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Mini review

An integrated instrumental and theoretical approach to quantitative electrode kinetic studies based on large amplitude Fourier transformed a.c. voltammetry: A mini review

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ABSTRACT

Herein, we emphasise the main advantages provided by Fourier transform assisted a.c. voltammetry over d.c. methods in quantitative electrode kinetic studies and report on the progress with integration of the a.c. approach with contemporary computer-assisted automated data analysis methods. In the mechanistically sensitive version of Fourier transformed a.c. voltammetry emphasised in this mini review, a large amplitude sinusoidal or another time dependent periodic function is superimposed onto the d.c. potential ramp. Using a sequence of Fourier Transform and filtering operations, both experimental and simulated data for the assumed mechanism are resolved into the aperiodic (d.c.) and a.c. harmonic components. Comparison of experiment and theory by heuristic or computer-assisted automated methods allows quantitative estimates to be provided of the relevant thermodynamic and kinetic parameters as well as of uncompensated resistance, double layer capacitance and other parameters present in the electrode kinetics model.

Contents

1. Introduction

Interpretation of the current-potential-time (*I*-*E*-*t*) relationship ensuing from the half-cell reaction at the working electrode is of prime interest in voltammetry. It is now very common in chemistry papers to provide cyclic voltammograms showing the redox transformations of a wide range of inorganic, organic or biologically important materials. However, many of these reports only give a qualitative description of the electrode processes and even where quantitative data are provided, commonly simple forms of theory based on peak potentials as a function of a scan rate (*e.g.* [1,2]) are employed.

In the d.c. form of cyclic voltammetry, a waveform of the kind shown in Fig. 1a is used. In a large amplitude a.c. voltammetric experiment which is the focus of this review, a sinusoidal (large amplitude in our case) or other time dependent periodic function is superimposed onto the d.c. ramp (Fig. 1b). Herein, we summarise the main advantages provided by using a combination of the a.c. and d.c. potential waveforms for voltammetric analysis and report on the progress in integration of a.c. voltammetry with contemporary computer-assisted data analysis methods.

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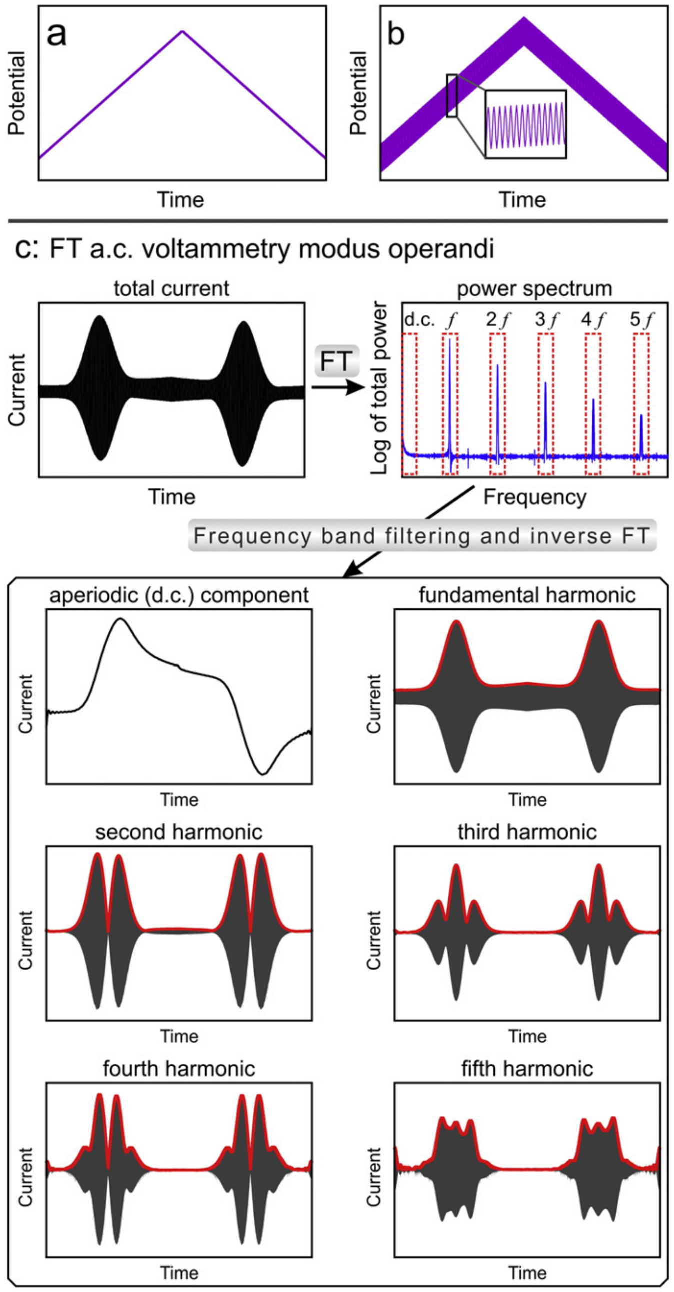

Fig. 1. Waveforms used in cyclic (a) d.c. and (b) a.c. voltammetry. (c) A.c. voltammetric data processing *via* the [FT – band selection and filtering – iFT] sequence of operations for a Red $\rightleftarrows$ Ox + e^- process. Red curves on top of the harmonic components portray the envelope presentation of the periodic current [3] preferred in this and many other publications.

2. D.c. and a.c. voltammetric electrode kinetic analysis

In order to describe the simplest case of a voltammogram for a process in which reactant, *R*, is transformed to product, *P*, *via* reaction

$$R \rightleftarrows P \pm e^-, \tag{1}$$

at least 10 parameters of the studied system have to be measured independently or estimated from theory *versus* experiment comparisons. The reversible formal potential (E^0), heterogeneous charge transfer rate constant at potential E^0 (k^0) and the charge transfer coefficient (α) or reorganisation energy (λ) [4] need to be established to define the electrode kinetics relevant to the electrode-solution interface used in the experiment. For the reactions involving dissolved species and occurring at a stationary disk electrode as often applies, the faradaic current is governed by diffusional mass transport. Mathematical description requires the use of Fick's laws and knowledge of the diffusivity (D) and concentration (c) of the reactant and the product(s), as well as the electrode geometry and its surface area (A). The background current also contributes to the total current and needs to be modelled. This can sometimes be approximated by a potential independent constant reflecting the capacitance of the double layer (C_{dl}), but in practice, knowledge of the potential dependence often is required. Finally, the voltammograms are strongly dependent on the uncompensated resistance (R_{u}) as defined by the Ohm's law, even if a three-electrode experimental mode is employed. R_{u} reflects mainly the resistance of the solution between the tip of the reference electrode and the working electrode. Thus, at a minimum, terms E^0, k^0, α (or λ), A, D_{Ox}, D_{Red}, c_{Ox}, c_{Red}, C_{dl}, and R_{u} need to be included in a model to describe the voltammetric response for a simplest faradaic electrode process (Eq. (1)). If the product is reactive, then chemical steps with their homogeneous rate constants also need to be included in the model.

To provide a quantitative account of an electrode process, it is necessary to compare experiment and theory and optimise the level of agreement. The model should fit the data very well at all concentrations, scan rates, frequencies and potentials. Of course, it is of great help if the experimental technique used is highly sensitive to all unknown parameters used in the simulations. It is just this and some other properties of the large amplitude Fourier transformed (FT) a.c. voltammetry that makes this method exceptionally valuable for quantitative electrode kinetic studies [5]. In d.c. cyclic voltammetry, typically the scan rate, $v = \frac{dE_{\mathrm{d.c.}}}{dt}$, is varied and a series of voltammograms are obtained and compared to simulations. However, in the case of the a.c. method as implemented with modern instrumentation, vast amounts of data are collected from a single experiment; *e.g.* when a sinewave having a frequency, f of 15 Hz with sufficiently large amplitude (say $\Delta E = 0.1$ V) is superimposed onto the d.c. ramp, then there will be a series of higher order harmonics at 30, 45, 60, and 75 Hz *etc.* each of which can be resolved by using a FT – band selection and filtering – inverse FT sequence of operations (Fig. 1c). Whilst the full data set would give a read out of a periodic response, the presentation in this format becomes very messy; we therefore widely use the envelope form of presentation [3] for clarity (Fig. 1c). Thus, with respect to establishing the thermodynamics and electrode kinetics, f and the higher harmonic content at $2f$, $3f$, *etc.* become a critical parameter rather than the d.c. potential scan rate. There is also an aperiodic component available from an a.c. voltammogram, which preserves the main attributes of a d.c. voltammetric experiment.

A feature that differs in FT a.c. voltammetry from the d.c. method, in addition to being able to collect all data from one experiment, is that the current magnitude is very sensitive to k^0 and R_{u}. Remarkably, while the background current is large in the fundamental harmonic, it is usually absent in the 3rd and higher order a.c. harmonics (Fig. 1c). Moreover, a.c. faradaic current is only negligibly influenced by the non-cottrellian diffusion effects arising from the edges of the ubiquitously used mm-sized embedded disk electrodes [6,7] and this allows use of a simple and easy to treat planar diffusion model.

There are other notable aspects of a.c. voltammetry that are not discussed in the text in the present review in the interest of brevity, but some of those are highlighted in Table 1. Table 2 highlights a few of the many experimental systems where combination of the FT a.c. and classical d.c. voltammetry is exceptionally useful. Further insights into the utility and diversity of the FT a.c. voltammetric method can be found in other papers from the Monash electrochemistry group and our colleagues (*e.g.* [8–11]).