

Voltammetric Analysis of Carbon Microelectrode Measurements based on the Hilbert Transform: A Theoretical and Experimental Study

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Keywords: Electrochemical detection, Hilbert transform, nonlinear reaction dynamics, voltammetric experiments

Electrochemical measurements relate the response of an electrode to an input signal and the chemical process occurring on the electrode surface. Electrochemistry holds a key position in analytical sciences since it offers the possibility to characterize chemical compounds both through thermodynamic or kinetic information by translating their current or voltage response to a specific form of excitation. Various combinations of electrode materials and input signals have been investigated in the past to improve selectivity and detection limits of techniques such as amperometry, voltammetry etc. (Bard and Faulkner, 2001). In recent years the remarkable progress in miniaturization techniques also had an impact on electrochemistry, extending electrochemical methodology into new domains of space (single cells, membrane pores), time (steady state, fast scan), and precision. Electrochemical sensing techniques have become essential for the elucidation of various phenomena, including physiological processes (Wightman et al., 1991) and biological detection (Cui et al., 2001).

In the beginning of the 1980's Wightman and co-workers first pointed out the advantages of conducting electrochemical measurements with ultramicroelectrodes, disc shaped "voltammetric" electrodes of less than 10 μ m radius, showing that they exhibit very

different properties than electrodes of conventional size (Wightman, 1981). At such small scales diffusion limitations are not nearly as severe thereby enabling in vivo experiments and measurement of faster heterogeneous rate constants. These very attractive features gave rise to the need for a more rigorous understanding of the physical processes occurring on the electrode interface.

In voltammetric techniques, a potential waveform is applied to an electrochemically active system and the current response is measured to identify the compound that underwent the electrochemical step. Various excitation waveforms of the potential have been studied in the past, such as linear, sawtooth, square wave, staircase etc (Bond, 1980). dc linear sweep and dc cyclic voltammetry have emerged as the most frequently used electrochemical techniques in analytical chemistry. In the first, the potential is swept linearly over the range of interest whereas in the second at a predetermined point the scan rate is inverted and the potential is scanned back.

Sinusoidal or ac voltammetry superimposes the ramp potential of dc cyclic voltammetry with an ac sinusoidal perturbation. ac voltammetry is an elegant and accurate method of electroanalysis when studying electrode processes and in many cases it has been shown to be superior to the widely used dc voltammetric methods (Bond, 1980) allowing the investigation of phenomena occurring on different time scales. Recently, Brazill et al. (2002) were able to achieve considerable improvement in selectivity by optimising the frequency and phase angle of the ac potential waveform to the analyte of interest. They used this method to study various biological molecules such as neurotransmitters, peptides etc.

The main reason that ac voltammetry has not become as popular as other electrochemical techniques is probably due to the lack of an appropriate theoretical framework on which data analysis can be based. The Fast Fourier Transform (FFT) has emerged as the most common method of analysis. The application of FFT when using a

harmonic excitation has allowed, amongst other things, good discrimination of the voltammetric signals from the background (Long and Weber, 1992). Nevertheless, even if the FFT analysis provides valuable insights into various process parameters, it has been shown that it cannot quantify adequately the nonlinear behaviour related to kinetic or thermodynamic dispersion or other phenomena which influence the thin-film process (Guo et al., 2004).

It is widely known that electrode potential strongly affects reaction kinetics occurring on the electrode surface. When investigating realistic electrochemical processes, total reversibility is rare and one must estimate the forward and backward reaction rates of the redox couple under investigation in order to predict concentration gradients and current response. The most popular method of estimating electrochemical kinetic constants is by using the highly nonlinear Butler-Volmer kinetic equations.

For these nonlinear processes, time-series analysis with tools which were developed for periodic, stationary and linear data-sets, such as most FFT methods, are not adequate. A nonlinear process does not obey the principle of superposition, nor does it have the property of frequency-preservation. Nonlinear systems can not be completely characterized by impulse or frequency response functions, nor can their output signals be derived by linear transform or convolution methods (Lynn, 1989).

Recently, a signal processing technique suitable for non-stationary non-periodic data series, the Hilbert transform, was utilised in the analysis of a population of electrochemical oscillators in order to measure emerging coherence (Kiss et al., 2002). Through the definition of the complex analytic signal using the Hilbert transform, we can define an instantaneous amplitude and phase, and from the phase an instantaneous frequency can be deduced. Arundell et al. (2004) were the first to use this technique for purely analytical purposes and showed, for voltammetric data, that the instantaneous amplitude and frequency of the current response can be related to electrochemical phenomena occurring

on electrode surface. Moreover, other electrode processes such as passivation could also be detected by the same technique.

Simulation results and experimental measurements show that the temporal analysis based on the Hilbert transform can offer valuable insight into electrochemical surface processes. By solving the nonlinear Butler-Volmer kinetic equation for a number of interesting excitation forms, we show that kinetic and thermodynamic parameters can be deduced from the analysis allowing the identification of the compounds adsorbed on the electrode surface. From the same analysis other parameters, such as bilayer capacitance, of the adsorbed film can also be obtained. Addition of white noise in the simulation results tests the robustness of the method. Experimental measurements on adsorbed species such as Prussian blue and azurin illustrate the simplicity of applying the technique on time-series and the quality of the results. It is shown that voltammetric detail can be seen even in the presence of large charging currents, which normally preclude quantitative analysis with conventional tools.

The same signal processing technique proves to be a valuable tool in systems where diffusion is the governing mechanism. Diffusion has a crucial impact on the electrochemical response in macroscopic systems especially when the kinetics of the reaction are faster than mass transport. At the microscale diffusion becomes significant when monitoring electrochemical processes *in vivo*, such as vesicular release in neurophysiology. Two-dimensional diffusion-reaction simulations are calculated for a number of excitations and the current response is treated with the Hilbert transform to show the impact of mass transport on the temporal analysis. Furthermore, we can deduce compound-specific parameters that can be used to characterise the species undergoing the electrochemical reaction. Finally we show that the conclusions deduced from the simulations can be applied to experimental measurements using hexaamineruthenium chloride.

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