PHYSICAL MATHEMATICS SEMINAR

LARGE-AMPLITUDE/HIGH-FREQUENCY VOLTAMMETRY: FROM NONLINEAR DYNAMICS AND SIGNAL PROCESSING TECHNIQUES TO NEUROTRANSMITTER MEASUREMENTS AND 'ELECTROCHEMICAL BUTTERFLIES'

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ABSTRACT:

In the last decades, electrochemical sensing techniques have been used in a plethora of applications. More specifically, voltammetry, where the electrode voltage is perturbed according to a predefined waveform, is the method of choice for a wide range of measurements, for instance in neuroscience. [1]

The major difficulty of voltammetric methods lies in their interpretation. Electrochemical signals are intrinsically nonlinear and nonstationary. For a long time voltammetric measurements were confined in small-amplitude perturbations to avoid nonlinear effects of electron transfer. Lately, ac voltammetry, which uses a 'slow' ramp superimposed on a 'faster' large amplitude sinusoid as voltage perturbation, has drawn considerable attention due to its enhanced voltammetric detail as well as its ability to investigate phenomena on different timescales. Such large-amplitude/high-frequency excitation waveforms though cause capacitance interference to the current to become substantial. Hitherto there have been few alternatives to the FFT technique for frequency analysis, although fundamental assumptions of the theory, namely periodicity and linearity, are not satisfied. As a result, ac voltammetric data-sets could either not be fully interpreted or their interpretation involves very complicated computations.

In this presentation a method will be introduced based on a nonstationary signal processing technique, the Hilbert transform [2], which is valid for analysing nonlinear phenomena. [3] It enables the accurate estimation of a set of species- and process-specific parameters in order to monitor the dynamical behaviour of the environment under investigation as well as the sensor/environment interface in the presence or absence of mass-transport effects. [4, 5] The proposed methodology proves very robust towards enhanced capacitance interference, mainly, and noise levels which normally preclude quantitative analysis with conventional tools. Experimental verification will be shown for (a) the immobilised blue-copper protein azurin, (b) freely diffusing $Ru(NH_3)_6^{2+/3+}$ and $Fe(CN)_6^{4-/3-}$ undergoing out-of-sphere electron transfer at the electrode surface and (c) neurotransmitter molecules such as dopamine and serotonin which play a fundamental role in cell signalling and are very difficult to discriminate *in vivo* with conventional voltammetric techniques.

Literature

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