BIOFUEL CELL POLARIZATION ESTIMATION: INVERSION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPIC MEASUREMENTS

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Application: Electrochemical Spectroscopy for Biofuels

Mathematical Model

Nonlinear Fitting

Linear Fitting
  Numerical Quadrature
    Integration by $t$
    Integration by $s$
    Right Preconditioner
  Regularization
    Parameter Choice
  Simulations

Nonnegative Least Squares
  Simulations

Conclusions
Physical Experiment: Microbial Electrolysis Cell for anaerobic bacteria

(a) Fuel cell

(b) Geobacter

(c) Microbial electrolysis cell

Figure: Geobacter, fuel cells, and waste water: Single-chamber microbial electrolysis cell consisting of a carbon fiber anode with a stainless steel current collector and a stainless steel cathode is used to convert food wastes into hydrogen in a single step.
ARB in fuel cell should be electrically self-sufficient

(a) Cyclic Voltammograms (CVs)

(b) Potential Loss inside ARB cell

Figure: (a) CVs of an ARB biofilm during its growth phase (7.8-11.8 d). Nernst-Monod relationship compared against the CVs (dotted lines). (b) CV explaining the potential profile for an ARB biofilm. The Nernst-Monod relationship (red dotted line) shows that most potential losses occur inside the ARB’s cell.
Figure: Schematic of the microbial electrochemical cells used for Electrochemical Impedance Spectroscopy (EIS)
Nyquist Plot of EIS impedance measurements

Figure: Nyquist plot and fitting by equivalent circuit model (ECM) for an ARB biofilm tested at -0.35 vs Ag/AgCl.
Goals

Given EIS measurements can we find

1. The underlying resistance
2. The equivalent circuit model
3. Number of resistances / processes
4. Chemical environment that minimizes ARB potential loss
Mathematical Model

Fredholm Integral Equation

- Small input current and measured output voltage leads to impedance measurements $Z(\omega)$ for angular frequency $\omega$

$$Z(\omega) = R_0 + R_{pol} \int_0^\infty \frac{g(t)}{1 + i \omega t} \, dt,$$

(1)

- Kernel $h(\omega, t) = \frac{1}{1 + i \omega t}$ - is not square integrable.
- $R_0$ and $R_{pol}$ are unknown parameters.
- Distribution function of relaxation times (DRT) $g(t)$

$$\int_0^\infty g(t) \, dt = 1 \text{ and } g(t) > 0 \text{ is unknown}$$
The DRT $g(t)$

**Simple Resistance - Capacitance Circuit**

Cole-Cole or ZARC element. (literature dependent)

$$g_{RQ}(t) = \frac{1}{2\pi t} \frac{\sin \beta \pi}{\cosh \left( \beta \ln \left( \frac{t}{t_0} \right) \right) + \cos \beta \pi},$$  \hspace{1cm} (2)

The impedance is analytically given

$$Z_{RQ}(\omega) = \frac{1}{1 + (i\omega t_0)^\beta},$$  \hspace{1cm} (3)

$0 < \beta < 1$ and distribution of time constants $t_0$.

Constant Phase element $Q$ and resistance $R$. 

![Diagram of simple resistance-capacitance circuit](image)
The DRT $g(t)$

Simple network of resistance - capacitance circuits

May also be realized by a lognormal distribution for the DRT

$$g_{LN}(t) = \frac{1}{t\sigma\sqrt{2\pi}} \exp \left( -\frac{(\ln(t) - \mu)^2}{2\sigma^2} \right).$$ (4)

No analytic form for the impedance is given.

Figure: Three lognormals and a weighted linear combination
Comparison of LN and RQ for one process chosen to align

(a) DRTs: $t$–space

(b) DRTs: $s$–space

(c) Nyquist plot

(d) Components $Z_1$

(e) Components $Z_2$

Figure: Simulated exact data measured at 65 logarithmically spaced points in $\omega$. In each case the solid line indicates the RQ functions and the $\diamond$ symbols the LN functions. $s = \log(t)$. 
Nonlinear Fitting

If analytic $Z(\omega)$ is known fitting to $Z$ is possible
No analytic form for $Z$ nonlinear fitting integrates the DRT
What error is incurred by a **wrong** choice of model?
The residuals are small

Figure: Residual norms fitting one process to the impedance spectrum of a DRT consisting of one process with white noise.
The impact

(a) RQ by LN

(b) LN by RQ

(c) RQ by LN:

(d) LN by RQ:

Figure: Fitting functions with the consistent mean values obtained over 50 noisy selections.

- True RQ $\beta = 0.72$, $t_0 = 0.1$, true LN $\sigma = 0.83$, $t_0 = 0.1$.
- RQ to LN gives $\beta = 0.86$ and $t_0 = 0.2$
- LN to RQ gives $\sigma = 1$ and $t_0 = 0.03$
- Location and height of peak is incorrect

Small residual does not imply good fitting
Linear Formulation: Integration in $t$

\[
Z(\omega) = Z_1(\omega) + iZ_2(\omega)
= \left( R^0 + R^{\text{pol}} \int_0^\infty \frac{g(t)}{1 + \omega^2 t^2} \, dt \right) - iR^{\text{pol}} \left( \int_0^\infty \frac{\omega t g(t)}{1 + \omega^2 t^2} \, dt \right),
= \left( R^0 + R^{\text{pol}} \int_0^\infty h_1(\omega, t) g(t) \, dt \right) - iR^{\text{pol}} \left( \int_0^\infty h_2(\omega, t) g(t) \, dt \right).
\]

Given $N$ quadrature points and $[T_{\text{min}}, T_{\text{max}}]$,

\[
\int_{T_{\text{min}}}^{T_{\text{max}}} g(t) h_k(\omega, t) \, dt \approx \sum_{n=1}^{N} a_n g(t_n) h_k(\omega, t) \tag{5}
\]

Matrices $(A_k)_{mn} = a_n h_k(\omega_m, t_n) \quad 1 \leq m \leq M, \ 1 \leq n \leq N$.

Measurements $(b_1)_m \approx Z_1(\omega_m) - R^0$ and $(b_2)_m \approx -Z_2(\omega_m)$

$(x)_n \approx g(t_n)$ satisfies the discrete linear systems

\[
A_k x \approx b_k, \quad k = 1, \ldots, 3, \quad A_3 = [A_1; A_2]
\]

Defining finer resolution also yields square $A_4 = [A_1^e, A_2^e]$
Systems are ill-conditioned whether Simpson’s or trapezium quadrature rules. Values for \( \omega = 2\pi f \) are based on logarithmic spacing on the interval \((f_{\text{min}}, f_{\text{max}}) = (10^{-1.7}, 10^5)\), consistent with the measured data.

Figure: The condition of matrices \( A_k, k = 1 \ldots 4 \) (\( \text{cond}(A_k) \)) plotted against the pairs \((l, j)\) indicating \([T_{\min}(l), T_{\max}(j)]\) with \( T_{\min} = [5e-2, 1e-2, 3e-3] \) and \( T_{\max} = [8e3, 4e4, 2e5] \) for both Simpson’s and trapezium quadrature rules. Values for \( \omega = 2\pi f \) are based on logarithmic spacing on the interval \((f_{\text{min}}, f_{\text{max}}) = (10^{-1.7}, 10^5)\), consistent with the measured data.
Model Error for the LN $g(t)$: integrating in $t$

Truncation error occurs due to semi-infinite integral: $E^\text{trunc}_k$

Quadrature error occurs due to limited sampling $E^\text{quad}_k$

Exact measurements $\hat{b}_k(\omega, t_0, \sigma)$ are contaminated

$$\hat{b}_k(\omega, t_0, \sigma) = \int_0^\infty g(t, t_0, \sigma) h_i(t, \omega) dt + E^\text{trunc}_k(\omega, T_{\text{min}}, T_{\text{max}}, t_0, \sigma)$$

$$+ E^\text{quad}_k(\omega, T_{\text{min}}, T_{\text{max}}, t_0, \sigma, N),$$

Figure: Larger error for $h_1$ than for $h_2$. Clearly depends on $g(t)$.
Transformation \( s = \ln(t) \)

Let \( s = \ln(t) \)

\[
Z(\omega) = \int_{0}^{\infty} h(\omega, t) g(t) \, dt = \int_{-\infty}^{\infty} h(\omega, e^{s}) f(s) \, ds, \quad f(s) := t g(t).
\]  

(7)

For the DRTs (2)-(4) we obtain the functions

\[
f_{\text{RQ}}(s) = \frac{1}{2\pi} \frac{\sin(\beta \pi)}{\cosh(\beta (s - \ln(t_0))) + \cos(\beta \pi)} \]

(8)

\[
f_{\text{LN}}(s) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{(s - \mu)^2}{2\sigma^2} \right), \quad \ln(t_0) = \mu - \sigma^2,
\]

(9)

Quadrature uses constant step in \( s \)

\[
\int_{-\infty}^{\infty} h(\omega, e^{s}) f(s) \, ds \approx \int_{s_{\text{min}}}^{s_{\text{max}}} h(\omega, e^{s}) f(s) \, ds \approx \Delta s \sum_{n=1}^{N} h(\omega, e^{s_{n}}) f(s_{n}).
\]

(10)
Figure: Quadrature error for a single RQ (left) LN(right) process with $N = 65$ for quadrature in $s$ and $t$ as a function of $\omega$, plotted on a log-log scale.
\[
\int_{-\infty}^{\infty} h_k(\omega, e^s) f(s) \, ds \approx \Delta s \sum_{n=1}^{N} h_k(\omega, e^{s_n}) f(s_n) + f(s_N) r_{k,N}(\omega, e^{s_N}) + f(s_1) r_{k,1}(\omega, e^{s_1}).
\] (11)

\[
r_{k,N}(\omega, e^{s_N}) := \begin{cases} 
\frac{1}{2} \ln(1 + (\omega e^{s_N})^{-2}) & k = 1 \\
\frac{\pi}{2} - \tan^{-1}(\omega e^{s_N}) & k = 2,
\end{cases}
\]

\[
r_{k,1}(\omega, e^{s_1}) := \begin{cases} 
\frac{1}{2} \Delta s h_1(\omega, e^{s_1}) & k = 1 \\
\tan^{-1}(\omega e^{s_1}). & k = 2.
\end{cases}
\]

yields with \( H_k(s) = h_k(\omega, s) f(s) \) and \( \int_{-\infty}^{s_1 - \Delta s} f(s) \, ds \leq \delta(f) \)

\[
E_k(\omega) \leq \begin{cases} 
\frac{\epsilon}{2} (\Delta s + \ln(2)) + \delta(f) + \frac{(s_N-s_1)^3}{12N^3} (N + 1) |H_1''(\zeta)| & k = 1 \\
\epsilon \pi + \frac{(s_N-s_1)^3}{12N^2} |H_2''(\zeta)|, & k = 2.
\end{cases}
\]
Impact on Conditioning

<table>
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<th>$A_2$</th>
<th>$A_3$</th>
<th>$A_4$</th>
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<td>1.4e + 13</td>
<td>7.5e + 12</td>
<td>4.1e + 20</td>
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<td>(10)</td>
<td>2.9e + 09</td>
<td>7.4e + 07</td>
<td>4.6e + 08</td>
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<td>2.8e + 09</td>
<td>7.4e + 07</td>
<td>4.6e + 08</td>
<td>9.0e + 18</td>
</tr>
</tbody>
</table>

**Table**: Comparing condition number of matrices with different quadratures for the optimal selection of the nodes for $t_n$, using $t = 1/\omega$.

Transformation acts as a **right** preconditioner on the system. Use matrix $A_3$ if sufficient data for resolution of the solution.
Right preconditioning separates frequencies of the basis

(a) $A_1$: $U$ above and $V$ below.  
(b) $A_1^s$: $U$ above and $V$ below.

Figure: Normalized Cumulative Periodograms and Kolmogorov-Smirnov 95% confidence bounds for white noise for the matrices $A_1$ and $A_1^s$. The NCPs for $A_2$ and $A_2^s$ show a similar separation of the frequency content of the respective basis vectors.
Why is the spectral decomposition important?

Consider mapping $A$ which takes solution $x$ to data $b$. $Ax = b$.

**Definition (Well - Posed (Hadamard in 1923))**

*Inverse problem of finding $x$ from $b$ is called well-posed if all*

- **Existence** a solution exists for any data $b$ in data space,
- **Uniqueness** the solution $x$ is unique
- **Stability** continuous dependence of $x$ on $b$: the inverse mapping $b \rightarrow x$ is continuous.

**Definition (Ill-Posed: according to Hadamard)**

*A problem is ill-posed if it does not satisfy all three conditions for well-posedness. Alternatively*

1. $b \not\in \text{range}(A)$
2. inverse is not unique because more than one image is mapped to the same data,
3. an arbitrarily small change in $b$ can cause an arbitrarily large change in $x$. 
Systems are Ill-conditioned - the discrete problem is ill-posed

Figure: An example solution for real data provide no useful information - the solution is sensitive to noise in the data and the floating point arithmetic calculations
Regularization

The improved matrices are still ill-conditioned and regularization is required.

\[ x = \arg \min \{ \|Ax - b\|^2 + \lambda^2 \|Lx\|^2 \} \] (12)

Tikhonov regularization controls the smoothness of the solution.

\( \lambda \) is a regularization parameter, many techniques exist to find \( \lambda \) - some require statistical properties of the data measurements.

\( L \) controls the smoothness - standard choices \( I \) or \( D_1 \) or \( D_2 \) - derivative operators.

Given \( \lambda \) an explicit solution is given with respect to the basis vectors, and solves the normal equations

\[(A^T A + \lambda^2 L^T L)x = A^T b\]
Example Solutions and Residuals - range of $\lambda$: regularizers $I$, $L_1$ and $L_2$
For a given residual norm there does not exist a solution with smaller semi-norm than the one provided by the L-Curve, in that sense the solution is optimal.
Residual Periodogram - uses power series to detect noise

Suppose for a given vector $y$ that it is a time series indexed by position, i.e. index $i$.

**Diagnostic 1** Does the histogram of entries of $y$ generate histogram consistent with $y \sim \mathbb{N}(0, 1)$? (i.e. independent normally distributed with mean 0 and variance 1) Not practical to automatically look at a histogram and make an assessment

**Diagnostic 2** Test the expectation that $y_i$ are selected from a white noise time series. Take the Fourier transform of $y$ and form cumulative periodogram $z$ from power spectrum $c$

$$c_j = |(\text{dft}(y)_j|^2, \quad z_j = \frac{\sum_{i=1}^{j} c_j}{\sum_{i=1}^{q} c_i}, \quad j = 1, \ldots, q,$$

**Automatic:** Test is the line $(z_j, j/q)$ close to a straight line with slope 1 and length $\sqrt{5}/2$?
Measure Deviation from Straight Line: Residual Vector : optimal black

Figure: **Low noise**: Testing for white noise: Calculate the cumulative periodogram and measure the deviation from the “white noise” line for several $\lambda$. The vector with highest white noise content indicates transfer of noise to the residual.
**Figure: High noise**: Testing for white noise: Calculate the cumulative periodogram and measure the deviation from the “white noise” line for several $\lambda$. The vector with highest white noise content indicates transfer of noise to the residual.
Simulations: Generate Data to test approach: RQ solid line, LN ◊.
Solutions by LLS: Minimum error red, LC · blue and NCP – green

Figure: Mean error and example LLS solutions. .1% noise, RQ-A data set, matrix $A_4$. 
Solutions by LLS: Minimum error red, LC · blue and NCP – green

Figure: Mean error and example LLS solutions. .1\% noise, LN-A data set, matrix $A_4$. 
Figure: Mean error and example LLS solutions. 0.1% noise, RQ-B data set, matrix $A_4$. 

(a) $L = I$  
(b) $L = L_1$  
(c) $L = L_2$  
(d) $L = I$  
(e) $L = L_1$  
(f) $L = L_2$
Figure: Mean error and example LLS solutions. 1% noise, LN-B data set, matrix $A_4$. 
Observations

1. Nonnegativity of $g(t)$ not maintained.
2. Boundary effects are observed
3. Important to impose additional constraints.
The DRT satisfies $g(t) > 0$. The transformed DRT, $f(s) = tg(t) > 0$ also. Hence nonnegative least squares:

$$x = \arg\min \{ \|Ax - b\|^2 + \lambda^2 \|Lx\|^2, \text{ s.t. } x \geq 0\}$$  \hspace{1cm} (13)$$

$$= \arg\min \left\{ \left\| \begin{pmatrix} A & b \end{pmatrix} \right\|_2^2, \text{ s.t. } x \geq 0 \right\}$$  \hspace{1cm} (14)$$

Depends on regularization parameter $\lambda$

Can be solved using a standard solver - Matlab \texttt{lsqnonneg}

Impose bounds on solution $x > 0$.

Parameter choice - solve for multiple $\lambda$ and pick solution as for the LS problem.
Measure Deviation from Straight Line: Residual Vector: optimal black

Figure: Low noise: Testing for white noise: Calculate the cumulative periodogram and measure the deviation from the “white noise” line for several $\lambda$. The vector with highest white noise content indicates transfer of noise to the residual.
Measure Deviation from Straight Line: Residual Vector : optimal black

Figure : High noise: Testing for white noise: Calculate the cumulative periodogram and measure the deviation from the “white noise” line for several $\lambda$. The vector with highest white noise content indicates transfer of noise to the residual.
Solutions by NNLS: Minimum error red, LC · blue and NCP – green

Figure: Mean error and example NNLS solutions. .1% noise, RQ-A data set, matrix $A_4$. 
Figure: Mean error and example NNLS solutions. $0.1\%$ noise, RQ-B data set, matrix $A_4$. 

Solutions by NNLS: Minimum error red, LC blue and NCP green.
Solutions by NNLS: Minimum error red, LC · blue and NCP – green

Figure: Mean error and example NNLS solutions. .1% noise, LN-A data set, matrix $A_4$. 

(a) $L = I$  
(b) $L = L_1$  
(c) $L = L_2$  

(d) $L = I$  
(e) $L = L_1$  
(f) $L = L_2$
Solutions by NNLS: Minimum error red, LC \cdot blue and NCP \textcolor{green}{} – green

\begin{align*}
(a) \quad L &= I \\
(b) \quad L &= L_1 \\
(c) \quad L &= L_2 \\
(d) \quad L &= I \\
(e) \quad L &= L_1 \\
(f) \quad L &= L_2
\end{align*}

\textbf{Figure}: Mean error and example NNLS solutions. .1\% noise, LN-B data set, matrix $A_4$. 
Observations

1. Nonnegativity of $g(t)$ is maintained.
2. Boundary effects better preserved
3. Additional constraints very helpful
4. Parameter choice extends easily to the NNLS case for small scale problem
5. Information on noise level would be helpful - allow other methods UPRE, $\chi^2$ etc
6. For high noise all solutions are smoothed

All work with undergraduates
Conclusions

**General**
- Small Scale problem - standard parameter choice can be used for regularization parameter estimation in NNLS
- Residual Periodogram extends successfully
- There is still work to do for 1d problems.

**EIS**
- The analysis of quadrature in this case demonstrates lack of model error despite low sampling
- Transformation is equivalent to a right preconditioning
- The ability to recognize more multiple processes in presence of noise is challenging
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