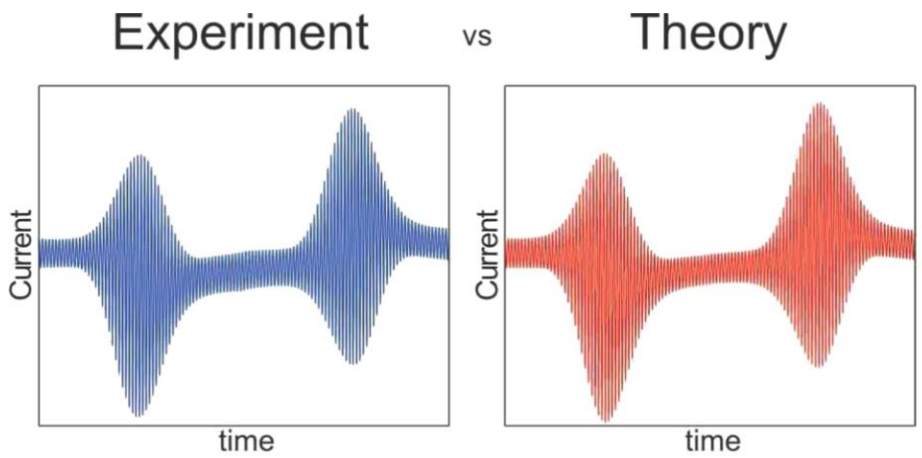
Modeling and Parameter Estimation of Single Electrode Redox Reaction

Electron transfer reactions (also known as reduction-oxidation, or redox reactions) are fundamental to life on Earth, mediating the biological energy pathways of both photosynthesis and respiration. Understanding these processes is essential for the development of synthetic alternatives, since the “natural” redox proteins and enzymes are built from sustainable resources, are optimized by evolution and operate effectively at room temperature and pressures, using water as a solvent.

The field of voltammetry is concerned with interrogating and analyzing redox reactions at electrodes. An input voltage signal is input to an electrochemical cell comprising of the chemical species in solution around an electrode. This species reacts at the electrode surface, generating an output current signal. This current signal is analyzed to determine the properties of the reaction. The behavior of many such reactions, and the parameters describing the kinetics, are well understood. However, for any given redox reaction, it remains a challenge to give an accurate, reliable estimation of these parameters.



$$\left[Fe(CN)_6\right]^{3-} + e^- \rightleftarrows \left[Fe(CN)_6\right]^{4-}$$

Project

The papers by Adamson et. al. [1] and Morris et. al. [2] provide mathematical models for a single electron transfer process either confined to a surface [1] or in solution [2]. The surface confined model consists of a differential-algebraic equation (DAE) that is solved over time. The solution model consists of a 1D diffusion process with a non-linear boundary condition at the electrode.

The candidate will:

- solve one or both of these models numerically in order to produce an accurate MATLAB implementation of the forward model, using a suitable time-stepping scheme and finite differences for the diffusion.
- attempt to recover the parameters (the so-called “inverse problem”) from simulated noisy “data” by minimizing a least squares cost function using MATLAB’s `fminsearch`.

Many extensions of this project are possible, depending on the interests of the candidate, for example:

- Using real experimental data (provided) for the inverse problem.
- Using an different non-linear optimization method such as CMA-ES, a genetic algorithm.
- Maximizing a Bayesian likelihood function instead of minimizing a cost function.

- Using MCMC sampling and the Bayesian likelihood to sample from the posterior distribution of the parameters, given the noisy data.
- Measuring the information content contained in the experimental data, using the Fisher Information matrix.
- Experimenting with different input voltage waveforms, comparing their information content and usefulness when recovering the parameters.

Pre-requisites

Knowledge/interest of MATLAB or another computing environment will be helpful, but this may be gained in Michaelmas Term. The project will involve 1D finite difference schemes and time-stepping methods (backward Euler is sufficient). These are covered in "Numerical Solution of Differential Equations I and II" but a candidate could also learn them as needed without too much difficulty.

References

[1] Adamson, H., Robinson, M., Bond, P. S., Soboh, B., Gillow, K., Simonov, A. N., ... & Parkin, A. (2017). Analysis of HypD Disulfide Redox Chemistry via Optimization of Fourier Transformed ac Voltammetric Data. Analytical chemistry, 89(3), 1565-1573.

[2] Morris, G. P., Simonov, A. N., Mashkina, E. A., Bordas, R., Gillow, K., Baker, R. E., ... & Bond, A. M. (2013). A comparison of fully automated methods of data analysis and computer assisted heuristic methods in an electrode kinetic study of the pathologically variable [Fe (CN) 6] 3–/4–process by AC voltammetry. Analytical chemistry, 85(24), 11780-11787.

[3] A. J. Bard and L. R. Faulkner. Electrochemical Methods: Fundamentals and Applications. John Wiley & Sons, Inc, 2001.

[4] K. W. Morton and D. F. Mayers. Numerical Solution of Partial Differential Equations: An Introduction. Cambridge University Press, 2005.