Electrochem. Comm. 118 (2020) 106810, doi: 10.1016/j.elecom.2020.106810

Analysis of adsorption-related voltammograms: Transformation to potential-program invariant form

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Abstract

A simple procedure is suggested by which cyclic voltammograms, CVs, characterizing adsorption processes can be analyzed. Using this procedure, from a set of CVs taken at varied scan-rates, two scan-rate independent, hysteresis-free functions of potential can be calculated. One of them characterizes the adsorption kinetics as if surface coverage were zero, the other is an adsorption isotherm. Because of the formal analogy, the procedure is applicable also for CVs of redox systems of finite quantity of reactants, e.g. surface confined redox systems.

Keywords: adsorption, kinetics, charge transfer, redox system

1. Introduction

Cyclic voltammograms, CVs, are usually complicated functions of the scan-rate; they often exhibit large hysteresis. Comparison of two CVs measured with different scan-rates is far from being trivial. The comparison is even more complicated if the scan-rate varies in time or when two voltammograms are measured with different, arbitrary waveforms of potential.

In rare, simple cases, however, there exist mathematical transformations by which CVs taken with different scan-rates can be transformed to the one-and-the-same potential-program invariant (PPI) function – which function is independent of the actual form of the potential-time function. For example, the CVs of reversible redox couples can be transformed to hysteresis-free sigmoid-shaped curves using semiintegration [1]. In contrast, the CVs of redox systems of slower kinetics – of the so-called quasi-reversible systems – cannot be transformed to a single PPI function. However, as it has recently been demonstrated in Refs. [2,3], by measuring a set of quasi-reversible CVs with varied scan-rates, two PPI functions can be obtained by a simple numerical procedure. One of them characterizes charge transfer kinetics, the other diffusion.

The subject of the present communication is the analysis of another important electrochemical situation: when the rate of the electrode process is limited by the finite quantity of reactants. The relevant equations are derived for the case of adsorption-desorption of charged species on an electrode surface with a finite density of adsorption sites. However, we keep in mind that there are analogous cases: the CVs of redox reactions of surface confined species and the CVs of redox reactions in a thin layer cell. The kinetics of all these types of processes manifest themselves as humps or peaks on the CVs and pseudocapacitances in the context of impedance analysis. As it is shown here using the example of the first case, the CVs can also be transformed to yield PPI functions.

2. Theory

Consider a CV measurement in a metal-electrolyte system where some electrolyte component A of concentration c is reversibly bound onto the surface. In what follows, we will use the term adsorption-desorption for this process. Denoting the unoccupied locations of the substrate as S, and considering also the electric charge change of A, the $\mathrm{A}^{z+} + \mathrm{S} \rightleftharpoons \mathrm{A}_\mathrm{S}^{(z+n)+} + n\mathrm{e}^-$ reaction proceeds; where the e^- are the excess electrons appearing on the metal. The density of adsorbed species on the substrate is expressed as surface concentration, Γ in mol/cm^2 units, or normalized by the total surface concentration of locations Γ_0, as a dimensionless coverage $\theta = \Gamma/\Gamma_0$.

The $E(t)$ potential program – of arbitrary waveform – starts in time t=0 from a sufficiently negative or positive value where adsorbate coverage is zero. The potential program crosses the $E = \varepsilon$ level more than once during the experiment (its possible ways are illustrated in Fig.1 of [3]).

In what follows, we analyze the rate equations at this particular ε potential. We adhere to the usual theorisation of electrochemical kinetics [4] but ignore all complication factors like IR drop, double-layer charging, transport hindering (i.e. adsorbate concentration in the vicinity of the surface is always the same as in the bulk, c). n is regarded to be a constant, integer number, though we should use the (negative of) the potential-dependent formal partial charge number [5] instead. Some of these complicating issues will be discussed in the Discussion section.

The current density j is always the time derivative of the electronic charge of the metal, q, which is – as double layer charging is out of our present scope – related to the change of the surface concentration, Γ. At any time instance t,

$$j(t) = \mathrm{d}q(t)/\mathrm{d}t = \partial q/\partial\Gamma \cdot \mathrm{d}\Gamma(t)/\mathrm{d}t = n\mathrm{F} \cdot \mathrm{d}\Gamma(t)/\mathrm{d}t = n\mathrm{F} \cdot \Gamma_0 \cdot \mathrm{d}\theta(t)/\mathrm{d}t \qquad (1)$$

where F is the Faraday constant. As the initial condition is $\Gamma(t \leq 0) = 0$, and hence $q(t \leq 0) = 0$; by integrating Eq.1 with respect to time, t, we get

$$q(t) = \int_0^t j(\tau)\mathrm{d}\tau = n\mathrm{F}\cdot\Gamma(t) = n\mathrm{F}\cdot\Gamma_0\cdot\theta(t) \qquad (2)$$

The net rate of adsorption, in the simplest way as usual in case of Langmuirian adsorption, is written as

$$\mathrm{d}\theta(t)/\mathrm{d}t = k_{\mathrm{ad}}(E) \cdot c \cdot [1 - \theta(t)] - k_{\mathrm{d}}(E) \cdot \theta(t) \qquad (3)$$

where k_{ad} and k_{d} are the rate coefficients of adsorption and desorption, respectively. Note that only the rate coefficients depend on E, in a yet unspecified way; the time dependence of j stems from that of θ (and an eventual dependence of the number of adsorption sites on potential is disregarded).

For time τ, when $E = \varepsilon$, by combining Eqs. 1 to 3, and introducing the symbol $H(\varepsilon) = k_{\mathrm{ad}}(\varepsilon)c + k_{\mathrm{d}}(\varepsilon)$ we get

$$j(\tau) = n\mathrm{F}\cdot\Gamma_0\cdot k_{\mathrm{ad}}(\varepsilon) \cdot c - H(\varepsilon) \cdot q(\tau) \qquad (4)$$

That is, if we measure a voltammogram which crosses some potential ε at least two times, then all the j vs q points (of the same ε potential) appear on one and the same $j = \mathrm{const}_1 - \mathrm{const}_2 \cdot q$ line. With increasing scan-rate, the points move towards the ordinate; the physical meaning of the ordinate intersect, const$_1$ is the adsorption rate – expressed as current density – as if the complete surface were completely uncovered, $\Gamma = 0$. As a limit value, it will be named as j_{lim}. The abscissa intersect of the line is $\mathrm{const}_1/\mathrm{const}_2 = n\mathrm{F}\cdot\Gamma_0\cdot 1/[1 + k_{\mathrm{d}}(\varepsilon)/(k_{\mathrm{ad}}(\varepsilon)c)]$, which has the physical meaning of the surface charge associated with the adsorption, in equilibrium; hence we denote it as q_{eq}..

With these denotions Eq.4 reads as

$$j(\tau) = j_{\mathrm{inf}}(\varepsilon) - H(\varepsilon) \cdot q(\tau) \qquad (5)$$

with $H(\varepsilon) = j_{\mathrm{lim}}(\varepsilon)/q_{\mathrm{eq}}(\varepsilon)$.

These are the key equations using which we can get j_{inf} and q_{eq} as a function of potential. Since they depend on potential only, they do not depend on the scan-rate, moreover the actual shape of the potential program, by which the js have been measured. In the same vein, since they are single-valued functions, they do not exhibit any hystereses.

3. Results of numerical tests

The properties of the transformation of Eq.5 is illustrated on simulated CVs in this Section. For the rate coefficients exponential dependences on potential were assumed, just as it has been usual in the previous theories since the sixties (representative studies are [6,7,8,9]). That is, the rate coefficients are $k_{\mathrm{ad}}(E) = k_{\mathrm{ad}}^0 \cdot \exp(\alpha_1 \mathrm{F}(E\text{-}E_0)/\mathrm{R}T)$ and $k_{\mathrm{d}}(E) = k_{\mathrm{d}}^0 \cdot \exp(-\alpha_2 \mathrm{F}(E\text{-}E_0)/\mathrm{R}T)$ where E_0 is the peak potential of the reversible peak ($E_0 = \mathrm{R}T/[(\alpha_1 + \alpha_2)\mathrm{F}] \cdot \ln\left(k_{\mathrm{d}}^0/c k_{\mathrm{ad}}^0\right)$, the other symbols have their usual meaning. The other simulation parameters are as follows: $\alpha_1 = \alpha_2 = 0.5, n = 1, c k_{\mathrm{ad}}^0 = 1\ \mathrm{s}^{-1}, \Gamma_0 = 2 \times 10^{-9}\ \mathrm{mol/cm}^2$**.** These CVs, normalized by the scan-rate, are displayed in Fig.1a; they are very similar to the ones in the literature (cf. Fig.8 of [6], Fig.4 of [7], Fig.2 of [8], and Fig.4 of [9]).

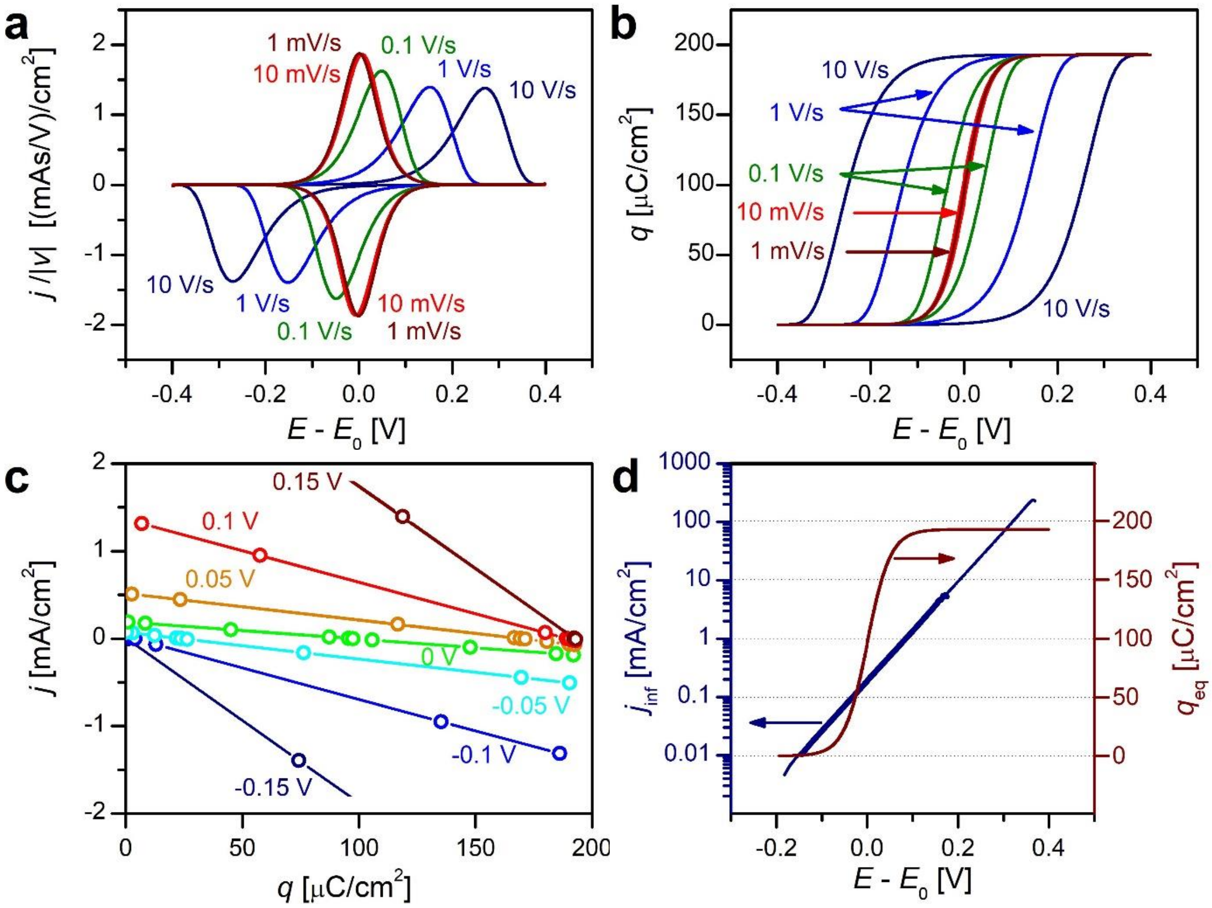

Figure 1.
Simulated adsorption-desorption CVs, and the procedure of calculation of the PPI representation. (a) The calculated scan-rate normalized CVs at scan-rates as indicated; (b) The integrated CVs; (c) The linear connection of j and q at potentials as indicated; (d) j_{inf} and q_{eq} as a function of potential. For demonstrating the absence of hysteresis, the anodic and the cathodic scans of the $j_{\mathrm{inf}} - E$ curve are drawn by thin and thick lines, respectively.

The steps of the procedure of getting the PPI forms are as follows: First, the integrated forms are calculated (see Fig.1b). As it is shown in Fig.1c for a couple of potentials, the $j - q$ dependence is linear. Finally, according to Eq. 5 straight lines were fitted to these points by a linear least squares program. Finally, from the fitted slopes and intercepts q_{eq} and j_{inf} values were calculated for each potential; these are shown in Fig.1d. Both curves are hysteresis-free; the characteristic values of the curves: j_{inf}, q_{eq} and the $\mathrm{d}\log(j_{\mathrm{inf}})/\mathrm{d}E$ slope at $E = 0$ are exactly the same as can be calculated from the input data.

4. Discussion

1. Apparently Eq. 4 is a simple combination of three basic equations known and used for decades. The novelty within this communication is that instead of calculating the $j(E)$ function of a single CV by employing exponential potential dependences for the rate coefficients as it was done in the previous studies [6,7,8], we set aside the potential dependence of the rate coefficients and evaluate a set of CVs with different scan-rates at the same potential together. This is how we can extrapolate to a rate with zero-coverage, and to adsorption equilibrium conditions at a certain potential. Hence this derivation is analogous to that of the quasireversible diffusion-controlled redox reaction case of Refs. [2,3] which also lead to the $j(t) = j_{\mathrm{inf}}(E) - H(E) \cdot T(t)$ equation where H is some parameter combination related to the kinetics and T is some integral transform of the measured current coefficient.

2. In general, Eq 5 holds without any constraint to the specific form of potential dependence of the rate coefficients. In the numeric example of the previous Section, exponential $k_{\mathrm{ad}}(E)$ and $k_{\mathrm{d}}(E)$ were assumed. However, other $k_{\mathrm{ad}}(E)$ and $k_{\mathrm{d}}(E)$ functions also lead to the two PPI functions, as it will be demonstrated in a next communication. This way, the analysis is applicable not only for the simplest Langmuirian adsorption; however, it is an open question whether or not Eq. 5 holds for the Temkin and Frumkin adsorption isotherms.

3. The theory with little changes applies also for redox reactions of surface confined species. For this, we denote the oxidised and reduced forms of some species as Ox and Red, taking part in the $\mathrm{Red}^{z+} \rightleftharpoons \mathrm{Ox}^{(z+n)+} + n\mathrm{e}^-$ reaction of rate coefficients $k_{\mathrm{ox}}(E)$ and $k_{\mathrm{red}}(E)$. The meaning of the symbols has somewhat to be changed, like Γ and Γ_0 are the surface concentration of Ox and the total concentration of Ox and Red, respectively; $H(E) = k_{\mathrm{ox}}(E) + k_{\mathrm{red}}(E)$. Eq 5. applies with these changes.

4. There might be complications mainly due to (i) the non-zero solution resistance (IR drop) and to (ii) double layer charging. The IR drop effect is easy to be corrected by determining the solution resistance R_{s} through measuring an impedance spectrum at sufficiently high frequencies. Since all ε potentials of this text are of interfacial nature, the IR drop must be subtracted from the applied potential; i.e. we have to plot $j(q)$ points corresponding to the same $\varepsilon - jR_{\mathrm{s}}$ potential, and analyse these plots to extract j_{inf} and q_{eq}. Note that one cannot perform the IR drop correction on the raw j-E plots by simply subtracting jR_{s} from the potentials [10]; one can do this correction only on the PPI j_{inf}. The charging current error can be corrected if the double layer capacitance, C_{dl}, is also known from the high frequency impedance measurements. As the charging current appears in the *rhs* of Eq.1 as a $C_{\mathrm{dl}}\, \mathrm{d}E/\mathrm{d}t$ term, one has to plot $j - C_{\mathrm{dl}}\, \mathrm{d}E/\mathrm{d}t$ vs q instead of Eq 5.

5. Since j_{inf} and q_{eq} are PPI functions, their $\partial/\partial E$ derivatives are also PPI – these derivatives are the reciprocal of the adsorption resistance and the adsorption capacitance (cf. Eqs A-123 and A-144 of [11]). This is how the large-signal and small-signal response functions (CV and impedance, respectively of the given systems) are related to each other through their PPI forms. This last correspondence is analogous to that of the quasireversible diffusion-controlled redox reaction [12].

5. Conclusions

The theory presented here, along with the illustrating simulations, shows how to transform adsorption-related voltammograms to yield two PPI functions. One of them is characteristic to adsorption kinetics, the other to adsorption equilibrium. From an algebra point of view, Eq. 5 is a simple combination of three well-known equations pertinent to the voltammetry of adsorption; however, by making use of the implicit scan-rate dependence of the current and of its integral at a constant potential we can extrapolate to the purely kinetics-controlled and purely equilibrium-based situations. These two PPI functions are determined from a set of voltammograms of different scan-rates or from voltammograms comprising a number of cycles with varied scan-rates.

The theory leading to Eq.5 opens a new route for the determination of adsorption rates and adsorption isotherms in electrochemical systems, just as for those of the analogous case of surface confined redox reactions.

Acknowledgements:

The research within project No. VEKOP-2.3.2-16-2017-00013 was supported by the European Union and the State of Hungary, co-financed by the European Regional Development Fund. Financial assistance of the National Research, Development and Innovation Office of through the project OTKA-NN-112034 is acknowledged.

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