

177d Determination of Electrochemical Parameters of Surface Confined Species: from Nonlinear Dynamics and Pattern Formation to Electron-Transfer Characteristics

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In the last decades, electrochemical sensing techniques have been used to investigate a plethora of biological processes [1-4]. For instance amperometry, where the electrode voltage is kept constant, and voltammetry, where the electrode voltage is perturbed according to a predefined waveform, are the methods of choice for a wide range of measurements in neuroscience [5-7]. From the current response of the electrode, information about the electron transfer characteristics and identity of the analyte can be drawn. While amperometric methods offer good temporal resolution they cannot discriminate between different molecules undergoing an electrochemical reaction step at the electrode [8]. On the other hand, a large number of physiological functions in biology are regulated by dynamic multicomponent systems and thus, a technique that is capable of monitoring different analytes simultaneously is required in order to study them. Voltammetric techniques have been shown to offer improved selectivity as well as improved discrimination against non-faradaic contributions to the signal. Ultramicroelectrodes (voltammetric electrodes of typically less than $10\ \mu\text{m}$) enable the accurate measurement of time-dependent currents and have proven to be a very useful tool for *in vivo* biological experiments offering unparalleled spatial and temporal resolution combined with good selectivity [9, 10].

From the electrode current response, information about the underlying mechanisms of electron transfer can be drawn. Nevertheless, the major difficulty of these methods lies in their interpretation. Electrochemical signals are intrinsically nonlinear and nonstationary. Additionally, double layer capacitance effects often distort the current response severely. Hitherto there have been few alternatives to the Fast Fourier Transform (FFT) technique for frequency analysis although fundamental assumptions of the theory, namely periodicity, continuity and linearity, are not satisfied.

The Hilbert transform (HT) offers an alternative tool of data analysis that can overcome these difficulties. It results in instantaneous frequency (f) and amplitude (a) as a function of time providing a viable method for nonstationary, nonlinear signal processing [11]. Recently, the HT was used to study the voltammetric time series of a population of electrochemical oscillators [12] as well as for purely electroanalytical purposes [13].

In this contribution we show how kinetic and thermodynamic properties of surface bound molecules can be estimated accurately using ac voltammetry as excitation perturbation and the time domain patterns resulting from the HT analysis. We will illustrate theoretically how the macroscopic parameters that characterise electron transfer, i.e. k_0 , α and E_0 from the Butler-Volmer methodology, can be estimated with high accuracy from our pattern formation analysis. This method proves extremely robust even in the presence of large charging currents, which normally preclude quantitative analysis with conventional tools. From the HT analysis of simulated voltammograms we introduce the characteristic pattern parameters (ω , ω_0) which allow the determination of these physical properties directly from the time domain [14]. Furthermore, we will attempt to show how microscopic electron-transfer parameters such as recombination energy ϵ or gating effects that are of significance in numerous biological/environmental processes influence our time domain-analysis. Additionally, we shall derive from our analysis the optimal voltage excitation parameters for the investigation of the analyte of interest. Experimental data with azurin, a model blue copper protein, will support our theoretical evidence. ‡

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