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 also applicable to CVs of redox systems with a finite quantity of reactants, e.g. surface-confined redox systems.

1. Introduction

Cyclic voltammograms, CVs, are usually complicated functions of the scan rate; they often exhibit large hysteresis. Comparison of two CVs measured at 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 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 semi-integration [1]. In contrast, the CVs of redox systems with slower kinetics – so-called quasi-reversible systems – cannot be transformed to a single PPI function. However, as recently 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. It is shown here, using the

example of the first case, that 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 $A^{z+} + S \rightleftharpoons A_s^{(z+n)+} + ne^-$ reaction proceeds, where the e^- are the excess electrons appearing on the metal. The density of the 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 at 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 potential ε. We adhere to the usual theorisation of electrochemical kinetics [4] but ignore all complicating factors such as 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 taken 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 considered 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,

$$j(t) = dq(t)/dt = \partial q/\partial \Gamma \cdot d\Gamma(t)/dt = nF \cdot d\Gamma(t)/dt = nF \cdot \Gamma_0 \cdot d\theta(t)/dt \quad (1)$$

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

$$q(t) = \int_0^t j(\tau)d\tau = nF \cdot \Gamma(t) = nF \cdot \Gamma_0 \cdot \theta(t) \quad (2)$$

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

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

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)–(3), and introducing the symbol $H(\varepsilon) = k_{ad}(\varepsilon)c + k_d(\varepsilon)$ we obtain

$$j(\tau) = nF \cdot \Gamma_0 \cdot k_{ad}(\varepsilon) \cdot c - H(\varepsilon) \cdot q(\tau) \quad (4)$$

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 $j = const_1 - const_2 q$ line. With increasing scan rate, the points move towards the ordinate; the physical meaning of the ordinate intersection, $const_1$, 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 intersection of the line is $const_1/const_2 = nF \cdot \Gamma_0 \cdot 1/[1 + k_d(\varepsilon)/(k_{ad}(\varepsilon)c)]$, which has the physical meaning of the surface charge associated with the adsorption, in equilibrium; hence we denote it as q_{eq}.

Using this notation, Eq. 4 reads

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

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

These are the key equations using which we can express j_{inf} and q_{eq} as a function of potential. Since they depend on potential only, they do not depend on the scan rate or 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) are illustrated using simulated CVs in this section. For the rate coefficients, exponential dependence on potential was assumed, as has been generally done in previous theories since the sixties (representative studies are [6–9]). That is, the rate coefficients are $k_{ad}(E) = k_{ad}^0 \cdot \exp(\alpha_1 F(E - E_0)/RT)$ and $k_d(E) = k_d^0 \cdot \exp(-\alpha_2 F(E - E_0)/RT)$ where E_0 is the peak potential of the reversible peak ($E_0 = RT/[(\alpha_1 + \alpha_2)F] \cdot \ln(k_d^0/ck_{ad}^0)$), and the other symbols have their usual meaning. The other simulation parameters are as follows: $\alpha_1 = \alpha_2 = 0.5$, $n = 1$, $ck_{ad}^0 = 1s^{-1}$, $\Gamma_0 = 2 \times 10^{-9} mol/cm^2$. These CVs, normalized by the scan rate, are displayed in Fig. 1a; they are very similar to ones reported in the literature (cf. Fig. 8 of [6], Fig. 4 of [7], Fig. 2 of [8], and Fig. 4 of [9]).

The steps in the procedure to obtain the PPI forms are as follows: First, the integrated forms are calculated (see Fig. 1b). As 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
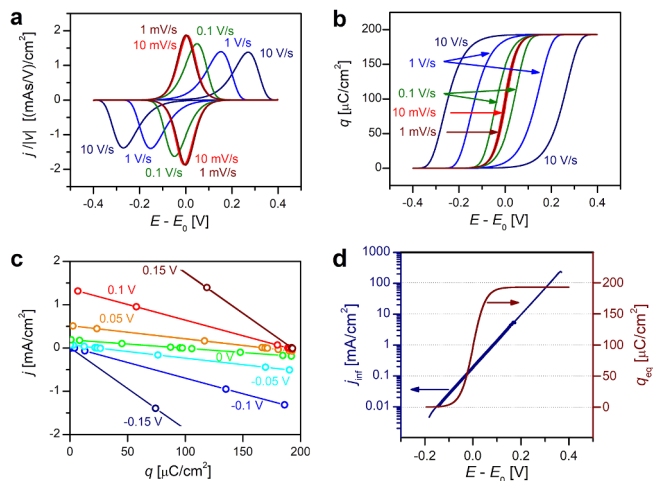
Fig. 1. Simulated adsorption–desorption CVs, and the procedure of calculation of the PPI representation. (a) The calculated scan-rate normalized CVs at the scan rates indicated; (b) The integrated CVs; (c) The linear connection of j and q at the potentials indicated; (d) j_{inf} and q_{eq} as a function of potential. To demonstrate the absence of hysteresis, the anodic and the cathodic scans of the j_{inf} – E curve are represented by thin and thick lines, respectively.

shown in Fig. 1d. Both curves are hysteresis-free; the characteristic values of the curves: j_{inf}, q_{eq} and the $d\log(j_{inf})/dE$ slope at $E = 0$ are exactly the same, as can be calculated from the input data.

4. Discussion

1. It appears that 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 in previous studies [6–8], 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 leads to the $j(t) = j_{inf}(E) - H(E) \cdot T(t)$ 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 on the specific form of potential dependence of the rate coefficients. In the numerical example in the previous section, exponential $k_{ad}(E)$ and $k_d(E)$ were assumed. However, other $k_{ad}(E)$ and $k_d(E)$ functions also lead to the two PPI functions, as will be demonstrated in a future communication. This way, the analysis is not limited to 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 small changes also applies to 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 $Red^{z+} \rightleftharpoons Ox^{(z+n)+} + ne^-$ reaction with rate coefficients $k_{ox}(E)$ and $k_{red}(E)$. The meaning of the symbols has to be changed somewhat – for example Γ and Γ_0 are the surface concentration of Ox and the total concentration of Ox and Red, respectively; $H(E) = k_{ox}(E) + k_{red}(E)$. Eq. (5). applies with these changes.

4. There might be complications due to (i) the non-zero solution resistance (IR drop) and to (ii) double-layer charging. The IR drop effect is easy to correct by determining the solution resistance R_s through measurement of an impedance spectrum at sufficiently high

frequencies. Since all ε potentials in this text are of an 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 $\varepsilon - jR_s$ 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 on the right-hand side of Eq. (1) as a $C_{dl} dE/dt$ term, one has to plot 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 illustrative simulations, shows how to transform adsorption-related voltammograms to yield two PPI functions. One of them is characteristic of adsorption kinetics, the other of adsorption equilibrium. From an algebraic 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 purely kinetics-controlled and purely equilibrium-based situations. These two PPI functions are determined from a set of voltammograms with 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, as well as for the analogous case of surface-confined redox reactions.

Declaration of Competing Interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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