



Further investigation of the equivalence of staircase and linear scan voltammograms. III-Averaged-current staircase voltammetry applied to electrochemical reactions involving adsorbed species

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ABSTRACT

Three voltammetric techniques are dealt with and compared in this work: first the linear scan voltammetry and next the staircase voltammetry used together with current sampling or current averaging on each step of the staircase signal. First, it can be stated that the averaged-current staircase voltammetry provides the same current data as a linear potential ramp, at the same potential scan rate, for any linear and time-invariant electrical/electrochemical dipole/system. Next, most electrochemical systems being nonlinear, the second aim is to show, through numerical simulation, that averaged-current staircase voltammograms well match linear scan voltammograms, taking the example of electrochemical reactions involving adsorbed species. Based on the relevant voltammetric models, theoretical investigation is carried out taking into account the Langmuir or Frumkin isotherm for adsorption, the reaction kinetics, the uncompensated resistance of the electrolyte, and the interfacial double-layer charging.

1. Introduction

In the two first parts of this work [1,2] we re-examined the sampling conditions that guarantee, within acceptable error, the equivalence of staircase voltammograms and linear scan voltammograms (SCV/LSV) or cyclic staircase voltammograms and cyclic voltammograms (CSCV/CV) plotted at the same potential scan rate, taking the example of electrochemical reactions involving soluble species. The input signals for LSV and SCV are schematized in Fig. 1a and b, respectively.

The experimentally controlled parameters for the staircase voltammetry technique (SCV/CSCV) are the potential step amplitude ΔE , the time length Δt following each potential step of the staircase signal, and the current sampling parameter γ . The current for the n th potential step is sampled at the time instant $t = (n + \gamma - 1)\Delta t$, where $\gamma \in [0, 1]$ and $n = 1, 2, \dots$. The equivalent potential scan rate is $v = \Delta E/\Delta t$. The initial and reversal (switching) potentials are additional variables for this technique.

Simplifications are possible for analysis of experimental SCV/CSCV current data provided the controlled parameters satisfy some conditions. First the condition,¹ $\gamma \Delta t \gg R_u C_{dl}$, should ensure that the sampled

current² I_{CSCV} is close to the Faradaic current for the same technique ($I_{CSCV} \approx I_{f, CSCV}$), with $I_{f, CSCV}$ being known analytically for reversible electrochemical reactions [3], and computed numerically otherwise. Next, the sampled CSCV current should be close to the Faradaic current for a linear or cyclic potential ramp ($I_{CSCV} \approx I_{f, CV}$), provided (i) $\gamma \Delta t \gg R_u C_{dl}$ is the sampling condition as above, (ii) the potential step amplitude is small enough, i.e. $\Delta E \ll RT_K/(|z|F)$ where z is the stoichiometric number of electron, R and F have their usual meaning and T_K is the absolute temperature, and (iii) slow electron transfer kinetics is satisfied at the electrode surface [2]. Main advantage is that $I_{f, CV}$ is well documented in the electrochemical literature [4]. Finally, the optimal sampling strategy thoroughly examined in our previous articles [1,2] should guarantee the global equivalence of SCV/CSCV and LSV/CV current data ($I_{CSCV} \approx I_{CV}$) within acceptable error. Main issue, however, is the dependence of the optimal sampling parameter (γ_{opt}) on the electron transfer kinetics, the mass transport process for redox species in the electrolyte, the Ohmic drop, the double-layer charging, and the potential scan rate v [1,2]. In addition, numerical experimentation is most often required for prediction of the optimal value of current sampling parameter as a function of v .

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¹ R_u and C_{dl} denote respectively the uncompensated resistance and the double-layer capacitance.

² For the sake of simplification of notation, I_{CSCV} refers here to both SCV and CSCV techniques.

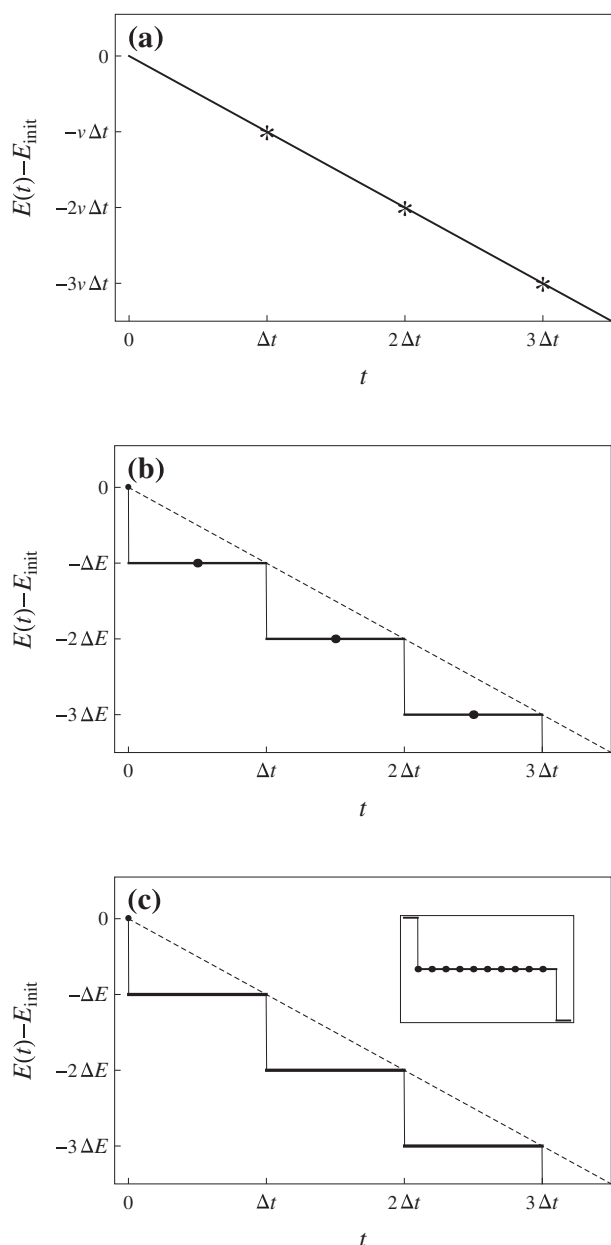


Fig. 1. Schematic representation of the input signals for the LSV, SCV and SCV_{av} techniques applied to a reduction reaction. (a) LSV: linear potential ramp (solid line) with slope $-v$. The current $I_{LSV}(t)$ is plotted versus the imposed potential $E(t) = E_{init} - vt$. For comparison purpose, the current $I_{LSV, n}$ can be evaluated at $t = n\Delta t$ (stars) for $n = 1, 2, \dots$ (b) SCV: staircase potential signal (solid line) with potential step amplitude $\Delta E = v\Delta t$. The current $I_{SCV, n}$ is sampled at $t = (n - 1 + \gamma)\Delta t$, with $\gamma = 0.5$ as an example (dots), and plotted versus the discrete value of potential $E_n = E_{init} - n\Delta E$, for $n = 1, 2, \dots$. The dashed line is the LSV input signal. (c) SCV_{av} : same input signal as SCV. The current is first sampled at $\delta t, 2\delta t, \dots$, with $\delta t = \Delta t/n_d$ and n_d being the number of current data collected for each potential step ($n_d = 10$ in the inset for example), next step-by-step averaged as $I_{SCV, n}^{av}$, and finally plotted versus the discrete value of potential $E_n = E_{init} - n\Delta E$, for $n = 1, 2, \dots$

Further complication should occur when adsorbed species are involved in electrochemical reactions. Stojek and Osteryoung [5] were probably the first authors to compare staircase and linear scan voltammograms for the case of reactants and products adsorbed,

crystallized or polymerized at the electrode surface. The SCV current was sampled at $\gamma = 0.25, 0.5$ and 1 , respectively. In practice, the SCV peaks were observed to decrease sharply in amplitude and finally disappear when the potential step amplitude ΔE is increased. These authors came to the following conclusion: “the conditions of equivalence between SCV and LSV curves cannot be given in a straightforward manner. Even application of small potential steps does not ensure reasonable agreement between SCV and LSV peak currents”.

Later, Komorsky-Lovric and Lovric [6] investigated both experimentally and theoretically the staircase voltammetric responses of surface redox reactions. They predicted the observation of a “quasi-reversible maximum” when the SCV peak current is plotted as a function of the decimal logarithm of the dimensionless standard rate constant $k^0\Delta t$, at constant ΔE . This maximum should depend on the amplitude ΔE of potential step, and the current sampling parameter γ . These authors came to the conclusion that “the SCV current response of surface redox reactions may entirely vanish if the reaction is fast and reversible”, and “the equivalence of SCV and LSV techniques for the above reactions cannot be obtained by changing the sampling parameter γ ”.

Next, Heering et al. [7] examined the applicability of staircase voltammetry to determine electron-transfer rate constants and their potential dependence for surface redox reactions. Their theoretical investigation was based on the analytical solution of the response to a potential step, iteratively used at each step of the staircase signal. These authors thoroughly examined the influence of the dimensionless rate constant of the electrochemical reaction on (i) the SCV peak current relative to the reversible CV peak current, (ii) the normalized SCV peak area, (iii) the dimensionless SCV peak width at half-height, and (iv) the dimensionless peak potential. Heering et al. successfully used the experimental study of reactions of redox-active centers in proteins as a model system.

More recently, Gonzalez et al. [8] derived analytical and fully explicit solutions of the multipotential pulse quasi-reversible $I-E-t$ and $Q-E-t$ responses (Q being the electrical charge involved) of strongly adsorbed redox molecules, i.e. the responses to an arbitrary sequence of electrode potentials, E_1, E_2, \dots , applied at the time instants, t_0, t_1, \dots , whatever the reversibility degree of the reaction kinetics. These authors also investigated the effect of the double-layer charging current on the $I-E-t$ and $Q-E-t$ responses of surface redox reactions, assuming that the total current is the sum of the Faradaic current without double-layer charging complication, and the double-layer charging current in the absence of electrochemical reaction, so-called “potential-step charging current” by Miaw and Perone [9]. It is worth noting that the above approximation is only valid when the uncompensated resistance R_u approaches zero, otherwise the “induced charging current” in the presence of Faradaic processes should be taken into account [9].

Gulaboski et al. [10] focused on the determination of the thermodynamic and kinetic parameters relevant to protein's physiological properties. These authors used the cyclic staircase voltammetry technique for theoretical investigation of protein-film redox mechanisms pertaining to EE, ECE and EEC_{cat} surface processes. The theoretical derivation was based on numerical solving of the integral forms for the mathematical solutions. The authors provided qualitative criteria for distinguishing a particular redox mechanism from the other two. They also proposed simple methods for the determination of the kinetic and thermodynamic parameters relevant to the electron transfer steps and the coupled chemical reactions.

Finally, in a recent article, Gulaboski and Mirceski [11] presented new aspects of the electrochemical-catalytic (EC') reaction mechanism in square-wave voltammetry and staircase voltammetry. Both diffusion-

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