Electrochemical Impedance Spectroscopy
with Application to Fuel Cells

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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. Time-Constant Dispersion
• Chapter 7. Regression Analysis
• Chapter 8. Error Structure
• Chapter 9. Kramers-Kronig Relations
• Chapter 10. Application to PEM Fuel Cells
• Chapter 11. Conclusions
• Chapter 12. Suggested Reading
• Chapter 13. Notation
Electrochemical Impedance Spectroscopy with Application to Fuel Cells

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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

1995

1998

2004

2007
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

\[ i_F = \overline{i}_{O_2} = n_{O_2} F k_{O_2} \overline{c}_{O_2} \exp \left\{ \frac{\alpha_{O_2} F}{RT} (\overline{V} - V_{O_2}) \right\} \]

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
- Faradaic current
- $C_{dl}$
- $R_e$
- $R_f$
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
• Chapter 2. Motivation
• Chapter 3. Impedance Measurement
• Chapter 4. Representations of Impedance Data
• Chapter 5. Development of Process Models
• Chapter 6. Time-Constant Dispersion
• Chapter 7. Regression Analysis
• Chapter 8. Error Structure
• Chapter 9. Kramers-Kronig Relations
• Chapter 10. Application to PEM Fuel Cells
• Chapter 11. Conclusions
• Chapter 12. Suggested Reading
• Chapter 13. Notation
Notation

- IUPAC Convention: Z’ and Z’’; i
- Present Work: Zr and Zj; j
Chapter 1. Introduction
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

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Steady-State Polarization Curve
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

\[ \Delta V = 10 \text{ mV} \]
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
  - \(<\sim 1\) kHz
Sinusoidal Perturbation

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

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

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

\[ i_f = f(V) \]

\[ V(t) \]
Sinusoidal Perturbation

Sinusoidal Perturbation

1 mHz

10 kHz

(V-V_0) / V_0

(i-i_0) / max(i-i_0)
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

![Graph showing Impedance Response with axes labeled Z_r and Z_j, and a peak at 100 Hz]
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

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

Chapter 2. Motivation

Impedance Spectrum

![Impedance Spectrum Graph](image)
Experimental Data

6 Repeated Measurements

Impedance, \( \Omega \)

Real

3% of \(|Z|\)

1% of \(|Z|\)

Imaginary

Frequency, Hz

0.1 1 10 100 1000 10000 100000
Impedance Spectroscopy vs. Step-Change Transients

- Information sought is the same
- Increased sensitivity
  - stochastic errors
  - frequency range
  - consistency check
- Better decoupling of physical phenomena
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**

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

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

\[ \frac{\omega}{2\pi} \int_{0}^{2\pi/\omega} AS \, dt = \frac{2A_0}{\pi} \cos(\phi_A - \phi_S) \quad \text{Has maximum value when} \quad \phi_A = \phi_S \]
Fourier Analysis:

equation: single-frequency input

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

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

\[ Z_r(\omega) = \text{Re} \left\{ \frac{V_r + jV_j}{I_r + jI_j} \right\} \]
\[ Z_j(\omega) = \text{Im} \left\{ \frac{V_r + jV_j}{I_r + jI_j} \right\} \]
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

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

\[ i(t) = i_0 \exp(baV) \]

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

\[ i_f = f(V) \]

\[ V(t) \]
Linearity

\( \frac{(I-I_0)}{\text{max}(I-I_0)} \)

\( \frac{(V-V_0)}{\Delta V} \)

- \( f = 1 \text{ mHz} \)
  - 1 mV
  - 20 mV
  - 40 mV

- \( f = 10 \text{ Hz} \)
  - 1 mV
  - 20 mV
  - 40 mV

- \( f = 100 \text{ Hz} \)
  - 1 mV
  - 20 mV
  - 40 mV

- \( f = 10 \text{ kHz} \)
  - 1 mV
  - 20 mV
  - 40 mV
Influence of Nonlinearity on Impedance

![Graph showing the influence of nonlinearity on impedance. The graph plots $Z_\text{r}$ vs. $Z_\text{j}$ with different voltage levels (1 mV, 20 mV, and 40 mV) indicated by different markers. There is also a model line.](image-url)
Influence of Nonlinearity on Impedance

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

| Voltage (mV) | \( |Z_j| / \Omega \text{ cm}^2 \) |
|-------------|----------------------------------|
| 1           |                                 |
| 20          |                                 |
| 40          |                                 |

- **Model**
- **1 mV**
- **20 mV**
- **40 mV**
**Guideline for Linearity**

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

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

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

\[ i_f = f(V) \]

\[ i(t)R_e \]

\[ \eta_s(t) \]

\[ V(t) \]
Influence of Ohmic Resistance

![Graph showing the influence of Ohmic Resistance](image)
Overpotential as a Function of Frequency

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

\[ i_f = f(V) \]

\[ \eta_s(t) \]

\[ V(t) \]

\[ i(t)R_e \]

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

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

\[ f / \text{Hz} \]

\[ |\eta_s| R_f / V (R_t + R_e) \]
Cell Design

- Use reference electrode to isolate influence of electrodes and membranes
• Seek uniform current/potential distribution
  – simplify interpretation
  – reduce frequency dispersion
Primary Current Distribution
Modulation Technique

• Potentiostatic
  – standard approach
  – linearity controlled by potential

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

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

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

• Galvanostatic
  – good for nonstationary systems
    • corrosion
    • drug delivery
  – requires variable perturbation amplitude to maintain linearity
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
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 EHD Experiment data]

- Data Set #2
- Data Set #4
- Data Set #1
Time per Frequency for 200 rpm

Frequency, Hz

Time per Measurement, s

△ Filter On
○ Filter Off
Impedance Scans

![Graph showing impedance scans with time intervals](image.png)
Impedance Scans

Elapsed Time / s

$\Delta \Theta$ Hz

$\square \Theta$ Hz

$\bigcirc \Theta$ Hz

$\bigtriangleup \Theta$ Hz

$f / \text{Hz}$
Time per Frequency Measured

\[ \frac{\Delta f}{s} \]

\[ f/\text{Hz} \]

- 5 cycles
- 3 cycles
- 5 seconds
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

\[ Z = Z_1 + Z_2 \]
\[ Y = \frac{1}{\frac{1}{Y_1} + \frac{1}{Y_2}} \]
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

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

Note:
\[ \omega = 2\pi f \]
\[ \omega \equiv \text{rad} / \text{s} \quad \text{or} \quad \text{s}^{-1} \]
\[ f \equiv \text{cycles} / \text{s} \quad \text{or} \quad \text{Hz} \]
Chapter 4. Representation of Impedance Data

**Impedance**

![Diagram showing an equivalent circuit with components R<sub>e</sub>, R<sub>f</sub>, and C<sub>dl</sub>](image)

Slope = 1

![Graph showing impedance magnitude and phase angle](image)

Slope = -1
Bode Representation

\[ Z = Z_r + jZ_j \]

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

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

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

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

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

Input & output are in phase

Input & output are out of phase
Constant Phase Element

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

\[ \frac{Z_j}{R_t} \]

\[ \frac{(Z_r - R_e)}{R_t} \]
CPE: Log Imaginary

Slope = + \( \alpha \)

Slope = - \( \alpha \)

Note: With a CPE (\( \alpha \neq 1 \), the asymptotic slopes are no longer \( \pm 1 \).
CPE: Modified Phase Angle

\[ \phi_{\text{adj}}(\infty) = -90(\alpha) \]

Note:
The high-frequency asymptote for the modified phase angle depends on the CPE coefficient \( \alpha \).
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

\[ Z'_r / \Omega \text{ cm}^2 \]

\[ Z_i / \Omega \text{ cm}^2 \]

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

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

\[ 0 \quad 10^{-3} \quad 10^{-2} \quad 10^{-1} \quad 10^0 \quad 10^1 \quad 10^2 \quad 10^3 \quad 10^4 \quad 10^5 \quad 10^6 \]

\[ f / \text{Hz} \]
**R_e-Corrected Bode Phase Angle**

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

\[ \phi_{adj}(\infty) = -90(\alpha) \]

\[ f / \text{Hz} \]

\[ \phi_{adj} \text{ / degree} \]

\[ \alpha = 1 \]
\[ \alpha = 0.7 \]
\[ \alpha = 0.5 \]
\[
|Z|_{\text{adj}} = \sqrt{(Z_r - R_{e,\text{est}})^2 + Z_j^2}
\]
Slope = $\alpha$

$\text{Log}(|Z_j|)$

$\text{slope} = \alpha$

$\text{slope} = -\alpha$

$\frac{|Z_j|}{\Omega \text{ cm}^2}$

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

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

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

![Graph showing impedance data for Mg alloy (AZ91) in 0.1 M NaCl.](image)
**Proposed Model**

\[
\begin{align*}
&Mg \xrightarrow{k_1} (Mg^+)_{ads} + e^- \\
&(Mg^+)_{ads} + H_2O \xrightarrow{k_2} Mg^{2+} + OH^- + \frac{1}{2} H_2 \quad \text{“negative difference effect” (NDE)} \\
&(Mg^+)_{ads} \xrightarrow{k_3} Mg^{2+} + e^- \\
&Mg^{2+} + 2OH^- \xrightarrow{k_4} Mg(OH)_2 \\
&Mg(OH)_2 \xrightarrow{k_5} MgO + H_2O
\end{align*}
\]

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\textsuperscript{2+}**
- **relaxation of (Mg\textsuperscript{+})\textsubscript{ads}**
- **intermediate**
\[ \log(|Z_j|) \]

Slope = \(-\alpha\)
Effective CPE Coefficient

\[ Q_{\text{eff}} = -\sin\left(\frac{\alpha \pi}{2}\right) \frac{1}{(2\pi f)^\alpha Z_j(f)} \]
R_e-Corrected Phase Angle

\[ \phi_{adj}(\infty) = -90\alpha \]

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

\( \alpha = 1 \) 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

![Graphs showing impedance data comparison to theory.](image)
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
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
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 electrolyte and interface with symbols](image-url)
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

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

\[ R_{t_2} = \delta_{t_2} / \kappa_{t_2} \]

<table>
<thead>
<tr>
<th>system</th>
<th>$\varepsilon$</th>
<th>$\delta / \text{Å}$</th>
<th>$C/\mu\text{F/cm}^{-2}$</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</td>
<td>6.7</td>
<td>120</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$ oxide</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

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

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

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

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

\[ A \rightarrow A^{z+} + ne^- \]

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

steady-state

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

oscillating component

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

\[ \tilde{i}_A = \frac{\bar{V}}{R_{t,A}} \]
\[ R_{t,A} = \frac{1}{K_A b_A \exp \left( b_A \bar{V} \right)} \]
Charging Current

\[ i = i_f + C_{dl} \frac{dV}{dt} \]
\[ \tilde{i} = \tilde{i}_f + j\omega C_{dl} \tilde{V} \]
\[ \tilde{i} = \frac{\tilde{V}}{R_{t,A}} + j\omega C_{dl} \tilde{V} \]
\[ = \tilde{V} \left( \frac{1}{R_{t,A}} + j\omega C_{dl} \right) \]
\[ \tilde{V} = \frac{R_{t,A}}{1 + j\omega R_{t,A} C_{dl}} \]
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 $R_{t,A}$

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

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

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

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

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

O + ne$^-$ → R

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

\[ \bar{i}_o = -n_o F D_o \frac{d\bar{c}_o}{dy} \bigg|_0 \]

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

\[ \tilde{i}_o = -n_o F D_o \frac{d\tilde{c}_o}{dy} \bigg|_0 \]

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

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

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

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

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

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

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

\[ \tilde{U} = \frac{\tilde{U}}{\tilde{i}} = \frac{\tilde{V}}{\tilde{i}} \]

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

\[ Z_O = R_e + \frac{R_{t,O} + z_{d,O}}{1+j\omega C_{dl} \left( R_{t,O} + z_{d,O} \right)} \]
Comparison to Circuit Analog

\[ Z_O = R_e + \frac{R_{t,O} + z_{d,O}}{1 + j \omega C_{dl} \left( R_{t,O} + z_{d,O} \right)} \]
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

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

reaction 2: formation of P

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

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

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

where

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

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

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

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

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

balance on $\gamma$

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

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

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

\[
= \frac{1}{R_t} + \frac{A}{j\omega + B}
\]

where

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

\[ R_e \quad C_{dl} \quad Z_f \]

\[ R = \frac{AR_f^2}{B + AR_f} \]

\[ L = \frac{1}{A} \quad R = \frac{A}{B} \]

\[ C = -\frac{1}{AR_f} \]
Corrosion of Steel

\[ i_f = i_{\text{Fe}} + i_{\text{H}_2} + i_{\text{O}_2} \]

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

\[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \]
Corrosion: \( \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \)

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

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

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

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

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

\[
\bar{i}_{Fe} = K_{Fe} \exp\left(\frac{2.303 \bar{V}}{\beta_{Fe}}\right)
\]

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

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

Important: Note the relationship among steady-state current density, Tafel slope, and charge transfer resistance.
H₂ Evolution: \[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \]

\[
\tilde{i}_{\text{H}_2} = -K_{\text{H}_2} \exp\left(-b_{\text{H}_2} \tilde{V}\right)
\]

\[
\tilde{i}_{\text{H}_2} = K_{\text{H}_2} b_{\text{H}_2} \exp\left(-b_{\text{H}_2} \tilde{V}\right) \tilde{\tilde{V}}
\]

\[
\tilde{i}_{\text{H}_2} = \frac{\tilde{\tilde{V}}}{R_{t,\text{H}_2}}
\]

\[
R_{t,\text{H}_2} = \frac{1}{K_{\text{H}_2} b_{\text{H}_2} \exp\left(-b_{\text{H}_2} \tilde{V}\right)}
\]
**O₂ Reduction:** \[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]

\[ \bar{i}_{\text{O}_2} = -K_{\text{O}_2} \bar{c}_{\text{O}_2,0} \exp\left(-b_{\text{O}_2} \bar{V}\right) \]

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

mass transfer: in terms of dimensionless gradient at electrode surface

\[
\tilde{i}_{O_2} = -n_{O_2} F D_{O_2} \frac{d\tilde{c}_{O_2}}{dy} \bigg|_0 \\
= -n_{O_2} F D_{O_2} \frac{\tilde{c}_{O_2,0}}{\delta_{O_2}} \tilde{\theta}'(0)
\]
O₂ Evolution: O₂ + 2H₂O + 4e⁻ → 4OH⁻

coupled expression

\[ \hat{i}_{O₂} = \frac{\tilde{V}}{R_{t,O₂} + \frac{\delta_{O₂}}{n_{O₂} F D_{O₂} \bar{c}_{O₂,0}} \frac{1}{b_{O₂}} \left( - \frac{1}{\bar{\theta}'(0)} \right)} \]

\[ = \frac{\tilde{V}}{R_{t,O₂} + z_{d,O₂}} \]

\[ z_{d,O₂} = \frac{\delta_{O₂}}{n_{O₂} F D_{O₂} \bar{c}_{O₂,0}} \frac{1}{b_{O₂}} \left( - \frac{1}{\bar{\theta}'(0)} \right) \]

\[ R_{t,O₂} = \frac{1}{K_{O₂} b_{O₂} \bar{c}_{O₂,0} \exp(-b_{O₂} \tilde{V})} \]
Capacitance and Ohmic Contributions

Faradaic

\[ \bar{i}_f = \sum i_f \]
\[ \tilde{i}_f = \sum \tilde{i}_f \]

Faradaic and Charging

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

Ohmic

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

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

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

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

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

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

\[ c_i = \bar{c}_i + \text{Re}\{\tilde{c}_i e^{j\omega t}\} \]

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

\[
\frac{1}{\theta_i'(0)} = - \frac{1}{\sqrt{j\omega\delta^2/D_i}}
\]
Rotating Disk
Chapter 5. Development of Process Models

Convective Diffusion

\[
\frac{\partial c_i}{\partial t} + v_r \frac{\partial c_i}{\partial r} + v_z \frac{\partial c_i}{\partial z} = D_i \left\{ \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial c_i}{\partial r} \right) + \frac{\partial^2 c_i}{\partial z^2} \right\}
\]

\[
v_z = \sqrt{\nu \Omega} \left\{ \frac{a \Omega}{\nu} z^2 + \frac{1}{3} \left( \frac{\Omega}{\nu} \right)^{3/2} z^3 + \frac{b}{6} \left( \frac{\Omega}{\nu} \right)^2 z^4 + \ldots \right\}
\]

\[
v_r = r \Omega \left\{ a \left( \frac{\Omega}{\nu} \right)^{1/2} z - \left( \frac{\Omega}{\nu} \right) \frac{z^2}{2} - \frac{b}{3} \left( \frac{\Omega}{\nu} \right)^{3/2} z^3 + \ldots \right\}
\]

\[
v_\theta = r \Omega \left\{ 1 - b \left( \frac{\Omega}{\nu} \right)^{1/2} z + a \left( \frac{\Omega}{\nu} \right)^{3/2} z^3 + \ldots \right\}
\]
Convective Diffusion in one-Dimension

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

\[
\sum_i s_i M_i^{z_i} = ne^-
\]

\[
c_i \rightarrow c_{i,\infty} \quad \text{as} \quad z \rightarrow \infty
\]

\[
D_i \frac{\partial c_i}{\partial z} = \frac{s_i i_f}{nF} \quad \text{at} \quad z = 0
\]

\[
i_f = f(\eta, c_i)
\]
**Sinusoidal Steady State**

\[ c_i = \bar{c}_i + \text{Re}\{\tilde{c}_i e^{j\omega t}\} \]

\[ j\omega \tilde{c} e^{j\omega t} + \nu_z \frac{d \bar{c}_i}{dz} + \nu_z \frac{d \tilde{c}_i}{dz} e^{j\omega t} - D_i \frac{d^2 \bar{c}_i}{dz^2} - D_i \frac{d^2 \tilde{c}_i}{dz^2} e^{j\omega t} = 0 \]

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

\[ K_i = \frac{\omega}{\Omega} \left(\frac{9\nu}{a^2 D_i}\right)^{1/3} = \frac{\omega}{\Omega} \left(\frac{9}{a^2}\right)^{1/3} \text{Sc}_i^{1/3} \]

\[ \xi = \frac{z}{\delta_i} \quad \delta_i = \left(\frac{3D_i}{a\nu}\right)^{1/3} \sqrt{\frac{\nu}{\Omega}} = \left(\frac{3}{a}\right)^{1/3} \frac{1}{\text{Sc}_i^{1/3}} \sqrt{\frac{\nu}{\Omega}} \]
Finite Length Warburg Impedance

\[ v_z \frac{\partial c_i}{\partial z} = 0 \]

\[ \ell = \sqrt{2.598 \nu^{1/3} D_i^{2/3}} \]

\[ z_d = z_d(0) \frac{\tanh \sqrt{j \omega \tau}}{\sqrt{j \omega \tau}} \]

\[ \tau = \frac{\ell^2}{D_i} = \frac{2.598 \text{Sc}^{1/3}}{\Omega} \]

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

\[
\frac{d^2 \tilde{\theta}_i}{d\xi^2} - v_z \frac{d\tilde{\theta}_i}{d\xi} - jK_i \tilde{\theta}_i = 0 \quad \tilde{\theta}_i(\xi) = \frac{\tilde{c}_i}{\tilde{c}_{i,0}}
\]

\[\tilde{\theta}_i \to 0 \quad \text{as} \quad \xi \to \infty\]

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

\[Z_D = -R_i \sum_i \left( \left. \frac{\partial f}{\partial c_{i,0}} \right|_{\eta, c_{j, j \neq i}} \right) s_i \frac{\delta_i}{nFD_i \tilde{\theta}_i'(0)} \]

\[Z_D = \frac{Z_D(0)}{\tilde{\theta}_i'(0)}\]
Numerical Solutions

Infinite Sc

One Term

\[ v_z = \sqrt{\nu \Omega} \left( -a \zeta^2 \right) \]
\[ \zeta = z \sqrt{\frac{\Omega}{\nu}}; \quad a = 0.51203 \]
\[ z_d = z_d(0) \left( -\frac{1}{\theta_0'(p \text{Sc}^{1/3})} \right) \]
\[ p = \frac{\omega}{\Omega} \]

Two Terms

\[ v_z = \sqrt{\nu \Omega} \left( -a \zeta^2 + \frac{1}{3} \zeta^3 \right) \]
\[ z_d = z_d(0) \left( -\frac{1}{\theta_0'(p \text{Sc}^{1/3})} + \frac{Z_1(p \text{Sc}^{1/3})}{\text{Sc}^{1/3}} \right) \]

Three Terms

\[ v_z = \sqrt{\nu \Omega} \left( -a \zeta^2 + \frac{1}{3} \zeta^3 + \frac{b}{6} \zeta^4 \right) \]
\[ b = -0.616 \]
\[ z_d = z_d(0) \left( -\frac{1}{\theta_0'(p \text{Sc}^{1/3})} + \frac{Z_1(p \text{Sc}^{1/3})}{\text{Sc}^{1/3}} + \frac{Z_2(p \text{Sc}^{1/3})}{\text{Sc}^{2/3}} \right) \]
**Coupled Diffusion Impedance**

\[
Z_d = \frac{Z_{d,outer} + \frac{D_{i,outer}}{D_{i,inner}} \frac{\delta_{i,inner}}{\delta_{i,outer}} Z_{d,inner}}{Z_{d,inner}Z_{d,outer} \left( j\omega \frac{\delta_{inner}^2}{D_{i,inner}} \right) + \frac{D_{i,outer}}{D_{i,inner}} \frac{\delta_{i,inner}}{\delta_{i,outer}}}
\]
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.
Basic Impedance Spectroscopy

Chapter 6. Time Constant Dispersion

- CPEs can arise from surface or axial distributions
- CPE parameters can be interpreted in terms of capacitance, depending on type of distribution
- Time-constant dispersions can be modeled explicitly.
Types of Distributions

• Surface

• Axial
Surface Distributions

(a) 

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

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

or

\[ R_e, Q, \alpha \]

(b) 

\[ R_{e,f}, C_{e,f} \]

\[ R_{\text{eff}}, C_{\text{eff}} \]
Axial Distributions
Relationship between $Q$ and $C$

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

• Surface Distribution

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

• Axial Distribution

$$C_{\text{eff}} = Q^{1/\alpha} R_f^{(1-\alpha)/\alpha}$$


Determination of Film Thickness

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

\[
\begin{array}{c|c}
R_1 & C \\
R_2 & C \\
R_3 & C \\
R_4 & C \\
R_5 & C \\
R_6 & C \\
\end{array}
\]

\[
\begin{array}{c|c}
& f_{RC} = (2\pi R_1 C)^{-1} \\
& f_{RC} = (2\pi R_2 C)^{-1} \\
& f_{RC} = (2\pi R_3 C)^{-1} \\
& f_{RC} = (2\pi R_4 C)^{-1} \\
& f_{RC} = (2\pi R_5 C)^{-1} \\
& f_{RC} = (2\pi R_6 C)^{-1} \\
\end{array}
\]
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
Porous Electrodes
deLevie Model

\[ R_0 = \frac{\rho}{\pi r^2} \]

\[ Z_0 = \frac{Z_{eq}}{2\pi r} \]

Under the assumption that \( Z_0 \) and \( R_0 \) are independent of \( x \)

\[ Z_{deLevie} = (R_0 Z_0)^{1/2} \coth(\ell \sqrt{\frac{R_0}{Z_0}}) \]

\[ Z = R_e + \frac{Z_{deLevie}}{n} \]

\[ Z = R_e + \frac{(\rho Z_{eq})^{1/2}}{\sqrt{2\pi nr^3/2}} \coth \left( \ell \sqrt{\frac{2\rho}{r Z_{eq}}} \right) \]
## Limiting Behavior

<table>
<thead>
<tr>
<th>$\ell \sqrt{2\rho / rZ_{eq}}$</th>
<th>$\coth\left(\ell \sqrt{2\rho / rZ_{eq}}\right)$</th>
<th>description</th>
<th>Parameters obtainable from regression</th>
</tr>
</thead>
<tbody>
<tr>
<td>large</td>
<td>1</td>
<td>Semi-infinite pores</td>
<td>$r^{3/2}n$</td>
</tr>
<tr>
<td>small</td>
<td>$\left(\ell \sqrt{2\rho / rZ_{eq}}\right)^{-1}$</td>
<td>Planar surface</td>
<td>$2\pi n \ell r$</td>
</tr>
<tr>
<td>intermediate</td>
<td>intermediate</td>
<td>Shallow pores</td>
<td>Two combinations of $r$, $n$, and $\ell$; i.e., $r^{3/2}n$ and $\ell / \sqrt{r}$</td>
</tr>
</tbody>
</table>
Consumption of Free Chlorine in Municipal Water Supplies

Cast Iron Pipes

Fe → Fe^{2+} + 2e^{-}

2Fe^{2+} + HOCl + H^+ ⇌ 2Fe^{3+} + Cl^- + H_2O

\[ \frac{1}{2}O_2 + 2H^+ + 2e^- ⇌ H_2O \]

**Issues**

- Coupled electrochemical reactions
- Surface films
- Convective diffusion
- History and time-dependent parameters
- Identification of corrosion rate

Diagram showing different rust types:
- Red Rust ($\alpha$-FeOOH, $\alpha$-Fe$_2$O$_3$)
- Green Rust & Carbonates ($\text{Fe}^{2+}$ and $\text{Fe}^{3+}$)
- Black Rust ($\text{Fe}_3\text{O}_4$)
- Evian® Water
- Cast Iron
Chapter 6. Time-Constant Dispersion

Model Development

No Free Chlorine

2 mg/l Free Chlorine
Model for Impedance Response

(a) \[ Z = R_e \]

(b) \[ Z_a = Z_c + \frac{Z_a}{Z_c} R_f \]

(c) \[ Z_D = C_{dl}^c R_{t_c} + Z_D \]

Z_c = \sqrt{R_0 Z_0} \coth\left(\frac{L}{\lambda}\right) \quad \lambda = \sqrt{\frac{Z_0}{R_0}}
**Impedance Data**

3 days

![Impedance Data for 3 days](image)

7 days

![Impedance Data for 7 days](image)

28 days

![Impedance Data for 28 days](image)
While use of a CPE may lead to improved regressions, the meaning can be ambiguous, and the physical system may not follow the specific distribution implied in the CPE model.

Distributed time-constant systems can be modeled explicitly.

Not all depressed semi-circles correspond to a CPE behavior.
Electrochemical Impedance Spectroscopy

Chapter 7. Regression Analysis

- Regression response surfaces
  - noise
  - incomplete frequency range
- Adequacy of fit
  - quantitative
  - qualitative

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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

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

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

\[ \chi^2 = \sum_{i=1}^{N_{\text{dat}}} \frac{(Z_i - Z(\omega_i \mid p))^2}{\sigma_i^2} \]

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

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

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

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.
Chapter 7. Regression Analysis

**Effect of Noisy Data**

**no noise**

**noise: 1% of modulus**

Note: use of log scale for parameters

All parameters fixed except \( R_3 \) and \( \tau_3 \)
Resulting Spectrum

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

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

- 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

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

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

-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  |
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

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

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

\[ -\frac{\mathcal{Z}_j}{\Omega} \]

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

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

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

\[
f / \text{Hz}
\]

±2\(\sigma\) noise level
Imaginary Residuals

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

\[ f / \text{Hz} \]

\[ \pm 2\sigma \text{ noise level} \]
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)

\[ Z_j / \Omega \]

\[ Z_r / \Omega \]
Phase Angle

\[ -\frac{Z_j}{\Omega} \]
Modified Phase Angle

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

![Graph showing the relationship between \(-Z_j/\Omega\) and \(f/\text{Hz}\).](image)

- For a given frequency \(f\), the variable \(-Z_j/\Omega\) is plotted on the vertical axis.
- The frequency \(f\) is shown on the horizontal axis, ranging from \(10^{-2}\) to \(10^4\) Hz.
- The graph demonstrates how the variable changes with different frequencies.
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.
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

inadequate model noise (frequency domain)
Weighting Strategies

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

<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</td>
</tr>
<tr>
<td>Proportional Weighting</td>
<td>( \sigma_r \neq \sigma_j ) ( \sigma_r = \alpha_r</td>
</tr>
<tr>
<td>Experimental</td>
<td>( \sigma_r = \sigma_j ) ( \sigma = \alpha</td>
</tr>
<tr>
<td>Refined Experimental</td>
<td>( \sigma_r = \sigma_j ) ( \sigma = \alpha</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 Fe(CN)$_6^{3-}$ on a Pt Disk, Imaginary Replicates @ 120 rpm, 1/4 $i_{lim}$
Reduction of Fe(CN)$_6^{3-}$ on a Pt Disk, Real Replicates @ 120 rpm, 1/4 $i_{lim}$
Reduction of Fe(CN)$_6^{3-}$ on a Pt Disk, Error Structure @ 120 rpm, $1/4 i_{lim}$
Reduction of Fe(CN)₆³⁻ on a Pt Disk,
Error Structure @ 120 rpm, 1/4 \( i_{\text{lim}} \)
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
Electrochemical Impedance Spectroscopy

Chapter 9. Kramers-Kronig Relations

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

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Contraints

• 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)

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

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

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

Kramers-Kronig in an expectation sense

\[ E(Z_j(\omega)) = \frac{2\omega}{\pi} E \left( \int_0^\infty \frac{Z_r(x) - Z_r(\omega) + \varepsilon_r(x) - \varepsilon_r(\omega)}{x^2 - \omega^2} \, dx \right) \]

\[ E(Z_r(\omega) - Z_r(\infty)) = E \left( \frac{2}{\pi} \int_0^\infty \frac{-xZ_j(x) + \omega Z_j(\omega) - x\varepsilon_j(x) + \omega\varepsilon_j(\omega)}{x^2 - \omega^2} \, dx \right) \]
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

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

\[
\frac{Z(x) - Z(\omega)}{(x^2 - \omega^2)}
\]

\[
\frac{Z(x) - Z(\omega)}{(x^2 - \omega^2)}
\]

f / Hz

Correct Value

Interpolated Value
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
Electrochemical Impedance Spectroscopy

Chapter 10. Application to PEM Fuel Cells

- Error analysis for EIS data
- Model development in terms of proposed reaction mechanisms
- Integration with Independent measurements

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**Issues for PEM Fuel Cell Impedance**

- Instrument artifacts
- Nonstationary behavior
- Nonuniform surfaces
- Complicated mass transfer geometry
- Side reactions
Sample Impedance Data

- Pure Inductance
- Mass Transfer
- Capacitive Loop
- Inductive Loop

Approach for Impedance Analysis

• Measurement Model
  – Assess stochastic error structure of data
  – Instrument artifacts
  – Nonstationary behavior

\[
\begin{align*}
\tau_1 &= R_1C_1 \\
\tau_2 &= R_2C_2 \\
\tau_k &= R_kC_k \\
\end{align*}
\]

\begin{align*}
(1) &\quad (2) &\quad \cdots &\quad (k) &\quad \cdots &\quad (K) \\
R_0 &\quad R_1 &\quad R_2 &\quad R_k &\quad R_K
\end{align*}

• Process Model
  – Based on proposed reactions
Experimental Results

Operating Conditions
T : 40°C, P : 1 atm.
Flow Rate : 0.1 l/m for H₂, 0.5 l/m for O₂

Steady State Measurement
Current Range : 0 – 0.5 A/cm²
Increment : 10 mA/30 Sec.

EIS Measurement
Galvanostatic Mode
Frequency : 0.001 – 3,000 Hz
Amplitude : 10 mA

![Graph showing polarization curve and Nyquist plot.](image-url)
Replicated Impedance Scans

![Graph showing impedance scans with various markers for different time points.](image-url)
Stochastic Error Structure

\[ \sigma_r = \sigma_j = \frac{\gamma |Z|^2}{R_m} \]

\[ \gamma = 6.7855 \times 10^{-01} \]

\[ R_m = 100 \]
Bias Errors at High Frequency

![Graph showing bias errors at high frequency](image)
High-frequency artifacts extend to negative imaginary values
Bias Error at Low Frequency

First Scan of Impedance Measurement

![Graphs showing impedance measurements over frequency](image-url)
Normalized Residual Errors

First Scan of Impedance Measurement
Bias Errors at Low Frequency

Second Scan of Impedance Measurement
Normalized Residual Errors

Second Scan of Impedance Measurement
Impedance Process Model
Development
Proposed Reactions

1. Hydrogen oxidation and oxygen reduction

2. Hydrogen oxidation and oxygen reduction with peroxide intermediate

3. Hydrogen oxidation and oxygen reduction with Pt deactivation
Assumptions:
- Uniform membrane properties
- Uniform surface overpotential
- No convection
- Diffusion through stagnant film of finite thickness
- Uniform surface and distribution of reactants and products
Steps in Model Development

- Reaction Mechanisms
- Steady-State Current Expressions
- Polarization Curve

Apply Sinusoidal Perturbation

- Faradaic Impedance
- Double Layer Capacitance
- Electrolyte Resistance
- Overall Impedance

Graphs showing potential vs. current and impedance vs. frequency.
Model Development: Case 1

- Oxygen Reduction

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

- Hydrogen Oxidation

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \]
Model 1: Simple Reaction Kinetics

[Diagram of a PEM fuel cell with labeled components: H₂, O₂, GDL, CAL, membrane, and O₂, H₂O. The diagram shows the flow of H₂ and O₂ to the anode and cathode.]
Model 1: Simple Reaction Kinetics

Diagram of a PEM fuel cell with labels for GDL, CAL, membrane, and connections for $H_2$, $O_2$, and $O_2, H_2O$.
Steady-State Current Density: 1

\[ \bar{i}_{H_2} = K_{H_2} \bar{C}_{H_2}(0) \exp(b_{H_2} \bar{\eta}_{H_2}) \]

\[ \bar{i}_{O_2} = -K_{O_2} \bar{C}_{O_2}(0) \exp(-b_{O_2} \bar{\eta}_{O_2}) \]

\[ i_{H_2} = -i_{O_2} \]
Model Predictions: Case 1

![Graphs showing model predictions compared to experimental data. The left graph plots potential (V) against current (A), while the right graph plots impedance (Z) against current density (J). Each graph includes data points and curves for both experimental data and Model 1.](image-url)
Model Development: Case 2

- Oxygen Reduction
  
  \[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \]
  
  \[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \]

- Hydrogen Oxidation
  
  \[ \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \]

Model 2: Peroxide Intermediate
Steady-State Current Density: 2

\[ \bar{i}_{O_2} = -K_{O_2} \bar{C}_{O_2}(0) \left( 1 - \bar{\gamma}_{H_2O_2} \right) \exp \left( -b_{O_2} \bar{\eta}_{O_2} \right) \]

\[ \bar{i}_{H_2O_2} = -K_{H_2O_2} \bar{C}_{H_2O_2}(0) \bar{\gamma}_{H_2O_2} \exp \left( -b_{H_2O_2} \bar{\eta}_{H_2O_2} \right) \]

\[ \bar{i}_{H_2} = K_{H_2} \bar{C}_{H_2}(0) \exp \left( b_{H_2} \bar{\eta}_{H_2} \right) \]

\[ i_{H_2} = - \left( i_{O_2} + i_{H_2O_2} \right) \]
Model 2 Response Compared with Data

**Graph 1:**
- **X-axis:** Current / A
- **Y-axis:** Potential / V
- **Legend:** Experimental data (circles), Model 2 (line)

**Graph 2:**
- **X-axis:** Resistance / Ω cm²
- **Y-axis:** Impedance / Ω cm²
- **Legend:** Experimental data (circles), Model 2 (line)
Model 2 Response Compared with Data

![Graph showing experimental data and model 2 response.](image_url)
Model 2 Response Compared with Data

Experimental data

Model 2

Potential / V

Current / A

Z_j / Ω cm^2

Z_r / Ω cm^2
Model Development: Case 3

• Oxygen Reduction

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]
\[ Pt + H_2O \rightleftharpoons 2H^+ + 2e^- + PtO \]
\[ PtO + 2H^+ \rightarrow Pt^{2+} + H_2O \]

• Hydrogen Oxidation

\[ H_2 \rightarrow 2H^+ + 2e^- \]

Model 3: Pt dissolution and formation of PtO

Diagram showing the flow of hydrogen (H₂) and oxygen (O₂) through different components of the PEM fuel cell, including GDL (Gas Diffusion Layer), CAL (Current collector and catalyst layer), and the membrane. The diagram includes symbols for the concentration of Pt at different locations (C₀,a, C₀,c, Z₀,a, Z₀,c, Z₁,c, Z₂,c, R_e) and the resistances and capacitances associated with the cell.
Steady-State Current Density: 3

\[
\bar{i}_{O_2,\text{Pt}} = -k_{\text{eff}} C_{O_2}(0) \exp(-b_{O_2} \bar{\eta}_{O_2})
\]

\[
\bar{i}_{Pt} = (1 - \bar{\gamma}_{PtO}) k_{Pt,f} \exp(b_{Pt} \bar{\eta}_{Pt}) - k_{Pt,b} \bar{\gamma}_{PtO} \exp(-b_{Pt} \bar{\eta}_{Pt})
\]

\[
r_{PtO} = k_{PtO} \bar{\gamma}_{PtO} C^{2}_{H^+}(0)
\]

\[
k_{\text{eff}} = k_{Pt} + (k_{PtO} - k_{Pt}) \bar{\gamma}_{PtO}
\]

\[
\bar{i}_{H_2} = k_{H_2} C_{H_2}(0) \exp(b_{H_2} \bar{\eta}_{H_2})
\]
Model 3 Response Compared with Data

The diagrams show the comparison between experimental data and Model 3 response for the polarization curves of PEM fuel cells. The graphs depict the relationship between current density and potential, with both experimental data and model predictions plotted. The data indicates a close match between the model predictions and the experimental results, demonstrating the effectiveness of Model 3 in simulating PEM fuel cell behavior.
Model 3 Response Compared with Data

![Graph showing comparison between experimental data and Model 3 response](image-url)

- **Z_j / Ω cm²**
- **Z_r / Ω cm²**

- Experimental data
- Model 3

![Graph showing comparison between potential and current](image-url)

- **Potential / V**
- **Current / A**
Model 3 Response Compared with Data

![Graph showing the comparison between Model 3 and experimental data](image)

The graph illustrates the comparison between the model prediction (Model 3) and experimental data for the impedance (Z) and potential. The graphs show the relationship between impedance (Z) and current (A) as well as potential (V) and current (A). The experimental data is represented by circles, and the model prediction is represented by a line.

- **Z / Ω cm²**: The real and imaginary parts of the impedance are plotted against each other. The graph shows a semicircular arc, which is characteristic of electrochemical impedance spectroscopy (EIS) data.
- **Potential / V**: This graph shows the change in potential with respect to current. The model and experimental data are closely aligned, indicating good agreement between the model and experimental results.

From the graphs, it is evident that Model 3 provides a reasonable fit to the experimental data, suggesting that the model accurately predicts the response of the PEM fuel cell under the conditions tested.
Model development suggests supporting experiments

- Formation of peroxide
- Signs of membrane degradation
- Formation of PtO
- Reduction in electrochemically active area
- Dissolved Pt in outflow
Evidence for PtO$_x$

Helena and Jason Weaver, University of Florida
Integrated Approach

Model

EIS Experiment

weighted regression analysis

Model and data agree

Model and data do not agree
Flooding and EIS response

EIS response as a function of current density collected at 40°C.

Effect of flooding is visible
EIS Response at 70°C

Effect of flooding is visible
Standard deviation of the Impedance

\[ \sigma_{r, \text{obs}} / \Omega \text{ cm}^2 \]

\[ \sigma_{j, \text{obs}} / \Omega \text{ cm}^2 \]

\[ 0.10 \text{ Hz} \]

\[ 10 \text{ Hz} \]

\[ 100 \text{ Hz} \]

Current Density / A cm\(^{-2}\)

Current Density / A cm\(^{-2}\)
Normalized Noise in Impedance Response

![Graph showing normalized noise in impedance response]

- Shows flooding - 10X more noise
- Shows need for better base error structure
Calculated Parameters
Fractional Surface Coverage of Intermediates

**Graph 1:**
- X-axis: Potential / V
- Y-axis: Fractional Surface Coverage
- Solid line: Hydrogen Peroxide
- Dashed line: Platinum Oxide

**Graph 2:**
- X-axis: Current / A
- Y-axis: Fractional Surface Coverage
- Solid line: Hydrogen Peroxide
- Dashed line: Platinum Oxide
Low-frequency Inductive Loops in PEM Fuel Cells

- Satisfy the Kramers-Kronig relations
- Are consistent with
  - Peroxide formation
  - Pt dissolution
- May provide a means to study reactions that limit lifetime
- Demonstrates synergistic approach
  - Error structure analysis
  - Model development
  - Use of supporting measurements
Chapter 11. Conclusions
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
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  – UF: O. Crisalle
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  – CIRIMAT: N. Pébère

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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 for application notes.
Suggested Reading
Process Models


Suggested Reading
Orazem group work on Fuel Cells

Suggested Reading
Measurement 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

Plotting

Chapter 13. Notation

Roman

$a$  coefficient in the Cochran expansion for velocity, $a = 0.51023$

$b$  coefficient in the Cochran expansion for velocity, $b = -0.61592$

$c_i$  concentration of reacting species $i$, mol/cm$^3$

$\bar{c}_i$  steady-state value of the concentration of reacting species $i$, mol/cm$^3$

$\ddot{c}_i$  Oscillating component of the concentration of reacting species $i$, mol/cm$^3$

$c_{i,o}$  concentration of species $i$ on the electrode surface, mol/cm$^3$

$\bar{c}_{i,o}$  steady-state value of the concentration of species $i$ on the electrode surface, mol/cm$^3$

$\ddot{c}_{i,o}$  Oscillating component of the concentration of species $i$ on the electrode surface, mol/cm$^3$

$c_\infty$  bulk concentration of the reacting species, mol/cm$^3$

$C_d$  double layer capacitance, F/cm$^2$

$C_{dl}$  double layer capacitance, F/cm$^2$

$D_i$  diffusion coefficient of species $i$, cm$^2$/s

$f$  arbitrary function, e.g., $i_f = f(V, c_i)$
### Chapter 14. Notation

- **$F$**: Faraday’s constant, C/equiv
- **$i$**: Total current density, A/cm²
- **$\bar{i}$**: Steady-state total current density, A/cm²
- **$\tilde{i}$**: Oscillating component of total current density, A/cm²
- **$i_f$**: Faradic current density, A/cm²
- **$\bar{i}_f$**: Steady-state Faradic current density, A/cm²
- **$\tilde{i}_f$**: Oscillating component of Faradic current density, A/cm²
- **$i_0$**: Exchange current density, A/cm²
- **$j$**: imaginary number, $\sqrt{-1}$
- **$k_A$**: rate constant for reaction identified by index $A$ (units depend on reaction stoichiometry)
- **$K$**: dimensionless frequency, $K_i = \frac{\omega}{\Omega} \left( \frac{9v}{a^2D_i} \right)^{\frac{1}{2}} = \frac{\omega}{\Omega} \left( \frac{9v}{a^2} \right)^{\frac{1}{2}} \text{Sc}_{i}^{1/3}$
- **$M_i$**: notation for species $i$
- **$n$**: number of electrons produced when one reactant ion or molecule reacts
- **$R$**: universal gas constant, J/mol/K
- **$R_e$**: Ohmic resistance, $\Omega$ cm²
- **$R_{i,A}$**: Charge-transfer resistance associated with reaction $A$, $\Omega$ cm²
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<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>
<tr>
<td>$Sc_i$</td>
<td>Schmidt number, $Sc_i = \frac{v}{D_i}$</td>
</tr>
<tr>
<td>$T$</td>
<td>electrolyte temperature, K</td>
</tr>
<tr>
<td>$t$</td>
<td>time, s</td>
</tr>
<tr>
<td>$v_r, v_z$</td>
<td>radial and axial velocity components, respectively, cm/s</td>
</tr>
<tr>
<td>$V$</td>
<td>potential, V</td>
</tr>
<tr>
<td>(\bar{V})</td>
<td>steady-state potential, V</td>
</tr>
<tr>
<td>$\tilde{V}$</td>
<td>oscillating contribution to potential, V</td>
</tr>
<tr>
<td>$Z$</td>
<td>impedance, $\Omega \text{ cm}^2$</td>
</tr>
<tr>
<td>$z$</td>
<td>axial position, cm</td>
</tr>
<tr>
<td>$z_d$</td>
<td>diffusion impedance, $\Omega \text{ cm}^2$</td>
</tr>
<tr>
<td>$z_i$</td>
<td>charge for species $i$</td>
</tr>
</tbody>
</table>

**Greek**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>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.</td>
</tr>
<tr>
<td>$\alpha_a$</td>
<td>apparent transfer coefficient for reaction A</td>
</tr>
</tbody>
</table>
$\beta_A$  Tafel slope for reaction A, V
$
\gamma_i$  Fractional surface coverage by species $i$
$\Gamma$  Maximum surface coverage
$\delta_i$  characteristic diffusion length for species $i$
$\bar{\theta}$  homogeneous solution to the oscillating dimensionless convective diffusion equation
$\bar{\theta}'(0)$  derivative of the solution to the oscillating dimensionless convective diffusion equation evaluated at the electrode surface
$\eta$  surface overpotential, V
$\kappa_\infty$  solution conductivity, $(\Omega \text{ cm})^{-1}$
$\ell$  characteristic length for a finite-length diffusion layer, $\ell = \sqrt{2.598 \nu^{1/3} D_i^{2/3} / \Omega}$
$\mu$  viscosity, g/cm s
$\nu$  kinematic viscosity, $\nu = \mu / \rho$, cm$^2$/s
$\rho$  density, g/cm$^3$
$\tau$  finite-length diffusion time constant, $\tau = \ell^2 / D_i$
$\xi$  normalized axial position, $\xi = z / \delta_i$
$\Phi$  ohmic potential, V
$\omega$  frequency of perturbation, rad/s
$\Omega$  rotation speed, rad/sec