Applications of Fourier Transformed large amplitude ac voltammetry for kinetics studies at stationary and rotating disc electrodes

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Dc voltammetric techniques are commonly classified as being based on stationary or hydrodynamic electrode configurations. The former are characterized by diffusion controlled mass transport and the later by convective mass transport. Both methods are widely used in studies of electrode kinetics and mechanisms[1,2,3] and each has well established advantages and disadvantages.[4,5,6] Another valuable method for quantitative evaluation of electrode kinetics is to use impedance spectroscopy in which a periodical small amplitude ac waveform is superimposed onto the dc ramp,[7] however, small amplitude doesn't provide access to the higher harmonics. On the other hand, large amplitude Fourier Transformed (FT)[8,9] ac voltammetry provides access to the higher order ac harmonic components essential for kinetic measurement. Here, we describe the use of large amplitude FT ac voltammetry for kinetics studies.

At rotating disc electrodes, resolution of time domain data into dc and ac harmonic components reveals that the mass transport for dc component is controlled by convective-diffusion, while the background current free higher order ac harmonic components are flow rate independent and governed by linear diffusion as shown in Figure 1. Thus, remarkable versatility is available; Levich behaviour of dc component limiting current provides diffusion coefficient values and access to higher harmonics allows fast electrode kinetics to be probed from one set of data.

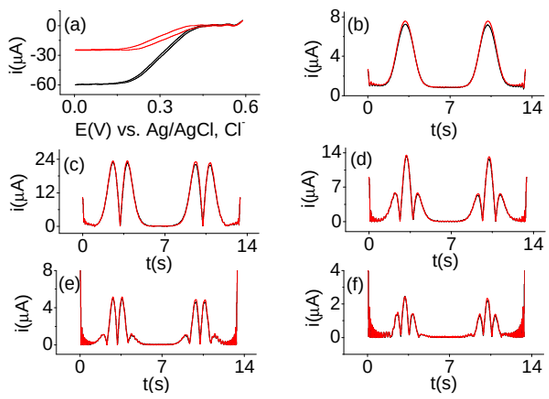

Figure 1: Comparison of dc and ac components for 0.98 mM $[Fe(CN)_6]^{3-}$ reduction in 3.0 M KCl at a glassy carbon electrode with rotation rates of (—)500 rpm and (—)3000 rpm, (a) dc component (b) 1st harmonic (b) 2nd harmonic (c) 3rd harmonic (d) 4th harmonic (e) 5th harmonic, (f) 6th harmonic, f = 9.0 Hz, ΔE = 80 mV, A = 0.07 cm^2, υ = 0.1V s^{-1}.

In the case of Fourier Transformed (FT) large amplitude ac voltammetry at stationary electrodes it is now well known that dc and ac sets of harmonics can be obtained from a single experiment and effect of uncompensated resistance and slow kinetics can be distinguished in higher harmonics.[10] Under stationary electrode conditions, electron transfer kinetics was extracted from higher ordered harmonic components. Upper limits of measurement under stationary electrode conditions are described in Figure 2 where use of appropriate conditions may lead to measurement of k^0 up to 1.0 cm s^{-1} at macro electrodes. Limitations associated with the electrode kinetics measurement and effects of experimental uncertainties in each case are also taken into account.

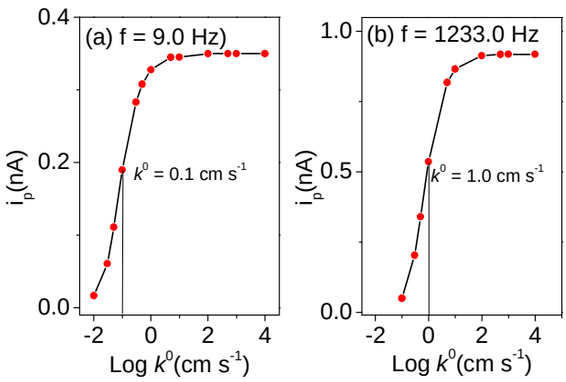

Figure 2: Peak currents of 5th harmonic versus Log k^0 obtained at frequencies (a) 9.0 Hz and (b) 1233 Hz, ΔE = 80 mV, C^* = 2.0 mM, R_u = 127 ohms, D = 2.0 × 10^{-5} cm^2 s^{-1}, C = 10 μF cm^{-2} and A = 0.00785 cm^2.

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