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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.

Key words: rate-determining step, EIS, impedance, adsorption

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

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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.

$$\mathrm{A} \rightleftharpoons \mathrm{B} \tag{1}$$

$$\mathrm{B} \rightleftharpoons \mathrm{C} \tag{2}$$

$$\mathrm{C} \xrightarrow{\text{rds}} \mathrm{D} \tag{3}$$

$$\mathrm{D} \xrightarrow{\text{fast}} \mathrm{E} \tag{4}$$

$$\mathrm{E} \xrightarrow{\text{fast}} \mathrm{F} \tag{5}$$

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:

$$\mathrm{A} \rightleftharpoons \mathrm{C} \tag{6}$$

$$\mathrm{C} \xrightarrow{\text{rds}} \mathrm{D} \tag{7}$$

$$\mathrm{D} \xrightarrow{\text{fast}} \mathrm{F} \tag{8}$$

(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 $K_1 K_2 k_{\text{rds}}[\mathrm{A}]$ 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 [2, 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.

1. 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].

$$R_{\mathrm{ct}} = \left(\frac{\partial j_{\mathrm{f}}}{\partial E} \right)^{-1}_{c_i, \theta_i} \tag{9}$$

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 $R_{\mathrm{s}}C_{\mathrm{dl}}$, 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 distinguished 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 $R_{\mathrm{ct}}C_{\mathrm{dl}}$ 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.)

$$R_{\mathrm{p}} = \lim_{\omega \to 0} Z(\omega) = \left(\frac{\mathrm{d}j_{\mathrm{ss}}}{\mathrm{d}E} \right)^{-1} \tag{10}$$

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 $\widehat{R}_{\mathrm{p}}$ and $\widehat{j}_{\mathrm{ss}}$ estimated by an *approximate* rds analysis.

1.1. Preequilibria

$$1.\ \mathrm{A}^-(\mathrm{aq}) \rightleftarrows \mathrm{A}(\mathrm{ads}) + \mathrm{e}^- \tag{11}$$

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 contant 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 $\theta_{\mathrm{A}}(E)$. Essentially, the potential and coverage move

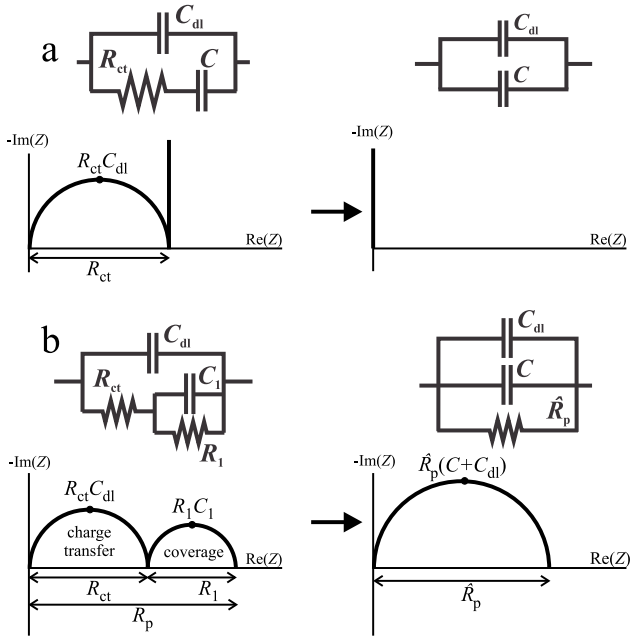

Figure 1: EIS simplifications. (a) an electrosorption reaction such as Eq. (11) in the limit of fast kinetics in both directions reduces to a pseudocapacitance. (b) a multistep reaction (here with a single adsorbate) under the assumptions that one step is rate determining collapses to a semicircle. (Labels at tops of semicircles are the approximate time constants corresponding to the top point frequency.)

along the equilibrium isotherm $\theta_{\mathrm{A}}(E)$ and are in phase.

$$K_1 = \frac{k_1}{k_{-1}} = \left[\mathrm{A}^-\right] \exp\left(\frac{F\left(E - E^{\circ}\right)}{RT}\right) = \frac{\theta_{\mathrm{A}}}{1 - \theta_{\mathrm{A}}} \tag{12}$$

$$\theta_{\mathrm{A}} = \frac{K_1}{1 + K_1} = \theta_{\mathrm{A}}(E) \tag{13}$$

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

$$\mathrm{d}\theta_{\mathrm{A}} = \frac{\mathrm{d}\theta_{\mathrm{A}}}{\mathrm{d}E}\mathrm{d}E \tag{14}$$

$$\Delta\theta_{\mathrm{A}} = \frac{\mathrm{d}\theta_{\mathrm{A}}}{\mathrm{d}E}\Delta E \tag{15}$$

As usual for a reversible adsorption process, charge flows immediately to effect a coverage change, and the *transient* current is the derivative of the isotherm

[7]. (The *steady-state* current is zero at every potential.)

$$\mathrm{d}\sigma = F\Gamma_\mathrm{m}\mathrm{d}\theta_\mathrm{A} \tag{16}$$

$$j_\mathrm{f} = \frac{\mathrm{d}\sigma}{\mathrm{d}t} = F + \mathrm{i}\omega C \tag{17}$$

$$\Delta j_\mathrm{f} = F\Gamma_\mathrm{m}\mathrm{i}\omega\Delta\theta_\mathrm{A} = F\Gamma_\mathrm{m}\mathrm{i}\omega\frac{\mathrm{d}\theta_\mathrm{A}}{\mathrm{d}E}\Delta E \tag{18}$$

$$Y_\mathrm{f} = \frac{\Delta j_\mathrm{f}}{\Delta E} = \mathrm{i}\omega\left(F\Gamma_\mathrm{m}\frac{\mathrm{d}\theta_\mathrm{A}}{\mathrm{d}E}\right) = \mathrm{i}\omega C \tag{19}$$

The faradaic impedance is just a capacitor, in fact its value is that of the steady-state pseudocapacitance, which is also the value of the capacitance in the impedance without the equilibrium approximation for a single-step reaction [8]. However, the charge-transfer resistance is now zero, consistent with the absence of any rate constants.

The case of multiple equilibria again leads to a capacitance. For example, if step 2 is added, then there are two equilibrium expressions in two coverages, which may be solved to give two coverage-potential relations, Eqs. (23) and (24).

$$2.\quad \mathrm{A(ads)} \rightleftharpoons \mathrm{B(ads)} + \mathrm{e}^- \tag{20}$$

$$K_1 = \frac{\theta_\mathrm{A}}{1-\theta_\mathrm{A}-\theta_\mathrm{B}} \tag{21}$$

$$K_2 = \frac{\theta_\mathrm{B}}{\theta_\mathrm{A}} \tag{22}$$

$$\theta_\mathrm{A} = \frac{K_1}{1+K_1+K_1K_2} = \theta_\mathrm{A}(E) \tag{23}$$

$$\theta_\mathrm{B} = \frac{K_1K_2}{1+K_1+K_1K_2} = \theta_\mathrm{B}(E) \tag{24}$$

Note that even if step 2 had no electron transfer so that K_2 were potential independent, θ_B would still depend on potential, because all the coverages are interdependent. Now the charge density change has to reflect the fact that adsorbate A requires one electron for its formation, and that adsorbate B requires two, Eq (25), and the modified derivation leads again to a capacitance.

$$\mathrm{d}\sigma = F\Gamma_\mathrm{m}\left(\mathrm{d}\theta_\mathrm{A} + 2\mathrm{d}\theta_\mathrm{B}\right) \tag{25}$$

$$Y_\mathrm{f} = \mathrm{i}\omega F\Gamma_\mathrm{m}\left(\frac{\mathrm{d}\theta_\mathrm{A}}{\mathrm{d}E} + 2\frac{\mathrm{d}\theta_\mathrm{B}}{\mathrm{d}E}\right) = \mathrm{i}\omega C \tag{26}$$

Note that if step 2 did not generate an electron, only one electron is needed to produce B(ads) and then $\mathrm{d}\sigma = F\Gamma_\mathrm{m}\left(\mathrm{d}\theta_\mathrm{A} + \mathrm{d}\theta_\mathrm{B}\right)$

1.2. Fast steps after the rds

To decouple the effect of preequilibria and fast steps, consider a three-step mechanism, Eqs. (27) - (29), in which preequilibria are absent and do not therefore generate adsorbate coverages.

$$3'.\ \mathrm{C^-(aq)} \xrightarrow{\text{rds}} \mathrm{C(ads)} + \mathrm{e^-} \tag{27}$$

$$4.\ \mathrm{2C(ads)} \xrightarrow{\text{fast}} \mathrm{C_2(ads)} \tag{28}$$

$$5.\ \mathrm{C_2(ads)} \xrightarrow{\text{fast}} \mathrm{C_2^+(aq)} + \mathrm{e^-} \tag{29}$$

The ac treatment is essentially the same as in a steady-state analysis. The net rate of production is assumed to be zero for the intermediate species after the rds, including those on the product side ot the rds, here $\mathrm{d}\theta_\mathrm{C}/\mathrm{d}t = \mathrm{d}\theta_{\mathrm{C}_2}/\mathrm{d}t = 0$. This is true exactly for steady state, but in the presence of the additional ac perturbation is the steady-state approximation: when species concentrations are small, their rates of production is set equal to zero. The fast removal of the product in one reaction by the next reaction reduces its coverage to zero. The rates of steps after the rds are then related back to the rate of the rds: $\Gamma_\mathrm{m}\mathrm{d}\theta_\mathrm{C}/\mathrm{d}t = v_{3'} - 2v_4 = 0 \Rightarrow v_4 = \frac{1}{2}v_{3'}$; $\Gamma_\mathrm{m}\mathrm{d}\theta_{\mathrm{A}_2}/\mathrm{d}t = v_4 - v_5 = 0 \Rightarrow v_5 = v_4 = \frac{1}{2}v_{3'}$. Therefore, in terms of current density:

$$j_\mathrm{f}/F = v_{3'} + v_5 \tag{30}$$

$$\widehat{j}_\mathrm{f}/F = v_{3'} + \frac{1}{2}v_{3'} = \frac{3}{2}v_{3'} \tag{31}$$

$$= \frac{3}{2}k_\mathrm{rds}\left(1 - \theta_\mathrm{A} - \theta_{\mathrm{A}_2}\right) \tag{32}$$

$$\approx \frac{3}{2}k_\mathrm{rds} \tag{33}$$

The rate law for the rds is just multiplied by a numerical factor that depends on the reaction stoichiometries; it is the number, n, of electrons crossing the interface each time the rds proceeds once. In terms of the impedance, there will be no semicircles reflecting the relaxation of coverage of species formed by the rds or subsequent steps. Impedance is blind to steps after the rds except that the "effective" rate constant of the overall reaction is the rate constant for the rds times n, which is 3/2 in this example.

For this example the rds occurs with electron transfer, which makes $k_{3'}$ depend on potential. It is evident from the current expression (33) that changes in potential lead to in-phase changes in faradaic current. More formally, the perturbation analysis leads to Y_f:

$$\widehat{j}_\mathrm{f} = \frac{3}{2}Fk_{3'} = f(E) \tag{34}$$

$$\mathrm{d}\widehat{j}_\mathrm{f} = \frac{\mathrm{d}f}{\mathrm{d}E}\mathrm{d}E \tag{35}$$

$$\Delta\widehat{j}_\mathrm{f} = \frac{\mathrm{d}f}{\mathrm{d}E}\Delta E \tag{36}$$

$$\widehat{Y}_\mathrm{f} = \frac{\Delta\widehat{j}_\mathrm{f}}{\Delta E} = \frac{\mathrm{d}f}{\mathrm{d}E} = \frac{1}{\widehat{R}_\mathrm{p}} \tag{37}$$

The derivative $\mathrm{d}f/\mathrm{d}E$ has no frequency dependence and therefore represents a resistor. Furthermore it is the derivative of the steady-state current potential curve, and so may be identified with $\widehat{R}_\mathrm{p}^{-1}$.Therefore the interfacial impedance $Z = (\mathrm{i}\omega C_\mathrm{dl} + \widehat{R}_\mathrm{p}^{-1})^{-1}$ is a semicircle of diameter $\widehat{R}_\mathrm{p}$.

1.3. The rds

To consider a more general case, the rds above (step 3′) is replaced with step 3, Eq. (38), which reacts two species A(ads) and B(ads) that are formed in preequilibria.

$$3.\ \ \mathrm{A(ads)} + \mathrm{B(ads)} \xrightarrow{\text{rds}} \mathrm{C(ads)} + \mathrm{e}^- \tag{38}$$

Specifically, assume that this rds is preceded by preequilibrium steps 1 and 2 (Eqs. (11) and (20)), and is followed by fast steps 4 and 5 (Eqs. (28) and (29)). The derivation of the admittance, Eqs. (39) - (43), proceeds similarly, but with added terms for coverages of A(ads) and B(ads).

$$j_\mathrm{rds} = Fv_\mathrm{rds} = Fk\theta_\mathrm{A}\theta_\mathrm{B} \tag{39}$$

$$\mathrm{d}j_\mathrm{rds} = \left(\frac{\partial j_\mathrm{rds}}{\partial E}\right)_{\theta_\mathrm{A},\theta_\mathrm{B}} \mathrm{d}E + \left(\frac{\partial j_\mathrm{rds}}{\partial \theta_\mathrm{A}}\right)_{\theta_\mathrm{B},E} \mathrm{d}\theta_\mathrm{A} + \left(\frac{\partial j_\mathrm{rds}}{\partial \theta_\mathrm{B}}\right)_{\theta_\mathrm{A},E} \mathrm{d}\theta_\mathrm{B} \tag{40}$$

$$= F\frac{\mathrm{d}k}{\mathrm{d}E}\theta_\mathrm{A}\theta_\mathrm{B}\mathrm{d}E + Fk\theta_\mathrm{B}\mathrm{d}\theta_\mathrm{A} + Fk\theta_\mathrm{A}\mathrm{d}\theta_\mathrm{B} \tag{41}$$

$$\Delta j_\mathrm{rds} = F\frac{\mathrm{d}k}{\mathrm{d}E}\theta_\mathrm{A}\theta_\mathrm{B}\Delta E + Fk\theta_\mathrm{B}\Delta\theta_\mathrm{A} + Fk\theta_\mathrm{A}\Delta\theta_\mathrm{B} \tag{42}$$

$$Y_\mathrm{rds} = F\frac{\mathrm{d}k}{\mathrm{d}E}\theta_\mathrm{A}\theta_\mathrm{B} + Fk\theta_\mathrm{B}\frac{\Delta\theta_\mathrm{A}}{\Delta E} + Fk\theta_\mathrm{A}\frac{\Delta\theta_\mathrm{B}}{\Delta E} \tag{43}$$

The admittance for the rds now has terms for the relaxation of the coverages of A(ads) and B(ads). These are in phase with the potential, and so $\Delta\theta_\mathrm{A}/\Delta E$ and $\Delta\theta_\mathrm{B}/\Delta E$ are replaced by $\theta_\mathrm{A}(E)$ and $\theta_\mathrm{B}(E)$ of Eqs. (23) and (24), which means that Y_rds represents a resistor. Scaling this by the number of electrons n that flow each time the rds turns over (including before the rds) gives

$$n\widehat{Y}_\mathrm{rds} = nF\frac{\mathrm{d}k}{\mathrm{d}E}\theta_\mathrm{A}\theta_\mathrm{B} + nFk\theta_\mathrm{B}\frac{\mathrm{d}\theta_\mathrm{A}}{\mathrm{d}E} + nFk\theta_\mathrm{A}\frac{\mathrm{d}\theta_\mathrm{B}}{\mathrm{d}E} \tag{44}$$

To see that this is actually the derivative of the steady-state current with potential, note that $j_\mathrm{ss} = nj_\mathrm{rds}$ and consider the total derivative

$$\frac{\mathrm{d}j_\mathrm{ss}}{\mathrm{d}E} = \left(\frac{\partial j_\mathrm{ss}}{\partial E}\right)_{\theta_\mathrm{A},\theta_\mathrm{B}} + \left(\frac{\partial j_\mathrm{ss}}{\partial \theta_\mathrm{A}}\right)_{\theta_\mathrm{B},E}\frac{\mathrm{d}\theta_\mathrm{A}}{\mathrm{d}E} + \left(\frac{\partial j_\mathrm{ss}}{\partial \theta_\mathrm{B}}\right)_{\theta_\mathrm{A},E}\frac{\mathrm{d}\theta_\mathrm{B}}{\mathrm{d}E} \tag{45}$$

$$= \left(\frac{\partial nj_\mathrm{rds}}{\partial E}\right)_{\theta_\mathrm{A},\theta_\mathrm{B}} + \left(\frac{\partial nj_\mathrm{rds}}{\partial \theta_\mathrm{A}}\right)_{\theta_\mathrm{B},E}\frac{\mathrm{d}\theta_\mathrm{A}}{\mathrm{d}E} + \left(\frac{\partial nj_\mathrm{rds}}{\partial \theta_\mathrm{B}}\right)_{\theta_\mathrm{A},E}\frac{\mathrm{d}\theta_\mathrm{B}}{\mathrm{d}E} \tag{46}$$

$$\frac{\mathrm{d}\widehat{j}_\mathrm{ss}}{\mathrm{d}E} = n\widehat{Y}_\mathrm{rds} \tag{47}$$

Therefore $n\widehat{Y}_{\mathrm{rds}}$ is equal to $\widehat{R}_{\mathrm{p}}^{-1}$ Intuitively, the capacitive current from the preequilibria is an additional contribution that must be added to the current that is controlled by the rds, so the total faradaic admittance is

$$\widehat{Y}_{\mathrm{f}} = n\widehat{Y}_{\mathrm{rds}} + \mathrm{i}\omega C = \frac{1}{\widehat{R}_{\mathrm{p}}} + \mathrm{i}\omega C \tag{48}$$

where C is the pseudocapacitance defined implicitly in Eq. (19). This addition of currents may be justified by a more mathematical treatment of the general case, which is now given.

1.4. The general case

Consider a mechanism of consecutive steps, for which the kinetics is given by a set of differential equations describing the net rate of production for each adsorbed species i:

$$\Gamma_{\mathrm{m}} \frac{\mathrm{d}\theta_i}{\mathrm{d}t} = |n_{ij}|\, v_j - |n_{ij'}|\, v_{j'} \tag{49}$$

Here the n_{ij} and $n_{ij'}$ are the stoichiometric coefficients for species i in reactions j and j', and specify how many moles of species i are formed in reaction j and removed in step j'. The current density is calculated from the rates of all the electron-transfer steps:

$$j_{\mathrm{f}} = F \sum_j n_{\mathrm{e}j} v_j \tag{50}$$

where $n_{\mathrm{e}j}$ is the stoichiometric number for the electrons in reaction j, positive for electrons as a product, negative for electrons as a reactant, and zero for a chemical step without electrons. The differential equations (49) may be used to convert each v_j in Eq. (50) to the rate of the rate-determining step and a multiple of the production rate of the species, leading to

$$j_{\mathrm{f}} = nFv_{\mathrm{rds}} + F\Gamma_{\mathrm{m}} \sum_{\mathrm{pre}\ i} m_i \frac{\mathrm{d}\theta_i}{\mathrm{d}t} - F\Gamma_{\mathrm{m}} \sum_{\mathrm{post}\ i} m'_i \frac{\mathrm{d}\theta_i}{\mathrm{d}t} \tag{51}$$

Here n is the number of electrons that pass through the interface each time the rds turns over, and pre i and post i refer to adsorbed species made in steps before the rds or removed in steps after the rds. The number m_i is the number of electrons produced when forming a pre-rds species i from reactants, and m'_i is the number of electrons produced when a post-rds species reacts further to give the final products. Note that at steady state, the time derivatives are zero, and the result is that the steady-state current density is just nFv_{rds}, as expected. To this point there is no approximation. Applying the steady-state approximation for species after the rds amounts to setting the second sum to zero, and making the preequilibrium approximation for species before the rds amounts to assuming the coverages of these species are uniquely determined by the potential through an equilibrium calculation. Under the latter assumption,

the derivative of the coverage with time may be recast in terms of a potential derivative, and the current density becomes:

$$\widehat{j}_{\mathrm{f}} = nFv_{\mathrm{rds}} + F\Gamma_{\mathrm{m}} \sum_{\text{pre } i} m_i \frac{\mathrm{d}\theta_i}{\mathrm{d}E} \frac{\mathrm{d}E}{\mathrm{d}t} \tag{52}$$

Now under small ac perturbation conditions $\mathrm{d}E/\mathrm{d}t$ becomes $\mathrm{i}\omega\Delta E$, and the faradaic admittance may be calculated:

$$\Delta\widehat{j}_{\mathrm{f}} = \frac{\mathrm{d}\left(nFv_{\mathrm{rds}}\right)}{\mathrm{d}E}\Delta E + \left(\mathrm{i}\omega\Delta E\right) F\Gamma_{\mathrm{m}} \sum_{\text{pre } i} m_i \frac{\mathrm{d}\theta_i}{\mathrm{d}E} \tag{53}$$

$$\widehat{Y}_{\mathrm{f}} = \frac{\Delta\widehat{j}_{\mathrm{f}}}{\Delta E} = \frac{\mathrm{d}\widehat{j}_{\mathrm{ss}}}{\mathrm{d}E} + \mathrm{i}\omega F\Gamma_{\mathrm{m}} \sum_{\text{pre } i} m_i \frac{\mathrm{d}\theta_i}{\mathrm{d}E} \tag{54}$$

$$= \frac{1}{\widehat{R}_{\mathrm{p}}} + \mathrm{i}\omega C \tag{55}$$

$$C = F\Gamma_{\mathrm{m}} \sum_{\text{pre } i} m_i \frac{\mathrm{d}\theta_i}{\mathrm{d}E} \tag{56}$$

In immediately writing the derivative $\mathrm{d}\left(nFv_{\mathrm{rds}}\right)/\mathrm{d}E$ without considering the coverages, the assumption has again been made that the coverages are known functions of the potential; see Eq. (45) for the justification. The capacitance found in the impedance is evidently the same as the steady-state capacitance: the derivative with respect to potential of the charge to form the equilibrium coverages of the adsorbed species, assuming the species after the rds are neglected. This capacitance is in parallel with the polarization resistance, and also with the double-layer capacitance as in Fig. 1b.

2. Discussion

The general derivation and examples above assume a strictly consecutive mechanism, in which an intermediate is produced in one step and removed in the next. However, the results will apply more generally. For example, the exact way in which the preequilibria interact is unimportant; the only requirement is that the reactant coverages in the rds can be related uniquely to the potential. Likewise, there could be branching in the steps after the rds without altering the conclusion. There does have to be a single reaction pathway, since the rate-determining step concept does not apply for parallel pathways. Intermediate species must not appear in both preequilibrium steps and steps after the rds: a species whose coverage is rapidly reduced to zero by a step after the rds cannot also be at equilibrium. (External species, whose concentrations are held constant, such as H^+ in a pH buffered solution, can be in both pre- and post-rds steps without conflict.)

The simplification of the impedance is based on a few simple ideas:

1. Species produced in the rds or subsequent steps are removed rapidly, and since their coverages do not build up they do not show relaxation features in EIS.
2. The coverages of species in preequilibrium steps oscillate in phase with the potential, which gives an out-of-phase pseudocapacitive contribution to the current.
3. For an electron-transfer rds, the potential oscillation leads to oscillation of the rate constant in the rds, which gives an in-phase contribution to the current of the rds.
4. The coverages of the reactants in the rds are oscillating in phase with the potential (according to 2), which leads to an in-phase contribution to the current of the rds.
5. The two in-phase currents of 3. and 4., scaled by the number of electrons in the mechanism, is a resistive contribution to the current.

This leads to a faradaic impedance that is the parallel combination of the polarization resistance $\widehat{R}_\mathrm{p}$ and a pseudocapacitance C. Both these are in parallel with the double-layer capacitance. The capacitors can be combined into a single capacitance of value $C + C_\mathrm{dl}$. Since C is typically much larger than C_dl, it dominates this combination. There are two special cases in which the contribution leading to C is absent. The first is when there are no adsorbed species in pre-equilibrium steps, usually because there are no such steps, as in the example of Eqs. (27) - (29). The second is if the preequilibria have no electron-transfer steps, so the coverages are fixed and not affected by potential.

To validate this theory, I compare the rds analysis with the exact analysis of a two-step mechanism (Eqs. (57) - (58) with simple Langmuir kinetics (59) - (64), for which the impedance is easily calculated by standard methods, e.g., [8].

$$1.\ \ \mathrm{A^-(aq)} \rightleftarrows \mathrm{A(ads)} + \mathrm{e^-} \tag{57}$$
$$2.\ \ \mathrm{A(ads)} \rightleftarrows \mathrm{A(aq)} \tag{58}$$

$$v_1 = k_1(1-\theta_\mathrm{A}) - k_{-1}\theta_\mathrm{A} \tag{59}$$
$$= k_1^\circ(1-\theta_\mathrm{A})\exp((1-\beta_1)F\left(E-E^\circ\right)/RT) \tag{60}$$
$$- k_{-1}^\circ\theta_\mathrm{A}\exp(-\beta_1 F\left(E-E^\circ\right)/RT) \tag{61}$$
$$v_2 = k_2\theta_\mathrm{A} - k_{-2}(1-\theta_\mathrm{A}) \tag{62}$$
$$\Gamma_\mathrm{m}\frac{\mathrm{d}\theta_\mathrm{A}}{\mathrm{d}t} = v_1 - v_2 \tag{63}$$
$$j_\mathrm{f} = Fv_1 = k_1(1-\theta_\mathrm{A}) - k_{-1}\theta_\mathrm{A} \tag{64}$$

Like any reaction mechanism with a single adsorbed species that leads to a nonzero steady-state current, a Nyquist plot of impedance comprises two semicircles

(Fig. 1b, left), and for a single-adsorbate mechanism with only one electron, the complication of an inductance cannot arise [9]. Consider first the case where the first step is a preequilibrium, and the second step is rate limiting. As in the usual Tafel analysis, the current is written in terms of the rate expression for the rds, Eq. (65), Then the coverage(s) of the reactants in the rds are expressed in terms of the preequilibrium constants, in this case using Eq. (12). Differentiation then leads to $\widehat{R}_{\rm p}$.

$$\widehat{j}_{\rm ss} = Fk_2\theta_{\rm A} \tag{65}$$

$$= Fk_2K_1/(1+K_1) \tag{66}$$

$$\frac{1}{\widehat{R}_{\rm p}} = \frac{{\rm d}\widehat{j}_{\rm ss}}{{\rm d}E} = \frac{F^2k_2}{RT(1+K_1)^2} \tag{67}$$

The coverage-potential relationships for the preequilibria, here Eq. (13), are differentiated and used to find the pseudocapacitance.

$$\frac{{\rm d}\theta_{\rm A}}{{\rm d}E} = \frac{F}{RT(1+K_1)^2} \tag{68}$$

$$C = F\Gamma_{\rm m}\frac{{\rm d}\theta_{\rm A}}{{\rm d}E} = \frac{F^2\Gamma_{\rm m}}{RT(1+K_1)^2} \tag{69}$$

$$\widehat{R}_{\rm p}C = \Gamma_{\rm m}/k_2 \tag{70}$$

For a preequilibrium steady-state current such as Eq. (65) to be a good approximation requires $k_2 \ll (k_1 + k_{-1})$ [10]; note that k_1 and k_{-1} do not both have to be much larger than k_2. However, Fig. 2a shows that for the impedance case, both k_1 and k_{-1} need to be much greater than k_2, otherwise equilibrium coverages are not achieved and the approximation is poor. At least in this case, closer agreement is obtained when the equilibrium lies to the left rather than to the right, e.g., when k_1 and k_{-1} are exchanged (not shown). Another interesting feature of this analysis that can be useful in practice is that the time constant, Eq. (70), will depend on potential only if the rds is an electron-transfer step. Fits to the impedance will yield $\widehat{R}_{\rm p}$ and $C+C_{\rm dl}$. Given that a pseudocapacitance (mF cm^{-2}) is typically much larger than a double-layer capacitance (μF cm^{-2}), $C + C_{\rm dl}$ may be approximated as C, and Eq. (70) used to extract k_2. The high capacitance is a sign that this semicircle represents coverage relaxation.

Consider now the case where the first step is the rds, and the second step is fast. From Eq. (37), the faradaic admittance is just the polarization resistance, Eq. (71), which is in parallel with the double-layer capacitance.

$$\frac{1}{\widehat{R}_{\rm p}} = \frac{{\rm d}\widehat{j}_{\rm ss}}{{\rm d}E} = F\frac{{\rm d}k_1}{{\rm d}E} = \frac{(1-\beta_1)F^2k_1}{RT} \tag{71}$$

Fig. 2b shows that k_1 and k_2 have to be significantly different: even for k_2 one hundred times larger than k_1 there is a noticeable discrepancy between the approximate and exact analyses; this disappears by $k_2 = 10^3k_1$. Fits to

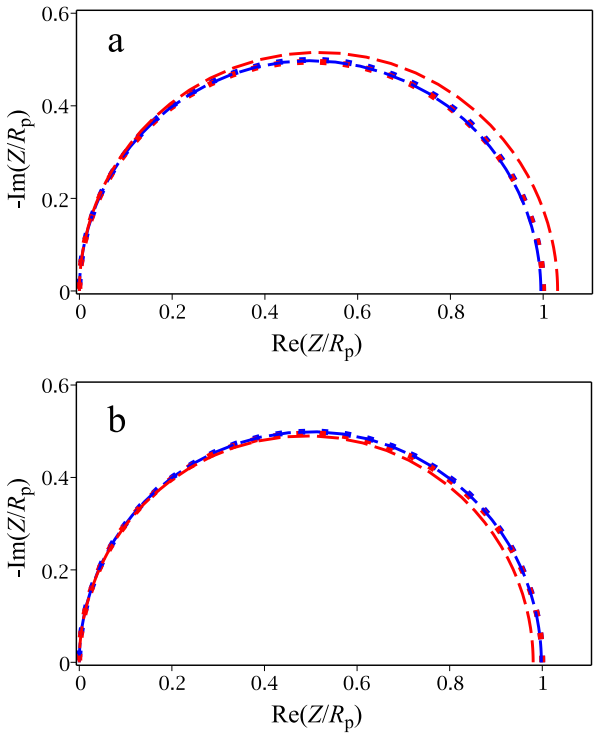

Figure 2: Comparison of approximate (dashed) and real (dotted) spectra. Mechanism of Eqs. (57) and (58). Dotted spectra are indistinguishable on this scale. (a) Step 2 rds. blue: $k_1 = 1 \times 10^{-5}$, $k_{-1} = 1 \times 10^{-5}$, $k_2 = 1 \times 10^{-7}$, $k_{-2} = 0$ mol cm^{-2} s^{-1}, $\Gamma_\mathrm{m} = 2.5$ nmol cm^{-2} s^{-1}, $C_\mathrm{dl} = 20$ μF cm^{-2}, $\beta_1 = 0.5$; red: same except $k_{-1} = 1 \times 10^{-6}$ mol cm^{-2} s^{-1} (b) Step 1 rds. blue: $k_1 = 1 \times 10^{-7}$, $k_2 = 1 \times 10^{-4}$, $k_{-1} = k_{-2} = 0$ mol cm^{-2} s^{-1}, others as in (a); red: same except $k_2 = 1 \times 10^{-5}$ mol cm^{-2} s^{-1}.

the semicircle would yield $\widehat{R}_\mathrm{p}$ and C_dl, and the small size of the latter should distinguish it from a pseudocapacitance. This is a sign that there is no significant coverage relaxation on the surface. Since the capacitance associated with this semicircle is C_dl, it is appropriate to ask if $\widehat{R}_\mathrm{p}$ can also be considered to be a charge-transfer resistance. Eq. (71) describes how the current changes with potential at a fixed surface condition (coverage effectively zero), and so both $\mathrm{d}j_\mathrm{f}/\mathrm{d}E = R_\mathrm{p}^{-1}$ and $(\partial j_\mathrm{f}/\partial E)_{\theta_i} = R_\mathrm{ct}^{-1}$ seem to apply. The true value of R_ct does reduce to the above expression under the assumed conditions, namely that the coverage is small and the back reaction of step 1 is negligible.

In this example, making appropriate rate constants much larger than the rate constant in the selected rds easily gives cases where two semicircles reduce to a single semicircle. The general framework developed can readily be applied to other cases of interest.

From the experimental point of view, one is presented with a complicated spectrum with a number of semicircles or other features. Electrochemical rate

constants change dramatically with potential, which typically means that at different potentials, different steps may be rate determining, and semicircles appear and disappear. A general theory is available that predicts the maximum number of features for an arbitrary adsorption reaction mechanism [11], and in principle these features are all distinct at equilibrium [12]. Moving away from equilibrium, there may be several regions with preequilibria and one or another step as rds, but at the highest overpotentials, all reactions will tend to be driven into irreversibility. For regions where the spectrum approximates a semicircle, the capacitance gives an indication of the state of coverage on the surface, or signals the absence of adsorbed species if it is the double-layer capacitance. The resistance gives information about the rds, as in a classical Tafel analysis, and the potential-dependence of the time constant may have similar information. Information from the different simplified regimes can then be used to build a more complete model of the reaction steps. This can then be tested more completely using conventional theory.

A detailed discussion of the criteria for simplification is outside the scope of this paper. However, a simple criterion for the preequilibrium approximation to apply is that the equilibria be achieved much faster than the oscillations are occurring. To estimate how large the rate constants must be for the preequilibria to be sustained at a given frequency ω, note that the approach to equilibrium occurs with time constant $\Gamma_{\mathrm{m}}/\left(k_j + k_{-j}\right)$ so that all preequilibria j need to satisfy Eq (72):

$$\Gamma_{\mathrm{m}}/\left(k_j + k_{-j}\right) \ll \omega^{-1} \tag{72}$$

This is a criterion for the features attributable to the preequilibrium kinetics to be small relative to the dominating semicircle. If these time constants are so short that they are less than the time constant for double-layer charging, then the features are not just small but are not measurable in principle. Sengoku et al [13] have considered this latter case in detail. Although they talk about fast and slow reactions, their method works by classifying species into fast and slow groups, and then using matrix methods to simplify the impedance. Their method is more quantitative than here regarding the conditions under which simplifications occur, but they do not explicitly use the idea of the rds or preequilibria.

Further work is required to refine the conditions under which simplification occurs. For example, when are the preequilibrium coverages so small that the capacitance may become comparable with the double-layer, and the prequilibria are not detected? How close are the approximate $\widehat{R}_{\mathrm{p}}$ and C to their true steady-state counterparts? What can be deduced from the time constants in the general case? Are there simple rules for the sequence in which features become small or large? The methodology here, and the answers to these types of questions will aid in the general problem of how to deduce a reaction mechanism from a series of observed spectra, which remains a difficult problem in EIS.

3. Conclusions

Under conditions in which one step in a reaction mechanism is rate-determining, the impedance simplifies to a semicircle whose associated resistance and capacitance can be simply calculated. The simplification occurs when the kinetics of the preequilibrium steps before the rds are very fast on the timescale of the applied frequency, so that the oscillations of the coverages of the preequiilibrium adsorbed species are in phase with the potential. This leads to a pseudocapacitance, which can be found by an equilibrium calculation. Coverages of species after the rds are small and are not detected by EIS. The diameter of the semicircle is the polarization resistance, which is determined by the slope of the steady-state current-potential curve, and gives information about the rds.

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