



# Probing Electrode Heterogeneity using Fourier-Transformed Alternating Current Voltammetry: Protocol Development



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## ABSTRACT

Fourier-transformed large amplitude alternating current voltammetry (FTACV) provides a sensitive analytical tool for the discrimination of electrode reactions that are complicated by surface heterogeneity. In this paper, it is shown how the FTACV response at a dual-electrode system comprised of different electrode materials having different heterogeneous charge transfer ( $k_1^0$  and  $k_2^0$ ) can be resolved into its individual electrode kinetics components without prior knowledge of the electrode size ratio ( $\theta_1:\theta_2$ ). This is possible when one process is reversible and the other is quasi-reversible; achievable by careful selection of the FTACV frequency. The applicability of the FTACV method over a wide range of electrode kinetic values and size ratios is considered for conditions under which numerical simulations based on a 1D diffusion model are adequate to describe the mass transport problem.

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## 1. Introduction

Modern developments in materials science has seen the advent of composite electrode materials which are highly heterogeneous in nature. Consequently, understanding the voltammetric response of electrochemically heterogeneous electrode surfaces has become essential [1–7]. However, the analysis of electrochemical responses at heterogeneous surfaces remains challenging due to the often random nature of surface-to-surface variations.

We have previously reported the use of Fourier-transformed large amplitude alternating current voltammetry (FTACV) [8–12] to resolve the heterogeneous charge transfer kinetics ( $k^0$  values) associated with the simple one-electron  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$  process derived at a dual (glassy carbon (GC)+polycrystalline boron-doped diamond (pBDD)) electrode configuration; a model system representing an electrode surface with two distinctly different activity domains [13]. The FTACV method was shown to provide advantages over techniques such as chronoamperometry [14,15] and direct current voltammetry (DCV) [2,3,16] for the elucidation of electrode kinetics at heterogeneous electrode surfaces due to the strong dependence of current magnitude on  $k^0$  in all AC harmonics [10,11,17].

In our previous work [13], the high kinetic sensitivity of the FTACV method on  $k^0$  allowed differences in the heterogeneous rate constants ( $k_1^0$  and  $k_2^0$  values) that differ by  $\sim 1$ -2 orders of magnitude in a dual - electrode configuration to be quantified and resolved into their individual responses. Significantly, all FTACV higher order harmonic data analysed to determined  $k^0$  values are derived from a single experiment [10] using the same electrode. In contrast, in traditional DCV, each data set is obtained in separate experiments at different scan rates such that the computation of  $k^0$  values is likely to be complicated by experiment-to-experiment variabilities [18].

In this study, we have generalised the application of our previously reported FTACV model [13] so that the standard rate constants,  $k_1^0$  and  $k_2^0$ , and size ratios,  $\theta_1:\theta_2$ , of two different activity domains of a dual - electrode surface do not limit the deconvolution of the current measured into the individual components. This is achievable provided that  $k_1^0$  is fully reversible and  $k_2^0$  is quasi - reversible on the FTACV timescale chosen. This outcome is possible as data obtained from a single FTACV experiment can be analysed with respect to each individual AC harmonic component which display a different level of kinetic sensitivity (different measurement timescales).

The applicability of this model is experimentally demonstrated with the deconvolution of the electrochemical response from a dual (Pt+pBDD) electrode configuration for the simple one-electron  $\text{FcCH}_2\text{OH}^{0/+}$  process. Conditions under which FTACV data can be treated by a 1D diffusion model are also discussed.

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## 2. Theory and Simulations

The common form of the FTACV technique and the one used in this paper comprises a sinusoidal potential waveform of amplitude,  $\Delta E/V$ , and frequency,  $f/Hz$ , superimposed onto a linear potential ramp,  $E_{DC}$ . The current includes the fundamental frequency component along with the higher order components,  $2f$ ,  $3f$ ,  $4f$ , etc. which are resolved using a Fourier transform (FT) – band filtering – inverse FT sequence of operation [8–12]. The FTACV data are then analysed by comparison of the resolved AC harmonic components to suitable models, analogous to the strategy adopted in modern DCV methods.

In this work, we are interested in comparing the voltammetric response for the oxidation of redox-active molecules undergoing simple outer - sphere electron transfer (ET) at a model surface containing two types of active sites under both DC and AC voltammetric conditions where no overlap of diffusion layers occurs between the two regions. In order to probe the implications of electrode surface heterogeneities on the voltammetric response, a surface consisting of two distinctly different kinetic properties ( $k^0_1, \alpha_1, k^0_2$  and  $\alpha_2$ ) can be modelled in terms of two regions which share a total surface area,  $A_{total}$ . The fractions of the total area of the two regions can be related by  $\theta_1$  and  $\theta_2 (= 1 - \theta_1)$ . Fick's 2<sup>nd</sup> law of planar diffusion was numerically solved to obtain time and spatial-dependence information for the concentration of the reduced species associated with the charge transfer process given by:

$$\frac{\partial c_i}{\partial t} = D \left( \frac{\partial^2 c_i}{\partial x^2} \right) \quad (1)$$

where  $D$  is the diffusion coefficient of the electroactive species of interest and  $c_i$  is the concentration of the electroactive species of interest at electrode material,  $i$ .

The electrode kinetics at both electrodes were assumed to obey the Butler-Volmer relationship which describes the potential - dependence of the ET rate at the electrode/electrolyte interface as follows:



In the above equation,  $k_{ox}$  and  $k_{red}$  are the oxidation and reduction rate constants given by:

$$k_{ox,i} = k_i^0 \exp \left[ \frac{(1 - \alpha_i) F \eta}{RT} \right] \quad (3)$$

$$k_{red,i} = k_i^0 \exp \left[ \frac{-\alpha_i F \eta}{RT} \right] \quad (4)$$

In equation 3 and 4,  $\alpha$  and  $k^0$  are the transfer coefficient (reasonably assumed to be 0.50 in this case) and the standard heterogeneous charge transfer rate constant at the formal reversible potential,  $E^0$ , of the redox couple,  $F$  is the Faraday constant,  $R$  is the universal constant,  $T$  is the absolute temperature and  $\eta = E(t) - E^0$  where  $E(t)$  is the potential applied to the electrode at time,  $t$ . In all simulations,  $E^0 = 0.00$  V and  $\alpha_i = 0.50$ .

For the voltammetric experiments described herein,  $E(t)$  is given by the sum of the DC voltage ramp,  $E_{DC}(t)$  and a sinusoidal component,  $E_{AC}(t)$ :

$$E(t) = E_{DC}(t) + E_{AC}(t) \quad (5)$$

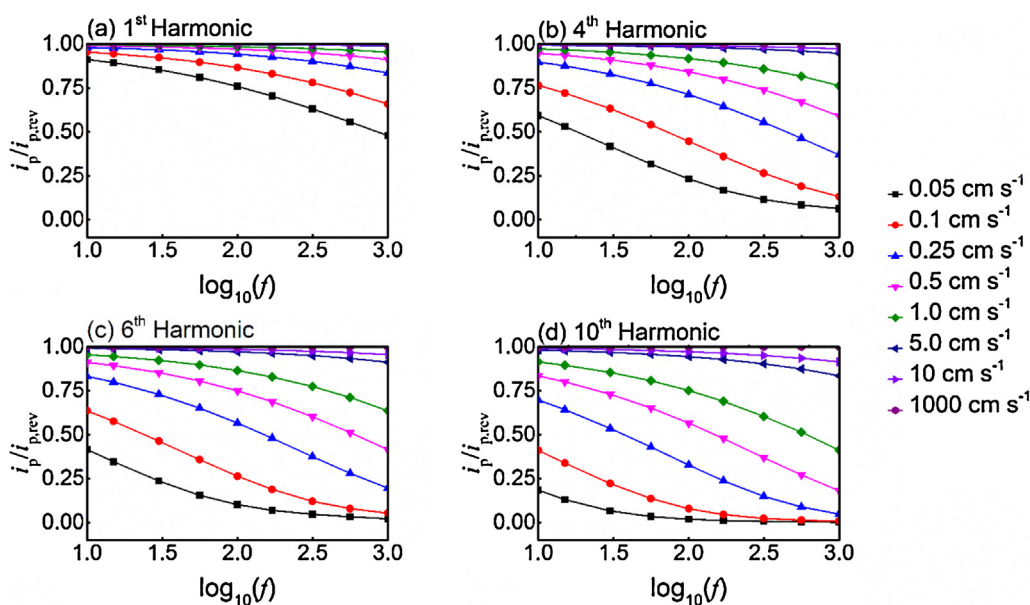
At any time,  $t$ , the potential is given by:

$$0 \leq t \leq t_s : E_{DC}(t) = E_{init} + vt \quad (6)$$

$$t_s < t \leq 2t_s : E_{DC}(t) = E_{init} + 2vt_s - vt \quad (7)$$

$$0 \leq t \leq 2t_s : E_{AC}(t) = \Delta E \sin(2\pi ft) \quad (8)$$

where  $E_{init}$  is the initial potential applied to the electrode,  $v$  is the potential scan rate,  $t_s$  is the time taken to complete a sweep in a single direction, and  $\Delta E$  and  $f$  are the amplitude and frequency of the AC waveform, respectively. In this study,  $\Delta E = 80.0$  mV and  $f = 10.0$  Hz are used for all FTACV simulations at a potential scan rate,  $v_{AC}$ , unless stated otherwise, or  $\Delta E = 0.0$  mV and  $f = 0.0$  Hz for conventional direct current cyclic voltammetry (DCCV) simulations at a potential scan rate,  $v_{DC}$ .



**Figure 1.** Simulated plots of  $i_p/i_{p,rev}$  versus  $\log_{10}f$  for the (a) 1<sup>st</sup>, (b) 4<sup>th</sup>, (c) 6<sup>th</sup> and (d) 10<sup>th</sup> AC harmonic components for an oxidation process at a homogeneous electrode surface with  $k^0 = 0.05, 0.1, 0.25, 0.5, 1.0, 5.0, 10$  and  $1000 \text{ cm s}^{-1}$ . Simulation parameters are as follows:  $c^0 = 1.0 \text{ mM}$ ,  $D = 1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ,  $\alpha = 0.50$ ,  $T = 295.0 \text{ K}$ ,  $v_{AC} = 0.1 \text{ V s}^{-1}$  and  $\Delta E = 80.0 \text{ mV}$ .

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