    • fewer frequencies takes less time
  – avoid line frequency and harmonic (±5 Hz)
    • takes a long time to measure on auto-integration
    • cannot use data anyway
  – select appropriate modulation technique
    • decide what you want to hold constant (e.g., current or potential)
    • system drift can increase measurement time on auto-integration
Reduce Instrument Bias Errors

- Faster potentiostat
- Short shielded leads
- Faraday cage
- Check results
  - against electrical circuit
  - against independently obtained parameters
Measurement Review
Improve Experimental Design

• Question
  – How can we isolate the role of positive electrode, negative electrode, and separator in a battery?

• Answer
  - Develop a very sophisticated process model.
  - Use a four-electrode configuration.
Improve Experimental Design

• Question
  - How can we reduce stochastic noise in the measurement?

• Answer

  - Use more cycles during integration.
  - Add at least a 2-cycle delay.
  - Ensure use of optimal current measuring resistor.
  - Check wires and contacts.
  - Avoid line frequency and harmonics.
  - Use a Faraday cage.
Improve Experimental Design

• Question
  – How can we determine the cause of variability between experiments?

• Answer

  - Use the Kramers-Kronig relations to see if data are self-consistent.
  - Change mode of modulation to variable-amplitude galvanostatic to ensure that the base-line is not changed by the experiment.
Facilitate Interpretation

• Question
  – How can we be certain that the instrument is not corrupting the data?

• Answer
  - Use the Kramers-Kronig relations to see if data are self-consistent.
  - Build a test circuit with the same impedance response and see if you get the correct result.
  - Compare results to independently obtained data (such as electrolyte resistance).
Experimental Considerations

- Frequency range
  - instrument artifacts
  - non-stationary behavior
- Linearity
  - low amplitude perturbation
  - depends on polarization curve for system under study
  - determine experimentally
- Signal-to-noise ratio
Can We Perform Impedance on Transient Systems?

• Timeframes for measurement
  – Individual frequency
  – Individual scan
  – Multiple scans
EHD Experiment

![Graph showing impedance data for different data sets.](image-url)
Time per Frequency for 200 rpm

- Time per Measurement, s
- Frequency, Hz

- Filter On
- Filter Off
Impedance Scans

The diagram shows the impedance scans over a series of time intervals.

- $Z_j / \Omega \text{ cm}^2$
- $Z_r / \Omega \text{ cm}^2$

Time Intervals:
- 0-1183 s
- 1183-2366 s
- 2366-3581 s
Impedance Scans

The graph shows the relationship between elapsed time (s) and frequency (Hz) for different curves. The x-axis represents frequency (Hz) on a logarithmic scale, ranging from $10^{-2}$ to $10^5$ Hz, while the y-axis represents elapsed time (s) with values ranging from 0 to 4000 s.
Time per Frequency Measured

\[ \Delta t_f / s \]

\[ f / \text{Hz} \]
Advanced Electrochemical Impedance Spectroscopy

Chapter 4. Representation of Impedance Data

- Electrical circuit components
- Methods to plot data
  - standard plots
  - subtract electrolyte resistance
- Constant phase elements

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Addition of Impedance

\[ Z = Z_1 + Z_2 \]

\[ Y = \frac{1}{1 + \frac{1}{\frac{1}{Y_1} + \frac{1}{Y_2}}} \]

\[ Z = \frac{1}{\frac{1}{Z_1} + \frac{1}{Z_2}} \]

\[ Y = Y_1 + Y_2 \]
Circuit Components

\[ Z = R_e \]

\[ Z = R_e + \frac{1}{j \omega C_{dl}} = R_e - j \frac{1}{\omega C_{dl}} \]

\[ j = \sqrt{-1} \]
Simple RC Circuit

\[ Z = R_e + \frac{1}{\frac{1}{R_t} + j\omega C_{dl}} \]

\[ = R_e + \frac{R_t}{1 + j\omega R_t C_{dl}} \]

\[ = R_e + \frac{R_t}{1 + (\omega R_t C_{dl})^2} - j \frac{\omega R_t^2 C_{dl}}{1 + (\omega R_t C_{dl})^2} \]

Note:
\[ \omega = 2\pi f \]
\[ \omega \equiv \text{rad} / \text{s} \quad \text{or} \quad \text{s}^{-1} \]
\[ f \equiv \text{cycles} / \text{s} \quad \text{or} \quad \text{Hz} \]
Impedance

\[ Z_r \text{ or } -Z_j / \Omega \]

**Slope = 1**

\[ Z_f / \Omega \]

**Slope = -1**

\[ Z_r / Z_j / \Omega \]

**Frequency / Hz**

- Real
- Imaginary
Bode Representation

\[ Z = Z_r + jZ_j \]

\[ Z_r = |Z| \cos(\phi) \]

\[ Z_j = |Z| \sin(\phi) \]
Modified Phase Angle

Input & output are in phase

\[ \phi^* = \tan^{-1}\left(\frac{Z_j}{Z_r - R_e}\right) \]

Note:
The modified phase angle yields excellent insight, but we need an accurate estimate for the solution resistance.

Input & output are out of phase

\[ \phi = \tan^{-1}\left(\frac{Z_j}{Z_r}\right) \]
**Constant Phase Element**

\[
Z - R_e \quad \frac{1}{R_t} = + \frac{1}{1 + (j\omega)^\alpha R_t Q}
\]

\[
\frac{Z_j}{R_t} = \frac{(Z_r - R_e)}{R_t}
\]

- \( \alpha = 1 \)
- \( \alpha = 0.9 \)
- \( \alpha = 0.8 \)
- \( \alpha = 0.7 \)
- \( \alpha = 0.6 \)
- \( \alpha = 0.5 \)
Note: With a CPE ($\alpha \neq 1$), the asymptotic slopes are no longer $\pm 1$. 
**CPE: Modified Phase Angle**

Note:

The high-frequency asymptote for the modified phase angle depends on the CPE coefficient $\alpha$. 

**Diagram:**

- Graph showing the modified phase angle $\phi^*$ in degrees as a function of $\omega/\tau$ with different $\alpha$ values: $\alpha=1$, $\alpha=0.9$, $\alpha=0.8$, $\alpha=0.7$, $\alpha=0.6$, $\alpha=0.5$.
Example for Synthetic Data

\[ Z(f) = R_e + \frac{R_t + z_d(f)}{1 + (j2\pi f)^\alpha Q_{dl}(R_t + z_d(f))} \]

\[ z_d(f) = z_d(f) \frac{\tanh \sqrt{j2\pi f \tau}}{\sqrt{j2\pi f \tau}} \]

Traditional Representation

**Graphs:**
- **Left:** Plot showing $Z_j$ vs. frequency $f$, with lines for $\alpha = 1$, $\alpha = 0.7$, and $\alpha = 0.5$. Markers indicate data points at specific frequencies: 1 Hz, 0.1 Hz, 10 mHz, 10 Hz, 100 Hz.
- **Right:** Diagram of a circuit with components $Q_{dl}$, $\alpha$, $R_e$, $Z_d$, and $R_t$.

**Equations:**
- $Z_j / \Omega \text{ cm}^2$
- $Z_r / \Omega \text{ cm}^2$
- $|Z| / \Omega \text{ cm}^2$
- $\phi / \text{degree}$

**Legend:**
- Solid line: $\alpha = 1$
- Dashed line: $\alpha = 0.7$
- Dash-dotted line: $\alpha = 0.5$
**Re-Corrected Bode Phase Angle**

\[
\phi_{adj} = \tan^{-1}\left(\frac{Z_j}{Z_r - R_{e,est}}\right)
\]

\[
\phi_{adj}(\infty) = -90(\alpha)
\]
**Re-Corrected Bode Magnitude**

\[ |Z|_{adj} = \sqrt{(Z_r - R_{e,est})^2 + Z_j^2} \]

Slope = \(-\alpha\)

\[ f / \text{Hz} \]

\[ |Z|_{adj} / \Omega \text{ cm}^2 \]

- \( \alpha = 1 \)
- \( \alpha = 0.7 \)
- \( \alpha = 0.5 \)
\[ \log(|Z_j|) \]

Slope = $\alpha$

- $\alpha = 1$
- $\alpha = 0.7$
- $\alpha = 0.5$

\[ |Z_j| / \text{cm}^2 \]

\[ f / \text{Hz} \]
Effective Capacitance or CPE Coefficient

\[ Z_{\text{CPE}} = \frac{1}{Q_{\text{CPE}} (j2\pi f)^\alpha} \]

\[ Q_{\text{eff}} = -\sin\left(\frac{\alpha \pi}{2}\right) \frac{1}{(2\pi f)^\alpha} Z_j(f) \]
Alternative Plots

• $R_e$-Corrected Bode Plots (Phase Angle)
  – Shows expected high-frequency behavior for surface
  – High-Frequency limit reveals CPE behavior

• $R_e$-Corrected Bode Plots (Magnitude)
  – High-Frequency slope related to CPE behavior

• $\log|Z_j|$
  – Slopes related to CPE behavior
  – Peaks reveal characteristic time constants

• Effective Capacitance
  – High-Frequency limit yields capacitance or CPE coefficient
Application
Mg alloy (AZ91) in 0.1 M NaCl
Proposed Model

\[
Mg \xrightarrow{k_1} (Mg^+)_{ads} + e^-
\]

\[
(Mg^+)_{ads} + H_2O \xrightarrow{k_2} Mg^{2+} + OH^- + \frac{1}{2} H_2 \quad \text{“negative difference effect” (NDE)}
\]

\[
(Mg^+)_{ads} \xrightarrow{k_3} Mg^{2+} + e^-
\xleftarrow{k_{-3}}

\[
Mg^{2+} + 2OH^- \xrightarrow{k_4} Mg(OH)_2
\xleftarrow{k_{-4}}

\[
Mg(OH)_2 \xrightarrow{k_5} MgO + H_2O
\xleftarrow{k_{-5}}
\]

Physical Interpretation

\[ \text{Mg} \xrightarrow{k_1} (\text{Mg}^+)_{\text{ads}} + e^- \]

\[ (\text{Mg}^+)_{\text{ads}} \xrightarrow{k_3} \text{Mg}^{2+} + e^- \]

- Diffusion of Mg\(^{2+}\)
- Relaxation of (Mg\(^{+}\))\(_{\text{ads}}\)
- Intermediate
Log(|Z_j|)

Slope = $-\alpha$
Effective CPE Coefficient

\[ Q_{\text{eff}} = -\sin\left(\frac{\alpha\pi}{2}\right) \frac{1}{(2\pi f)^\alpha Z_j(f)} \]
$\phi_{adj}(\infty) = -90\alpha$

$\phi_{adj} = \tan^{-1}\left( \frac{Z_j}{Z_r - R_{e,est}} \right)$

**Diagram:**

- Plot of $|Z|_{adj}$ vs. $f$/Hz
- Log-log scale
- Time points: 0.5, 3.0, 6.0 hours
- Graph shows the change in phase angle with frequency and time.
Physical Parameters

<table>
<thead>
<tr>
<th>Immersion Time / h</th>
<th>0.5</th>
<th>3.0</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ / dimensionless</td>
<td>0.856</td>
<td>0.872</td>
<td>0.877</td>
</tr>
<tr>
<td>$Q_{\text{eff}}/M\Omega^{-1}\text{cm}^{-2}s^\alpha$</td>
<td>22.7</td>
<td>19.1</td>
<td>18.5</td>
</tr>
<tr>
<td>$R_e/\Omega\text{cm}^2$</td>
<td>10.65</td>
<td>10.45</td>
<td>11.4</td>
</tr>
</tbody>
</table>
Experimental device for LEIS

\[ Z_{local} = \frac{\Delta V_{applied}}{\Delta i_{local}} \]
Mg alloy (AZ91) in Na$_2$SO$_4$ 10$^{-3}$ M at the corrosion potential after 1 h of immersion. Electrode radius 5500 µm.

Global impedance analyzed with a CPE ($\alpha = 0.91$). Only the HF loop of the diagram is analyzed.

Local impedance \( \alpha = 1 \) to 0.92
Mg alloy (AZ91) in Na$_2$SO$_4$ 10$^{-3}$ M at the corrosion potential after 1 h of immersion. Electrode radius 5500 µm

The local impedance has a pure RC behavior.

The CPE is explained by a 2d distribution of the resistance as shown in the figure.
Comparison to Theory
Graphical Representation of Impedance Data

• Expanded Range of Plot Types
  – Facilitate model development
  – Identify features without complete system model

• Suggested Plots
  – $R_e$-Corrected Bode Plots (Phase Angle)
    • Shows expected high-frequency behavior for surface
    • High-Frequency limit reveals CPE behavior
  – $R_e$-Corrected Bode Plots (Magnitude)
    • High-Frequency slope related to CPE behavior
  – $\log|Z_j|$
    • Slopes related to CPE behavior
    • Peaks reveal characteristic time constants
  – Effective Capacitance
    • High-Frequency limit yields capacitance or CPE coefficient
Plots based on Deterministic Models
Convective Diffusion to a RDE

low-frequency asymptote

Reduction of Fe(CN)$_6^{3-}$ on a Pt Disk, $i/i_{lim} = 1/2$
Figure 4.1: Normalized Impedance Plane

Note: We again need an accurate estimate for the solution resistance.
Normalized Real

\[ p = \frac{\omega}{\Omega} \]

\[ \frac{(Z_r - R_e)}{(Z_{r,max} - R_e)} \]

- ○ 120 rpm
- △ 600
- ▽ 1200
- ▲ 2400
Normalized Imaginary

\[ \frac{-Z_j}{(Z_{r,\text{max}} - R_e)} \]

Graph showing normalized imaginary impedance data for different speeds: 120 rpm, 600, 1200, and 2400 rpm.
Straight line at low frequency

Slope at low frequency yields $D_i$

$$\lim_{p \to 0} \left( \frac{d \text{Re}\{Z\}}{dp \text{Im}\{Z\}} \right) = \lambda \text{Sc}^{1/3} = s$$

$$\lambda = 1.2261 + 0.84 \text{Sc}^{-1/3} + 0.63 \text{Sc}^{-2/3}$$

$\text{Sc} = 1090.6$
n-GaAs Diode: scaling based on Arrhenius relationship
Normalized Real

\[ f^* = \frac{f}{f_0} \exp\left( \frac{E}{kT} \right) \]

Normalized Imaginary

Normalized Imaginary

\[ \frac{-Z_j}{|Z_{\text{max}}|} \]

- 320 K
- 340 K
- 360 K
- 380 K
- 400 K
Normalized Log Real

\[ \frac{Z_r}{|Z_{\text{max}}|} \]

\[ f^* \]

- ○ 320 K
- △ 340 K
- ▽ 360 K
- ▲ 380 K
- ▼ 400 K
Normalized Log Imaginary

\[\frac{-Z_j}{|Z_{\text{max}}|}\]

\[f^*\]
Superlattice Structure

- $Z_r, \Omega$
- $Z_j, \Omega$

-4.0E+08 to 4.0E+08
-2.0E+08 to 2.0E+08
0.0E+00 to 0.0E+00

-4.0E+07 to 4.0E+07
-2.0E+07 to 2.0E+07
0.0E+00 to 0.0E+00

Temperatures:
- 298.8
- 290
- 285
- 270
- 260
Chapter 4. Representation of Impedance Data

Normalized Real Part

\[ f^* = \frac{f}{f_0} \exp\left(\frac{E}{kT}\right) \]
Normalized Imaginary Part

\[ f^* = \frac{f}{f_0} \exp \left( \frac{E}{kT} \right) \]
Choice of Representation

- Plotting approaches are useful to show governing phenomena
- Complement to regression of detailed models
- Sensitive analysis requires use of properly weighted complex nonlinear regression
Advanced Electrochemical Impedance Spectroscopy

Chapter 5. Development of Process Models

- Use of Circuits to guide development
- Develop models from physical grounds
- Model case study
- Identify correspondence between physical models and electrical circuit analogues
- Account for mass transfer

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Use circuits to create framework
Addition of Potential

[Diagram showing an electrical circuit with labels: Electrolyte, Interface, $R_e$, $R_{ei}$, $Z_{int}$, and $V$.]
Addition of Current
Equivalent Circuit at the Corrosion Potential
Equivalent Circuit for a Partially Blocked Electrode
Equivalent Circuit for an Electrode Coated by a Porous Layer
Equivalent Electrical Circuit for an Electrode Coated by Two Porous Layers

\[ C_{\ell_2} = \frac{\varepsilon \varepsilon_0}{\delta}; \varepsilon_0 = 8.8452 \times 10^{-14} \text{ F/cm} \]

\[ R_{\ell_2} = \frac{\delta_{\ell_2}}{\kappa_{\ell_2}} \]

<table>
<thead>
<tr>
<th>system</th>
<th>( \varepsilon )</th>
<th>( \delta/\text{Å} )</th>
<th>( C/\mu\text{Fcm}^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>double layer on bare metal</td>
<td>-</td>
<td>-</td>
<td>10-50</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 ) oxide(^{27} )</td>
<td>6.7</td>
<td>120</td>
<td>0.5</td>
</tr>
<tr>
<td>( \text{Fe}_2\text{O}_3 ) oxide(^{28} )</td>
<td>7</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>( \text{Ni}_2\text{O}_5 ) oxide</td>
<td>42</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>asphalt coatings</td>
<td>2.6</td>
<td>( 5 \times 10^7 )</td>
<td>( 5 \times 10^{-7} )</td>
</tr>
<tr>
<td>epoxy cast resin</td>
<td>3.6</td>
<td>( 5 \times 10^6 )</td>
<td>( 6 \times 10^{-6} )</td>
</tr>
</tbody>
</table>
Use kinetic models to determine expressions for the interfacial impedance
Approach

- identify reaction mechanism
- write expression for steady state current contributions
- write expression for sinusoidal steady state
- sum current contributions
- account for charging current
- account for ohmic potential drop
- account for mass transfer
- calculate impedance
General Expression for Faradaic Current

\[ i_f = f(V, c_{i,0}, \gamma_i) \]

\[ i = \tilde{i} + \text{Re}\{\tilde{i} e^{j\omega t}\} \]

\[ \tilde{i}_f = \left( \frac{\partial f}{\partial V} \right)_{c_{i,0}, \gamma_k} \tilde{V} + \sum_i \left( \frac{\partial f}{\partial c_{i,0}} \right)_{V, c_j, j \neq i, \gamma_k} \tilde{c}_{i,0} \]

\[ + \sum_k \left( \frac{\partial f}{\partial \gamma_k} \right)_{V, c_j \gamma_j, j \neq k} \tilde{\gamma}_k \]
Reactions Considered

• Dependent on Potential
• Dependent on Potential and Mass Transfer
• Dependent on Potential, Mass Transfer, and Surface Coverage
• Coupled Reactions
Irreversible Reaction: Dependent on Potential

\[ A \rightarrow A^{z+} + n e^- \]

- Potential-dependent heterogeneous reaction
- Two-dimensional surface
- No effect of mass transfer
Current Density

steady-state

\[ i_A = n_A F k_A \exp\left(\frac{\alpha_A F}{RT} \bar{V}\right) \quad i_A = K_A \exp(b_A \bar{V}) \]

oscillating component

\[ \tilde{i}_A = K_A b_A \exp(b_A \bar{V}) \bar{V} \]

\[ \tilde{i}_A = \frac{\bar{V}}{R_{t,A}} \]

\[ R_{t,A} = \frac{1}{K_A b_A \exp(b_A \bar{V})} \]
### Charging Current

![Circuit Diagram]

\[
i = i_f + C_{dl} \frac{dV}{dt}
\]

\[
\tilde{i} = \tilde{i}_f + j\omega C_{dl} \tilde{V}
\]

\[
\tilde{i} = \frac{\tilde{V}}{R_{t,A}} + j\omega C_{dl} \tilde{V}
\]

\[
\tilde{V} = \tilde{V} \left( \frac{1}{R_{t,A}} + j\omega C_{dl} \right)
\]

\[
\frac{\tilde{V}}{\tilde{i}} = \frac{R_{t,A}}{1 + j\omega R_{t,A} C_{dl}}
\]
Ohmic Contributions

\[ U = iR_e + V \]
\[ \tilde{U} = \tilde{i} R_e + \tilde{V} \]
\[ Z_A = \frac{\tilde{U}}{\tilde{i}} = R_e + \frac{\tilde{V}}{\tilde{i}} \]
\[ = R_e + \frac{R_{t,A}}{1+j\omega R_{t,A} C_{dl}} \]
Steady Currents in Terms of $R_{t,A}$

\[ \bar{i}_A = K_A \exp(b_A \bar{V}) \quad \beta_A = 2.303 / b_A \]

\[ \bar{i}_A = K_A \exp(2.303 \bar{V} / \beta_A) \]

\[ R_{t,A} = \frac{1}{K_A b_A \exp(b_A \bar{V})} = \frac{\beta_A}{2.303 \bar{i}_A} \]

\[ \bar{i}_A = \frac{\beta_A}{2.303 R_{t,A}} \]

\[ \beta_A = 2.303 R_{t,A} \bar{i}_A \]
**Irreversible Reaction:** Dependent on Potential and Mass Transfer

- Irreversible potential-dependent heterogeneous reaction
- Reaction on two-dimensional surface
- Influence of transport of O to surface

\[
O + ne^- \rightarrow R
\]
Current Density

steady-state

$$\bar{i}_o = -K_o \bar{c}_{o,0} \exp(-b_o \bar{V})$$

oscillating component

$$\tilde{i}_o = K_o b_o \bar{c}_{o,0} \exp(-b_o \bar{V}) \tilde{V} - K_o \exp(-b_o \bar{V}) \tilde{c}_{o,0}$$

$$= \frac{\tilde{V}}{R_{t,o}} - K_o \exp(-b_o \bar{V}) \tilde{c}_{o,0}$$

$$R_{t,o} = \frac{1}{K_o \bar{c}_{o,0} \exp(-b_o \bar{V})}$$
Mass Transfer

\[
\bar{i}_O = -n_0 F D_0 \left. \frac{d\tilde{c}_O}{dy} \right|_0
\]

\[
i_O = \bar{i}_O + \text{Re}\left\{\tilde{i}_O e^{i\omega t}\right\}
\]

\[
\tilde{i}_O = -n_0 F D_0 \left. \frac{d\tilde{c}_O}{dy} \right|_0
\]

\[
\tilde{i}_O = -n_0 F D_0 \frac{\tilde{c}_O,0}{\delta_O} \tilde{\theta}'(0)
\]
Combine Expressions

\[\tilde{i}_o = \frac{\tilde{V}}{R_{t,o}} - K_o \exp(b_o \tilde{V}) \tilde{c}_{O,0}\]

\[\tilde{c}_{O,0} = -\frac{\tilde{i}_o \delta_o}{n_o F D_o \tilde{\theta}'(0)}\]
Current Density

\[
\tilde{i}_O = \frac{\tilde{V}}{R_{t,O} + \frac{\delta_O}{n_O F D_O \bar{c}_{O,0}} \frac{1}{b_O} \left( -\frac{1}{\tilde{\theta}'(0)} \right)}
\]

\[
\tilde{V} = \frac{\tilde{V}}{R_{t,O} + z_{d,O}}
\]

\[
z_{d,O} = \frac{\delta_O}{n_O F D_O \bar{c}_{O,0}} \frac{1}{b_O} \left( -\frac{1}{\tilde{\theta}'(0)} \right)
\]

\[
R_{t,O} = \frac{1}{K_O \bar{c}_{O,0} \exp \left( -b_O \tilde{V} \right)}
\]
Calculate Impedance

\[ i = i_f + C_{dl} \frac{dV}{dt} \]
\[ \tilde{i} = \tilde{i}_O + j\omega C_{dl}\tilde{V} \]

\[ U = iR_e + V \]
\[ \tilde{U} = \tilde{i}R_e + \tilde{V} \]

\[ Z_O = \frac{\tilde{U}}{\tilde{i}} = R_e + \frac{\tilde{V}}{\tilde{i}} \]
\[ = R_e + \frac{R_{t,O} + z_{d,O}}{1+j\omega C_{dl}} \frac{1}{R_{t,O} + z_{d,O}} \]

\[ \tilde{i} = \frac{\tilde{V}}{R_{t,O} + z_{d,O}} + j\omega C_{dl}\tilde{V} \]
Comparison to Circuit Analog

\[ Z_O = R_e + \frac{R_{t,O} + Z_{d,O}}{1 + j\omega C_{dl} (R_{t,O} + Z_{d,O})} \]
Irreversible Reaction: Dependent on Potential and Adsorbed Intermediate

B $\xrightarrow{k_1} X + e^-$

$X \xrightarrow{k_2} P + e^-$

- Potential-dependent heterogeneous reactions
- Adsorption of intermediate on two-dimensional surface
- Maximum surface coverage
Steady-State Current Density

reaction 1: formation of X

$$\bar{i}_1 = K_1 (1 - \bar{\gamma}) \exp \left( b_1 (\bar{V} - V_1) \right)$$

reaction 2: formation of P

$$\bar{i}_2 = K_2 \bar{\gamma} \exp \left( b_2 (\bar{V} - V_2) \right)$$

total current density

$$\bar{i} = \bar{i}_1 + \bar{i}_2$$
Steady-State Surface Coverage

balance on $\gamma$

$$\Gamma \frac{d\gamma}{dt} = \frac{i_1}{F} - \frac{i_2}{F} = 0$$

steady-state value for $\gamma$

$$\bar{\gamma} = \frac{K_1 \exp\left(b_1 \left(\bar{V} - V_1\right)\right)}{K_1 \exp\left(b_1 \left(\bar{V} - V_1\right)\right) + K_2 \exp\left(b_2 \left(\bar{V} - V_2\right)\right)}$$
Steady-State Current Density

\[
\bar{i} = K_1 (1 - \bar{\gamma}) \exp(b_1 (\bar{V} - V_1)) + K_2 \bar{\gamma} \exp(b_2 (\bar{V} - V_2))
\]

where

\[
\bar{\gamma} = \frac{K_1 \exp(b_1 (\bar{V} - V_1))}{K_1 \exp(b_1 (\bar{V} - V_1)) + K_2 \exp(b_2 (\bar{V} - V_2))}
\]
Oscillating Current Density

\[
\bar{i} = K_1(1 - \bar{\gamma}) \exp\left( b_1(\bar{V} - V_1) \right) + K_2\bar{\gamma} \exp\left( b_2(\bar{V} - V_2) \right)
\]

\[
\tilde{i} = \left( \frac{1}{R_{t,1}} + \frac{1}{R_{t,2}} \right)\tilde{V} + \left( K_2 \exp\left( b_2(\bar{V} - V_2) \right) - K_1 \exp\left( b_1(\bar{V} - V_1) \right) \right)\tilde{\gamma}
\]

\[
R_{t,1} = \left[ K_1 b_1 (1 - \bar{\gamma}) \exp\left( -b_1 (\bar{V} - V_1) \right) \right]^{-1}
\]

\[
R_{t,2} = \left[ K_2 b_2 \bar{\gamma} \exp\left( -b_2 (\bar{V} - V_2) \right) \right]^{-1}
\]
Need Additional Equation

balance on $\gamma$

$$\Gamma j\omega \tilde{\gamma} = \frac{1}{F} \left( \frac{1}{R_{t,1}} - \frac{1}{R_{t,2}} \right) \tilde{V} - \left( K_1 \exp\left( b_1 (\overline{V} - V_1) \right) + K_2 \exp\left( b_2 (\overline{V} - V_2) \right) \right) \tilde{\gamma}$$

$$\tilde{\gamma} = \frac{R_{t,1}^{-1} - R_{t,2}^{-1}}{F\Gamma j\omega + \left( K_1 \exp\left( b_1 (\overline{V} - V_1) \right) + K_2 \exp\left( b_2 (\overline{V} - V_2) \right) \right)} \tilde{V}$$
Impedance

\[
\frac{1}{Z} = \frac{1}{R_t} + \frac{\left[K_2 \exp\left(b_2 \left(\overline{V} - V_2\right)\right) - K_1 \exp\left(b_1 \left(\overline{V} - V_1\right)\right)\right]}{F \Gamma j \omega + F \left(K_1 \exp\left(b_1 \left(\overline{V} - V_1\right)\right) + K_2 \exp\left(b_2 \left(\overline{V} - V_2\right)\right)\right)} \left[ R_{t,1}^{-1} - R_{t,2}^{-1} \right] \\
= \frac{1}{R_t} + \frac{A}{j \omega + B}
\]

where

\[
\frac{1}{R_t} = \frac{1}{R_{t,M}} + \frac{1}{R_{t,X}}
\]
Chapter 5. Development of Process Models
Corrosion of Steel

\[ i_f = i_{Fe} + i_{H_2} + i_{O_2} \]

- \( 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \)
- \( O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \)
- \( Fe \rightarrow Fe^{2+} + 2e^- \)
Corrosion: \( \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \)

\[
\dot{i}_{\text{Fe}} = K_{\text{Fe}} \exp\left( b_{\text{Fe}} \bar{V} \right)
\]

\[
\tilde{i}_{\text{Fe}} = K_{\text{Fe}} b_{\text{Fe}} \exp\left( b_{\text{Fe}} \bar{V} \right) \tilde{V}
\]

\[
\tilde{i}_{\text{Fe}} = \frac{\tilde{V}}{R_{t,\text{Fe}}}
\]

\[
R_{t,\text{Fe}} = \frac{1}{K_{\text{Fe}} b_{\text{Fe}} \exp\left( b_{\text{Fe}} \bar{V} \right)}
\]
Steady Currents in Terms of $R_t$

$$\bar{i}_{Fe} = K_{Fe} \exp\left( b_{Fe} \bar{V} \right)$$

$$\beta_{Fe} = 2.303 / b_{Fe}$$

$$\bar{i}_{Fe} = K_{Fe} \exp\left( 2.303\bar{V} / \beta_{Fe} \right)$$

$$R_{t,Fe} = \frac{1}{K_{Fe} b_{Fe} \exp\left( b_{Fe} \bar{V} \right)} = \frac{\beta_{Fe}}{2.303\bar{i}_{Fe}}$$

$$\bar{i}_{Fe} = \frac{\beta_{Fe}}{2.303R_{t,Fe}}$$

Important: Note the relationship among steady-state current density, Tafel slope, and charge transfer resistance.
H₂ Evolution: 2H₂O + 2e⁻ → H₂ + 2OH⁻

\[ i_{H₂} = -K_{H₂} \exp(-b_{H₂} \bar{V}) \]

\[ \tilde{i}_{H₂} = K_{H₂} b_{H₂} \exp(-b_{H₂} \bar{V}) \tilde{\bar{V}} \]

\[ \tilde{i}_{H₂} = \frac{\tilde{\bar{V}}}{R_{t,H₂}} \]

\[ R_{t,H₂} = \frac{1}{K_{H₂} b_{H₂} \exp(-b_{H₂} \bar{V})} \]
\( \overline{i_{O_2}} = -K_{O_2} \overline{c_{O_2,0}} \exp(-b_{O_2} \overline{V}) \)

\( \tilde{i}_{O_2} = K_{O_2} b_{O_2} \overline{c_{O_2,0}} \exp(-b_{O_2} \overline{V}) \tilde{V} - K_{O_2} \exp(-b_{O_2} \overline{V}) \tilde{c}_{O_2,0} \)
**O₂ Evolution:** \( \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \)

mass transfer: in terms of dimensionless gradient at electrode surface

\[
\tilde{i}_{O_2} = -n_{O_2} F D_{O_2} \left. \frac{d\tilde{c}_{O_2}}{dy} \right|_0
\]

\[
= -n_{O_2} F D_{O_2} \frac{\tilde{c}_{O_2,0}}{\delta_{O_2}} \tilde{\theta}'(0)
\]
O₂ Evolution: \( \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \)

coupled expression

\[
\tilde{i}_{\text{O}_2} = \frac{\tilde{V}}{R_{t,\text{O}_2} + \frac{\delta_{\text{O}_2}}{n_{\text{O}_2} F D_{\text{O}_2} c_{\text{O}_2,0}} \frac{1}{b_{\text{O}_2}} \left(-\frac{1}{\tilde{\theta}'(0)}\right)}
\]

\[
= \frac{\tilde{V}}{R_{t,\text{O}_2} + z_{d,\text{O}_2}}
\]

\[
z_{d,\text{O}_2} = \frac{\delta_{\text{O}_2}}{n_{\text{O}_2} F D_{\text{O}_2} c_{\text{O}_2,0}} \frac{1}{b_{\text{O}_2}} \left(-\frac{1}{\tilde{\theta}'(0)}\right)
\]

\[
R_{t,\text{O}_2} = \frac{1}{K_{\text{O}_2} b_{\text{O}_2} c_{\text{O}_2,0} \exp\left(-b_{\text{O}_2} \tilde{V}\right)}
\]
**Capacitance and Ohmic Contributions**

Faradaic

\[ i_f = \sum_i i_f \]
\[ \tilde{i}_f = \sum_i \tilde{i}_f \]

Faradaic and Charging

\[ i = i_f + C_d \frac{dV}{dt} \]
\[ \tilde{i} = \tilde{i}_f + j\omega C_d \tilde{V} \]

Ohmic

\[ U = iR_e + V \]
\[ \tilde{U} = \tilde{i} R_e + \tilde{V} \]
Process Model

\[ Z = \frac{\tilde{U}}{\tilde{i}} = Z_r + jZ_j \]

\[ = \frac{1}{\left( \frac{1}{R_{t,\text{Fe}}} + \frac{1}{R_{t,H_2}} \right) + \frac{1}{R_{t,O_2} + z_{d,O_2}}} + j\omega C_d \]

\[ = \frac{1}{R_{\text{eff}}} + \frac{1}{R_{t,O_2} + z_{d,O_2}} + j\omega C_d \]

\[ \frac{1}{R_{\text{eff}}} = \frac{1}{R_{t,\text{Fe}}} + \frac{1}{R_{t,H_2}} \]
Development of Impedance Models

- identify reaction mechanism
- write expression for steady state current contributions
- write expression for sinusoidal steady state
- sum current contributions
- account for charging current
- account for ohmic potential drop
  - account for mass transfer
- calculate impedance
Mass Transfer
Film Diffusion

\[ \frac{\partial c_i}{\partial t} = D_i \left\{ \frac{\partial^2 c_i}{\partial z^2} \right\} \]

steady state

\[ \bar{c}_i \rightarrow c_{i,\infty} \quad \text{as} \quad z \rightarrow \delta_f \]

\[ \bar{c}_i = c_{i,0} \quad \text{at} \quad z = 0 \]

\[ \bar{c}_i = c_{i,0} + \frac{z}{\delta_f} \left( c_{i,\infty} - c_{i,0} \right) \]
Film Diffusion

\[
\frac{\partial c_i}{\partial t} = D_i \left\{ \frac{\partial^2 c_i}{\partial z^2} \right\} \\
c_i = \bar{c}_i + \text{Re}\{ \tilde{c}_i e^{j\omega t} \}
\]

\[
j\omega \tilde{c}_i e^{j\omega t} = D_i \frac{d^2 \bar{c}_i}{dz^2} + D_i \frac{d^2 \tilde{c}_i}{dz^2} e^{j\omega t}
\]

\[
j\omega \bar{c}_i e^{j\omega t} = D_i \frac{d^2 \tilde{c}_i}{dz^2} e^{j\omega t}
\]

\[
j\omega \bar{c} = D_i \frac{d^2 \tilde{c}_i}{dz^2}
\]

\[
\xi = \frac{z}{\delta_i}
\]

\[
K_i = \frac{\omega \delta_i^2}{D_i}
\]

\[
\tilde{\theta}_i = \frac{\bar{c}_i}{\bar{c}_i(0)}
\]

\[
\frac{d^2 \tilde{\theta}_i}{d \xi^2} - jK_i \tilde{\theta}_i = 0
\]
Warburg Impedance

\[ \frac{d^2 \tilde{\theta}_i}{d \xi^2} - jK_i \tilde{\theta}_i = 0 \]

\[ \tilde{\theta}_i = A \exp \left( \xi \sqrt{jK_i} \right) + B \exp \left( -\xi \sqrt{jK_i} \right) \]

\[ \tilde{\theta}_i = 0 \quad \text{at} \quad \xi = 1 \]

\[ \tilde{\theta}_i = 1 \quad \text{at} \quad \xi = 0 \]

\[ \frac{1}{\theta_i'(0)} = - \frac{\tanh \sqrt{jK_i}}{\sqrt{jK_i}} \]

\[ \frac{1}{\theta_i'(0)} = - \frac{\tanh \sqrt{\frac{j \omega \delta^2}{D_i}}}{\sqrt{\frac{j \omega \delta^2}{D_i}}} \]

\[ \tilde{\theta}_i = 0 \quad \text{at} \quad \xi = \infty \]

\[ \tilde{\theta}_i = 1 \quad \text{at} \quad \xi = 0 \]

\[ \frac{1}{\theta_i'(0)} = - \frac{1}{\sqrt{jK_i}} \]

\[ \frac{1}{\theta_i'(0)} = - \frac{1}{\sqrt{\frac{j \omega \delta^2}{D_i}}} \]
Concentration

\[ \frac{c(\xi)}{c(\infty)} \]

- Diffusion Impedance Only (infinite)
- Diffusion Impedance Only (finite)
- Complete Impedance

\[
\begin{align*}
\frac{c(\xi)}{c(\infty)} &= \frac{1 - e^{-\frac{\xi}{\delta}}}{1 - e^{-\frac{\infty}{\delta}}} \\
&= 1 - e^{-\frac{\xi}{\delta}} \\
&= 1 - e^{-t/K}
\end{align*}
\]

- \( t = 0, \frac{2\pi}{K} \)
- \( t = \frac{n\pi}{K} \)
- \( t = \frac{0.5n\pi}{K} \)
- \( t = \frac{1.5n\pi}{K} \)

\( K = 1 \)

\( K = 100 \)
Coupled Diffusion Impedance

\[ z_d = \frac{z_{d, outer} + \frac{D_{i, outer}}{D_{i, inner}} \frac{\delta_{i, inner}}{\delta_{i, outer}} z_{d, inner}}{z_{d, inner} z_{d, outer} \left( j\omega \frac{\delta_{i, inner}^2}{D_{i, inner}} \right) + \frac{D_{i, outer}}{D_{i, inner}} \frac{\delta_{i, inner}}{\delta_{i, outer}}} \]
Interpretation Models for Impedance Spectroscopy

- Models can account rigorously for proposed kinetic and mass transfer mechanisms.
- There are significant differences between models for mass transfer.
- Stochastic errors in impedance spectroscopy are sufficiently small to justify use of accurate models for mass transfer.
Chapter 6. Constant Phase Elements

• The origin of CPEs is ambiguous
• CPEs can arise from surface or axial distributions
• CPE parameters can be interpreted in terms of capacitance, depending on type of distribution
Page deliberately left blank
Types of Distributions

- Surface
- Axial
Surface Distributions

\[ R_{e,i}, \quad R_i, C_i \]

\[ (\sum Y_i)^{-1} \]

\[ R_e \quad \text{or} \quad Q, \alpha \]

\[ R_{e,\text{eff}}, C_{\text{eff}} \]

(a)

(b)
Axial Distributions
Relationship between Q and C

\[ Z(\omega) = R_e + \frac{R_t}{1 + (j\omega)^\alpha QR_t} \]

- Surface Distribution

\[ C_{eff} = Q^{1/\alpha} \left( \frac{R_eR_t}{R_e + R_t} \right)^{(1-\alpha)/\alpha} \]

- Axial Distribution

\[ C_{eff} = Q^{1/\alpha} R_f^{(1-\alpha)/\alpha} \]


Determination of Film Thickness

\[
C_{\text{eff}} = \frac{\varepsilon \varepsilon_0}{\delta}
\]

<table>
<thead>
<tr>
<th>R_1</th>
<th>C</th>
<th>( f_{RC} = (2\pi R_1 C)^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_2</td>
<td>C</td>
<td>( f_{RC} = (2\pi R_2 C)^{-1} )</td>
</tr>
<tr>
<td>R_3</td>
<td>C</td>
<td>( f_{RC} = (2\pi R_3 C)^{-1} )</td>
</tr>
<tr>
<td>R_4</td>
<td>C</td>
<td>( f_{RC} = (2\pi R_4 C)^{-1} )</td>
</tr>
<tr>
<td>R_5</td>
<td>C</td>
<td>( f_{RC} = (2\pi R_5 C)^{-1} )</td>
</tr>
<tr>
<td>R_6</td>
<td>C</td>
<td>( f_{RC} = (2\pi R_6 C)^{-1} )</td>
</tr>
</tbody>
</table>
Constant Phase Elements

- Origin is ambiguous
- Can arise from surface or axial distributions
- CPE parameters can be interpreted in terms of capacitance, depending on type of distribution
Advanced Electrochemical Impedance Spectroscopy

Chapter 7. Regression Analysis

- Regression response surfaces
  - noise
  - incomplete frequency range
- Adequacy of fit
  - quantitative
  - qualitative
Test Circuit 1: 1 Time Constant

- $R_0 = 0$
- $R_1 = 1 \, \Omega \, \text{cm}^2$
- $\tau_1 = \tau_{RC} = 1 \, \text{s}$
Linear optimization surface roughly parabolic

\[ f(p) = \sum_{i=1}^{N_{dat}} \frac{(Z_{r,dat} - Z_{r,mod})^2}{\sigma_r^2} + \sum_{k=1}^{N_{dat}} \frac{(Z_{j,dat} - Z_{j,mod})^2}{\sigma_j^2} \]
**Nonlinear Regression**

\[
f(p) = f(p_0) + \sum_{j=1}^{N_p} \frac{\partial f}{\partial p_j} \bigg|_{p_0} \Delta p_j + \frac{1}{2} \sum_{j=1}^{N_p} \sum_{k=1}^{N_p} \frac{\partial^2 f}{\partial p_j \partial p_k} \bigg|_{p_0} \Delta p_j \Delta p_k + \ldots
\]

For our purposes:

\[
\chi^2 = \sum_{i=1}^{N_{\text{dat}}} \frac{(y_i - y(x_i \mid p))^2}{\sigma_i^2}
\]

\[
\beta = \alpha \cdot \Delta p
\]

\[
\beta_k = \sum_{i=1}^{N_{\text{dat}}} \frac{y_i - y(x_i \mid p)}{\sigma_i^2} \frac{\partial y(x_i \mid p)}{\partial p_k}
\]

\[
\alpha_{j,k} \approx \sum_{i=1}^{N_{\text{dat}}} \frac{1}{\sigma_i^2} \left[ \frac{\partial y(x_i \mid p)}{\partial p_j} \frac{\partial y(x_i \mid p)}{\partial p_k} \right]
\]

Variance of data

Derivative of function with respect to parameter
Methods for Regression

• Evaluation of derivatives
  – method of steepest descent
  – Gauss-Newton method
  – Levenberg-Marquardt method

• Evaluation of function
  – simplex
Effect of Noisy Data

Add noise: 1% of modulus

- response surface remains parabolic
- value at minimum increases
Test Circuit 2: 3 Time Constants

- \( R_0 = 1 \, \Omega \, \text{cm}^2 \)
- \( R_1 = 100 \, \Omega \, \text{cm}^2 \)
- \( \tau_1 = 0.001 \, \text{s} \)
- \( R_2 = 200 \, \Omega \, \text{cm}^2 \)
- \( \tau_2 = 0.01 \, \text{s} \)
- \( R_3 = 5 \, \Omega \, \text{cm}^2 \)
- \( \tau_3 = 0.05 \, \text{s} \)

Note: 3rd Voigt element contributes only 1.66% to DC cell impedance.
Effect of Noisy Data

All parameters fixed except $R_3$ and $\tau_3$

Note: use of log scale for parameters
Resulting Spectrum

![Graph showing the resulting spectrum with labels for $Z_j / \Omega \text{ cm}^2$ and $Z_r / \Omega \text{ cm}^2$ with two models: one with 1% noise and one with no noise.](image)

- Model with 1% noise added
- Model with no noise
Test Circuit 3: 3 Time Constants

- $R_0 = 1 \ \Omega \ \text{cm}^2$
- $R_1 = 100 \ \Omega \ \text{cm}^2$
- $\tau_1 = 0.01 \ \text{s}$
- $R_2 = 200 \ \Omega \ \text{cm}^2$
- $\tau_2 = 0.1 \ \text{s}$
- $R_3 = 100 \ \Omega \ \text{cm}^2$
- $\tau_3 = 10 \ \text{s}$

Note: 3rd Voigt element contributes 25% to DC cell impedance. The time constant corresponds to a characteristic frequency $\omega_3=0.1 \ \text{s}^{-1}$ or $f_3=0.016 \ \text{Hz}$. 
Resulting Test Spectra

\[
\frac{Z_j}{\Omega \text{ cm}^2}
\]

\[
\frac{Z_r}{\Omega \text{ cm}^2}
\]

-100

0

0 100 200 300 400

0.01 Hz to 100 kHz

1 Hz to 100 kHz
Effect of Truncated Data

0.01 Hz to 100 kHz

1 Hz to 100 kHz

All parameters fixed except $R_3$ and $\tau_3$
Conclusions from Test Spectra

• The presence of noise in data can have a direct impact on model identification and on the confidence interval for the regressed parameters.

• The correctness of the model does not determine the number of parameters that can be obtained.

• The frequency range of the data can have a direct impact on model identification.

• The model identification problem is intricately linked to the error identification problem. In other words, analysis of data requires analysis of the error structure of the measurement.
When Is the Fit Adequate?

- Chi-squared statistic
  - includes variance of data
  - should be near the degree of freedom
- Visual examination
  - should look good
  - some plots show better sensitivity than others
- Parameter confidence intervals
  - based on linearization about solution
  - should not include zero
Test Case: Mass Transfer to a RDE

\[ Z(\omega) = R_e + \frac{R_t + z_d(\omega)}{1 + (j\omega C)(R_t + z_d(\omega))} \]

Single reaction coupled with mass transfer. Consider model for a Nernst stagnant diffusion layer:

\[ z_d(\omega) = z_d(\omega) \frac{\tanh \sqrt{j\omega \tau}}{\sqrt{j\omega \tau}} \]
## Evaluation of $\chi^2$ Statistic

| $\sigma|Z(\omega)|$ | 1   | 0.1 | 0.05 | 0.03 | 0.01 |
|---------------------|-----|-----|------|------|------|
| $\chi^2$            | 0.0408 | 4.08 | 16.32 | 45.32 | 408   |
| $\chi^2/\nu$        | 0.00029 | 0.029 | 0.12 | 0.32 | 2.9   |
Comparison of Model to Data

Impedance Plane (Nyquist)

Value of $\chi^2$ has no meaning without accurate assessment of the noise level of the data.
Modulus

\[ |Z| / \Omega \]

\[ f / \text{Hz} \]
Phase Angle

\[ \phi / \text{degrees} \]

\[ f / \text{Hz} \]
Imaginary

\[-Z_j/\Omega\]

\[f/\text{Hz}\]
Slope = -1
for RC
Modified Phase Angle

\[ \phi^* = \tan^{-1} \left( \frac{Z_j}{Z_r - R_e} \right) \]
Real Residuals

\[ \frac{\varepsilon_r}{Z_r} \]

\[ f / \text{Hz} \]

\pm 2\sigma \text{ noise level}
Plot Sensitivity to Quality of Fit

- **Poor Sensitivity**
  - **Modulus**
  - **Real**

- **Modest Sensitivity**
  - **Impedance-plane**
    - only for large impedance values
  - **Imaginary**
  - **Log Imaginary**
    - emphasizes small values
    - slope suggests new models
  - **Phase Angle**
    - high-frequency behavior is counterintuitive due to role of solution resistance
  - **Modified Phase Angle**
    - high-frequency behavior can suggest new models
    - needs an accurate value for solution resistance

- **Excellent Sensitivity**
  - **Residual error plots**
    - trending provides an indicator of problems with the regression
Test Case: Better Model for Mass Transfer to a RDE

\[ Z(\omega) = R_e + \frac{R_t + z_d(\omega)}{1 + (j\omega)\alpha Q(R_t + z_d(\omega))} \]

Consider 3-term expansion with CPE to account for more complicated reaction kinetics:

\[ z_d = z_d(0) \left( \frac{1}{\theta_0'(pSc^{1/3})} + \frac{Z_1(pSc^{1/3})}{Sc^{1/3}} + \frac{Z_2(pSc^{1/3})}{Sc^{2/3}} \right) \]

\[ \chi^2/\nu = 4.86 \]
Comparison of Model to Data

Impedance Plane (Nyquist)
Phase Angle

![Phase Angle Graph]

$$-\angle Z_j / \Omega$$

$$f / \text{Hz}$$
Modified Phase Angle

$$\phi^* = \tan^{-1}\left(\frac{Z_j}{Z_r - R_e}\right)$$
Log Imaginary

\[ -\frac{Z_j}{\Omega} \]

\[ f \text{ / Hz} \]
Real Residuals

\[ \frac{\varepsilon_r}{Z_r} \]

\[ f/ \text{Hz} \]

\[ \pm 2\sigma \]
Imaginary Residuals

\[ \frac{\varepsilon_j}{Z_j} \]

\[ f / \text{Hz} \]

\[ \pm 2\sigma \]
Confidence Intervals

- Based on linearization about trial solution
- Assumption valid for good fits
  - for normally distributed fitting errors
  - small estimated standard deviations
- Can use Monte Carlo simulations to test assumptions
Regression of Models to Data

• Regression is strongly influenced by
  – stochastic errors in data
  – incomplete frequency range
  – incorrect or incomplete models

• Some plots more sensitive to fit quality than others.
• Quantitative measures of fit quality require independent assessment of error structure.
• The model identification problem is intricately linked to the error identification problem.
Chapter 8. Error Structure

Advanced Electrochemical Impedance Spectroscopy

Chapter 8. Error Structure

- Contributions to error structure
- Weighting strategies
- General approach for error analysis
- Experimental results

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Contributions to Error Structure

• Sampling Errors

• Stochastic Phenomena

• Bias Errors
  – Lack of Fit
  – Changing baseline (non-stationary processes)
  – Instrumental artifacts
Time-domain $\rightarrow$ Frequency Domain

1 mHz

10 Hz

100 Hz

10 kHz
Error Structure

\[ \varepsilon_{\text{resid}}(\omega) = Z_{\text{obs}}(\omega) - Z_{\text{model}}(\omega) \]

\[ = \varepsilon_{\text{fit}}(\omega) + \varepsilon_{\text{bias}}(\omega) + \varepsilon_{\text{stochastic}}(\omega) \]

- fitting error
- inadequate model
- noise (frequency domain)

experimental errors: inconsistent with the Kramers-Kronig relations
# Weighting Strategies

\[
J = \sum_k \frac{(Z_{r,k} - \hat{Z}_{r,k})^2}{\sigma_{r,k}^2} + \sum_k \frac{(Z_{j,k} - \hat{Z}_{j,k})^2}{\sigma_{j,k}^2}
\]

<table>
<thead>
<tr>
<th>Strategy</th>
<th>Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Weighting</td>
<td>(\sigma_r = \sigma_j) (\sigma = \alpha)</td>
</tr>
<tr>
<td>Modulus Weighting</td>
<td>(\sigma_r = \sigma_j) (\sigma = \alpha |Z|)</td>
</tr>
<tr>
<td>Proportional Weighting</td>
<td>(\sigma_r \neq \sigma_j) (\sigma_r = \alpha_r |Z_r|); (\sigma_j = \alpha_j |Z_j|)</td>
</tr>
<tr>
<td>Experimental</td>
<td>(\sigma_r = \sigma_j) (\sigma = \alpha |Z_j| + \beta |Z_r| + \gamma |Z|^2/R_m)</td>
</tr>
<tr>
<td>Refined Experimental</td>
<td>(\sigma_r = \sigma_j) (\sigma = \alpha |Z_j| + \beta |Z_r| - R_{sol} + \gamma |Z|^2/R_m + \delta)</td>
</tr>
</tbody>
</table>
Assumed Error Structure often Wrong

Data obtained by T. El Moustafid, CNRS, Paris, France
Reduction of Fe(CN)$_6^{3-}$ on a Pt Disk, 120 rpm
Reduction of $\text{Fe(CN)}_6^{3-}$ on a Pt Disk, Imaginary Replicates @ 120 rpm, $1/4 \, i_{\text{lim}}$
Reduction of $\text{Fe(CN)}_6^{3-}$ on a Pt Disk, Real Replicates @ 120 rpm, $1/4 \ i_{\text{lim}}$
Reduction of $\text{Fe(CN)}_6^{3-}$ on a Pt Disk, Error Structure @ 120 rpm, $1/4 i_{\text{lim}}$
Reduction of Fe(CN)$_6^{3-}$ on a Pt Disk, Error Structure @ 120 rpm, 1/4 $i_{lim}$
Interpretation of Impedance Spectra

• Need physical insight and knowledge of error structure
  – stochastic component
    • weighting
    • determination of model adequacy
    • experimental design
  – bias component
    • suitable frequency range
    • experimental design

• Approach is general
  – electrochemical impedance spectroscopies
  – optical spectroscopies
  – mechanical spectroscopies
Advanced Electrochemical Impedance Spectroscopy

Chapter 9. Kramers-Kronig Relations

• Mathematical form and interpretation
• Application to noisy data
• Methods to evaluate consistency

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Constraints

• Under the assumption that the system is
  – Causal
  – Linear
  – Stable

• A complex variable $Z$ must satisfy equations of the form:

$$Z_j(\omega) = \frac{2\omega}{\pi} \int_0^\infty \frac{Z_r(x) - Z_r(\omega)}{x^2 - \omega^2} dx$$

$$Z_r(\omega) = Z_r(\infty) + \frac{2\omega}{\pi} \int_0^\infty \frac{-xZ_j(x) + \omega Z_j(\omega)}{x^2 - \omega^2} dx$$
Use of Kramers-Kronig Relations

• Concept
  – if data do not satisfy Kramers-Kronig relations, a condition of the derivation must not be satisfied
    • stationarity / causality
    • linearity
    • stability
  – interpret result in terms of
    • instrument artifact
    • changing baseline
  – if data satisfy Kramers-Kronig relations, conditions of the derivation may be satisfied
For real data (with noise)

\[ Z_{ob}(\omega) = Z(\omega) + \varepsilon(\omega) \]
\[ = (Z_r(\omega) + \varepsilon_r(\omega)) + j(Z_j(\omega) + \varepsilon_j(\omega)) \]

where
\[ \varepsilon(\omega) = \varepsilon_r(\omega) + j\varepsilon_j(\omega) \]

\[ E(Z(\omega)_{ob}) = Z(\omega) \quad \text{If and only if} \quad E(\varepsilon(\omega)) = 0 \]

Kramers-Kronig in an expectation sense

\[ E(Z_j(\omega)) = \frac{2\omega}{\pi} E \left( \int_0^\infty \frac{Z_r(x) - Z_r(\omega) + \varepsilon_r(x) - \varepsilon_r(\omega)}{x^2 - \omega^2} \, dx \right) \]
\[ E(Z_r(\omega) - Z_r(\infty)) = E \left( \frac{2}{\pi} \int_0^\infty \frac{-\omega Z_j(x) + \omega Z_j(\omega) - x\varepsilon_j(x) + \omega\varepsilon_j(\omega)}{x^2 - \omega^2} \, dx \right) \]
The Kramers-Kronig relations can be satisfied if

\[ E(\varepsilon(\omega)) = 0 \quad \text{and} \quad E\left( \frac{2\omega}{\pi} \int_{0}^{\infty} \frac{\varepsilon_r(x)}{x^2 - \omega^2} dx \right) = 0 \]

- This means
  - the process must be stationary in the sense of replication at every measurement frequency.
  - As the impedance is sampled at a finite number of frequencies, \( \varepsilon_r(x) \) represents the error between an interpolated function and the “true” impedance value at frequency \( x \). In the limit that quadrature and interpolation errors are negligible, the residual errors \( \varepsilon_r(x) \) should be of the same magnitude as the stochastic noise \( \varepsilon_r(\omega) \).
Chapter 9. Kramers-Kronig Relations

Meaning of

\[
E \left( \frac{2\omega}{\pi} \int_0^\infty \frac{\varepsilon_r(x)}{x^2 - \omega^2} \, dx \right) = 0
\]
Use of Kramers-Kronig Relations

- Quadrature errors
  - require interpolation function
- Missing data at low and high frequency
Methods to Resolve Problems of Insufficient Frequency Range

• Direct Integration
  – Extrapolation
    • single RC
    • polynomials
    • $1/\omega$ and $\omega$ asymptotic behavior
  – simultaneous solution for missing data

• Regression
  – proposed process model
  – generalized measurement model
Advanced Electrochemical Impedance Spectroscopy

Chapter 10. Use of Measurement Models

- Generalized model
- Identification of stochastic component of error structure
- Identification of bias component of error structure
Approach

• Experimental design
  – quality (signal-to-noise, bias errors)
  – information content

• Process model
  – account for known phenomena
  – extract information concerning other phenomena

• Regression
  – uncorrupted frequency range
  – weighting strategy

• Error analysis - measurement model
  – stochastic errors
  – bias errors
**Error Structure**

\[ Z_{\text{obs}} - Z_{\text{model}} = \varepsilon_{\text{res}} \]

\[ Z_{\text{obs}} - Z_{\text{model}} = \varepsilon_{\text{fit}} + \varepsilon_{\text{bias}} + \varepsilon_{\text{stoch}} \]

- Stochastic errors
- Bias errors
  - lack of fit
  - experimental artifact
    - Kramers-Kronig consistent
    - Kramers-Kronig inconsistent
Measurement Model

- Superposition of lineshapes

\[ Z = R_0 + \sum_{k=1}^{n} \frac{R_k}{1 + j\omega R_k C_k} \]
Identification of Stochastic Component of Error Structure

How?
• Replicate impedance scans.
• Fit measurement model to each scan:
  – use modulus or no-weighting options.
  – same number of lineshapes.
  – parameter estimates do not include zero.
• Calculate standard deviation of residual errors.
• Fit model for error structure.

Why?
• Weight regression.
• Identify good fit.
• Improve experimental design.
Replicated Measurements

![Graph showing replicated measurements with axes labeled as $Z_r / \Omega$ and $-Z_j / \Omega$.]
1 Voigt Element

-\( Z_j / \Omega \)

\( Z_r / \Omega \)
2 Voigt Elements

\[ Z_r / \Omega \]

\[ -Z_j / \Omega \]
3 Voigt Elements
4 Voigt Elements

- $Z_j / \Omega$

$Z_r / \Omega$
5 Voigt Elements
6 Voigt Elements

\[ -Z_j / \Omega \]

\[ Z_r / \Omega \]
10 Voigt Elements

\[ Z_j / \Omega \]

\[ Z_r / \Omega \]
Residual Errors

- Imaginary component
- Real component

Frequency / Hz

Residual Errors

- Imaginary component
- Real component

Frequency / Hz
Residual Sum of Squares

\[ \sum \left( \frac{\varepsilon^2}{\sigma^2} \right) \]

# Voigt Elements

The graph illustrates the decrease in residual sum of squares as the number of Voigt elements increases. The mathematical expression represents the sum of the squared residuals divided by the variance, which is a measure of the goodness of fit for a model.
Fit to Repeated Data Sets

![Graph showing fit to repeated data sets with axes labeled $Z_r / \Omega$ on the x-axis and $-Z_j / \Omega$ on the y-axis.]
Residual Errors

Real

\( \varepsilon_r / Z_r \)

Frequency / Hz

\( 0.01 \) \( 0.1 \) \( 1 \) \( 10 \) \( 100 \) \( 1000 \) \( 10000 \) \( 100000 \)
Standard Deviation

- Standard Deviation
- Imaginary
- Real

Direct calculation of standard deviation

Standard deviation obtained from measurement model analysis

Frequency, Hz

0.001 0.01 0.1 1 10 100 1000 10000 100000
Comparison to Impedance

![Graph showing comparison to impedance.](image)

- **Z or \(\sigma, \Omega\)** vs. **Frequency, Hz**

  - Red dots represent the real part.
  - Red triangles represent the imaginary part.
  - Blue dashed line represents 3% of |Z|.

The graph illustrates the comparison of the measured values (Z or \(\sigma, \Omega\)) against the expected impedance values as a function of frequency. The data points and curves allow for a visual assessment of the accuracy and consistency of the measurement models over the specified frequency range.
Identification of Bias Component of Error Structure

How?

• Fit measurement model to real component:
  – predict imaginary component.
  – Use Monte Carlo calculations to estimate confidence interval.

• Fit measurement model to imaginary component:
  – predict real component.
  – Use Monte Carlo calculations to estimate confidence interval.

Why?

• Identify suitable frequency range for regression.
• Improve experimental design.
1st of Repeated Measurements

Imaginary

![Graph showing frequency vs. imaginary impedance](image)
1st of Repeated Measurements

Real

Frequency / Hz

Z_r / Ω
Fit to Imaginary Part

\[ -Z_j / \Omega \]

Frequency / Hz
Fit to Imaginary Part

\[ \frac{\xi}{Z_j} \]

Frequency / Hz

-0.03
0
0.03

0.01 0.1 1 10 100 1000 10000 100000
Chapter 10. Use of Measurement Models

Predict Real Part

![Graph showing the relationship between frequency and impedance](image)

- Frequency / Hz
- $Z_r / \Omega$
Predict Real Part

![](chart.png)

- Frequency / Hz
- $\varepsilon_r / Z_r$
Validation of Measurement Model
Approach
The error structure identified should be independent of measurement model used.

Voigt:

\[ Z(\omega) = R_0 + \sum_{i=1}^{N} \frac{R_i}{1+(j\omega)\tau_i} \]

Transfer Function:

\[ Z(\omega) = \frac{\sum_{i=0}^{M} b_i (j\omega)^{ni}}{\sum_{j=0}^{n} a_j (j\omega)^{nj}} \quad n = 1/2 \]

\[ Z(\omega) = \frac{b_0 + b_1 (j\omega)^{1/2} + b_2 (j\omega) + \ldots + b_M (j\omega)^{M/2}}{a_0 + a_1 (j\omega)^{1/2} + a_2 (j\omega) + \ldots + (j\omega)^{P/2}} \quad M = P; \quad a_P = 1 \]
Convective Diffusion to a RDE
Reduction of Fe(CN)$_6^{3-}$ on a Pt Disk: $i/i_{\text{lim}} = \frac{1}{4}$; 120 rpm
Convective Diffusion to a RDE
Reduction of Fe(CN)$_6^{3-}$ on a Pt Disk: $i/i_{\text{lim}} = \frac{1}{4}$; 120 rpm

real part

imaginary part
Data Sets for Analysis

Current / mA vs. time / h

- Measurement
  - Before impedance scan
  - After impedance scan

The graph shows the current (in mA) over time (in hours) with measurements taken before and after an impedance scan. The data points are distributed across different time intervals, indicating changes or trends over time.
Regression Results for Set #1: 0-1 h

- **Data:**
  - 74 frequencies
  - 148 data points

- **Voigt Model:**
  - 10 elements + $R_e$
  - 21 parameters

- **Transfer Function:**
  - $5a_i + 6b_i$
  - 11 parameters
Stochastic Error Structure for Set #1: Voigt

\[ \sigma_{Z_i}, \frac{\sigma_{Z_j}}{\Omega} \]

\[ f / \text{Hz} \]
Stochastic Error Structure for Set #1: Voigt & Transfer Function

\[ \sigma_{\text{VMM}} \]

\[ \frac{\sigma_{z_i}}{\Omega} \]

\[ f / \text{Hz} \]
Regression Results for Set #3: 8.9-9.9 h

- **Data:**
  - 74 frequencies
  - 148 data points

- **Voigt Model:**
  - 9 elements + $R_e$
  - 19 parameters

- **Transfer Function:**
  - $5 a_i + 6 b_i$
  - 11 parameters
Stochastic Error Structure for Set #3: Voigt
Stochastic Error Structure for Set #3: Voigt & Transfer Function

![Graph showing a plot of \( \sigma Z_r, \sigma Z_j / \Omega \) vs. frequency \( f / \text{Hz} \). The graph includes data for real and imaginary components, with markers for TMM and VMM.]
Identification of Stochastic Component of Error Structure

• Direct evaluation of standard deviation includes significant contributions from changes in system behavior
• The error structure identified was independent of measurement model used
• Selection of measurement model
  – Ease of identification of initial parameters → Voigt
  – Number of parameters → Transfer Function


Evaluation of Consistency with the Kramers-Kronig relations

• Approach
  – Fit measurement model to imaginary component
  – Use experimental variance to weight regression
  – Predict real component
  – Compare prediction to measured data
  – Use Monte Carlo calculations to estimate confidence interval

• Assumption
  – Measurement model satisfies the Kramers-Kronig relations
Voigt Measurement Model: Data 1

- 20 parameters, guessed value for $R_e$
- Tight confidence interval at low frequency
- Justify deleting 5 data points at lowest frequency
Voigt Measurement Model: Data 5

- 20 parameters, guessed value for $R_e$
- Justify keeping all data points
Interpretation of Impedance Spectra

• Physical insight and knowledge of error structure
  – stochastic component
    • weighting
    • determination of model adequacy
    • experimental design
  – bias component
    • suitable frequency range
    • experimental design

• Measurement model approach is general
  – electrochemical impedance spectroscopies
  – optical spectroscopies
  – mechanical spectroscopies
Advanced Electrochemical Impedance Spectroscopy

Chapter 11. Conclusions

- Overview of Course
- Credits

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Overview of Course

- Chapter 1. Introduction
- Chapter 2. Motivation
- Chapter 3. Impedance Measurement
- Chapter 4. Representations of Impedance Data
- Chapter 5. Development of Process Models
- Chapter 6. Constant Phase Elements
- Chapter 7. Regression Analysis
- Chapter 8. Error Structure
- Chapter 9. Kramers-Kronig Relations
- Chapter 10. Use of Measurement Models
- Chapter 11. Conclusions
- Chapter 12. Suggested Reading
- Chapter 13. Notation
Impedance Spectroscopy

- Electrochemical measurement of macroscopic properties
- Example of a generalized transfer-function measurement
- Can be used to extract contributions of
  - electrode reactions
  - mass transfer
  - surface layers
- Can be used to estimate
  - reaction rates
  - transport properties
- Interpretation of data
  - graphical representations
  - regression
  - process models
  - error analysis
Integrated Approach

- Other Observations
- Model
- EIS Experiment
- Error Analysis

Weighted regression analysis

- Model and data agree
- Model and data do not agree

Publication
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  – The Electrochemical Society
  – The Fuel Cell Seminar
Advanced Electrochemical Impedance Spectroscopy

Chapter 12. Suggested Reading

- General
- Process Models
- Orazem group work on Fuel Cells
- Measurement Models
- CPE
- Plotting

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Suggested Reading

General


• Other Sources
  – See instrument vendor websites for application notes.
Suggested Reading
Process Models


Suggested Reading

CPE


- C. H. Hsu and F. Mansfeld, Technical Note: “Concerning the Conversion of the Constant Phase Element Parameter \( Y_0 \) into a Capacitance,” *Corrosion*, **57** (2001), 747-748.


Suggested Reading

Measurement Models


Suggested Reading
Plotting

Advanced Electrochemical Impedance Spectroscopy

Chapter 13. Notation

- Roman
- Greek
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>coefficient in the Cochran expansion for velocity, $a = 0.51023$</td>
</tr>
<tr>
<td>$b$</td>
<td>coefficient in the Cochran expansion for velocity, $b = -0.61592$</td>
</tr>
<tr>
<td>$c_i$</td>
<td>concentration of reacting species $i$, mol/cm$^3$</td>
</tr>
<tr>
<td>$\bar{c}_i$</td>
<td>steady-state value of the concentration of reacting species $i$, mol/cm$^3$</td>
</tr>
<tr>
<td>$\tilde{c}_i$</td>
<td>Oscillating component of the concentration of reacting species $i$, mol/cm$^3$</td>
</tr>
<tr>
<td>$c_{i,o}$</td>
<td>concentration of species $i$ on the electrode surface, mol/cm$^3$</td>
</tr>
<tr>
<td>$\bar{c}_{i,o}$</td>
<td>steady-state value of the concentration of species $i$ on the electrode surface, mol/cm$^3$</td>
</tr>
<tr>
<td>$\tilde{c}_{i,o}$</td>
<td>Oscillating component of the concentration of species $i$ on the electrode surface, mol/cm$^3$</td>
</tr>
<tr>
<td>$c_\infty$</td>
<td>bulk concentration of the reacting species, mol/cm$^3$</td>
</tr>
<tr>
<td>$C_d$</td>
<td>double layer capacitance, F/cm$^2$</td>
</tr>
<tr>
<td>$C_{dl}$</td>
<td>double layer capacitance, F/cm$^2$</td>
</tr>
<tr>
<td>$D_i$</td>
<td>diffusion coefficient of species $i$, cm$^2$/s</td>
</tr>
<tr>
<td>$f$</td>
<td>arbitrary function, e.g., $i_f = f(V, c_i)$</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant, C/equiv</td>
</tr>
<tr>
<td>$i$</td>
<td>Total current density, A/cm$^2$</td>
</tr>
<tr>
<td>$\bar{i}$</td>
<td>Steady-state total current density, A/cm$^2$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\tilde{i}$</td>
<td>Oscillating component of total current density, A/cm²</td>
</tr>
<tr>
<td>$i_f$</td>
<td>Faradic current density, A/cm²</td>
</tr>
<tr>
<td>$\overline{i}_f$</td>
<td>Steady-state Faradic current density, A/cm²</td>
</tr>
<tr>
<td>$\tilde{i}_f$</td>
<td>Oscillating component of Faradic current density, A/cm²</td>
</tr>
<tr>
<td>$i_0$</td>
<td>Exchange current density, A/cm²</td>
</tr>
<tr>
<td>$j$</td>
<td>Imaginary number, $\sqrt{-1}$</td>
</tr>
<tr>
<td>$k_A$</td>
<td>Rate constant for reaction identified by index A (units depend on reaction stoichiometry)</td>
</tr>
<tr>
<td>$K_i$</td>
<td>Dimensionless frequency, $K_i = \frac{\omega}{\Omega} \left( \frac{9\nu}{a^2D_i} \right)^{\frac{1}{2}} = \frac{\omega}{\Omega} \left( \frac{9}{a^2} \right)^{\frac{1}{2}} Sc_i^{\frac{1}{3}}$</td>
</tr>
<tr>
<td>$M_i$</td>
<td>Notation for species $i$</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrons produced when one reactant ion or molecule reacts</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant, J/mol/K</td>
</tr>
<tr>
<td>$R_e$</td>
<td>Ohmic resistance, $\Omega$ cm²</td>
</tr>
<tr>
<td>$R_{\text{t},A}$</td>
<td>Charge-transfer resistance associated with reaction A, $\Omega$ cm²</td>
</tr>
<tr>
<td>$r$</td>
<td>Radial coordinate, cm</td>
</tr>
<tr>
<td>$r_0$</td>
<td>Radius of disk, cm</td>
</tr>
<tr>
<td>$s_i$</td>
<td>Stoichiometric coefficient for species $i$, ($s_i &gt; 0$ for a reactant and $s_i &lt; 0$ for a product)</td>
</tr>
</tbody>
</table>
Chapter 13. Notation

$\text{Sc}_i$  Schmidt number, $\text{Sc}_i = \nu / D_i$

$T$  electrolyte temperature, K

$t$  time, s

$v_r, v_z$  radial and axial velocity components, respectively, cm/s

$V$  potential, V

$\overline{V}$  steady-state potential, V

$\dot{V}$  oscillating contribution to potential, V

$Z$  impedance, $\Omega \text{ cm}^2$

$z$  axial position, cm

$z_d$  diffusion impedance, $\Omega \text{ cm}^2$

$z_i$  charge for species $i$

**Greek**

$\alpha$  coefficient used in the exponent for a constant-phase element. When $\alpha = 0$, the element behaves as an ideal capacitor in parallel with a resistor.

$\alpha_A$  apparent transfer coefficient for reaction $A$

$\beta_A$  Tafel slope for reaction $A$, V

$\gamma_i$  Fractional surface coverage by species $i$
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma )</td>
<td>Maximum surface coverage</td>
</tr>
<tr>
<td>( \delta_i )</td>
<td>Characteristic diffusion length for species ( i )</td>
</tr>
<tr>
<td>( \hat{\theta} )</td>
<td>Homogeneous solution to the oscillating dimensionless convective diffusion equation</td>
</tr>
<tr>
<td>( \hat{\theta}'(0) )</td>
<td>Derivative of the solution to the oscillating dimensionless convective diffusion equation evaluated at the electrode surface</td>
</tr>
<tr>
<td>( \eta )</td>
<td>Surface overpotential, V</td>
</tr>
<tr>
<td>( \kappa_\infty )</td>
<td>Solution conductivity, ( (\Omega \text{ cm})^{-1} )</td>
</tr>
<tr>
<td>( \ell )</td>
<td>Characteristic length for a finite-length diffusion layer, ( \ell = \sqrt[3]{2.598 \nu^{1/3} D_i^{2/3} / \Omega} )</td>
</tr>
<tr>
<td>( \mu )</td>
<td>Viscosity, ( \text{g/cm s} )</td>
</tr>
<tr>
<td>( \nu )</td>
<td>Kinematic viscosity, ( \nu = \mu / \rho ), ( \text{cm}^2/\text{s} )</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Density, ( \text{g/cm}^3 )</td>
</tr>
<tr>
<td>( \tau )</td>
<td>Finite-length diffusion time constant, ( \tau = \ell^2 / D_i )</td>
</tr>
<tr>
<td>( \xi )</td>
<td>Normalized axial position, ( \xi = z / \delta_i )</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>Ohmic potential, ( \text{V} )</td>
</tr>
<tr>
<td>( \omega )</td>
<td>Frequency of perturbation, ( \text{rad/s} )</td>
</tr>
<tr>
<td>( \Omega )</td>
<td>Rotation speed, ( \text{rad/sec} )</td>
</tr>
</tbody>
</table>