Correction factors for the analysis of voltammetric peak currents measured using staircase voltammetry

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A B S T R A C T

The use of staircase voltammetry for the measurement of reversible diffusional redox species under a linear mass-transport regime leads to significant suppression of the peak currents (up to 20% for larger step sizes) and an increase in the peak-to-peak separation (cf. ΔE_{pp} ~ 70 mV at the reversible limit as opposed to 57 mV). These discrepancies between the voltammetric results of a staircase and true analogue voltammogram may lead to mis-interpretation of data. This work provides an overview of the differences between the two techniques in the macro-electrode reversible limit and provides new expressions which allow the peak current of a staircase voltammogram to be quantitatively analysed. Moreover, clear guidance is provided about which conditions the application of the provided equation is valid in the terms of mass-transport edge effects to the macro-electrode.

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1. Introduction

The analysis of cyclic voltammograms either by the use of analytical expressions [1] or numerical simulation [2–4] almost invariably assumes that the applied potential is a true linear ramp i.e., dE/dt is taken to be a constant. For the majority of modern commercial potentiostats available today the basic cyclic voltammetric method available with the equipment in fact applies a staircase ramping potential. Commonly, the assumption is that for sufficiently small step sizes then the results of the two methodologies converge. At a qualitative level this assumption is often reasonably valid but as will be discussed within this work, for the measurement of physically correct experimental parameters and the extraction of quantitative data, insight into the differences between these two voltammetric methodologies is required.

From the mid-80s till the early 90s Osteryoung, amongst others, [5, 6] published a series of important papers focused on the discrepancies between staircase and true linear sweep voltammetry [7–12]. As with many pulse techniques [13] the initial motivation for interest in the application of staircase voltammetry was in order to facilitate and improve the measurement of Faradaic processes over capacitive [14]. This improved resolution between the two current sources may be achieved for *diffusional* species by exploiting the difference in the currents' time constants. Crudely the current associated with the capacitive charging of the electrode varies exponentially with time ($I = f(e^{-kt})$) whereas for a diffusion limited process (under a linear diffusion regime) the current varies with the square-root of time ($I = f(t^{-0.5})$). In running a staircase voltammogram the potentiostat is in effect performing a series of short

sequential chronoamperograms. Fig. 1 depicts a comparison of the voltage waveforms used by the two different voltammetric techniques. For the staircase waveform (red) the point at which the current is sampled during the course of each step influences the shape of the voltammetric response. By convention the sampling position is define by the dimensionless value alpha, where an alpha of one corresponds to sampling the current at the end of a potential step and conversely an alpha of zero corresponds to sampling at the start. It is worth noting that this sampling alpha value should not be conflated with the transfer coefficient 'alpha' used within the Butler–Volmer equation.

As the potentiostat applies the staircase voltage ramp, the actual current passed at the electrode will exhibit sharp pulses associated with the application of each potential step. By sampling the current once during each potential step (as is commonly done), or alternatively averaging the recorded response, the large fluctuations in the current may be omitted and the current response will more closely resemble that found for conventional 'true' linear sweep voltammetry. For the majority of basic potentiostat procedures the current is sampled once at the end of the step (sampling alpha = 1.0) hence due to their differing time constants the relative magnitude of the Faradaic current is greater than the capacitive current as compared to true analogue cyclic voltammetry. However, although this method facilitates discrimination between diffusional Faradaic and capacitive currents under most conditions the resulting voltammogram is not equivalent to true linear sweep voltammetry as implemented using an analogue potentiostat. For staircase voltammetry the procedure used for sampling the current significantly influences the resulting voltammogram and importantly leads to attenuated peak currents and increased peak-to-peak separations. These disparities between the recorded voltammograms will have certainly caused some researchers to conclude on a basis of their
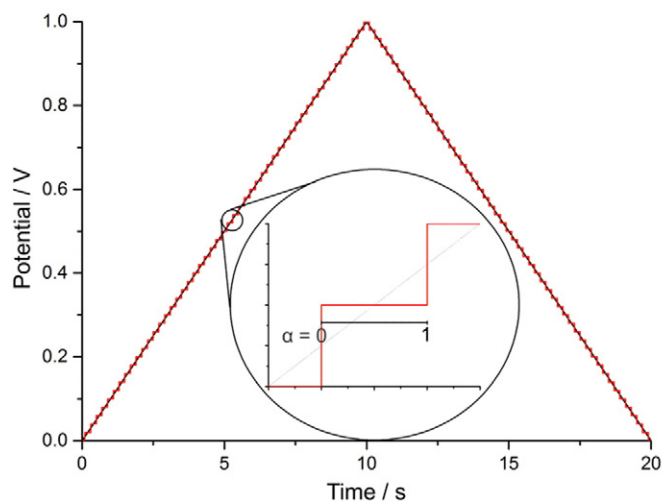
Fig. 1. Comparison of the voltage wave forms used for staircase (red) and true analogue (black) cyclic voltammetry. Zoomed inlay depicts an individual step showing the sampling alpha scale, when $\alpha = 1$ the current is sampled at the end of the step alternatively, $\alpha = 0$ implies a current measurement at the beginning of the step. Data depicts the wave form used for a cyclic voltammogram (0–1 V) at a scan rate of 0.1 V s^{-1} and with a step potential of 20 mV. Image taken from Ref. [2].

experimental data that a reversible redox couple is only quasi-reversible (or that the system exhibits ohmic distortions) and/or to under report the diffusion coefficient by ca. 20%.

This work will focus upon the voltammetry of reversible diffusional redox couples and demonstrates both theoretically and experimentally the influence of the parameters used within staircase voltammetry. Consequently, correction factors for the Randles–Ševčík equation are provided, allowing quantitative analysis of voltammetric data of reversible species to be measured from staircase voltammetry without the direct need for simulation. Furthermore, this work also serves to clearly state the conditions under which a voltammetric system can be suitably and quantitatively analysed using these equations.

2. Experimental

2.1. Chemicals

Potassium chloride and hexaammineruthenium(III) chloride were supplied by Sigma-Aldrich. All solutions were made using ultrapure water from Millipore with a resistivity not less than 18.2 M cm at 298 K.

2.2. Electrochemistry

A three electrode system in a Faraday cage was used for all electrochemical experiments. A μAutolab II from Metrohm Autolab B.V., Utrecht, The Netherlands was used as the potentiostat. The working electrode was a glassy carbon disk, BASi, (radius = 1.5 mm), the electrode was polished on alumina (1.0, 0.3 μm, Buehler, Lake Bluff, IL, USA) and rinsed with deionised water thoroughly between each experiment. A saturated calomel electrode (SCE), BASi, was used as the reference and a graphite rod was used as the counter.

2.3. Simulations

The theoretical work in this paper utilises two models, first a one-dimensional system is provided where the electrode potential increases along a staircase ramp. Second, a two-dimensional model with an analogue ramp is used to define the dimensionless scan rate at which the radial diffusion contributions to the current should be considered. The one dimension simulations use a script written in Python 2.7 whereas

the two dimensional model was implemented in Julia, [15] a high performance scripting language. Further details of the models can be found within the SI Section 1.

3. Results and discussion

Fig. 2 depicts the simulated response of a one-electron reversible redox couple at a macro-electrode (1D) to an applied staircase potential. The scan starts at $+0.2$ V and the potential is reduced cathodically in increments of 5 mV. The current for ease of comparison has been normalized against the expected peak current for a reversible one-electron system. Unlike a regular voltammogram this staircase potential ramp results in significant pulsing of the current. At low overpotentials the magnitude of these current pulses is not significant, however as the formal potential of the redox couple is approached their magnitude increases. This increase in the magnitude of the pulsing simply reflects the change in the composition of the reactants and products at the interface as determined by the Nernst equation. As the potential is reduced further the depletion of the reactant at the electrode surface causes the reaction to become diffusion limited. Hence the redox response becomes less sensitive to the electrode potential and as such the magnitude of the pulsing decreases and the current tends to its diffusion limited value. Upon reverse of the potential scan (at -0.2 V) the process is repeated in the anodic direction as the product is oxidised back to the starting material. The inlay depicts a zoomed region of the staircase voltammogram showing three individual steps. During the course of each step the current decreases, consequently depending upon how and when the current is sampled dramatically, different voltammograms may be recorded.

The convention for many modern potentiostats is to sample the current at the end of each potential step; this is reportedly to improve the resolution of the Faradaic signal above that of the capacitive background. However, as is clear from Fig. 2, sampling the current at the end of the potential step will result in the recording of a current significantly less than would be attained if a true linear ramp was used. Fig. 3 depicts the simulated results for the same (as shown in Fig. 2) one-electron redox couple however here the current has only been sampled once per potential step. The position at which the current is sampled is
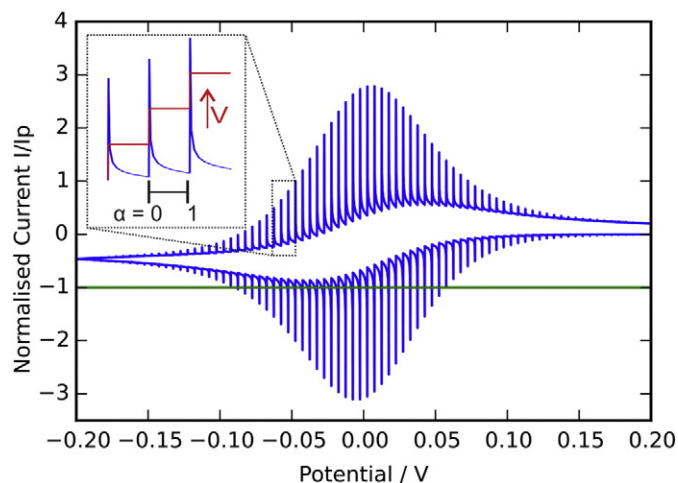

Fig. 2. The voltammetric response of a reversible one-electron redox couple to a staircase potential ramp (5 mV potential step, 0.1 V s^{-1}) under a linear diffusion regime. Green line represents the expected current for an analogue cyclic voltammogram. For ease of understanding the current has been plotted against the potential that would have been applied if an analogue potential ramp had been used. Inlay depicts a zoomed section of the voltammogram depicting three individual potential steps, showing both the variation of the potential (red line) and the scale used for the sampling value 'alpha'. Such that an alpha of one corresponds to a measurement at the end of a potential step and a value of zero corresponds to a measurement at the beginning of the step.