



The rate-determining step in electrochemical impedance spectroscopy



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ABSTRACT

The concept of the rate-determining step (rds) is applied to electrochemical impedance spectroscopy (EIS). For consecutive (sequential) reaction steps with adsorption and fast mass transport, if the rds is preceded by rapid preequilibria and followed by fast steps then the EIS spectrum reduces to a single semicircle in the complex plane. The diameter of this semicircle is the polarization resistance and is related to the kinetics of the rds. The capacitance associated with this semicircle is the sum of the double-layer capacitance and a pseudocapacitance associated with the coverages of species in the preequilibria.

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1. Introduction

Complicated and wonderful shapes of Nyquist plots of impedance spectra in electrochemical impedance spectroscopy (EIS) have been predicted and found for multistep mechanisms. The methodology to calculate impedance spectra from arbitrary multistep reaction mechanisms is well understood, and in general the more chemical species are involved, the more complicated the spectra will be. However, a survey of the literature shows that complicated spectra are the exception rather than the rule. I propose here that the concept of the rate-determining step can be used to rationalize why semicircles in Nyquist plots are “missing”. Specifically, the case of reactions with many adsorbed species but without mass transport limitations is considered. When there is a slow rds and the other steps are fast, then the spectra reduce to just one semicircle. These predictions are validated by comparing the rds-simplified spectra with the exact results from conventional theory. Preliminary calculations have been presented previously [1]. The goal is not just to show how some impedance spectra simplify when one step or another is the rds, since specific cases are frequently dealt with in the literature, but to gain a general understanding of what it is about the concentration oscillations that lead to this simplification.

There are two common approximation methods in conventional chemical kinetics: the steady-state approximation and the preequilibrium approximation. The preequilibrium method works for a sequence of consecutive reaction steps, of which the slowest

step (smallest rate constant, highest peak on the reaction coordinate) is known as the rate-determining step (rds), e.g., step (3) in the mechanism of reactions (1)–(5). It is assumed to be much slower than all the other steps.



At steady state, steps before the rds are assumed to be much faster, and so achieve an approximate equilibrium state (a preequilibrium) in which the intermediates “queue up” and wait to ascend to the transition state of the rds. Consequently, the concentrations of the intermediates in these steps, including the reactants of the rds, may build up and may have significant concentrations. Skiing down from the transition state, the moguls of the fast subsequent steps present little impediment, and the concentrations of the intermediates after the rds are therefore assumed to be negligible. In this scenario, provided the rate constants of the subsequent steps are much faster than the rate constant of the rds, their exact values do not enter the overall rate expressions. Because neither their rate constants nor their neglected intermediate concentrations matter, these subsequent steps may be combined into a single composite step. Likewise, multiple preequilibrium steps may be combined into a single preequilibrium, and most mechanisms can be converted into a variation of a three step mechanism such as the simplification of the above scheme to:

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(It is important to remember the presence of the intermediate B in this combined scheme if it has an appreciable concentration.) In this way, the overall rate law is reduced to a composite rate constant involving the equilibrium constants and the forward rate constant of the rds multiplied by some combination of reactant concentrations, e.g., in the case of the above stoichiometry the overall rate will be $K_1 K_2 k_{\text{rds}} [A]$ and a first-order analysis can be used. The ease of analysis of first-order reactions is such that much of the conventional organic and inorganic chemical kinetic literature arranges concentrations and other conditions to afford this type of simplification. In electrochemistry, this type of analysis was popularized by Bockris and Nagy [2] and Bockris and Reddy [3], and is widely used in steady-state mechanisms to estimate Tafel slopes. The simplifying assumption that intermediates in the preequilibria have low concentrations is typically made, but is not an essential part of the method, and will not be assumed in this work.

A significant complication arises in adapting this type of analysis to EIS. The sinusoidal modulation of the potential in general leads to modulation of all the intermediate concentrations. At high enough frequencies that the rds does not respond, the concentrations of the intermediates in the preequilibrium steps may be modulated independently of the rds, i.e., the ac components of the concentrations are no longer enslaved to the rate of the rds. This does not prevent simplification, but does make the conditions for simplification more stringent than in a steady-state analysis. A staged strategy is used to present the theory. I consider in turn preequilibria, fast steps after the rds, the rds itself and then the synthesis of all of these. The proposed approximate analysis is then validated against known solutions for some simple cases. The main thrust will be to enable qualitative understanding of what approximations are appropriate under what conditions, and use this to predict when the spectra may be simplified.

2. Theory

In interpreting the meaning of the semicircles, I will make frequent references to the charge-transfer and polarization resistances, and so a brief review of their meaning is in order; see [4] for a more detailed discussion. The charge-transfer resistance is defined by Eq. (9) [5].

$$R_{\text{ct}} = \left(\frac{\partial j_f}{\partial E} \right)_{c_i, \theta_i}^{-1} \quad (9)$$

where j_f is the faradaic current density. The charge-transfer resistance tells how the rates of the electron-transfer steps, which the faradaic current density j_f is made up from, respond to a change in the potential, with the concentrations and coverages at the interface kept constant. In the ideal case, the potential can be changed instantly while the interfacial condition is frozen, and it is possible to prove that R_{ct} is the high-frequency limit of the faradaic impedance for any reaction mechanism [6]. In practice, the potential can only be changed as fast as the double-layer can be charged, which has a time constant of the order of $R_s C_{\text{dl}}$, where R_s is the solution resistance. Typically, R_s is arranged to be small, and it is omitted here without consequence. Faradaic processes that are faster than double layer charging cannot be seen, or more accurately impedance experiments cannot be used to distinguish them from double-layer charging currents. Unless such faster processes hide R_{ct} , the highest-frequency semicircle in the impedance will always be

associated with the $R_{\text{ct}} C_{\text{dl}}$ time constant. In this semicircle, the faradaic current will oscillate in phase with the potential, and there should be no oscillation of the coverages or concentrations. Because all electron-transfer steps change their free-energies of activation immediately as the potential is changed, there is no queuing, and the concept of a rate-determining step does not apply. Therefore, a Tafel plot of R_{ct} does not have the same diagnostic significance as a Tafel plot of the steady-state current [4]. This argument assumes that the highest-frequency semicircle can be detected, no matter how small it is. The detectability of a small semicircle may have a lot to do with experimental considerations, but in general the collapse of an experimental spectrum to a single semicircle is frequently a sign that one step has become rate determining, as I show below.

Semicircles at lower frequencies than the R_{ct} semicircle are due to relaxations of the surface coverages, i.e., at lower frequencies, the coverages can oscillate. In the dc limit, the interfacial concentrations and coverages have time to fully relax to the value appropriate to the potential as the potential oscillates, and so will be in phase with the potential. The current as a function of potential is then just the steady-state curve, and so the zero-frequency resistance is just the inverse slope of the steady-state current–potential curve, i.e., it is the polarization resistance, Eq. (10). (See Ref. [4] for a more formal proof.)

$$R_p = \lim_{\omega \rightarrow 0} Z(\omega) = \left(\frac{dj_{\text{ss}}}{dE} \right)^{-1} \quad (10)$$

Since R_p reflects the steady-state behavior, its Tafel behavior reflects the rds in the same way as a classical Tafel analysis. Although R_p defined above in terms of the *true* steady-state current–potential curve will be approximately the same as the inverse slope of the current–potential curve resulting from an approximate rds analysis, I will use a caret to specify \hat{R}_p and \hat{j}_{ss} estimated by an *approximate* rds analysis.

2.1. Preequilibria



A single electrosorption reaction such as Eq. (11) has a faradaic impedance that consists of the charge transfer resistance in series with a capacitance [8]. Coupled with the double-layer capacitance, the Nyquist plot shows a high-frequency semicircle with a vertical rise at low frequencies owing to the blocking capacitor, Fig. 1a. Now consider the limit in which forward and reverse rates are so fast that this reaction is always at equilibrium. Then the potential-dependent equilibrium constant is just a rearrangement of the Nernst equation, Eq. (12). (Solution concentrations are constant and included in equilibrium or rate constants in this work.) The equilibrium coverage adjusts immediately to a change in potential according to Eq. (13). Although the Langmuir isotherm is assumed in these equations, the treatment applies to other isotherms by specifying a different function $\theta_A(E)$. Essentially, the potential and coverage move along the equilibrium isotherm $\theta_A(E)$ and are in phase.

$$K_1 = \frac{k_1}{k_{-1}} = [A^-] \exp\left(\frac{F(E - E^0)}{RT}\right) = \frac{\theta_A}{1 - \theta_A} \quad (12)$$

$$\theta_A = \frac{K_1}{1 + K_1} = \theta_A(E) \quad (13)$$

A small perturbation in potential dE leads to a small perturbation in coverage $d\theta_A$, Eq. (14), and in the case of sinusoidal perturbations, perturbations dx are replaced by the sinusoidal oscillating form $\Delta x = \tilde{x} \exp(i\omega t)$. Therefore the ac coverage change may be related to the ac potential change by Eq. (15).

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