Electrochemical Impedance Spectroscopy

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Preface

These notes were prepared for a brief course (8-10 lectures) on electrochemical impedance spectroscopy given at the Norwegian University of Science and Technology (NTNU), Trondheim, in the fall of 2004. Despite thinking about impedance for about twenty-five years, the only times I taught it were as a small section of a graduate course in electrochemistry that only had time to deal with a few simple cases, and as a directed studies graduate course composed mainly of readings related to circuit theory and fitting. I took this opportunity to expand the short section of notes that I had for the former course, and create notes on some of the topics in the latter course. I also took the opportunity to try to present the method for arbitrary multistep reaction mechanisms in a more pedagogical way, since in my papers on this topic there is never time to be as tutorial as I would like. Also, my thinking about which variables present the theory in the most consistent way, and how to best deal with static species has evolved over time. Owing to time constraints, some topics I would have liked to include in these notes have been omitted. Some parts could be improved, so I would appreciate any feedback on what is not clear or other suggestions for improvement[1].

Most of the notes require mathematics only at the level of knowledge of complex numbers and differentiation. Partial derivatives appear frequently, but aside from the ability to evaluate them as derivatives keeping some things constant, there is no significant multivariable calculus. Occasionally a result is proven using Laplace transformation, but usually the result is more important than the proof. Determinants appear in the formulation of the impedance in Chapter 4. Only in Sec. 4.1.1 is some matrix manipulation involved, and this section is mainly reference material that is not used elsewhere. On the other hand, the reader will find it easier with a basic understanding of basic electrochemistry, such as potentiostats, symmetry factors, exchange current densities, and Fick's laws.

I thank NTNU for providing some funding for the visit to Trondheim. I especially thank Reidar Tunold and Frode Seland for their continued hospitality to me during my stays, and apologize to Frode for any inverse relationship between time spent on this course and time spent on research. NTNU has a lot of good students and I enjoy interacting with them. Ruth Latham's requirement for a directed reading course forced me to collect papers and my thoughts on several of the topics here, and I thank her for a positive interaction in both that course and her research work on impedance data analysis.

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[1] I know already there are too many footnotes.

Chapter 1

Introduction

Electrochemical Impedance Spectroscopy (EIS) is a technique that has matured a lot in the last twenty years; its areas of application have broadened and better instrumentation and software has made it more accessible to the nonspecialist. Despite this, the interpretation of impedance spectra remains a difficult issue, and very often the state of data analysis is to fit an equivalent circuit and then guess at the meaning of its elements. This process has a number of pitfalls, and so there is some benefit in a careful introduction to both the derivation of impedance for electrochemical systems, and some elements of circuit theory. The focus on circuit theory is perhaps unusual in a review of EIS, but I hope to show that it guides the way in choosing equivalent circuits and aids in the interpretation of impedance data.

In the derivation of impedance expressions, the focus is on reaction mechanisms under fairly ideal conditions, and many other important topics such as porous electrodes or passive films are simply ignored. However, many of the principles involved in reaction kinetics are the same as in these other topics. This is especially true for corrosion, in the case where the point-defect model is used. In fact, the approach here is to develop a general methodology in the hope that other systems can be fearlessly tackled by the student.

There is some difficulty in teaching a course to a mix of students, some of whom know nothing of impedance, and others who are experienced practitioners who would like to learn some more of the subtleties. I have dealt with this mix by making the notes fairly rigorous mathematically, and trying not to gloss over points that are significant to the interpretation, making them useful as a reference work. The beginner can gloss over some of the details and the asides in the footnotes. A downside of this strategy is the large number of equations; I hope that this is not in itself daunting. More experienced practitioners will find that the presentation is very straightforward, and may want to think about some deeper issues. There are several "points to ponder" (PtP) given in footnotes that are intended to stimulate. In some cases, the answer can be found with a bit of careful thought but some others are almost research questions for which I have no answer. In contrast, the exercises are intended to be straightforward.

1.1 Overview of EIS

In the potentiostatic version of EIS (Fig. 1.1), the stimulus is a small ac sine wave in potential applied on top of the d.c. potential. The current response of the electrochemical system contains an a.c component, whose phase is in general shifted from the phase of the potential. The phase and magnitude of the a.c.components of the potential and current are treated as the phase and magnitudes of complex numbers $\widetilde{E}$ and $\widetilde{j}$, and their ratio gives the impedance, from which kinetic

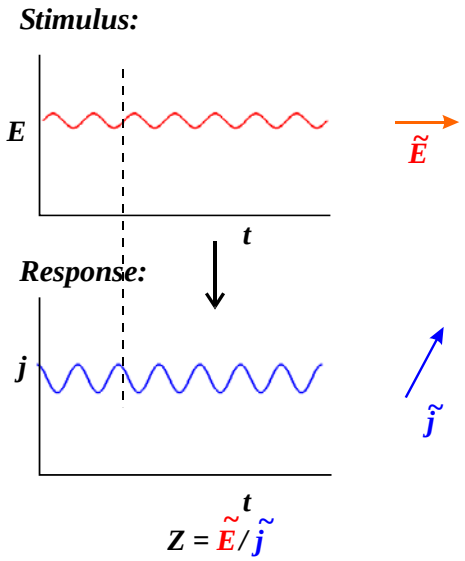


Figure 1.1: The principle of potentiostatic EIS

information may be derived. From the experimental point of view (Fig. 1.2), a function generator generates the small amplitude sine wave voltage, typically 5 mV rms (the *perturbation*). This is applied, together with a d.c. voltage, to the electrochemical cell via a potentiostat. The response to this potential program is a current, which in general consists of both a.c. and d.c. components. The current is measured (in the current-to-voltage converter of the potentiostat, or by measuring the voltage across a resistor in series with the cell), and an instrument such as a Frequency Response Analyzer (FRA) measures the amplitude and phase of the a.c. component of both the current and the potential. These are converted into a value of the impedance at the frequency of the sine wave. The measurement is then repeated at a series of different frequencies, thus building up an impedance *spectrum*.

The objective is to determine some kinetic parameters of the electrochemical system. The basic idea is that the different processes occurring in the electrochemical system have different characteristic time constants. For low enough frequencies of the applied perturbation, all the processes can "keep up" with the perturbation. As the frequency is increased beyond the reciprocal of the time constant of the process, the process struggles to keep up and responds with less amplitude and an increasing phase shift, and, at higher frequencies yet, ceases to respond. As the frequency is progressively increased, more and more processes "drop out" – the frequency at which they do so is a measure of their kinetics – and the kinetic behavior of the whole system is mapped out. This is seen most clearly on a plot of the magnitude of the impedance versus the frequency (Fig. 1.3), which shows characteristic bends or "break frequencies" that occur at the reciprocals of the system's time constants [1,2]. The slopes of the straight sections are characteristic of the types of elements in the equivalent circuit, which is an electrical analog of the electrochemical system under study. For example, slope of zero = resistor, slope of -1 = capacitor, slope of -1/2 = Warburg (diffusional) element.

[1] Strictly, only some of them are "system time constants" in the sense of linear systems theory.

[2] PtP: But the impedance is getting smaller as we go to higher frequencies, indicating the current response is *increasing* in magnitude as we go to higher frequencies.

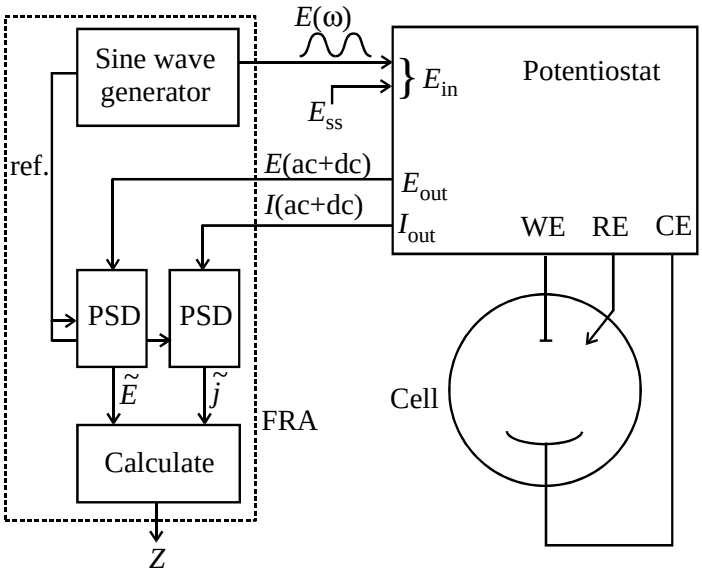


Figure 1.2: Experimental setup for potentiostatic EIS

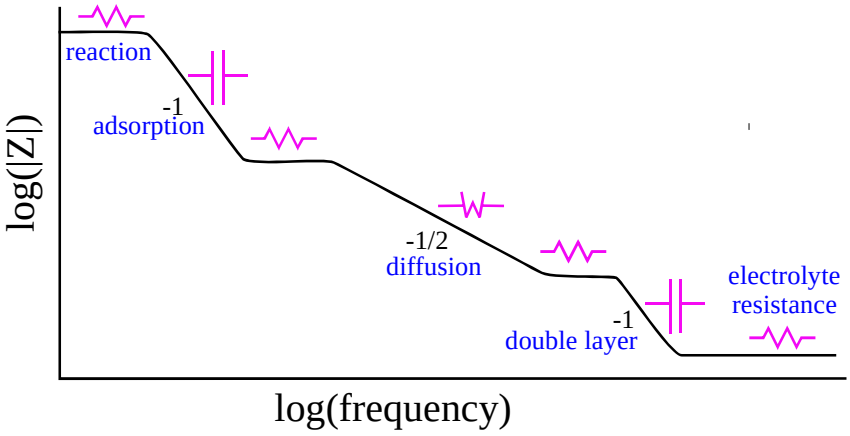


Figure 1.3: Typical log magnitude vs log frequency plot.

The Bode plot is a pair of plots, of the log of the magnitude of the impedance and of its phase[3], each versus the log of the frequency. The phase plot typically has peaks like a spectrum, perhaps justifying the name Electrochemical Impedance *Spectroscopy*, (apparently coined by Florian Mansfeld in a 1983 paper) but the analogy with an optical spectrum becomes clearer if the magnitude spectrum is differentiated twice.

EIS may be compared with the other potentiostatic method for extracting kinetic parameters, namely chronoamperometry. It has several advantages (most of these are advantages over any other transient methods):

- It is featureful: the semicircles and other features are usually visually obvious and easily distinguishable by a data analysis computer program; compare this to distinguishing mono- and bi-exponential decays in a current transient.
- A single instrument can typically measure time constants over many orders of magnitude; in a current transient, a single oscilloscope could not work on both the microsecond and kilosecond time scales.
- The instruments have extremely good noise rejection: The transient current of a system after 100 s is typically lost in the noise, but the a.c. component at 10 mHz is readily measured.
- Because the kinetic equations are linearized in the analysis, it is always possible solve the equations to find the equivalent circuit, so that numerical values of parameters can almost always be found.
- Because it applies only a small perturbation from steady-state, it can monitor electrochemical systems such as batteries and fuel cells in their operating conditions.

Against this, there are several disadvantages:

- Because the kinetic equations are linearized in the analysis, some information is lost and only certain combinations of rate parameters can be extracted. (This is often true for other methods as well.) A full analysis of parameters at all potentials can lead to complete parameter extraction but such an analysis is not usually attempted.
- Because software can easily fit equivalent circuits, it has become common to intuitively assign meaning to equivalent circuit elements and their values, without a rigorous justification. This can lead to erroneous interpretation.
- The method requires that the system comes to a steady state for the time scale of the measurement, which is typically quite long.
- Although prices are coming down, some instrumentation remains outragously expensive.

1.2 Notation

All our quantities will be normalized for the area of the electrode, since this is essential for comparing data between different workers using differently sized electrodes. For current, we will be explicit and use j for current density. To avoid confusion with the square root of -1, we will denote the latter quantity by i (note that this is not italicized). For capacitance, resistance,

[3] These are the real and imaginary parts of the log of impedance, $\ln(Z) = \ln(|Z|\exp(\mathrm{i}\,\varphi)) = \ln|Z| + \mathrm{i}\,\varphi$.

impedance and other quantities, the normalization with respect to area is implicit, e.g., C denotes capacitance per unit area (F m^{-2}), impedance Z is in Ohms times square meters (Ω m^2).

The real and imaginary parts of complex numbers will be denoted $\mathrm{Re}(X)$ and $\mathrm{Im}(X)$, or sometimes X_r and X_i. We will avoid the nomenclature Z' and Z'' for real and imaginary parts of impedance, since in the electrical engineering literature $Z = Z' - \mathrm{i}\,Z''$ and $Y = Y' + \mathrm{i}\,Y''$, but elsewhere $Z = Z' + \mathrm{i}\,Z''$ and $Y = Y' + \mathrm{i}\,Y''$. Where we need to be clear that a quantity is complex, we use a tilde, $\widetilde{X}$, but Z and Y are always assumed complex, so we omit the tildes for these.

The applied potential perturbs the system about its steady state with frequency f, and angular frequency $\omega = 2\pi f$. The potential perturbation induces many other variables to oscillate about their steady state values. We write the perturbation $X - X_\mathrm{ss} = \Delta X$ [4]. This symbol is used variously by different authors; here it is a time varying quantity that may include several harmonics[5]:

$$X = X_\mathrm{ss} + \Delta X = X_\mathrm{ss} + X(\omega) + X(2\omega) + \cdots \tag{1.1}$$

We write the a.c. component at a single frequency as

$$\begin{aligned} X(\omega) &= |X|\sin(\omega t + \varphi) && (1.2)\\ &= |X|[\cos(\varphi)\sin(\omega t) + \sin(\varphi)\cos(\omega t)] && (1.3)\\ &= [|X|\cos(\varphi)]\sin(\omega t) + [|X|\sin(\varphi)]\cos(\omega t) && (1.4)\\ &= X_\mathrm{r}\sin(\omega t) + X_\mathrm{i}\cos(\omega t) && (1.5) \end{aligned}$$

where X_r and X_i terms are known as the in-phase and quadrature components. It is natural to associate $X(\omega)$ with a complex number

$$\begin{aligned} \widetilde{X} &= X_\mathrm{r} + \mathrm{i}\,X_\mathrm{i} && (1.6)\\ |\widetilde{X}| &= |X| && (1.7)\\ \arg(\widetilde{X}) &= \varphi && (1.8)\\ \mathrm{Re}(\widetilde{X}) &= X_\mathrm{r} = |X|\cos(\varphi) && (1.9)\\ \mathrm{Im}(\widetilde{X}) &= X_\mathrm{i} = |X|\sin(\varphi) && (1.10)\\ \widetilde{X} &= |X|\exp(\mathrm{i}\,\varphi) && (1.11) \end{aligned}$$

A little thought shows that it is possible to also get the right mapping to a complex number if instead we define $X(\omega) = |X|\cos(\omega t - \varphi)$.[6]. However, the convention we have chosen is that of the instrument makers, who define zero phase at a positive-going zero crossing [7].

1.3 Defining Impedance

In potentiostatic EIS the applied potential is a steady (d.c.) potential and a small amplitude sine wave at some angular frequency ω. The current density flowing through the cell in response to this will be the sum of a steady-state current density j_ss, an a.c. component at angular frequency ω, and higher frequency components at angular frequencies $2\omega, 3\omega, \cdots$.

[4] In cases of Faradaic rectification, we should distinguish the original steady state value before switching on the perturbation, X_ss from the dc component of the signal in the presence of the perturbation, X_dc.

[5] Many of our results apply whether or not ΔX is periodic, and require only that it be small. However, in the interests of simplicity we assume small periodic signals throughout.

[6] Perhaps surprisingly, engineering texts do not take much care in defining the reference point and sign of the phase.

[7] I'm glad you've made the effort to read the footnotes. Remind me to tell the phase story!

We are usually most interested in the current response at ω, denoted $j(\omega)$. We are interested in both the magnitude and phase (relative to the phase of the a.c. component of the potential); so we have

$$\begin{aligned} E &= E_{\rm ss} + E(\omega) && (1.12)\\ j &= j_{\rm ss} + j(\omega) + j(2\omega) + \cdots && (1.13)\\ E(\omega) &= |E|\sin(\omega t) && (1.14)\\ j(\omega) &= |j|\sin(\omega t + \varphi) = |j|[\cos(\varphi)\sin(\omega t) + \sin(\varphi)\cos(\omega t)] && (1.15) \end{aligned}$$

As above, we can represent the potential and current density components at ω by complex numbers:

$$\begin{aligned} \widetilde{E} &= |E|\exp(0) = E_{\rm r} + {\rm i}\,E_{\rm i} = E_{\rm r} && (1.16)\\ \widetilde{j} &= |j|\exp({\rm i}\,\varphi) = j_{\rm r} + {\rm i}\,j_{\rm i} && (1.17) \end{aligned}$$

where $j_{\rm r} = |j|\cos(\varphi)$ and $j_{\rm i} = |j|\sin(\varphi)$. $E_{\rm i} = 0$ because we have defined the phase φ as relative to the potential, i.e., the potential has zero phase. We define the impedance, Z, and the admittance, Y, as ratios of the complex numbers for current density and potential[8].

$$\begin{aligned} Z &= \frac{\widetilde{E}}{\widetilde{j}} = \frac{E_{\rm r} + {\rm i}\,E_{\rm i}}{j_{\rm r} + {\rm i}\,j_{\rm i}} = \frac{E_{\rm r}}{j_{\rm r} + {\rm i}\,j_{\rm i}} && (1.18)\\ Y &= \frac{1}{Z} = \frac{\widetilde{j}}{\widetilde{E}} = \frac{j_{\rm r} + {\rm i}\,j_{\rm i}}{E_{\rm r} + {\rm i}\,E_{\rm i}} = \frac{j_{\rm r} + {\rm i}\,j_{\rm i}}{E_{\rm r}} && (1.19) \end{aligned}$$

(The final form for the impedance is not explicitly in the form $a + {\rm i}\,b$; this can be remedied by multiplying the numerator and denominator of the impedance by the complex conjugate of the denominator:

$$Z = \frac{E_{\rm r}}{j_{\rm r} + {\rm i}\,j_{\rm i}} = \frac{E_{\rm r}}{(j_{\rm r} + {\rm i}\,j_{\rm i})}\frac{(j_{\rm r} - {\rm i}\,j_{\rm i})}{(j_{\rm r} - {\rm i}\,j_{\rm i})} = \frac{E_{\rm r}j_{\rm r} - {\rm i}\,E_{\rm r}j_{\rm i}}{j_{\rm r}^2 + j_{\rm i}^2} \qquad (1.20)$$

Note that $\mathrm{Re}(Z) \neq 1/\mathrm{Re}(Y)$.)

Although we have defined the phase of the current relative to a positive-going zero crossing in the ac component of the potential for mathematical simplicity, the numerical value of the impedance in independent of the reference point for the phase. The definition of impedance that we have used here is readily extended to the case of higher order impedances dealing with higher harmonics, for example, the second-order admittance[9] may be defined as

$${}^2Y = \frac{j_{2\rm r} + {\rm i}\,j_{2\rm i}}{E_{\rm r}^2} \qquad (1.21)$$

where $j_{2\rm r}$ and $j_{2\rm i}$ are the in-phase and quadrature coefficients of the second harmonic $j(2\omega)$[10].

[8] Instruments are always calibrated in rms amplitude, which is $1/\sqrt{2}$ times the amplitude defined here. Once we take the ratio to get admittance or impedance, we get the same answer.

[9] By analogy with nonlinear optics, this should be called the hyperadmittance.

[10] PtP: the reference point for the phase does matter for the higher-order impedances, so one needs to know exactly what one's instrument does.

1.4 Impedance of a capacitor

In general, the impedance and admittance are both functions of frequency. As an example, consider a capacitor for which the fundamental relationship between current and potential is[11]

$$j = C\frac{dE}{dt} \tag{1.22}$$

The steady-state solution is that the current density is zero for any steady potential

$$j_{\rm ss} = 0 = C\frac{dE_{\rm ss}}{dt} \tag{1.23}$$

We now derive the impedance of a capacitance by some different methods.

1.4.1 Using real signals

This is the right way to do it. Substituting $E = E_{\rm ss} + |E|\sin(\omega t)$ in the fundamental relationship gives

$$j = \omega C|E|\cos\omega t = \omega C|E|\sin(\omega t + \pi/2) \tag{1.24}$$

As expected, the steady-state current is zero, there are no harmonics and there is a phase shift of 90°. Working with the complex numbers:

$$\widetilde{j} = \omega C|E|\exp(\mathrm{i}\,\pi/2) = \mathrm{i}\,\omega C|E| = \mathrm{i}\,\omega C\widetilde{E} \tag{1.25}$$

$$Z_C = \frac{\widetilde{E}}{\widetilde{j}} = \frac{1}{\mathrm{i}\,\omega C} \tag{1.26}$$

$$\boxed{Y_C = \mathrm{i}\,\omega C} \tag{1.27}$$

1.4.2 Using complex exponentials

This is the easy way to do it. All that stuff with trig relationships seems complicated. The math is simpler if we imagine that

$$E = E_{\rm ss} + \Delta E \approx E_{\rm ss} + \widetilde{E}\exp(\mathrm{i}\,\omega t) \tag{1.28}$$

$$j = j_{\rm ss} + \Delta j \approx j_{\rm ss} + \widetilde{j}\exp(\mathrm{i}\,\omega t) \tag{1.29}$$

the broken equals denoting our delusional use of a complex signal when we really only have a real signal[12]. Substituting these into the fundamental equation (1.22) gives

$$j_{\rm ss} + \widetilde{j}\exp(\mathrm{i}\,\omega t) = C\frac{d(E_{\rm ss} + \widetilde{E}\exp(\mathrm{i}\,\omega t))}{dt} \tag{1.30}$$

$$= C\frac{dE_{\rm ss}}{dt} + C\frac{d(\widetilde{E}\exp(\mathrm{i}\,\omega t))}{dt} \tag{1.31}$$

[11] The sign convention used in circuit theory is that an arrow is written in one direction through the component, arbitrarily chosen. Positive current applies if the current flows in the arrow direction. The potential difference is defined as the potential at the tail of the arrow minus the potential at the head of the arrow.

[12] In the case of the current density, we are also assuming that the response has only the fundamental harmonic, usually a reasonable approximation.

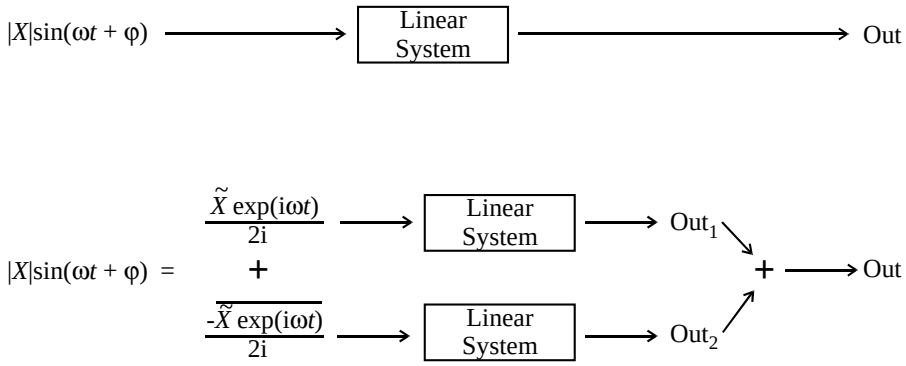


Figure 1.4: Decomposition of a real signal into two complex ones. Top and bottom diagrams are equivalent.

Subtracting the steady-state equation (1.23) gives

$$\widetilde{j}\exp(\mathrm{i}\,\omega t) = C\frac{d(\widetilde{E}\exp(\mathrm{i}\,\omega t))}{dt} \tag{1.32}$$

$$= \mathrm{i}\,\omega C\widetilde{E}\exp(\mathrm{i}\,\omega t) \tag{1.33}$$

Cancelling $\exp(\mathrm{i}\,\omega t)$ from each side and then dividing each side by $\widetilde{E}$ gives the result we got before

$$\widetilde{j} = \mathrm{i}\,\omega C\widetilde{E} \tag{1.34}$$

$$\frac{\widetilde{j}}{\widetilde{E}} = \mathrm{i}\,\omega C \tag{1.35}$$

$$Y = \mathrm{i}\,\omega C \tag{1.36}$$

Why are we allowed to get away with this? Well we replaced the correct $|X|\sin(\omega t+\varphi) = X_\mathrm{r}\sin(\omega t) + X_\mathrm{i}\cos(\omega t)$ (Eq. 1.5) by $\widetilde{X}\exp(\mathrm{i}\,\omega t)$, which is

$$\widetilde{X}\exp(\mathrm{i}\,\omega t) = (X_\mathrm{r} + \mathrm{i}\,X_\mathrm{i})(\cos(\omega t) + \mathrm{i}\sin(\omega t)) \tag{1.37}$$

$$= X_\mathrm{r}\cos(\omega t) - X_\mathrm{i}\sin(\omega t) + \mathrm{i}(X_\mathrm{r}\sin(\omega t) + X_\mathrm{i}\cos(\omega t)) \tag{1.38}$$

or

$$X_\mathrm{r}\sin(\omega t) + X_\mathrm{i}\cos(\omega t) = \mathrm{Im}(\widetilde{X}\exp(\mathrm{i}\,\omega t)) = \frac{\widetilde{X}\exp(\mathrm{i}\,\omega t) - \overline{\widetilde{X}\exp(\mathrm{i}\,\omega t)}}{2\,\mathrm{i}} \tag{1.39}$$

where the bar indicates complex conjugate. For a linear system

$$\mathrm{Response}(aA + bB) = a\mathrm{Response}(A) + b\mathrm{Response}(B) \tag{1.40}$$

so that the if we know the response to $\widetilde{X}\exp(\mathrm{i}\,\omega t)$ and the response to $\overline{\widetilde{X}\exp(\mathrm{i}\,\omega t)}$ (for which the derivation is only trivially different) then we know the response to $X_\mathrm{r}\sin(\omega t) + X_\mathrm{i}\cos(\omega t)$, which is a linear combination of these (Fig. 1.4)

This method does not work for non-linear systems, and although we will make use of it for its mathematical simplicity, we must remember to abandon it for any work with higher harmonics or large amplitude signals in real systems.

1.4.3 Transfer Function method

This is the method for those who like to invoke higher mathematics. Taking Laplace transforms of the fundamental capacitor equation (1.22) gives immediately the same result as before (Eq. (1.34))

$$\widetilde{j} = sC\widetilde{E} \tag{1.41}$$

if we interpret the tilde as meaning the Laplace-transformed quantity, $s = \mathrm{i}\,\omega$ and throw away the initial condition part of the transform of a derivative ($\mathfrak{L}(dx/dt) = s\mathfrak{L}(x) - x(0+)$). The transfer function is the transformed output over the transformed input, and in this case is the admittance

$$Y = sC \tag{1.42}$$

Admittance and impedance are often calculated (and defined) in this way, but again *this only works for linear systems.* Careful use of transform methods requires consideration of a number of subtle points: Why is $s = \mathrm{i}\,\omega$ used above yet the Laplace variable also has a real part ($s = \mathrm{i}\,\omega+\sigma$)? What is the difference between ω, the applied angular frequency, and ω, the variable in s? Why did we discard the initial condition part? On the other hand, we can go a long way in the intuitive way we applied the transform above.

1.5 Resistors and Inductors

From here on, we assume that higher harmonics are negligible, and we use the complex exponential method. We first practice it for the resistor and inductor. For an inductor, from the fundamental relationship $E = Ldj/dt$ we proceed by

1. Substituting in $E = E_{\mathrm{ss}} + \Delta E$ and $j = j_{\mathrm{ss}} + \Delta j$

$$\begin{aligned} E_{\mathrm{ss}} + \Delta E &= Ld(j_{\mathrm{ss}} + \Delta j)/dt & (1.43)\\ &= Ldj_{\mathrm{ss}}/dt + Ld\Delta j/dt & (1.44)\end{aligned}$$

2. Subtracting the relationship at steady state.

$$\begin{aligned} \text{subtract:} \quad & E_{\mathrm{ss}} = Ldj_{\mathrm{ss}}/dt & (1.45)\\ \text{leaves:} \quad & \Delta E = Ld\Delta j/dt & (1.46)\end{aligned}$$

3. Express the Δ quantities as complex exponentials and cancel $\exp(\mathrm{i}\,\omega t)$

$$\begin{aligned} \widetilde{E}\exp(\mathrm{i}\,\omega t) &= Ld[\widetilde{j}\exp(\mathrm{i}\,\omega t)]/dt & (1.47)\\ &= \mathrm{i}\,\omega L\widetilde{j}\exp(\mathrm{i}\,\omega t) & (1.48)\\ \widetilde{E} &= \mathrm{i}\,\omega L\widetilde{j} & (1.49)\end{aligned}$$

4. Divide through all terms by $\widetilde{E}$.

$$\begin{aligned} 1 &= \mathrm{i}\,\omega L\widetilde{j}/\widetilde{E} & (1.50)\\ Y_L &= 1/\mathrm{i}\,\omega L & (1.51)\end{aligned}$$

$$\boxed{Z_L = \mathrm{i}\,\omega L} \tag{1.52}$$

For a resistor, we have no differentiation to do and so we can simplify things by recognizing that

$$\frac{\Delta j}{\Delta E} = \frac{\widetilde{j}\exp(\mathrm{i}\,\omega t)}{\widetilde{E}\exp(\mathrm{i}\,\omega t)} = \frac{\widetilde{j}}{\widetilde{E}} \tag{1.53}$$

From the fundamental relationship for a resistor, $E = jR$, steps 1 and 2 give

$$\Delta E = (\Delta j)R \tag{1.54}$$

We can immediately divide through by ΔE

$$1 = \frac{\Delta j}{\Delta E}R = YR \tag{1.55}$$

$$Y = 1/R \tag{1.56}$$

$$\boxed{Z_R = R} \tag{1.57}$$

Now that we have done the impedances for the linear circuit elements, we can finish elementary circuit theory by adding the rules that impedances in series add and admittances in parallel add. So for a resistor R in series with a capacitor C we have

$$Z = R + \frac{1}{\mathrm{i}\,\omega C} \tag{1.58}$$

for the parallel combination we have

$$Y = \mathrm{i}\,\omega C + 1/R \tag{1.59}$$

1.6 A Δ Calculus

A consideration of the above examples suggests that we need never actually expand the ΔX quantities as complex exponentials, if we just use the differentiation rule directly:

$$\frac{d\Delta X}{dt} = \mathrm{i}\,\omega \Delta X \tag{1.60}$$

We also note that since the equations must be satisfied at steady state, we can always subtract the steady state parts of each variable, so it is possible to immediately move from the variable to its perturbation. So we can abbreviate the method to "*perturb, differentiate, divide by* ΔE"

So we can essentially do the inductor in one step

$$E = Ldj/dt \tag{1.61}$$

$$\frac{\Delta E}{\Delta E} = L\,\mathrm{i}\,\omega\frac{\Delta j}{\Delta E} \tag{1.62}$$

$$1 = \mathrm{i}\,\omega LY \tag{1.63}$$

$$Y = \frac{1}{\mathrm{i}\,\omega L} \tag{1.64}$$

For the perturb step, we may sometimes need to use a Taylor series to find the perturbation.

$$f(E_{\mathrm{ss}} + \Delta E) = f(E_{\mathrm{ss}}) + \left(\frac{df}{dE}\right)_{E=E_{\mathrm{ss}}}\Delta E + \cdots \tag{1.65}$$

$$\Delta f \approx \left(\frac{df}{dE}\right)_{E=E_{\mathrm{ss}}}\Delta E \tag{1.66}$$

For example, for a diode

$$j = j_0[\exp(aE) - 1] = f(E) \tag{1.67}$$

$$\begin{aligned} \text{perturb: } \Delta j &= \left(\frac{df}{dE}\right)_{E=E_{\text{ss}}} \Delta E && (1.68)\\ &= aj_0 \exp(aE_{\text{ss}})\Delta E && (1.69)\\ \text{divide by } \Delta E\text{: } Y &= aj_0 \exp(aE_{\text{ss}}) && (1.70) \end{aligned}$$

In the case of multiple variables, we use the multivariable form of Taylor's series. For example, for a rate v that depends on both potential and a concentration c

$$\begin{aligned} v &= v(c, E) && (1.71)\\ v(c + \Delta c, E + \Delta E) &= v_{\text{ss}} + \left(\frac{\partial v}{\partial c}\right)_E \Delta c + \left(\frac{\partial v}{\partial E}\right)_c \Delta E && (1.72)\\ \Delta v &= \left(\frac{\partial v}{\partial c}\right)_E \Delta c + \left(\frac{\partial v}{\partial E}\right)_c \Delta E && (1.73) \end{aligned}$$

where, as before, the partial derivatives are evaluated at the steady state, but we have not encumbered the notation to indicate this.

Chapter 2

Simple Electrochemical Systems

2.1 The Electrochemical Interface

We recall the potential profile in an electrochemical cell (Fig. 2.1). We define the distance from the electrode as z, positive away from the electrode. All fluxes away from the electrode are also considered positive. Currents in this direction are also positive, in accord with the IUPAC convention of anodic currents being positive. Recall that the electrode potential differs from the potential drop at the interface only by a constant, so that changes in the potential drop are equal to changes in the electrode potential

$$E = \Delta\phi_{\mathrm{m-s}} + \text{ constant} \tag{2.1}$$

Since our principal interest here is kinetics and not the subtle nature of the structure of the interface, we will assume a parallel-plate capacitor model of the double-layer capacitance (Fig. 2.2).

We now consider ways of charging and discharging the double layer. From the picture in Fig. 2.2, bringing positive charges in from the wire constitutes a positive current and makes the charge on the metal σ_{m} more positive. On the other hand, electrons leaping across the interface from right to left constitutes a positive (oxidation) current that makes the charge on the metal more negative, and so appears with a negative sign in the equation below. This electron-transfer

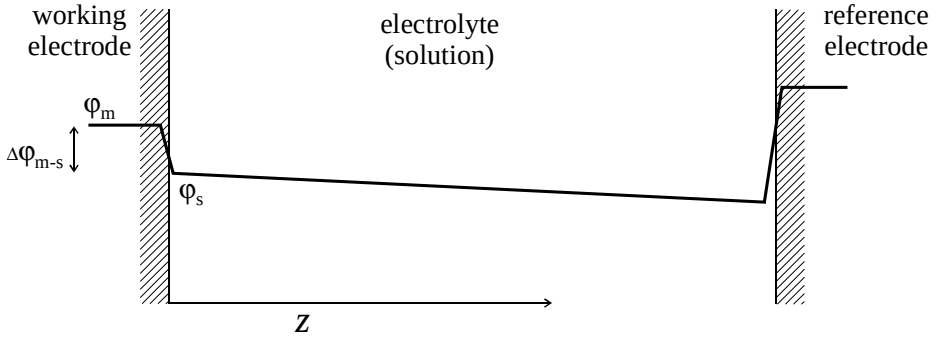


Figure 2.1: Potential profile in an electrochemical cell

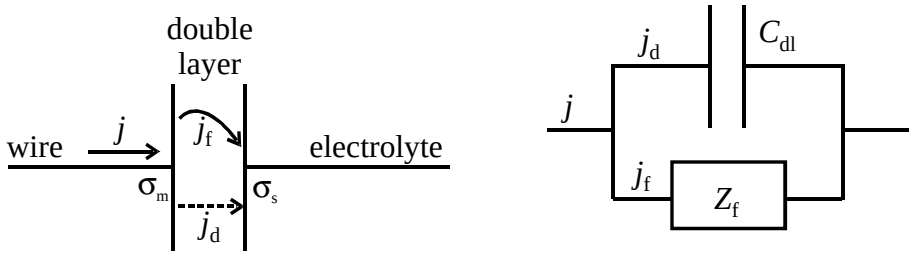


Figure 2.2: Currents at the double-layer capacitance and the equivalent circuit of the interface.

reaction current j_f is the Faradaic current.

$$\frac{d\sigma_\mathrm{m}}{dt} = j - j_\mathrm{f} \tag{2.2}$$

This equation is just a statement of the conservation of charge.

At steady-state, the left-hand side of Eq. (2.2) must be zero and the current flowing through the wire is equal to the Faradaic current. But as the system is changing, the current we measure, that through the wire, is not equal to the reaction current as we would like it to be. Thus although the double layer is to some the most fascinating part of electrochemistry, to most of us it's just a nuisance, and we need to work hard to minimize its effect.

If displacement currents are included, then current is conserved. Displacement current is not a real current in the sense that real charges are moving, but is defined in terms of changes in electric field $\boldsymbol{E}$

$$\boldsymbol{j}_\mathrm{d} = \varepsilon_0 \frac{d\boldsymbol{E}}{dt} \tag{2.3}$$

$$j_\mathrm{d} = \varepsilon_0 \frac{dE_z}{dt} \quad \text{(1-D)} \tag{2.4}$$

Gauss's law shows that

$$E_z = \frac{\sigma_\mathrm{m}}{\varepsilon_0} \tag{2.5}$$

Then the displacement current is

$$j_\mathrm{d} = \frac{d\sigma_\mathrm{m}}{dt} \tag{2.6}$$

so from Eq. 2.2,

$$j = j_\mathrm{d} + j_\mathrm{f} \tag{2.7}$$

which is just a statement of conservation of current since it says that the current in the wire is equal to the current crossing the interface. We identify the displacement current with the double-layer charging current; the subscript "d" can also mean double-layer. Thus, under some very non-restrictive assumptions, we have proven that the measured current is the sum of the Faradaic current and the double-layer charging current[1]. Thus the electric circuit analog or equivalent circuit is a parallel arrangement of the double-layer impedance and the Faradaic impedance (whose form depends on the nature of the reaction).

[1] PtP: What exactly is the minimum set of assumptions that we need to make? How are these affected by adsorption?

The double-layer capacitance is defined as[2]

$$C_{\mathrm{d}} = \frac{d\sigma_{\mathrm{m}}}{d\Delta\phi_{\mathrm{m-s}}} = \frac{d\sigma_{\mathrm{m}}}{dE} \tag{2.8}$$

and provided that the charge depends only on the potential we can convert this to

$$C_{\mathrm{d}} = \frac{d\sigma_{\mathrm{m}}}{dt} \Big/ \frac{dE}{dt} \tag{2.9}$$

$$j_{\mathrm{d}} = C_{\mathrm{d}} dE/dt \tag{2.10}$$

as expected for a capacitor. (It follows from Eq. (2.8) that for the double-layer capacitance (or any capacitance)

$$\Delta E = \frac{\Delta\sigma_{\mathrm{m}}}{C_{\mathrm{d}}} \tag{2.11}$$

$$\widetilde{E} = \frac{\widetilde{\sigma}_{\mathrm{m}}}{C_{\mathrm{d}}} \tag{2.12}$$

i.e., the charge is in phase with the potential.) From the current conservation equation (2.7) and Eq. (2.10), we show that the equivalent circuit of the Fig. 2.2 applies:

$$Y = \frac{\widetilde{j}}{\widetilde{E}} = \frac{\widetilde{j_{\mathrm{d}}} + \widetilde{j_{\mathrm{f}}}}{\widetilde{E}} = \mathrm{i}\,\omega C_{\mathrm{d}} + Y_{\mathrm{f}} \tag{2.13}$$

And the total measured impedance between the working electrode and the reference electrode, including the solution resistance is

$$Z_{\mathrm{tot}} = \frac{\widetilde{E} + \widetilde{E}_{\mathrm{s}}}{\widetilde{j}} = Z + R_{\mathrm{s}} = \frac{1}{\mathrm{i}\,\omega C_{\mathrm{dl}} + Y_{\mathrm{f}}} + R_{\mathrm{s}} \tag{2.14}$$

where R_{s} is the resistance of the solution between the working electrode and the reference electrode (also called R_{u}, the uncompensated resistance).

Now we consider several different types of reactions, and calculate Z_{f} for them.

2.2 One-Step Reaction without Diffusion or Adsorption

Suppose we have a single elementary reaction, with rapid diffusion of product and reactants, and no adsorption at the electrode surface.

$$\mathrm{A(aq)} + \mathrm{e}^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{A}^-\mathrm{(aq)} \tag{2.15}$$

$$v_1 = k_1[\mathrm{A}] - k_{-1}[\mathrm{A}^-] \tag{2.16}$$

The rate v_1 is a surface rate, in mol m^{-2} s^{-1}, and we define it as the net rate in the direction written, i.e., it is positive if the reaction goes forward and negative if the reaction goes backward. As usual in electrochemistry, the rate constants depend exponentially on potential

$$k_1 = k_1^0 \exp\left(-\frac{\beta_1 F(E-E^0)}{RT}\right) = k_1^{\mathrm{eq}} \exp\left(-\frac{\beta_1 F\eta}{RT}\right) \tag{2.17}$$

$$k_{-1} = k_{-1}^0 \exp\left(+\frac{(1-\beta_1) F(E-E^0)}{RT}\right) = k_{-1}^{\mathrm{eq}} \exp\left(+\frac{(1-\beta_1) F\eta}{RT}\right) \tag{2.18}$$

[2] According the IUPAC, the subscript here means neither displacement nor double layer, but "differential".

where k_1^{eq} is the rate constant at the equilibrium potential. The form with superscript "eq" is less commonly used[3] than the standard rate constant k_1^0, but has some advantages for multistep mechanisms. The overpotential η is unambiguous here, but in the case of multistep mechanisms it needs to be remembered that η is the overpotential for the overall reaction. With rapid diffusion, the concentrations of A and A^- at the surface are fixed, so that the rate depends only on the potential. The current is related to the rate by

$$j_{\mathrm{f}} = -Fv_1 \tag{2.19}$$

Proceeding as before

$$Y_{\mathrm{f}} = \frac{\Delta j_{\mathrm{f}}}{\Delta E} = \frac{-F\Delta v_1}{\Delta E} = \frac{-F(dv_1/dE)_{E=E_{\mathrm{ss}}}\Delta E}{\Delta E} = -F\left(\frac{dv_1}{dE}\right)_{E=E_{ss}} \tag{2.20}$$

Now $(dv_1/dE)_{E=E_{\mathrm{ss}}}$ is negative (rate of a cathodic reaction decreases with increasing potential) and it also does not depend on frequency. Thus the Faradaic impedance is a positive constant, $Y_{\mathrm{f}} = 1/R_{\mathrm{ct}}$, i.e., the Faradaic reaction acts like a resistor, the *charge transfer resistor*. From the assumed potential dependence of the rate constants, we can calculate the potential dependence of this resistor:

$$\frac{dv_1}{dE} = \frac{dv_1}{d\eta} = \left(-\frac{\beta_1 F}{RT}\right) k_1^{\mathrm{eq}} \exp\left(-\frac{\beta_1 F\eta}{RT}\right)[\mathrm{A}] \tag{2.21}$$

$$-\left(+\frac{(1-\beta_1)F}{RT}\right) k_{-1}^{\mathrm{eq}} \exp\left(+\frac{(1-\beta_1)F\eta}{RT}\right)[\mathrm{A}^-] \tag{2.22}$$

$$= -\left(\frac{\beta_1 F}{RT}\right) k_1[\mathrm{A}] - \left(\frac{(1-\beta_1)F}{RT}\right) k_{-1}[\mathrm{A}^-] \tag{2.23}$$

$$\frac{1}{R_{\mathrm{ct}}} = \left(\frac{\beta_1 F}{RT}\right) k_1[\mathrm{A}] + \left(\frac{(1-\beta_1)F}{RT}\right) k_{-1}[\mathrm{A}^-] \tag{2.24}$$

Now at equilibrium ($\eta = 0$) we have $v_1 = 0$ since the forward and reverse rates are equal (this is a definition of equilibrium) and

$$k_1^{\mathrm{eq}}[\mathrm{A}] = k_{-1}^{\mathrm{eq}}[\mathrm{A}^-] = \frac{j_0}{F}$$

where j_0 is the exchange current density. Therefore

$$\frac{1}{R_{\mathrm{ct}}} = \frac{j_0 F}{RT}\left[\beta_1 \exp\left(-\frac{\beta_1 F\eta}{RT}\right) + (1-\beta_1)\exp\left(+\frac{(1-\beta_1)F\eta}{RT}\right)\right] \tag{2.25}$$

If $\beta = \frac{1}{2}$ then this curve is symmetrical with respect to the minimum at $\eta = 0$. At $\eta = 0$, $R_{\mathrm{ct}} = RT/j_0F$, i.e., we can find the exchange current density from an impedance measurement. The faster the reaction (higher j_0), the lower the resistance. Note that this is the same result we would have found if we defined a resistance from the steady-state current-potential curve.

$$\frac{1}{R_{\mathrm{ct}}} = \frac{dj_{\mathrm{ss}}}{dE} \tag{2.26}$$

Far from equilibrium, a log plot enables extraction of β_1. Note that the charge-transfer resistance is a *differential* resistance; it is not the same as E/j_{ss}.

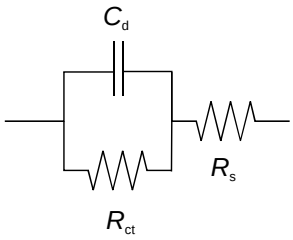


Figure 2.3: Equivalent circuit for a simple electron-transfer reaction.

Combining this with the rest of the interface gives the equivalent circuit of Fig. 2.3.

This makes intuitive sense - the reaction resistor provides a way to discharge the capacitor, since electrons cross the interface. A few words about this equivalent circuit are in order:

- We were able to derive this form of the equivalent circuit without much regard to the detailed form of the potential dependence of the rate constants – Eq. 2.20 tells us the reaction is represented by a resistor without knowing the exact potential dependence of v_1. Our subsequent manipulation used the conventional Tafel forms of the rate constants, but other forms could have been used (e.g., the Marcus form). This is true in general: The form of the equivalent circuit depends on the linking of variables, and only when calculating the potential dependence of the elements do we need the intimate details of the rate laws.

- As noted, the charge-transfer resistor here is a differential resistor, reflecting the slope of the current-potential curve at the steady-state potential at which the impedance experiment is carried out. In general, it cannot be used to predict the results of other types of experiments[4].

- As a particular case of the above point, this equivalent circuit can not be used for d.c. currents. Suppose it could be: We measure R_{ct} in an a.c. experiment in which the steady-state current is j_{ss}. Then we conclude that the potential drop across the interface is $j_{ss}R_{ct}$ – we have just measured the absolute potential drop at the interface, a goal that has eluded electrochemists for years!

A Bode plot is a plot of $\log|Z|$ vs $\log f$ (or $\log\omega$), together with a plot of the phase vs $\log f$ (Fig. 2.4 for this circuit). The two resistors lead to two horizontal regions on the magnitude plot, and the capacitor leads to the central region with slope -1. At high frequencies, the double-layer capacitance acts like a wire, so only the solution resistance has any effect. At low frequencies, C_d acts as an open circuit, so that the effective circuit is R_{ct} and R_s in series. Note that often, as here, the phase is considered positive when in fact it is negative; really we are plotting the phase of the admittance.

In a Nyquist plot, we plot $-\mathrm{Im}(Z)$ vs $\mathrm{Re}(Z)$ with frequency as a parameter (Fig. 2.5 for the above circuit). A semicircle is observed with high-frequency intercept on the real axis of R_s and diameter R_{ct}.

[3] Frankly, I'm the only person who uses it.

[4] Actually, because there are no concentrations or surface coverages involved in this simple case that might vary depending on the way we did the experiment, this case is an exception and probably could be used to predict the results of, say, a potential step experiment.

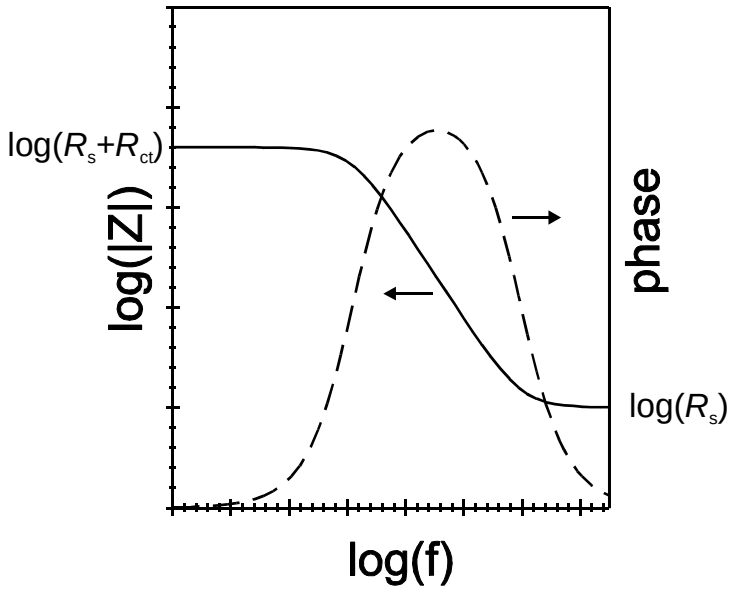


Figure 2.4: Bode plot for simple electron-transfer reaction.

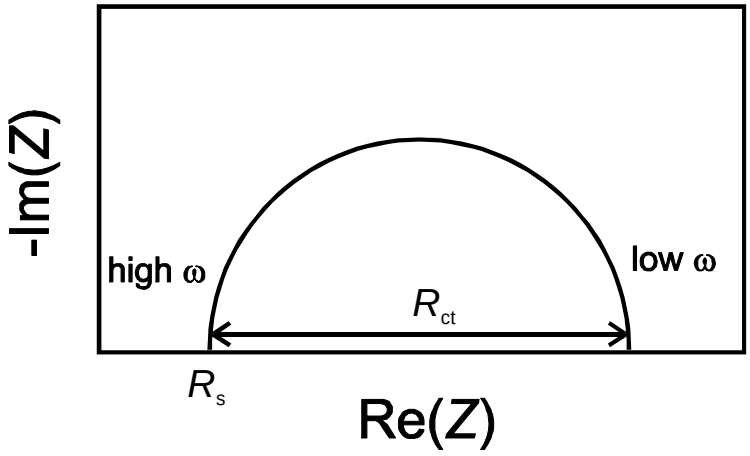


Figure 2.5: Nyquist plot for a simple electron transfer reaction.

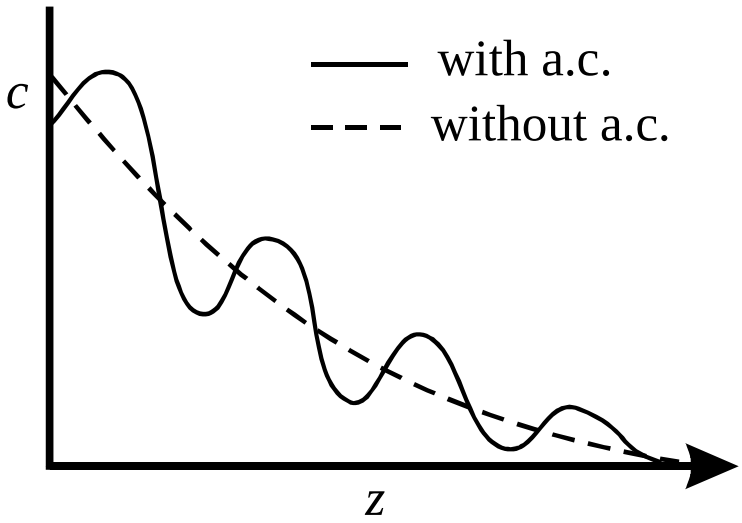


Figure 2.6: Concentration profile of a reaction product.

2.3 Mathematics of A.C. Diffusion

With an a.c. perturbation, the concentration of a diffusing species will also have an a.c. component, whose amplitude decays as we get further from the electrode (Fig. 2.6)

We suppose $c(x,t) = c_{\rm ss}(x) + \Delta c(x,t) = c_{\rm ss}(x) + \widetilde{c}(x)\exp(\mathrm{i}\,\omega t)$, and since the diffusion equation is linear, the a.c. part must be a solution (as well as the steady-state part[5]).

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{2.27}$$

and we solve in our usual way (only differentiation with respect to *time* extracts $\mathrm{i}\,\omega$)

$$\text{perturb: } \frac{\partial \Delta c}{\partial t} = D\frac{\partial^2 \Delta c}{\partial x^2} \tag{2.28}$$

$$\frac{\partial[\widetilde{c}(x)\exp(\mathrm{i}\,\omega t)]}{\partial t} = D\frac{\partial^2[\widetilde{c}(x)\exp(\mathrm{i}\,\omega t)]}{\partial x^2} \tag{2.29}$$

$$\text{differentiate: } \mathrm{i}\,\omega\widetilde{c}(x)\exp(\mathrm{i}\,\omega t) = \exp(\mathrm{i}\,\omega t)D\frac{\partial^2\widetilde{c}(x)}{\partial x^2} \tag{2.30}$$

$$\text{cancel } \exp(\mathrm{i}\,\omega t)\text{: } \mathrm{i}\,\omega\widetilde{c}(x) = D\frac{\partial^2\widetilde{c}(x)}{\partial x^2} = D\frac{d^2\widetilde{c}(x)}{dx^2} \tag{2.31}$$

where we have replaced the partial differentiation with ordinary differentiation, since $\widetilde{c}$ depends only on x, not t. Reorganizing this, we recognize it as the harmonic oscillator differential equation,

$$\frac{d^2\widetilde{c}(x)}{dx^2} = \frac{\mathrm{i}\,\omega}{D}\widetilde{c}(x) \tag{2.32}$$

[5] Actually, we are cheating here, since the semiinfinite diffusion problem doesn't have a true steady-state solution.

which has the general solution:

$$\widetilde{c}(x) = A\exp\left(-\sqrt{\frac{\mathrm{i}\,\omega}{D}}x\right) + B\exp\left(+\sqrt{\frac{\mathrm{i}\,\omega}{D}}x\right) \tag{2.33}$$

A and B are determined from the boundary conditions. The first is that the amplitude of the a.c. concentration drops to zero far from the electrode, i.e., $\widetilde{c}(\infty) = 0$. This implies that $B = 0$. Now the value of $\widetilde{c}(x)$ at the surface we denote $\widetilde{c}_\mathrm{s}$, and by substituting $x = 0$, we see that this must be equal to A. Therefore

$$\widetilde{c}(x) = \widetilde{c}_\mathrm{s}\exp\left(-\sqrt{\frac{\mathrm{i}\,\omega}{D}}x\right) \tag{2.34}$$

which tells us how the amplitude and phase of the a.c. component of the concentration change as we move away from the electrode.

Now we consider the flux (Fick's first law),

$$J = -D\frac{\partial c}{\partial x} \tag{2.35}$$

and proceed in a similar manner to give

$$\begin{aligned}
\widetilde{J}(x) &= -D\frac{d\widetilde{c}(x)}{dx} && (2.36)\\
&= -D\frac{d}{dx}\left[\widetilde{c}_\mathrm{s}\exp\left(-\sqrt{\frac{\mathrm{i}\,\omega}{D}}x\right)\right] && (2.37)\\
&= D\widetilde{c}_\mathrm{s}\sqrt{\frac{\mathrm{i}\,\omega}{D}}\exp\left(-\sqrt{\frac{\mathrm{i}\,\omega}{D}}x\right) && (2.38)
\end{aligned}$$

We are interested only in the relationship between the flux and concentration at the surface, which is all that the electrode senses.

$$\boxed{\widetilde{J}_\mathrm{s} = \widetilde{c}_\mathrm{s}\sqrt{\mathrm{i}\,\omega D}} \tag{2.39}$$

Note that

$$\begin{aligned}
\sqrt{\mathrm{i}} &= (\cos\pi/2 + \mathrm{i}\sin\pi/2)^{1/2} && (2.40)\\
&= \cos\pi/4 + \mathrm{i}\sin\pi/4 && (2.41)\\
&= \frac{1}{\sqrt{2}} + \frac{\mathrm{i}}{\sqrt{2}} && (2.42)\\
&= \frac{1}{\sqrt{2}}(1 + \mathrm{i}) && (2.43)
\end{aligned}$$

so there is a 45° phase shift between the surface flux and the surface concentration. This expression for the flux can then be combined with the reaction kinetics.

The above results are all for semi-infinite diffusion, where the diffusing species move far from the electrode surface, and the boundary condition away from the electrode is at $z = \infty$. Another important case is that of finite diffusion, where we assume the diffusion layer extends from $z = 0$ to $z = d$. If mass transport is fast outside this zone, then the a.c. component should drop to zero amplitude there, $\widetilde{c}(z = d) = 0$. The general solution is the same (Eq. (2.33)), but B is no

longer zero. The mathematics is more complicated in detail though not in principle, and leads to the flux-concentration relationship:

$$\widetilde{J}_\mathrm{s} = \widetilde{c}_\mathrm{s}\sqrt{\mathrm{i}\,\omega D}\coth\left(d\sqrt{\frac{\mathrm{i}\,\omega}{D}}\right) \tag{2.44}$$

for which the phase shift is no longer 45° but depends on d, ω and D. The finite diffusion results below follow fairly simply from the semi-infinite results by replacing $\sqrt{\mathrm{i}\,\omega D}$ with $\sqrt{\mathrm{i}\,\omega D}\coth\left(d\sqrt{\frac{\mathrm{i}\omega}{D}}\right)$. For some systems, a no-flux (blocking) boundary condition is used instead, $\widetilde{J}(z=d)=0$, but we will not consider this case further.

2.4 One-Step Reaction with Diffusion

Consider an irreversible one-step reaction with reactant diffusion:

$$\mathrm{A(aq)} + \mathrm{e}^- \xrightarrow{k_1} \mathrm{A}^-\mathrm{(aq)} \tag{2.45}$$

We now need the matching condition between reaction rate and diffusive flux. This is simply that (in the absence of adsorption)

$$r_\mathrm{A} = J_\mathrm{A,s} \tag{2.46}$$

where r_A means the reaction rate of production of species A, and $J_\mathrm{A,s}$ is the diffusive flux of A at the surface. Now since a reaction event removes a molecule of A, we have

$$r_\mathrm{A} = -v_1 \tag{2.47}$$

As the reaction proceeds in the forward direction (v_1 positive), A is consumed by the reaction (r_A negative) as it reaches the surface from the solution ($J_\mathrm{A,s}$ negative).

We now expand v_1 in a Taylor series in two variables because v_1 depends both on the potential and on the *surface* concentration of A (we will drop the subscripts "s" to simplify the notation).

$$\widetilde{v}_1 = \left(\frac{\partial v_1}{\partial c_\mathrm{A}}\right)_E \widetilde{c}_\mathrm{A} + \left(\frac{\partial v_1}{\partial E}\right)_{c_\mathrm{A}} \widetilde{E} \tag{2.48}$$

But using the flux-concentration equation (2.39) as the flux matching we have

$$\left(\frac{\partial v_1}{\partial c_\mathrm{A}}\right)_E \widetilde{c}_\mathrm{A} + \left(\frac{\partial v_1}{\partial E}\right)_{c_\mathrm{A}} \widetilde{E} = \widetilde{v}_1 = -\widetilde{J}_\mathrm{A} = -\widetilde{c}_\mathrm{A}\sqrt{\mathrm{i}\,\omega D} \tag{2.49}$$

which can be solved to find $\widetilde{c}_\mathrm{A}$:

$$\widetilde{c}_\mathrm{A} = \frac{-\left(\partial v_1/\partial E\right)_{c_\mathrm{A}}\widetilde{E}}{\left(\partial v_1/\partial c_\mathrm{A}\right)_E + \sqrt{\mathrm{i}\,\omega D}} \tag{2.50}$$

Substituting this back into the expression for faradaic current gives

$$\begin{aligned}
\widetilde{j_{\mathrm{f}}} &= -F\widetilde{v}_1 = F\widetilde{J}_{\mathrm{A}} = F\widetilde{c}_{\mathrm{A}}\sqrt{\mathrm{i}\,\omega D} \\
&= F\frac{-\left(\partial v_1/\partial E\right)_{c_{\mathrm{A}}}\widetilde{E}\sqrt{\mathrm{i}\,\omega D}}{\left(\partial v_1/\partial c_{\mathrm{A}}\right)_E + \sqrt{\mathrm{i}\,\omega D}} \\
Y_{\mathrm{f}} &= \frac{\widetilde{j_{\mathrm{f}}}}{\widetilde{E}} = -F\sqrt{\mathrm{i}\,\omega D}\frac{\left(\partial v_1/\partial E\right)_{c_{\mathrm{A}}}}{\left(\partial v_1/\partial c_{\mathrm{A}}\right)_E + \sqrt{\mathrm{i}\,\omega D}} \\
Z_{\mathrm{f}} &= 1/Y_{\mathrm{f}} = -\frac{\left(\partial v_1/\partial c_{\mathrm{A}}\right)_E + \sqrt{\mathrm{i}\,\omega D}}{F\sqrt{\mathrm{i}\,\omega D}\left(\partial v_1/\partial E\right)_{c_{\mathrm{A}}}} \\
&= -\frac{\left(\partial v_1/\partial c_{\mathrm{A}}\right)_E}{F\sqrt{\mathrm{i}\,\omega D}\left(\partial v_1/\partial E\right)_{c_{\mathrm{A}}}} - \frac{1}{F\left(\partial v_1/\partial E\right)_{c_{\mathrm{A}}}}
\end{aligned}$$

The second term is the charge transfer resistance

$$\frac{1}{R_{\mathrm{ct}}} = -F\left(\partial v_1/\partial E\right)_{c_{\mathrm{A}}} = \left(\partial j_{\mathrm{ss}}/\partial E\right)_{c_{\mathrm{A}}} \tag{2.51}$$

This time it is a partial derivative of the steady-state current with potential at constant c_{A}. In general the charge-transfer resistor tells how fast we can modify the rate at which electrons cross the interface as we adjust the potential, *keeping everything else constant.*

The first term is an impedance due to diffusion, known as the Warburg impedance; it is in series with the change transfer resistance. It has the form

$$Z_{\mathrm{W}} = \frac{\sigma'}{\sqrt{\mathrm{i}\,\omega}} = \frac{\sqrt{2}\sigma'}{(1+\mathrm{i})\omega^{1/2}} = \frac{\sqrt{2}\sigma'}{(1+\mathrm{i})\omega^{1/2}} \tag{2.52}$$

$$= \frac{\sqrt{2}\sigma'}{(1+\mathrm{i})\omega^{1/2}}\frac{(1-\mathrm{i})}{(1-\mathrm{i})} = \frac{\sqrt{2}\sigma'\,(1-\mathrm{i})}{2\omega^{1/2}} \tag{2.53}$$

$$= \sigma\,(1-\mathrm{i})\,\omega^{-1/2} \tag{2.54}$$

It is evident that the real and imaginary part are the same maginitude, and a plot of this function in the Nyquist plot gives a 45° line. On a Bode plot, it presents as a region of slope -$\frac{1}{2}$. The complete equivalent circuit is known as the Randles equivalent circuit (Fig. 2.7).

As before, the details of the mechanism are not required in deducing the form of the equivalent circuit; we have not bothered here to expand out the details of the partial derivatives. For example, step one could be quasi-reversible rather than irreversible. Logically, to consider the reverse reaction without invoking diffusion of the product would have to mean that the product had a high concentration even though the reactant had a low concentration, which seems contrived. Much less obviously, even if we have a quasi-reversible reaction with product diffusion as well as reactant diffusion, the equivalent circuit turns out to be the same, but the expression for the Warburg σ parameter is different.

In the case of a finite diffusion layer, the Warburg impedance has the form

$$Z_{\mathrm{W}} = \frac{\sigma'}{\sqrt{\mathrm{i}\,\omega}}\tanh\left(d\sqrt{\frac{\mathrm{i}\,\omega}{D}}\right) \tag{2.55}$$

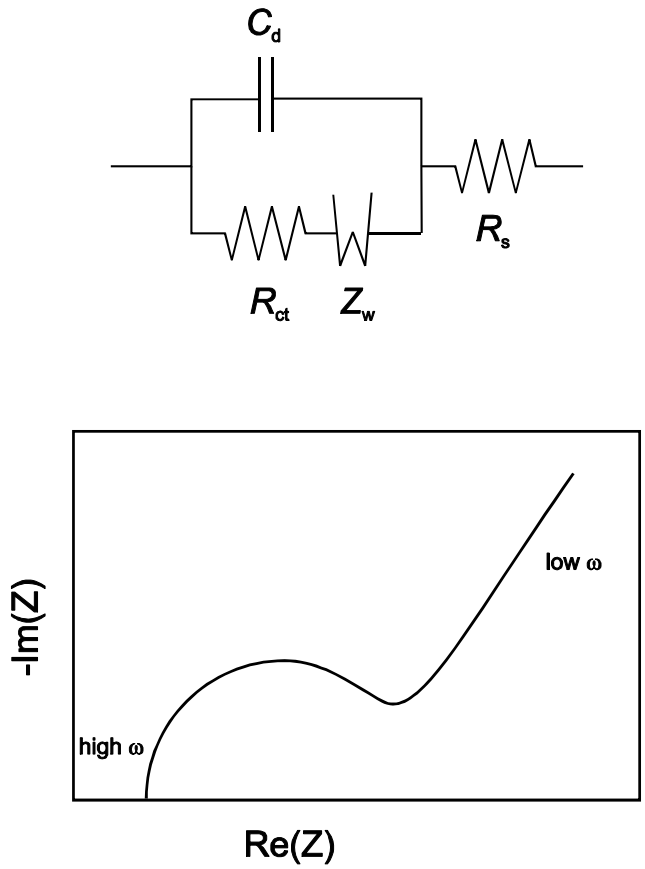


Figure 2.7: Randles Equivalent Circuit and its Nyquist Plot

2.5 One Step Reaction with Adsorption

Consider a one-step reaction with fast diffusion but which produces an adsorbed product, e.g., the underpotential adsorption of hydrogen on Pt:

$$\mathrm{Pt(site)} + \mathrm{H^+(aq)} + \mathrm{e^-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{PtH(ads)} \tag{2.56}$$

$$\begin{aligned} v_1 &= k_1\varphi - k_{-1}\theta & (2.57)\\ &= k_1(1-\theta) - k_{-1}\theta & (2.58) \end{aligned}$$

Here the fast diffusion ensures that the concentration of H^+ at the surface is constant, and we have subsumed its constant concentration into the value of the rate constant k_1. The concentration of adsorbed hydrogen, θ, is expressed as a surface coverage, the number of atoms of H adsorbed divided by the number of atoms in the top layer of Pt atoms:

$$\theta = \frac{\Gamma_\mathrm{H}}{\Gamma_\mathrm{m}} \tag{2.59}$$

where Γ means a surface concentration in mol m^{-2}, and "m" means monolayer. Note the following:

- We explicitly include the reaction sites in the reaction equation, to remind us that adsorbing a hydrogen removes an active site.
- In writing PtH(ads) we are implying that each hydrogen requires one Pt and the saturation coverage is one hydrogen per Pt. If the adsorbing H occupied two Pt atoms on adsorption, we would write Pt_2H(ads).
- Inclusion of the sites as a separate reaction species in a mass action form of the kinetics (Eq. (2.57)) is equivalent to making the usual assumptions for the Langmuir isotherm (localized adsorption sites, no lateral interactions)
- The conversion of the mass action kinetics (Eq. (2.57)) to the more usual Langmuir kinetics[6] (Eq. 2.58) also has the hidden assumption of one H per Pt. For Pt_2H, we would have $\varphi = 1 - 2\theta$.
- Our definition of θ is that usually used in surface science and has the "unit" ML for monolayers. It allows consistency in all our subsequent manipulations of stoichiometric matrices and the like. It differs from the fractional coverage, which would define the coverage as a fraction of the saturation coverage and would lead to $\varphi = 1 - \theta$ regardless of adsorption stoichiometry.

The current density ("rate of production of electrons") and rate of production of the adsorbed species are related simply to the rate:

$$\begin{aligned} j_\mathrm{f}/F &= -v_1 & (2.60)\\ \Gamma_\mathrm{m}\frac{d\theta}{dt} &= v_1 & (2.61) \end{aligned}$$

[6] The term Langmuir kinetics is preferred to Langmuir isotherm in the present context, since the latter term it implies an equilibrium relationship.

where Γ_{m} converts the $d\theta/dt$ to mol m^{-2} s^{-1}. Remembering that v_1 depends on the two oscillating variables E and θ, we may process these two equations in our usual way

$$\frac{Y_{\mathrm{f}}}{F} = \frac{\widetilde{j}_{\mathrm{f}}/F}{\widetilde{E}} = \frac{-\widetilde{v}_1}{\widetilde{E}} = -\left[\left(\frac{\partial v_1}{\partial E}\right)_\theta \frac{\widetilde{E}}{\widetilde{E}} + \left(\frac{\partial v_1}{\partial \theta}\right)_E \frac{\widetilde{\theta}}{\widetilde{E}}\right] \tag{2.62}$$

$$\mathrm{i}\,\omega\Gamma_{\mathrm{m}}\frac{\widetilde{\theta}}{\widetilde{E}} = \frac{\widetilde{v}_1}{\widetilde{E}} = \left[\left(\frac{\partial v_1}{\partial E}\right)_\theta \frac{\widetilde{E}}{\widetilde{E}} + \left(\frac{\partial v_1}{\partial \theta}\right)_E \frac{\widetilde{\theta}}{\widetilde{E}}\right] \tag{2.63}$$

The second equation may be solved for $\widetilde{\theta}/\widetilde{E}$, which may then be substituted into the first equation:

$$\frac{\widetilde{\theta}}{\widetilde{E}} = \frac{(\partial v_1/\partial E)_\theta}{\mathrm{i}\,\omega\Gamma_{\mathrm{m}} - (\partial v_1/\partial\theta)_E} \tag{2.64}$$

$$Y_{\mathrm{f}} = -F\left[(\partial v_1/\partial E)_\theta + \frac{(\partial v_1/\partial\theta)_E\,(\partial v_1/\partial E)_\theta}{\mathrm{i}\,\omega\Gamma_{\mathrm{m}} - (\partial v_1/\partial\theta)_E}\right] \tag{2.65}$$

$$= \frac{-F\left[(\partial v_1/\partial E)_\theta\,(\mathrm{i}\,\omega\Gamma_{\mathrm{m}} - (\partial v_1/\partial\theta)_E) + (\partial v_1/\partial\theta)_E\,(\partial v_1/\partial E)_\theta\right]}{\mathrm{i}\,\omega\Gamma_{\mathrm{m}} - (\partial v_1/\partial\theta)_E} \tag{2.66}$$

$$= \frac{-F\left[(\partial v_1/\partial E)_\theta\,\mathrm{i}\,\omega\Gamma_{\mathrm{m}}\right]}{\mathrm{i}\,\omega\Gamma_{\mathrm{m}} - (\partial v_1/\partial\theta)_E} \tag{2.67}$$

To see what circuit this corresponds to we convert to the impedance

$$Z_{\mathrm{f}} = \frac{\mathrm{i}\,\omega\Gamma_{\mathrm{m}} - (\partial v_1/\partial\theta)_E}{-F\left[(\partial v_1/\partial E)_\theta\,\mathrm{i}\,\omega\Gamma_{\mathrm{m}}\right]} \tag{2.68}$$

$$= -\frac{1}{F\,(\partial v_1/\partial E)_\theta} + \frac{(\partial v_1/\partial\theta)_E}{F\,(\partial v_1/\partial E)_\theta\,\mathrm{i}\,\omega\Gamma_{\mathrm{m}}} \tag{2.69}$$

$$= R_{\mathrm{ct}} + \frac{1}{\mathrm{i}\,\omega C} \tag{2.70}$$

The faradaic impedance is the series combination of a resistance and a capacitance (Fig. 2.8). The resistance can be recognized as the charge transfer resistance, since it satisfies the form

$$\frac{1}{R_{\mathrm{ct}}} = \left(\frac{\partial j_{\mathrm{ss}}}{\partial E}\right)_\theta \tag{2.71}$$

The capacitor

$$C = \frac{F\Gamma_{\mathrm{m}}\,(\partial v_1/\partial E)_\theta}{(\partial v_1/\partial\theta)_E} \tag{2.72}$$

turns out in this particular case to be equal to the steady-state adsorption pseudocapacitance

$$C_{\mathrm{ss}} = -F\Gamma_{\mathrm{m}}\frac{d\theta_{\mathrm{ss}}}{dE} \tag{2.73}$$

This relationship between a capacitance in an equivalent circuit and the adsorption pseudocapacitance is not true in general. Although not obvious, this is related to the fact that there is no resistance bridging the capacitance, and is due to the cancellation of terms between Eqs. (2.66) and (2.67). As before, the form of the equivalent circuit is independent of the details of the rate law and would be the same even if we had non-Tafel potential dependence of the rate constants or isotherms other than the Langmuir isotherm.

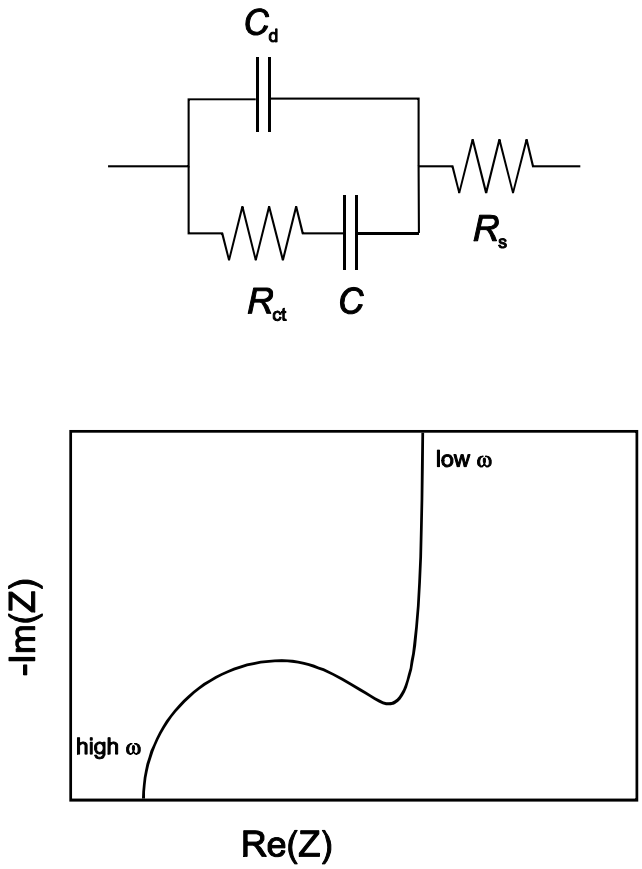


Figure 2.8: Equivalent circuit for the simple adsorption reaction and its Nyquist plot.

2.6 One Step Reaction with Adsorption and Diffusion

Now let's see how we put diffusion and adsorption together. Consider UPD adsorption of silver on Pt.

$$\mathrm{Pt(site)} + \mathrm{Ag^+(aq)} + \mathrm{e^-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{PtAg(ads)} \tag{2.74}$$

The governing equations that we need are ones we have seen before

$$\text{electrons:} \qquad j_\mathrm{f} = -Fv_1 \tag{2.75}$$

$$\mathrm{PtAg(ads)}: \qquad \Gamma_\mathrm{m}\frac{d\theta}{dt} = v_1 \tag{2.76}$$

$$\mathrm{Ag^+(aq)}: \qquad J_{\mathrm{Ag^+,s}} = -v_1 \tag{2.77}$$

and we can find the admittance by the same strategy: solve the last two equations for the oscillating concentrations $\widetilde{\theta}/\widetilde{E}$ and $\widetilde{c}/\widetilde{E}$ and substitute back into the first equation. We write c instead of $c_{\mathrm{Ag^+,s}}$ for simplicity. The only significant difference from the previous cases is that the rate v_1 now depends on three things: E, θ, and c.

$$\frac{Y_\mathrm{f}}{F} = \frac{\widetilde{j_\mathrm{f}}/F}{\widetilde{E}} = \frac{-\widetilde{v}_1}{\widetilde{E}} = -\left[\left(\frac{\partial v_1}{\partial E}\right)_{\theta,c}\frac{\widetilde{E}}{\widetilde{E}} + \left(\frac{\partial v_1}{\partial \theta}\right)_{E,c}\frac{\widetilde{\theta}}{\widetilde{E}} + \left(\frac{\partial v_1}{\partial c}\right)_{E,\theta}\frac{\widetilde{c}}{\widetilde{E}}\right] \tag{2.78}$$

$$\mathrm{i}\,\omega\Gamma_\mathrm{m}\frac{\widetilde{\theta}}{\widetilde{E}} = \frac{\widetilde{v}_1}{\widetilde{E}} = \left[\left(\frac{\partial v_1}{\partial E}\right)_{\theta,c}\frac{\widetilde{E}}{\widetilde{E}} + \left(\frac{\partial v_1}{\partial \theta}\right)_{E,c}\frac{\widetilde{\theta}}{\widetilde{E}} + \left(\frac{\partial v_1}{\partial c}\right)_{E,\theta}\frac{\widetilde{c}}{\widetilde{E}}\right] \tag{2.79}$$

$$\frac{\widetilde{J}_{\mathrm{Ag^+,s}}}{\widetilde{E}} = \frac{\widetilde{c}\sqrt{\mathrm{i}\,\omega D}}{\widetilde{E}} = -\left[\left(\frac{\partial v_1}{\partial E}\right)_{\theta,c}\frac{\widetilde{E}}{\widetilde{E}} + \left(\frac{\partial v_1}{\partial \theta}\right)_{E,c}\frac{\widetilde{\theta}}{\widetilde{E}} + \left(\frac{\partial v_1}{\partial c}\right)_{E,\theta}\frac{\widetilde{c}}{\widetilde{E}}\right] \tag{2.80}$$

In the last equation, we have used the flux-concentration relationship that we derived earlier for semi-infinite diffusion (Eq. 2.39). We do not carry out the step-by-step manipulations to get to the faradaic impedance for this case, since we will generalize and simplify the notation later. The result is that

$$Z_\mathrm{f} = -\frac{1}{F\left(\partial v_1/\partial E\right)_{\theta,c}} - \frac{\left(\partial v_1/\partial c\right)_{E,\theta}}{F\left(\partial v_1/\partial E\right)_{\theta,c}\sqrt{\mathrm{i}\,\omega D}} + \frac{\left(\partial v_1/\partial \theta\right)_{E,c}}{F\Gamma_\mathrm{m}\left(\partial v_1/\partial E\right)_{\theta,c}\mathrm{i}\,\omega} \tag{2.81}$$

$$= R_\mathrm{ct} + \frac{\sigma'}{\sqrt{\mathrm{i}\,\omega}} + \frac{1}{\mathrm{i}\,\omega C} \tag{2.82}$$

where the expressions for R_ct, σ' and C are the same as before, except that a second variable is held constant in the partial derivatives. Therefore we have the equivalent circuit and Nyquist plot of Fig. 2.9. Note that the capacitance (vertical line in the Nyquist plot) dominates in the limit of zero frequency, rather than the Warburg element. This can be seen from the equation for the faradaic impedance, in which ω goes to zero faster than $\omega^{1/2}$, so that the capacitance term eventually dominates over the Warburg term. This is a general result for all mechanisms with diffusion and a dc current of zero (blocking capacitor).

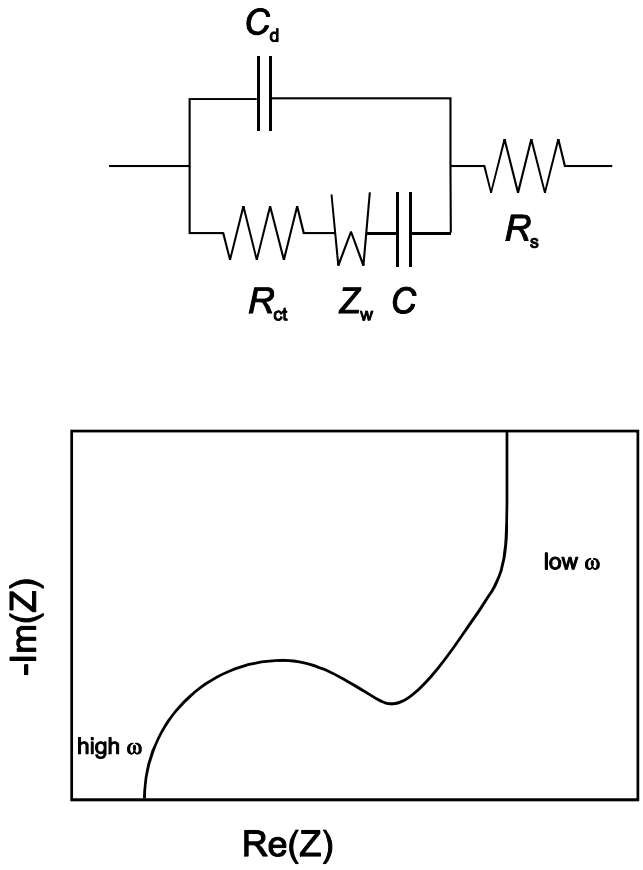


Figure 2.9: Equivalent circuit and Nyquist plot for one-step reaction with adsorption and diffusion.

Chapter 3

Circuits

We present here some elementary properties of circuits that are useful in understanding some of the capabilities and limitations of the analysis of impedance data. Suppose that we construct a circuit from a finite number of resistors, capacitors, and inductors, all connected together[1]. This circuit is passive (can't generate energy), lumped (components are small compared to the wavelength[2]), and linear (doubling the amplitude of the perturbation doubles the response). We find two places along the wires that we call the terminals, and we designate one of the terminals as a reference terminal (this might often be ground, though this is not necessary in our analysis) and the other as the working terminal. We apply an a.c. perturbation and measure the a.c. voltage across the two terminals (working relative to the reference) and measure the a.c. current into the working terminal (current through the reference terminal is the negative of this). Then we calculate the impedance, which for this two-terminal arrangement (sometimes called a 1-port) is called a *driving point impedance.*

The impedances of the individual elements are

$$Z_R = R \tag{3.1}$$
$$Z_C = 1/sC \tag{3.2}$$
$$Z_L = sL \tag{3.3}$$

where $s = \mathrm{i}\omega$. It is useful to consider the limiting behavior of these elements at low and high frequencies. Of course, the resistor has the same value at any frequency. At low frequencies a capacitor looks like an open circuit (the plates of the capacitor act like a gap to d.c.), but at high frequencies the capacitor passes current with more facility, and at infinite frequencies, it appears like a wire. In contrast, at low frequencies, the inductor acts like a wire (the coiled nature of the wire is irrelevant). At higher frequencies it resists changes, and at infinite frequency it is blocking and acts as an open circuit.

We combine the impedances of these components according to the rules that impedances in series add, and admittances in parallel add. If the resulting expression for the impedance is

[1] We assume this interconnectedness in all cases henceforth. We don't want to always have to mention that two unconnected pieces aren't of interest. Along the same lines, we aren't interested in a circuit element that is attached with only one end, the other end unconnected to anything.

[2] This is the wavelength inside the component. Another definition is that the current into the device is exactly equal to the current out of the device.

simplified, it is a rational function (ratio of two polynomials) in s.

$$Z(s) = \frac{a_n s^n + a_{n-1} s^{n-1} + \cdots + a_1 s + a_0}{s^m + b_{m-1} s^{m-1} + \cdots + b_1 s + b_0} \tag{3.4}$$

$$= \frac{\rho(s-\alpha_1)(s-\alpha_2)\cdots(s-\alpha_n)}{(s-\beta_1)(s-\beta_2)\cdots(s-\beta_m)} \tag{3.5}$$

Consideration of the type of simplification operations that are used to get this form shows that all the coefficients $a_0, a_1, \cdots, a_n, b_0, b_{1,\cdots}, b_{m-1}$ are non-negative.

If we replace s with $\mathrm{i}\omega$, then Z is the actual impedance of the circuit, but it is convenient also to think of Z as a function of the complex variable s, and allow s to have real and imaginary parts. The qualitative behavior of Z turns out to depend on the locations of the *zeroes*, $\alpha_1, \alpha_2, \cdots, \alpha_n$ (values of s for which the impedance becomes zero, $Z(s \to \alpha_i) = 0$) and the *poles*, $\beta_1, \beta_2, \cdots, \beta_m$ (values of s for which the impedance becomes infinite, $Z(s \to \beta_i) = \infty$) in the complex s plane. If $s = \alpha_1$, then $Z = 0$, but of course if α_1 has a non-zero real part, then it is never true that $\mathrm{i}\omega = \alpha_1$ – the poles and zeroes characterize the impedance spectrum in a rather roundabout way.

3.1 *RC* Circuits

We consider first the case of *RC* circuits, i.e., circuits with only resistors and capacitors. Consider first the limiting cases at high and low frequencies. At very high frequencies, the capacitors act like wires and short circuit some of the other elements in the circuit. It is fairly easy to see that the result is the same as a bunch of resistors connected together, which can be simplified to a single resistor. Thus the impedance at very high frequencies is real, finite and non-negative. For the impedance to be finite when $\omega = \infty$ ($s = \infty$), the degree of the numerator polynomial cannot exceed the degree than the denominator polynomial, $n \leq m$. The impedance might be zero, if the capacitors are arranged in such a way as to short circuit the whole thing; in this case $n < m$, otherwise $n = m$. The condition $Z(s \to \infty) = 0$ may be interpreted as the presence of a zero at infinity. If we accept this definition, then the numbers of poles and zeros of the impedance are always equal[3]. If Z is an interfacial impedance with a parallel combination of the double-layer capacitance and the faradaic impedance, then we know that there must be the zero at infinity, and $n = m - 1$: not counting the pole at infinity there is one more pole than zero.

At zero frequency, the capacitors act as open circuit and may be effectively be removed from the circuit, leaving only resistors. Usually then the impedance simplifies to a single resistance. However, if a capacitor is located in such a way that its removal splits the circuit into two pieces, then the resulting impedance will be infinite. Another way of stating this is that the d.c. current through the circuit is zero. Then we have $Z(s \to 0) = \infty$, i.e., there is a pole at zero. An example of this is the simple adsorption reaction circuit, Fig. 2.8, where there is no d.c. current, and the impedance tends to infinity at low frequencies.

Although we will not prove them all, we summarize the properties of the poles and zeroes of *RC* circuits (Fig. 3.1):

- All poles and zeros are real and non-positive, i.e., they lie on the negative real axis in the complex s plane.
- Poles and zeroes are simple (are all distinct) and alternate or "interlace".

[3] In fact we haven't proven that there can't be two or more zeroes at infinity. It can be shown that m and n can differ by no more than one for any *RLC* circuit.

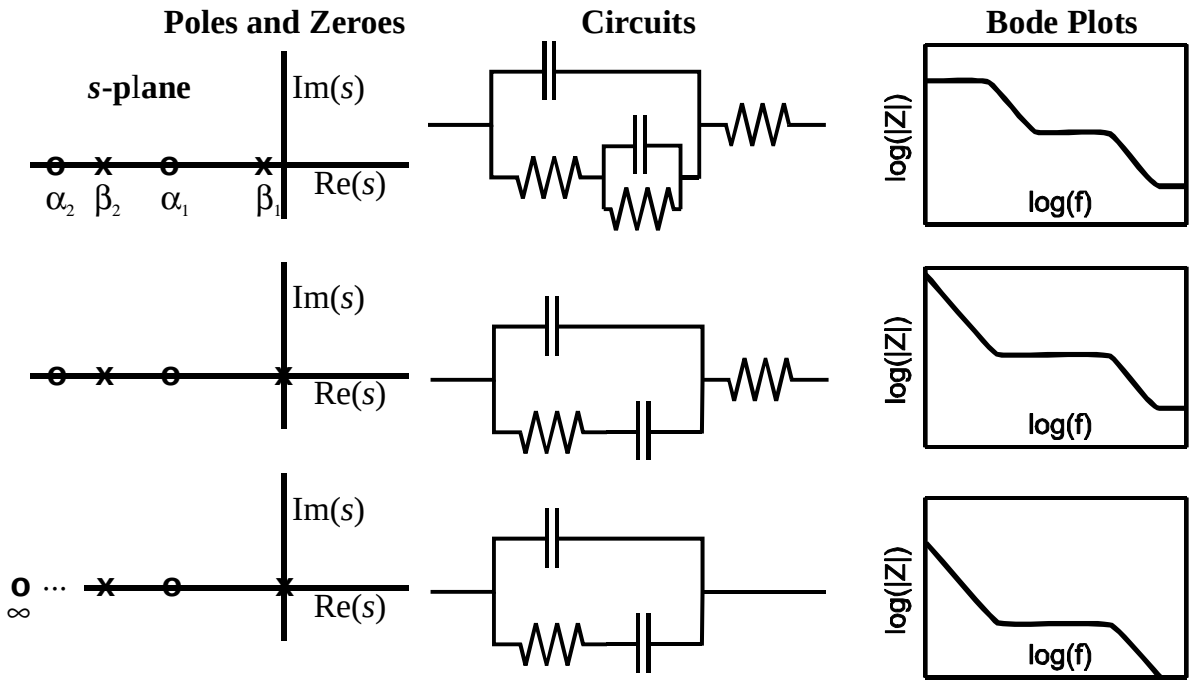


Figure 3.1: Pole-zero and Bode plots for some RC circuits.

- The smallest (nearest the origin) is a pole, which may be at the origin.
- The largest is a zero, which may be at infinity.

It is evident from the above discussion that a pole at the origin means a blocking circuit (high impedance) at low frequencies, and the Bode plot has a limiting slope of -1 (capacitor) at low frequency. A zero at infinity means that the high-frequency behavior is capacitive leading to a value of zero impedance at infinite frequency. A closer look at the relationship between the poles and zeroes and the Bode plot is revealed by thinking about the impedance for the first case in Fig. 3.1:

$$Z = \frac{\rho(s-\alpha_1)(s-\alpha_2)}{(s-\beta_1)(s-\beta_2)}, \qquad \alpha_2 < \beta_2 < \alpha_1 < \beta_1 < 0 \tag{3.6}$$

We suppose that all the poles and zeroes are widely separated. The value of Z for frequencies close to zero is approximately $\rho\alpha_1\alpha_2/\beta_1\beta_2$, i.e., the impedance approximates a resistor with this value. For s much larger in magnitude than β_1, but much smaller than α_1, then the factor $(s-\beta_1)$ is approximately s. On the other hand, the factor $(s-\alpha_1)$ is approximately $-\alpha_1$. Evaluating all the factors in this way shows that Z may be approximated as

$$Z \approx \frac{\rho(-\alpha_1)(-\alpha_2)}{(s)(-\beta_2)}, \qquad \alpha_1 \ll |s| \ll \beta_1 \tag{3.7}$$

$$= \frac{1}{sC}, \qquad C = -\beta_2/\rho\alpha_1\alpha_2 \tag{3.8}$$

so in this frequency range the Bode plot has a slope of -1, characteristic of a capacitance. The transition from the resistance to capacitance is a bend on the Bode plot, occurring roughly at a

frequency $\omega \sim |\beta_1|$. Similarly

$$Z \approx \frac{\rho(s)(-\alpha_2)}{(s)(-\beta_2)}, \qquad \beta_2 \ll |s| \ll \alpha_1 \tag{3.9}$$

$$= \rho\alpha_2/\beta_2 \tag{3.10}$$

so the next region on the Bode plot is a horizontal region corresponding to a resistor. Evidently, for an RC circuit, the Bode plot alternates between horizontal (resistive) regions and regions of slope -1 (capacitive). The bends in the Bode plot are thus a direct indication of where the poles and zeroes are located. We can play a similar game with the phases. The phase in a resistive section is zero, and in a capacitive section is 90°. At the bends in the magnitude plot, the phase is transitioning between the two values.

We supposed that the poles and zeroes were widely separated, but if they are not, all that happens is that the bends are less distinct and harder to distinguish. In practice, the phase plot often has more visual separation of the regions. It should be noted that if a capacitive section is short, the phase may not rise to the full 90° [4].

For the Nyquist plot, we first consider a parallel combination of a resistor and capacitor. Straightforward algebra shows that $(\mathrm{Re}(Z) - R/2)^2 + \mathrm{Im}(Z)^2 = (R/2)^2$, i.e., the Nyquist plot is has the equation of a circle of radius $R/2$ centered at $R/2$. Since $\mathrm{Im}(Z) \leq 0$, this is a semicircle in the first quadrant as conventionally plotted. The time constant for this combination is the product $RC = \tau$ and the frequency at the top of the semicircle corresponds to an angular frequency that is the reciprocal of this:

$$\omega_{\mathrm{top}} = 1/\tau = 1/RC \tag{3.11}$$

$$f_{\mathrm{top}} = \frac{1}{2\pi RC} \tag{3.12}$$

Adding several such RC combinations in series produces a semicircle per parallel RC unit. An additional series resistor displaces everything to the right, and an additional series capacitor adds a vertical section at the low-frequency limit. This exhausts the possible forms for Nyquist plots of RC circuits. To see why this is so, we note that this form of RC circuit is a canonical form (the first Foster form) in the *network synthesis* problem. That is, given a rational function in s whose poles and zeroes satisfy the above conditions, there is an algorithm that will generate a first Foster form circuit. But there are several other algorithms, to give other canonical forms, and indeed algorithms that give mixed forms. Since these can all be derived from the same rational function in s that can be realized as a first Foster form, all these circuits must have the same form of Nyquist plot. From the network synthesis point of view, none of these circuits are any better than others.

As an example, consider the impedance

$$Z = \frac{2s^2 + \frac{17}{21}s + \frac{2}{35}}{s^2 + \frac{32}{105}s + \frac{1}{210}} \tag{3.13}$$

This can be written in several ways, corresponding to the different realizations in Fig. 3.2:

[4] This should not be confused with a CPE, where the full 90° is not reached because $\alpha < 1$.

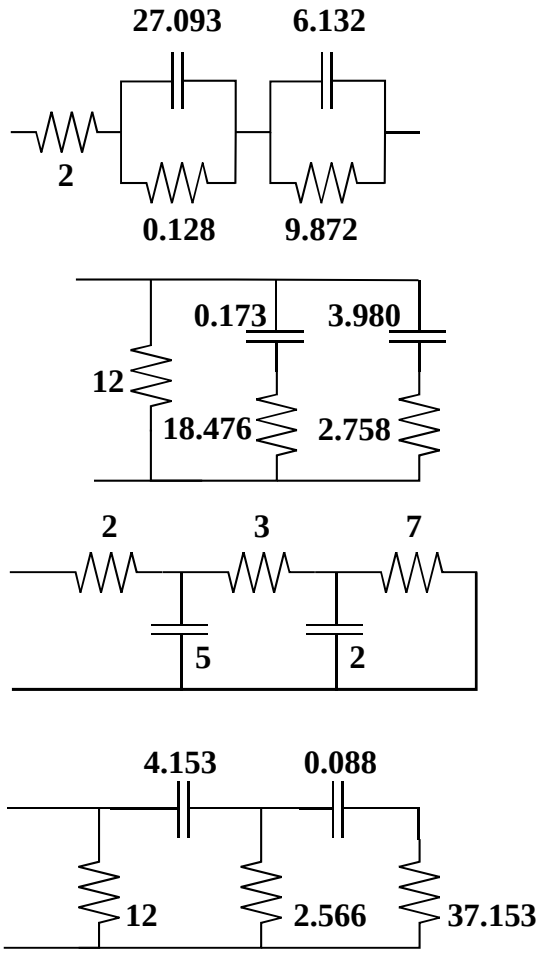


Figure 3.2: Standard *RC* circuits. Foster 1, Foster 2, Cauer 1, Cauer 2.

$$\text{First Foster:} \qquad Z = 2 + \frac{1}{27.093s + \frac{1}{0.128}} + \frac{1}{6.132s + \frac{1}{9.872}} \tag{3.14}$$

$$\text{Second Foster:} \qquad Z = \left[\frac{1}{12} + \frac{1}{18.476 + \frac{1}{0.173s}} + \frac{1}{2.758 + \frac{1}{3.980s}}\right]^{-1} \tag{3.15}$$

$$\text{First Cauer:} \qquad Z = 2 + \frac{1}{5s + \frac{1}{3 + \frac{1}{2s + \frac{1}{7}}}} \tag{3.16}$$

$$\text{Second Cauer:} \qquad Z = \frac{1}{\frac{1}{12} + \frac{1}{\frac{1}{4.153s} + \frac{1}{\frac{1}{2.566} + \frac{1}{\frac{1}{0.088s} + 37.153}}}}} \tag{3.17}$$

These four circuits all have the same impedance spectra; from an electrical point of view they behave exactly the same. One can convert any one to any other one by simplifying the impedance

to the rational function form and then following one of the four standard algorithms. Some of the relationships between circuit elements are immediately obvious by thinking about the low-frequency and high-frequency limiting behavior. For example, at zero frequency where we omit the capacitors, we can simplify each of the circuits to a resistor. Therefore the series combination of the three resistors in the first and third circuits are the same, $2+0.128+9.872 = 2+3+7 = 12$, which is the value of the first resistor in circuits two and four. Likewise for the infinite frequency behavior, where the capacitors act like wires, the first resistor in the first and third circuits equals the parallel combinations in the second and fourth circuits: $(12^{-1} + 18.476^{-1} + 2.758^{-1})^{-1} = (12^{-1} + 2.566^{-1} + 37.153^{-1})^{-1} = 2$.

The circuits of Fig. 3.2 are for a case with no pole at zero or zero at infinity. If there is a pole at zero (no d.c. path) then the Foster 1 form has an initial series capacitor, the Foster 2 form has no first parallel resistor, the Cauer 1 form terminates with a capacitor, and the Cauer 2 form has an initial series capacitor. For the zero at infinity (shorting capacitors), the Foster 1 form has no initial series resistor, the Foster 2 form has an initial parallel capacitor, the Cauer 1 form has no initial series resistor, and the Cauer 2 form has a short instead of the terminal resistor.

The algorithms for realizing the different canonical forms may be found in books on network synthesis; for the Cauer 1 form we give the algorithm in an appendix. Some general notes about the network synthesis problem are in order.

1. These algorithms generate circuits with the minimum number of elements. We could of course have other circuits with more elements by replacing a single resistor (capacitor) by an equivalent combination of many resistors (capacitors), but since we don't achieve anything by this, we will consider only minimal forms.

2. It is possible to switch from one form to another somewhere in the middle of the generating algorithm, so that there are other minimal circuits possible (for only a few elements there may not be very much choice).

3. The different canonical forms are not all equivalent from the point of view of the simplicity of the circuit element values. If the coefficients of the polynomials are specified (Eq. (3.4)), then the poles and zeroes are, in general, rather complicated functions of the coefficients, since they are the roots of polynomials (Eq. (3.5)). Even for simple polynomials, the roots involve square roots or other surds; for polynomials of higher degrees there are no analytical solutions. The element values in the Foster forms are derived from partial fraction expansions, and are related to the polynomial roots, but the Cauer form element values are related more simply to the polynomial coefficients.

4. The number of circuit elements in a minimal form is equal to the number of parameters in the impedance function.

5. The number of capacitors in a minimal circuit is equal to the number of poles.

6. The number of resistors in a minimal circuit is equal to the number of poles plus one, minus one if there is a pole at zero (no d.c. path), minus one if there is a zero at infinity (shorting capacitors).

Note that if we write down any *RC* circuit with the minimal number of elements and the correct limiting behavior at zero and inifinite frequencies, then we can find valid element values to realize a rational function impedance with the same number of parameters (and correct limiting behavior). In this sense, almost any equivalent circuit is acceptable.

Finally, from the point of view of electrochemical equivalent circuits, especially for mechanistic schemes, the Cauer 1 from has some distinct advantages. Firstly, the first resistor and capacitor are in the right place for the solution resistance and double-layer capacitance (note that the third circuit in Fig. 3.2 is a disguised form of the first circuit in Fig. 3.1). Secondly, point 3 above means that the element values can be simply related to the coefficients, which, as we will see, are simply related to the rate parameters. If we were to use a Foster (or partially Foster) form, then it might be impossible to give an analytical expression relating element values to rate parameters.

3.2 Inductors

We will not deal with the rules for RL or LC circuits separately, but move directly to the general case of RLC circuits. (The inclusion of transformers M can be easily accommodated because an $RLCM$ circuits is equivalent to (but simpler than) an RLC circuit.) Since inductors are like wires at low frequency, an inductor can bridge other components and lead to $Z(s \to 0) = 0$, i.e., zeroes at zero are now possible. Inductors at high frequency can act like a break, and so a series inductor added to a circuit leads to $Z(s \to \infty) = \infty$, i.e., a pole at infinity. This pole at infinity arises when the degree of the numerator exceeds the degree of the denominator, so we can now have $n = m + 1$ in Eq. (3.4) as well as the $n = m$ and $n = m - 1$ we had previously.

The inductor gives a slope of $+1$ in the Bode magnitude plot, together with a phase of $-90°$. We can now access the fourth quadrant of the Nyquist plot in the conventional representation ($-\operatorname{Im}(Z)$ up). A parallel RL combination gives a semicircle below the axis; the top point frequency is again related to the time constant, which is now $L/R = \tau$. A series inductor (pole at infinity) gives a vertical line down at high frequencies, in contrast to the vertical line up for a series capacitor[5] at low frequencies.

Not every rational impedance function that we can write down corresponds to a circuit; there are some conditions imposed that we investigate below. But suppose we can make a circuit, i.e., the impedance is *realizable*. Then if the pole-zero pattern is not that corresponding to an RC circuit (alternating poles and zeroes on the negative real axis), the circuit must contain an inductor. Apparently there are two ways in which this can happen: (I) If the poles and zeroes remain real and negative, but no longer interlace, or (II) the poles or zeroes become complex. In fact the constraint on poles and zeroes for RC circuits are rather severe, so in some loose sense we might expect inductors to appear in circuits fairly often. In the context of EIS, it is fairly hard to find a reaction mechanism that *cannot* show inductive behavior.

We will say that an impedance function is "inductive" or shows "inductive behavior" if it can be realized as a circuit containing an inductor. A more loose usage, common in the literature, is to say that the behavior is inductive if the impedance goes below the real axis in a Nyquist plot. This differs from our definition in two ways. Firstly, an impedance may go below the axis but not be realizable as a circuit at all. Secondly, the circuit may have an inductor, but the inductor may not dominate the behavior enough to bring it below the axis; a common example of this is a loop crossing itself in the first quadrant.

3.3 Power, Stability, and PR

No, this isn't a section on the influence of the media on regime change. Rather, we want to consider some general constraints on the impedance, which are required for it to be realizable

[5] PtP: Can we have a circuit without a series inductor that has a pole at infinity?

as an RLC circuit. The first is simply that an RLC circuit can dissipate or store energy, but cannot create it from nothing.

3.3.1 Power

Consider a capacitor, to which we apply a potential $E = E_{\rm ss} + |E|\sin(\omega t) = E_{\rm ss} + E_{\rm r}\sin(\omega t)$, and for which the current response is $j = |j|\cos(\omega t) = j_{\rm i}\cos(\omega t)$. The instantaneous power (per unit area) is $E(t)j(t)$, and we may integrate this over a cycle to find the average power per cycle:

$$\begin{aligned}
\overline{P} &= \frac{1}{2\pi/\omega}\int_{t=0}^{t=2\pi/\omega} (E_{\rm ss} + E_{\rm r}\sin(\omega t))\, j_{\rm i}\cos(\omega t)dt && (3.18)\\
&= \frac{\omega}{2\pi}\int_{t=0}^{t=2\pi/\omega} E_{\rm ss} j_{\rm i}\cos(\omega t)dt + \frac{\omega}{2\pi}\int_{t=0}^{t=2\pi/\omega} E_{\rm r} j_{\rm i}\sin(\omega t)\cos(\omega t)dt && (3.19)\\
&= 0 + 0 = 0 && (3.20)
\end{aligned}$$

This is as expected, since a capacitor stores energy in an electric field and doesn't dissipate it into heat. (Mathematically, the 90° phase shift means that the response function $\cos(\omega t)$ is orthogonal to the input function $\sin(\omega t)$). A similar result obtains for an inductor, which stores magnetic energy. In contrast, for a resistor the response is a sin function and:

$$\begin{aligned}
\overline{P} &= \frac{\omega}{2\pi}\int_{t=0}^{t=2\pi/\omega} (E_{\rm ss} + E_{\rm r}\sin(\omega t))\,(j_{\rm ss} + j_{\rm r}\sin(\omega t))\, dt && (3.21)\\
&= E_{\rm ss} j_{\rm ss} + \frac{\omega}{2\pi}\int_{t=0}^{t=2\pi/\omega} E_{\rm r} j_{\rm r}\sin(\omega t)\sin(\omega t)dt && (3.22)\\
&= P_{\rm ss} + \frac{1}{2}E_{\rm r} j_{\rm r} && (3.23)
\end{aligned}$$

The impedance of the resistor is $R = \widetilde{E}/\widetilde{j} = E_{\rm r}/j_{\rm r}$, so we can write this result as

$$\overline{P} = P_{\rm ss} + \frac{1}{2}Rj_{\rm r}^2 = P_{\rm ss} + \frac{1}{2}\,{\rm Re}(Z)|j|^2 \qquad (3.24)$$

where we have used the fact that there is no imaginary part of the current density. The a.c. power is positive for a resistor, reflecting the fact that a resistor dissipates energy as heat. The last form is actually quite general for a linear system[6]. In the capacitor and inductor cases, the real part of the impedance is zero and we obtain the result that the a.c. power is zero. To prove the general case, we consider a response $j_{\rm ss} + j_{\rm r}\sin(\omega t) + j_{\rm i}\cos(\omega t)$ and carry out the same steps – as for the capacitor, the $j_{\rm i}\cos(\omega t)$ term won't contribute – and we find the same result. Now it is a thermodynamic result that the power in a passive circuit is nonnegative[7], and we expect the a.c. power to be nonnegative in its own right, since switching on the a.c. signal should not decrease the power dissipation. Therefore we conclude that the real part of the impedance must be positive[8].

[6] PtP: The analysis is not as straightforward if we are generating harmonics.

[7] Power is related to the rate of entropy production, $P = Td\sigma/dt \geq 0$.

[8] PtP: Could the real part be slightly negative, so that the a.c. power was negative but the overall power $\overline{P}$ was positive?

3.3.2 Stability

The second constraint, that is to some extent interlinked and implied by the power constraint, is stability. This is the idea that a small perturbation from steady state leads to relaxation back to the steady state, rather than to an increasing response. In general, the response of a linear circuit to a perturbation is a sum of exponentials, perhaps multiplied by sine waves. As a simple example, consider a system with transfer function

$$\frac{\mathrm{Out}(s)}{\mathrm{In}(s)} = \frac{1}{s-a} \tag{3.25}$$

and a input of a delta function[9], which has a Laplace transform of 1. Then the output is the inverse Laplace transform of $1/(s-a)$, which is $\exp(at)$. Now if $a > 0$, we have unstable behavior; if $a < 0$, we have stable behavior. If a is purely imaginary, the response is oscillating, a halfway case that we term semistable. More precisely, the condition for stability is $\mathrm{Re}(a) < 0$. The generalization of this is that all poles of the transfer function must have negative real parts for stability. We need to remember that since we are dealing with potentiostatic experiments, the response is the current and therefore the transfer function is the admittance function, not the impedance function. So in terms of the impedance, the requirement for stability is that all the *zeroes* of the impedance must have negative real parts.

3.3.3 The Positive Real Condition

The formal condition for an impedance function to be realizable as an $RLCM$ or RLC circuit (this includes RC and other special cases) is that the impedance is a positive real (PR) rational function in s. The condition that it be a real rational function has to do with the components being lumped, the only case we are considering in detail. For such a function, PR means that $\mathrm{Re}(Z(s)) \geq 0$ if $\mathrm{Re}(s) \geq 0$. The PR condition can be written in several other equivalent ways; for our purposes the most useful set is[10,11]:

$$\text{For all } \omega,\ \mathrm{Re}(Z(\mathrm{j}\omega)) \geq 0 \tag{3.26}$$

$$\text{All poles and zeroes of } Z(s) \text{ are in the closed left-half plane (LHP)}^{12} \tag{3.27}$$

$$\text{Any imaginary axis poles and zeroes are simple}^{13} \text{ with positive residues}^{14} \tag{3.28}$$

The first condition is immediately recognizable as the power condition that the circuit can only dissipate or store energy; its practical implication is that the impedance must stay in the first or fourth quadrants of the Nyquist plot and cannot wander into the left-hand side. The second condition is just the stability condition (the zeroes for potentiostatic control and the poles for galvanostatic control). From an EIS point of view we can assume this is always satisfied in an experiment, since we need stability to achieve steady state before turning the a.c. pertubation on. The third condition is more important for resonant circuits, and rarely needs to be considered in electrochemical contexts, except for the case of poles and zeros at zero or infinity ($s = 0$ and $s = \infty$ are on the imaginary axis) that we have already discussed.

These conditions tell us that we can find a circuit. To actually find a circuit, there are some standard algorithms. The Brune synthesis produces an $RLCM$ circuit. The Bott-Duffin synthesis produces an RLC circuit with more elements in than the Brune synthesis. In these days, for the

[9] also known as a short, sharp kick.

[10] This is not a minimum set: if the second and third statements apply to the poles then they must apply to the zeroes and vice-versa.

[11] PtP: Find an example which satisfies the second condition but not the first.

relatively simple circuits that are encountered in EIS, it is possible to carry out the synthesis by a brute force method using a symbolic algebra program such as Maple or Mathematica. A circuit that has the correct pole-zero behaavior is chosen, and its impedance written down using the series/parallel rules. This is then simplified to the rational function form (Eq. (3.4)), and the coefficients from this procedure are equated with the coefficients of the desired impedance function. Solution of this set of equations then gives the element values of the circuit.

Finally, we note that all our treatments have been for lumped components, and so the impedance has been a rational function of s. But in electronics, sometimes we need to think in terms of electromagnetic waves, for example in the propagation of fast pulses down a coaxial cable. The coaxial cable is an example of a transmission line. This is a device that can be thought of an infinitely repetitive arrangement of lumped elements taken in the limit that their dimensions shrink to zero. There are more complicated positive real conditions that apply to transmission lines and some circuits containing them.

3.4 The Kramers-Kronig Conditions

Now you may have decided that in an a.c. experiment, you get two numbers at each potential and frequency (real and imaginary parts of the impedance) and so you are doing better that other types of experiments where you get one number at each potential and time (a current). Alas, you don't get something for nothing, and it turns out that there is a relationship between the real and imaginary parts of a nicely-behaving impedance. Specifically, if you know the real part *at every frequency*, you can calculate the imaginary part at any frequency, using the Kramers-Kronig transforms, and vice-versa:

$$\mathrm{Im}(Z(\omega)) = \frac{2\omega}{\pi}\int_0^\infty \frac{\mathrm{Re}(Z(x)) - \mathrm{Re}(Z(\omega))}{x^2-\omega^2}dx \tag{3.29}$$

$$\mathrm{Re}(Z(\omega)) = \mathrm{Re}(Z(0)) - \frac{2\omega}{\pi}\int_0^\infty \frac{(\omega/x)\,\mathrm{Im}(Z(x)) - \mathrm{Im}(Z(\omega))}{x^2-\omega^2}dx \tag{3.30}$$

$$\mathrm{Re}(Z(\omega)) = \mathrm{Re}(Z(\infty)) - \frac{2}{\pi}\int_0^\infty \frac{x\,\mathrm{Im}(Z(x)) - \omega\,\mathrm{Im}(Z(\omega))}{x^2-\omega^2}dx \tag{3.31}$$

These relationships mean that, in principle, one could measure only the real parts and then calculate the imaginary parts. But since the measurement usually easily gives the real and imaginary parts together, one can instead check whether or not the above relationships hold. If they do not, it means that the assumptions under which they hold are violated, which may mean that the data is bad in some way, e.g. the system is slowly changing on the time scale on which a spectrum is collected. The assumptions required to derive the Kramers-Kronig relationships are:

Linearity: The system is linear: $\mathrm{Response}(aA+bB) = a\mathrm{Response}(A) + b\mathrm{Response}(B)$. Usually this is satisfied if the amplitude of the potential is small enough.

Causality: This just means that the response to an input cannot precede the input. Mathematically, it can be related to the absence of certain types of poles[15] in the right half of the s plane.

[15] Strictly, these are poles of the admittance, or zeroes of the impedance. The KK transforms should really be written in terms of the admittance for potentiostatic control.

Stability: We've seen this one before.

Finite: The real and imaginary parts[16] must be finite over the entire frequency range.

In practice, the integrals can be hard to evaluate for experimental data, mainly because some sort of extrapolation scheme is required to extend the data all the way to zero frequency and infinite frequency. There have been several schemes proposed to solve this extrapolation problem. These complications in evaluating the transforms can often be avoided in practice:

1. If the data can be fitted to an *RLC* circuit, then if must satisfy the four conditions and therefore the KK check is not required. (This conclusion can be extended to some other components as well, including the Warburg impedance)

2. Even if an equivalent circuit cannot be found, the data can be fitted to an equivalent circuit of a standard form (with the right pole/zero behavior at zero and infinity) having a large number of time constants. These time constants can be chosen to be spread out logarithmically over the experimental frequency range. Then if the data fits to this circuit, it must satisfy the KK relationships. A Foster 1 circuit (also known as a *Voight* circuit) is particularly suitable since it can be fitted computationally efficiently using a *linear* least-squares fitting procedure:
$$Z = R_0 + \frac{X_0}{\mathrm{i}\,\omega} + \sum_k \frac{R_k}{1 + \mathrm{i}\,\omega\tau_k} \tag{3.32}$$
where the fitting is linear in the parameters R_0 (series resistor), X_0 (1/series capacitor) and R_k because the τ_k are prescribed.

We note that, at least for lumped circuits, the KK and PR relationships are equivalent, but since the KK relationships do not only hold for lumped components, they are more general. Finally, we note that if the data is considered good, the KK relationships may be used to extrapolate experimental data to zero and infinite frequencies; this capability exists in at least one commercial fitting program.

3.5 Low-Frequency Behavior

We have seen that for *RLC* circuits, the low-frequency behavior is qualitatively determined by the presence or absence of poles or zeroes at zero. We can be more specific about the value of the resistance at zero frequency (in the absence of a pole), and generalize this result for any linear system (not just a lumped one). Intuitively, zero frequency is "d.c." and so we expect the resistance at zero frequency to be related to the steady-state behavior. Since the resistors in EIS are differential, we might expect:
$$\frac{1}{R_\mathrm{p}} = \frac{1}{\lim_{s\to 0} Z(s)} = \frac{dj_\mathrm{ss}}{dE} \tag{3.33}$$

(We use Laplace transforms to show this. Because we are using a linearized system rather that a true linear system, we cannot just calculate the d.c. current from the d.c. potential, but we can calculate the current increment δj a long time after stepping the potential a small amount δE. The Laplace transform of this small potential step at time $t = 0$ is $\delta E/s$. Therefore the Laplace transform of the current output

[16] Again, this should be for the admittance for potentiostatic control.

is $Y(s)\delta E/s$ The value of this at steady state can be found by using the final value theorem $f(t=\infty) = \lim_{s\to 0} sF(s)$, which in this case gives $\delta j = \lim_{s\to 0} sY(s)\delta E/s = \lim_{s\to 0} Y(s)\delta E = \delta E \lim_{s\to 0} Y(s)$ or $\delta j/\delta E = \lim_{s\to 0} Y(s)$.)[17]

Note that we can loosely say that this result also applies when there is pole at zero (blocking capacitor). There the steady-state current is zero independently of potential, so $dj_{\mathrm{ss}}/dE = 0$ and $R_{\mathrm{p}} = \infty$. The inverse of the slope of the steady state current-potential relationship is known as the polarization resistance, and EIS provides an easy way to measure it. In some cases, e.g., corrosion measurments, the polarization resistance is the primary quantity of interest and so it is not necessary to measure the whole frequency range.

It is often stated that the polarization resistance is the low frequency limit of the impedance minus the high-frequency limit (the solution resistance) and although this difference may be the quantity with kinetic significance, the above derivation shows that the inverse slope of the measured steady-state curve is the low-frequency intercept only. The resolution to this apparent paradox is that the low frequency-limit is the slope of the steady-state curve uncorrected for solution resistance; the difference quantity gives the slope of the corrected steady-state curve.

One application of this result is to decide when an impedance spectrum has been measured down to a low enough frequency that no features have been missed. The apparent low frequency intercept is compared with the slope of the measured steady-state current potential, and if they agree, there can be nothing significant missing at low frequencies.[18]

3.6 Warburg Impedance as a Transmission Line

The Warburg impedance may be thought of as a transmission line. This is a limiting case of the circuit in Fig. 3.3. We suppose that the transmission line, of infinite length, is divided into small sections of length δz, each of which has one capacitor of value $C = c\delta z$ and one resistor of value $R = r\delta z$, where c and r are capacitance and resistance per unit length. Looking at the problem recursively, as in the bottom of the figure, we see that Z_{W} may be found by solving the equation:

$$Z_{\mathrm{W}} = \frac{1}{\mathrm{i}\,\omega c\delta z + \frac{1}{r\delta z + Z_{\mathrm{W}}}} \tag{3.34}$$

Collecting the Z_{W} on the same side of the equation and simplifying gives a rational function in $\mathrm{i}\,\omega$ whose numerator must be zero:

$$\mathrm{i}\,\omega c Z_{\mathrm{W}}^2 + \mathrm{i}\,\omega r c Z_{\mathrm{W}}\delta z - r = 0 \tag{3.35}$$

Since we are interested in the limiting case where $\delta z \to 0$, we drop the term with δz and solve for Z_{W}:

$$Z_{\mathrm{W}} = \sqrt{\frac{r}{\mathrm{i}\,\omega c}} \tag{3.36}$$

which is the Warburg form.

Perhaps not surprisingly, a finite diffusion impedance can be represented as a finite transmission line, with a terminating element that depends on the the boundary condition at $z = d$. For the $\widetilde{c}(z=d) = 0$ condition, this is just a short at the end of the line; for the $\widetilde{J}(z=d) = 0$ condition it is an open circuit. Transmission lines are also used to model porous electrodes.

[17] The final value theorem requires stability, i.e., the absence of poles in the closed right half plane.

[18] This can be a circular argument, since a slow time constant not measured by impedance could also be missed by not waiting long enough for true steady state.

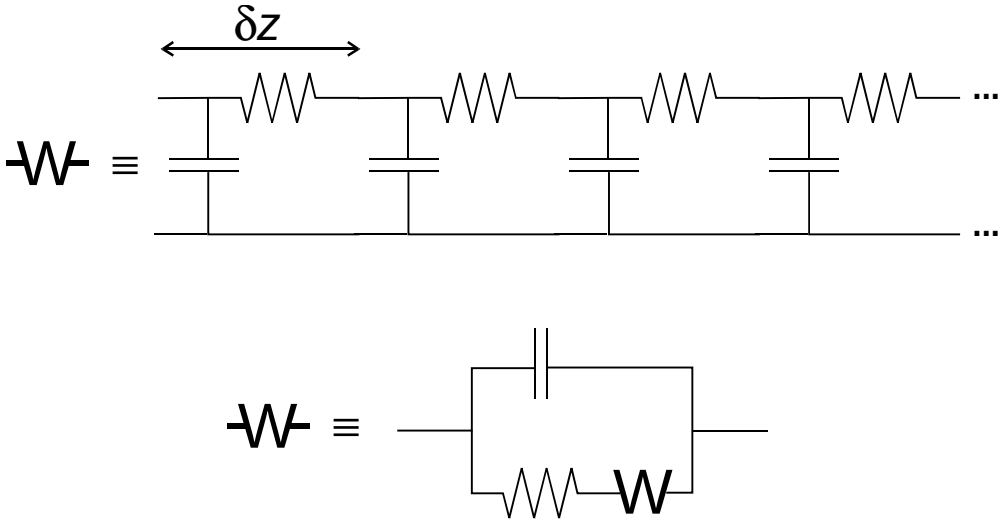


Figure 3.3: Transmission line view of the Warburg impedance. Top: infinite respresentation. Bottom: recursive representation.

Chapter 4

Multistep Reaction Mechanisms

We now generalize the rules we had for the simple one-step reaction to the case of multistep[1] reaction mechanisms with several elementary reactions. At first we will dealt with the mechanics of working out the impedance for an arbitrary reaction mechanism, but later we will give some general rules relating to the inverse problem: For a given EIS spectrum, which mechanisms can give rise to it? and which can be eliminated from further consideration? We first recall the one-step reaction with adsorption and diffusion. We had three types of species that were treated differently: electrons, adsorbed species, and diffusing species. (Implicitly, there was another type of species, *static* or *external* aqueous species whose mass transport was sufficiently fast that we included their concentrations in the rate constants and then forgot about them, e.g., H^+ in the one-step reaction with adsorption.) In each case, there was a relationship with v_1, the reaction rate for the step. Later v_1 was recognized as a function of some concentrations and potential, and its perturbation in terms of these variables was considered. A little thought shows that if several reaction steps are involved, there will be a composite rate that will replace v_1, but which will still depend on some concentrations and can be dealt with in much the same way.

We illustrate this for the example of the hydrogen evolution reaction (HER) at a Pt electrode

$$\begin{aligned} \underset{\varphi}{\mathrm{Pt(site)}} + \underset{[\mathrm{H^+}]}{\mathrm{H^+}} + \mathrm{e^-} \quad &\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \quad \underset{\theta}{\mathrm{PtH(ads)}} \\ \underset{\theta}{\mathrm{PtH(ads)}} + \underset{[\mathrm{H^+}]}{\mathrm{H^+}} + \mathrm{e^-} \quad &\underset{k_2}{\overset{k_2}{\rightleftarrows}} \quad \underset{\varphi}{\mathrm{Pt(site)}} + \underset{c}{\mathrm{H_2(aq)}} \\ 2\underset{\theta}{\mathrm{PtH(ads)}} \quad &\underset{k_3}{\overset{k_3}{\rightleftarrows}} \quad 2\underset{\varphi}{\mathrm{Pt(site)}} + \underset{c}{\mathrm{H_2(aq)}} \end{aligned} \tag{4.1}$$

$$\begin{aligned} v_1 &= k_1'\varphi[\mathrm{H^+}] - k_{-1}\theta \\ v_2 &= k_2'\theta[\mathrm{H^+}] - k_{-2}'\varphi c \\ v_3 &= k_3'\theta^2 - k_{-3}'\varphi^2 c \end{aligned} \tag{4.2}$$

We are treating the reaction sites and adsorbed hydrogen as two distinct species, in contrast to the way we did the single-step reactions[2]. We assume that the hydrogen mass transport in the

[1] IUPAC prefers "composite" to "multistep".

[2] This means that the quantities $(\partial v/\partial\theta)_E$ and $(\partial v/\partial\theta)_{E,\varphi}$ are not the same, and similarly for other partial derivatives. For a discussion about this, see D.A. Harrington, J. Electroanal. Chem., 449 (1998) 29, Appendix A.

solution is diffusive, but that the H^+ has fast mass transport, and so its concentration at the surface is constant and is subsumed into the rate constants:

$$\begin{aligned} v_1 &= k_1\varphi - k_{-1}\theta \\ v_2 &= k_2\theta - k_{-2}\varphi c \\ v_3 &= k_3\theta^2 - k_{-3}\varphi^2 c \end{aligned} \tag{4.3}$$

We write equations for each species (except the static ones). For electrons, we can think of the faradaic current density as proportional to the "rate of production of electrons"

$$\text{electrons: } j_\mathrm{f}/F = \frac{"d[\mathrm{e}^-]"}{dt} = r_\mathrm{e} \tag{4.4}$$

where r_e is a combination of the rates of the component steps

$$r_\mathrm{e} = -v_1 - v_2 \tag{4.5}$$

reflecting the fact that electrons are removed once in step 1 and once in step 2. For the adsorbed species, and for the sites which are treated like adsorbed species we write:

$$\mathrm{PtH(ads)} \quad : \quad \Gamma_\mathrm{m}\frac{d\theta}{dt} = r_\theta = v_1 - v_2 - 2v_3 \tag{4.6}$$

$$\mathrm{Pt(site)}: \quad \Gamma_\mathrm{m}\frac{d\varphi}{dt} = r_\varphi = -v_1 + v_2 + 2v_3 \tag{4.7}$$

where the 2 reflects the fact that two PtH are removed in step 3 or that two Pt(sites) are produced in step 3. (We probably should have used notation like r_PtH instead of r_θ.) For the diffusing hydrogen we have

$$\mathrm{H_2}\text{: } J_{\mathrm{H_2}} = r_{\mathrm{H_2}} = v_2 + v_3 \tag{4.8}$$

For each species, the rates of production due to reaction are combinations of the rates of the individual reaction steps, with the coefficients being the stoichiometric coefficients in the steps. We can summarize these relationships in a matrix form

$$\boldsymbol{r} = \boldsymbol{N}\boldsymbol{v} \tag{4.9}$$

$$\begin{bmatrix} r_\mathrm{e} \\ r_\theta \\ r_\varphi \\ r_{\mathrm{H_2}} \end{bmatrix} = \begin{bmatrix} -1 & -1 & 0 \\ 1 & -1 & -2 \\ -1 & 1 & 2 \\ 0 & 1 & 1 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \\ v_3 \end{bmatrix} \tag{4.10}$$

where $\boldsymbol{N}$ is the stoichiometric matrix[3], with one column for each reaction, and one row for each species. The matrix is easiest to generate by columns from the reaction scheme (recall that stoichiometric coefficients for reactants are negative), and then the rows can be read off to find the production rate for the species.

To find the impedance, we begin by following the perturb, differentiate, divide by E procedure

[3] $\boldsymbol{N}$ is capital nu here, since stoichiometric coefficients should have the symbol ν. But to avoid confusion between ν and v we use n for individual stoichiometric coefficients.

and use the flux-concentration relationship for H_2 (Eq. (2.39)):

$$\text{electrons: } \frac{Y_\mathrm{f}}{F} = \frac{1}{F}\frac{\widetilde{j}_\mathrm{f}}{\widetilde{E}} = \frac{\widetilde{r}_\mathrm{e}}{\widetilde{E}} = \left[\left(\frac{\partial r_\mathrm{e}}{\partial E}\right)_{\theta,\varphi,c}\frac{\widetilde{E}}{\widetilde{E}} + \left(\frac{\partial r_\mathrm{e}}{\partial \theta}\right)_{E,c,\varphi}\frac{\widetilde{\theta}}{\widetilde{E}} + \left(\frac{\partial r_\mathrm{e}}{\partial \varphi}\right)_{E,c,\theta}\frac{\widetilde{\varphi}}{\widetilde{E}} + \left(\frac{\partial r_\mathrm{e}}{\partial c}\right)_{E,\theta,\varphi}\frac{\widetilde{c}}{\widetilde{E}}\right] \tag{4.11}$$

$$\text{PtH(ads): } \mathrm{i}\,\omega\Gamma_\mathrm{m}\frac{\widetilde{\theta}}{\widetilde{E}} = \frac{\widetilde{r}_\theta}{\widetilde{E}} = \left[\left(\frac{\partial r_\theta}{\partial E}\right)_{\theta,\varphi,c}\frac{\widetilde{E}}{\widetilde{E}} + \left(\frac{\partial r_\theta}{\partial \theta}\right)_{E,c,\varphi}\frac{\widetilde{\theta}}{\widetilde{E}} + \left(\frac{\partial r_\theta}{\partial \varphi}\right)_{E,c,\theta}\frac{\widetilde{\varphi}}{\widetilde{E}} + \left(\frac{\partial r_\theta}{\partial c}\right)_{E,\theta,\varphi}\frac{\widetilde{c}}{\widetilde{E}}\right] \tag{4.12}$$

$$\text{Pt(site): } \mathrm{i}\,\omega\Gamma_\mathrm{m}\frac{\widetilde{\varphi}}{\widetilde{E}} = \frac{\widetilde{r}_\varphi}{\widetilde{E}} = \left[\left(\frac{\partial r_\varphi}{\partial E}\right)_{\theta,\varphi,c}\frac{\widetilde{E}}{\widetilde{E}} + \left(\frac{\partial r_\varphi}{\partial \theta}\right)_{E,c,\varphi}\frac{\widetilde{\theta}}{\widetilde{E}} + \left(\frac{\partial r_\varphi}{\partial \varphi}\right)_{E,c,\theta}\frac{\widetilde{\varphi}}{\widetilde{E}} + \left(\frac{\partial r_\varphi}{\partial c}\right)_{E,\theta,\varphi}\frac{\widetilde{c}}{\widetilde{E}}\right] \tag{4.13}$$

$$H_2\text{: } \frac{\widetilde{J}_{\mathrm{H_2,s}}}{\widetilde{E}} = \frac{\widetilde{c}\sqrt{\mathrm{i}\,\omega D}}{\widetilde{E}} = \frac{\widetilde{r}_c}{\widetilde{E}} = \left[\left(\frac{\partial r_c}{\partial E}\right)_{\theta,\varphi,c}\frac{\widetilde{E}}{\widetilde{E}} + \left(\frac{\partial r_c}{\partial \theta}\right)_{E,c,\varphi}\frac{\widetilde{\theta}}{\widetilde{E}} + \left(\frac{\partial r_c}{\partial \varphi}\right)_{E,c,\theta}\frac{\widetilde{\varphi}}{\widetilde{E}} + \left(\frac{\partial r_c}{\partial c}\right)_{E,\theta,\varphi}\frac{\widetilde{c}}{\widetilde{E}}\right] \tag{4.14}$$

We could use the procedure we used before: solve the last three equations for the three unknowns $\widetilde{\theta}/\widetilde{E}$, $\widetilde{\varphi}/\widetilde{E}$ and $\widetilde{c}/\widetilde{E}$, and then substitute these into the first equation to get the faradaic admittance[4]. However, we probably want the impedance including the double layer, since that is what we observe experimentally (R_s is easily corrected for), so we modify the strategy to produce this directly. We also take the opportunity to streamline the procedure and notation to bring out the full generality of the procedure.

Firstly, we substitute $Y_\mathrm{f} = Y - \mathrm{i}\,\omega C_\mathrm{d}$ in the first equation, and then collect terms in all three equations in a suggestive way:

$$\text{electrons: } -\left[\left(\frac{\partial r_\mathrm{e}}{\partial E}\right)_{\theta,\varphi,c} + \frac{\mathrm{i}\,\omega C_\mathrm{d}}{F}\right] = -\frac{Y}{F} + \left(\frac{\partial r_\mathrm{e}}{\partial \theta}\right)_{E,c,\varphi}\frac{\widetilde{\theta}}{\widetilde{E}} + \left(\frac{\partial r_\mathrm{e}}{\partial \varphi}\right)_{E,c,\theta}\frac{\widetilde{\varphi}}{\widetilde{E}} + \left(\frac{\partial r_\mathrm{e}}{\partial c}\right)_{E,\theta,\varphi}\frac{\widetilde{c}}{\widetilde{E}} \tag{4.15}$$

$$\text{PtH(ads): } -\left(\frac{\partial r_\theta}{\partial E}\right)_{\theta,\varphi,c} = \left[\left(\frac{\partial r_\theta}{\partial \theta}\right)_{E,c,\varphi} - \mathrm{i}\,\omega\Gamma_\mathrm{m}\right]\frac{\widetilde{\theta}}{\widetilde{E}} + \left(\frac{\partial r_\theta}{\partial \varphi}\right)_{E,c,\theta}\frac{\widetilde{\varphi}}{\widetilde{E}} + \left(\frac{\partial r_\theta}{\partial c}\right)_{E,\theta,\varphi}\frac{\widetilde{c}}{\widetilde{E}} \tag{4.16}$$

$$\text{Pt(site): } -\left(\frac{\partial r_\varphi}{\partial E}\right)_{\theta,\varphi,c} = \left(\frac{\partial r_\varphi}{\partial \theta}\right)_{E,c,\varphi}\frac{\widetilde{\theta}}{\widetilde{E}} + \left[\left(\frac{\partial r_\varphi}{\partial \varphi}\right)_{E,c,\theta} - \mathrm{i}\,\omega\Gamma_\mathrm{m}\right]\frac{\widetilde{\varphi}}{\widetilde{E}} + \left(\frac{\partial r_\varphi}{\partial c}\right)_{E,\theta,\varphi}\frac{\widetilde{c}}{\widetilde{E}} \tag{4.17}$$

$$H_2\text{: } -\left(\frac{\partial r_c}{\partial E}\right)_{\theta,\varphi,c} = \left(\frac{\partial r_c}{\partial \theta}\right)_{E,c,\varphi}\frac{\widetilde{\theta}}{\widetilde{E}} + \left(\frac{\partial r_c}{\partial \varphi}\right)_{E,c,\theta}\frac{\widetilde{\varphi}}{\widetilde{E}} + \left[\left(\frac{\partial r_c}{\partial c}\right)_{E,\theta,\varphi} - \sqrt{\mathrm{i}\,\omega D}\right]\frac{\widetilde{c}}{\widetilde{E}} \tag{4.18}$$

We can express the equations in matrix form:

$$\frac{C_\mathrm{d}}{F\Gamma_\mathrm{m}}\begin{bmatrix} -\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}}\left(\frac{\partial r_\mathrm{e}}{\partial E}\right)_{\theta,\varphi,c} - \mathrm{i}\,\omega\Gamma_\mathrm{m} \\ -\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}}\left(\frac{\partial r_\theta}{\partial E}\right)_{\theta,\varphi,c} \\ -\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}}\left(\frac{\partial r_\varphi}{\partial E}\right)_{\theta,\varphi,c} \\ -\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}}\left(\frac{\partial r_c}{\partial E}\right)_{\theta,\varphi,c} \end{bmatrix} = \begin{bmatrix} -\frac{1}{F} & \left(\frac{\partial r_\mathrm{e}}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_\mathrm{e}}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_\mathrm{e}}{\partial c}\right)_{E,\theta,\varphi} \\ 0 & \left(\frac{\partial r_\theta}{\partial \theta}\right)_{E,c,\varphi} - \mathrm{i}\,\omega\Gamma_\mathrm{m} & \left(\frac{\partial r_\theta}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_\theta}{\partial c}\right)_{E,\theta,\varphi} \\ 0 & \left(\frac{\partial r_\varphi}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_\varphi}{\partial \varphi}\right)_{E,c,\theta} - \mathrm{i}\,\omega\Gamma_\mathrm{m} & \left(\frac{\partial r_\varphi}{\partial c}\right)_{E,\theta,\varphi} \\ 0 & \left(\frac{\partial r_c}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_c}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_c}{\partial c}\right)_{E,\theta,\varphi} - \sqrt{\mathrm{i}\,\omega D} \end{bmatrix}\begin{bmatrix} Y \\ \frac{\widetilde{\theta}}{\widetilde{E}} \\ \frac{\widetilde{\varphi}}{\widetilde{E}} \\ \frac{\widetilde{c}}{\widetilde{E}} \end{bmatrix} \tag{4.19}$$

We can use Cramer's rule to solve for Y: the first unknown is the determinant of the matrix with its first column replaced by the constants (the vector on the left) divided by the determinant of

[4] This would be the state space way of doing things.

the matrix:

$$Y = \frac{\frac{C_\mathrm{d}}{F\Gamma_\mathrm{m}} \begin{vmatrix} -\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}} \left(\frac{\partial r_\mathrm{e}}{\partial E}\right)_{\theta,\varphi,c} - \mathrm{i}\,\omega\Gamma_\mathrm{m} & \left(\frac{\partial r_\mathrm{e}}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_\mathrm{e}}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_\mathrm{e}}{\partial c}\right)_{E,\theta,\varphi} \\ -\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}} \left(\frac{\partial r_\theta}{\partial E}\right)_{\theta,\varphi,c} & \left(\frac{\partial r_\theta}{\partial \theta}\right)_{E,c,\varphi} - \mathrm{i}\,\omega\Gamma_\mathrm{m} & \left(\frac{\partial r_\theta}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_\theta}{\partial c}\right)_{E,\theta,\varphi} \\ -\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}} \left(\frac{\partial r_\varphi}{\partial E}\right)_{\theta,\varphi,c} & \left(\frac{\partial r_\varphi}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_\varphi}{\partial \varphi}\right)_{E,c,\theta} - \mathrm{i}\,\omega\Gamma_\mathrm{m} & \left(\frac{\partial r_\varphi}{\partial c}\right)_{E,\theta,\varphi} \\ -\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}} \left(\frac{\partial r_c}{\partial E}\right)_{\theta,\varphi,c} & \left(\frac{\partial r_c}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_c}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_c}{\partial c}\right)_{E,\theta,\varphi} - \sqrt{\mathrm{i}\,\omega D} \end{vmatrix}}{\begin{vmatrix} -\frac{1}{F} & \left(\frac{\partial r_\mathrm{e}}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_\mathrm{e}}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_\mathrm{e}}{\partial c}\right)_{E,\theta,\varphi} \\ 0 & \left(\frac{\partial r_\theta}{\partial \theta}\right)_{E,c,\varphi} - \mathrm{i}\,\omega\Gamma_\mathrm{m} & \left(\frac{\partial r_\theta}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_\theta}{\partial c}\right)_{E,\theta,\varphi} \\ 0 & \left(\frac{\partial r_\varphi}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_\varphi}{\partial \varphi}\right)_{E,c,\theta} - \mathrm{i}\,\omega\Gamma_\mathrm{m} & \left(\frac{\partial r_\varphi}{\partial c}\right)_{E,\theta,\varphi} \\ 0 & \left(\frac{\partial r_c}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_c}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_c}{\partial c}\right)_{E,\theta,\varphi} - \sqrt{\mathrm{i}\,\omega D} \end{vmatrix}} \tag{4.20}$$

We simplify the bottom determinant by expanding down the first column, and then we flip the whole thing upside down to get Z:

$$Z = -\frac{\Gamma_\mathrm{m}}{C_\mathrm{d}} \frac{\begin{vmatrix} \left(\frac{\partial r_\theta}{\partial \theta}\right)_{E,c,\varphi} - \mathrm{i}\,\omega\Gamma_\mathrm{m} & \left(\frac{\partial r_\theta}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_\theta}{\partial c}\right)_{E,\theta,\varphi} \\ \left(\frac{\partial r_\varphi}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_\varphi}{\partial \varphi}\right)_{E,c,\theta} - \mathrm{i}\,\omega\Gamma_\mathrm{m} & \left(\frac{\partial r_\varphi}{\partial c}\right)_{E,\theta,\varphi} \\ \left(\frac{\partial r_c}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_c}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_c}{\partial c}\right)_{E,\theta,\varphi} - \sqrt{\mathrm{i}\,\omega D} \end{vmatrix}}{\begin{vmatrix} -\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}} \left(\frac{\partial r_\mathrm{e}}{\partial E}\right)_{\theta,\varphi,c} - \mathrm{i}\,\omega\Gamma_\mathrm{m} & \left(\frac{\partial r_\mathrm{e}}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_\mathrm{e}}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_\mathrm{e}}{\partial c}\right)_{E,\theta,\varphi} \\ -\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}} \left(\frac{\partial r_\theta}{\partial E}\right)_{\theta,\varphi,c} & \left(\frac{\partial r_\theta}{\partial \theta}\right)_{E,c,\varphi} - \mathrm{i}\,\omega\Gamma_\mathrm{m} & \left(\frac{\partial r_\theta}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_\theta}{\partial c}\right)_{E,\theta,\varphi} \\ -\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}} \left(\frac{\partial r_\varphi}{\partial E}\right)_{\theta,\varphi,c} & \left(\frac{\partial r_\varphi}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_\varphi}{\partial \varphi}\right)_{E,c,\theta} - \mathrm{i}\,\omega\Gamma_\mathrm{m} & \left(\frac{\partial r_\varphi}{\partial c}\right)_{E,\theta,\varphi} \\ -\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}} \left(\frac{\partial r_c}{\partial E}\right)_{\theta,\varphi,c} & \left(\frac{\partial r_c}{\partial \theta}\right)_{E,c,\varphi} & \left(\frac{\partial r_c}{\partial \varphi}\right)_{E,c,\theta} & \left(\frac{\partial r_c}{\partial c}\right)_{E,\theta,\varphi} - \sqrt{\mathrm{i}\,\omega D} \end{vmatrix}} \tag{4.21}$$

Each row and column of the determinants corresponds to one of the species in a rather obvious way. Note that the top determinant is the bottom one with its first row and column (corresponding to the electron) deleted. It is clear that this procedure is rather general, and allows us to consider reaction mechanisms with a mixture of diffusing and adsorbed species. A few points are worth noting:

- We have assumed that the double-layer is treated as a capacitor in parallel with the faradaic impedance. However this holds under most conditions, as shown above. (Note that we haven't made any assumptions about the potential dependence of this capacitance.)
- We have not yet made any assumptions about the specific form of the potential dependence of the rate constants.
- We have not yet made any assumption about the "isotherm", whether Langmuir kinetics applies or some other form of the rate law with coverage.
- We have not yet shown any advantage for treating the sites as separate species; we could have used the single variable θ (rather than θ and φ) as we did in the single-step adsorption reaction.

- The case of finite diffusion ($\widetilde{c}(z=d)=0$ boundary condition) is easily accommodated by replacing $\sqrt{\mathrm{i}\,\omega D}$ with $\sqrt{\mathrm{i}\,\omega D}\coth\left(d\sqrt{\frac{\mathrm{i}\,\omega}{D}}\right)$.
- If there are several diffusing species, then they can each have their own diffusion coefficient D_i, or we can make the common approximation that they are all the same.

The fact that we have not made very many assumptions is an advantage in that we can put a variety of rate law forms into our computer and crank out the impedance with the above expression as a starting point. On the other hand we need to make some more specific assumptions if we are going to make any global statements about what types of mechanisms give what types of equivalent circuits. If we add in only information about the stoichiometry, and none about the rate laws (dependence on coverages, concentrations or potential)[5], then we can still make some general statements, though we will not prove them:

1. More complex impedance spectra do not necessarily result from mechanisms with more species.
2. The number of reaction steps per se is not important.
3. Mechanisms with the same number and type of species may give different types of spectra.
4. At high frequencies, the faradaic impedance simplifies to a charge-transfer resistor

$$\frac{1}{R_{\mathrm{ct}}}=F\left(\frac{\partial r_{\mathrm{e}}}{\partial E}\right)_{\theta_i,c_k}=\left(\frac{\partial j_{\mathrm{ss}}}{\partial E}\right)_{\theta_i,c_k} \tag{4.22}$$

   which means that the highest frequency feature in the Nyquist plot (aside from the solution resistance) is always part of a semicircle representing the charge-transfer resistance in parallel with the double-layer capacitance.
5. Since r_{e} is a combination of the rates of the electron-transfer steps, the charge transfer resistance is a parallel combination of the charge-transfer resistances of the individual electron-transfer steps.
6. The limiting low-frequency behavior is determined by a parameter X, which is determined by playing a game with the available species (including the external ones).
   (a) If the electrons and the external species can be combined to form a balanced reaction, then $X=2$ and the low frequency behavior is resistive, otherwise:
   (b) If the electrons and the soluble species (external or diffusing) can be combined to form a balanced reaction, then $X=1$ and the low frequency behavior is Warburg, otherwise:
   (c) If any reaction with electrons must include an adsorbed species, $X=0$, and the low frequency behavior is capacitive (blocking).

The fact that the the high-frequency behavior is the charge-transfer resistance with this form should not surprise us. As soon as we change the potential drop across the double-layer, we change the activation barrier for the electrons to cross the interface and therefore the rate at which the electrons transfer is in phase with the potential, i.e., we have a resistor. This resistor depends

[5] Note that by associating electrons with potential, we are implicitly assuming that the rate of a reaction step without electrons is independent of potential.

on a partial derivative with the various coverages and surface concentrations held constant – to adjust these is slow and so at a high enough frequency their concentrations are frozen and only the electron-transfer rate can be influenced. The rate at which we can change the field in the double layer depends on how fast we can charge and discharge the double-layer capacitance, which is limited by how fast we can bring ions to and from the solution to the double layer – this happens with time constant $R_\mathrm{s}C_\mathrm{d}$.

Based on what we have seen in circuit theory, the low-frequency behavior depends on the poles or zeros at zero, and the rule about X really just characterizes the pole at zero, $Z \sim 1\Big/\left(\sqrt{\mathrm{i}\,\omega}\right)^{2-X}$. For $X = 0$, $Z \sim 1/s$, which we have seen leads to a blocking capacitor. It is gratifying that this is precisely the case where the reaction mechanism has no d.c. current flow, since the requirement for an adsorbed species on the surface in the reaction means that we adsorb to the steady-state coverage and then the reaction can proceed no further. In the $X = 2$ case (no pole at zero), the reaction we construct is a viable candidate for an overall reaction, i.e. our mechanism is electrocatalytic and a d.c. current can pass, leading to non-blocking resistive behavior. The $X = 1$ case is an intermediate case, where our overall reaction rate is limited by diffusion, and we get Warburg behavior at low frequencies. Note that the way the rule is applied, blocking behavior dominates over Warburg behaviour at low frequencies, as we saw previously for the reaction

$$\mathrm{Pt(site)} + \mathrm{Ag^+(aq)} + \mathrm{e^-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{PtAg(ads)} \tag{4.23}$$

No reaction can be made from $\mathrm{Ag^+(aq)}$ and $\mathrm{e^-}$, so we decide that $X = 0$ and the behavior is capacitive at the lowest frequencies, even though diffusion may be apparent at higher frequencies.

4.1 Mechanisms with Adsorption and Fast Mass Transport

To be able to make some more specific statements about impedance behavior and specific circuits, we make some simplifying assumptions. Firstly, we notice that the diffusing species with the square roots $\sqrt{\mathrm{i}\,\omega}$ are rather different from the adsorbed species, and this means that it is very hard to make general statements about mechanisms with both diffusing and adsorbed species. So we focus our attention on mechanisms where mass transport does not play a role. Once we omit diffusing species (i.e., make them external), then we notice that we can make a further simplification by factoring out Γ_m. For the hydrogen evolution reaction with $\mathrm{H^+}$ and $\mathrm{H_2}$ both considered external, we can simplify Eq. 4.21 to[6]

$$Z = -\frac{1}{C_\mathrm{d}} \frac{\begin{vmatrix} \frac{1}{\Gamma_\mathrm{m}}\left(\frac{\partial r_\theta}{\partial \theta}\right)_{E,\varphi} - s & \frac{1}{\Gamma_\mathrm{m}}\left(\frac{\partial r_\theta}{\partial \varphi}\right)_{E,\theta} \\ \frac{1}{\Gamma_\mathrm{m}}\left(\frac{\partial r_\varphi}{\partial \theta}\right)_{E,\varphi} & \frac{1}{\Gamma_\mathrm{m}}\left(\frac{\partial r_\varphi}{\partial \varphi}\right)_{E,\theta} - s \end{vmatrix}}{\begin{vmatrix} -\frac{F}{C_\mathrm{d}}\left(\frac{\partial r_\mathrm{e}}{\partial E}\right)_{\theta,\varphi} - s & \frac{1}{\Gamma_\mathrm{m}}\left(\frac{\partial r_\mathrm{e}}{\partial \theta}\right)_{E,\varphi} & \frac{1}{\Gamma_\mathrm{m}}\left(\frac{\partial r_\mathrm{e}}{\partial \varphi}\right)_{E,\theta} \\ -\frac{F}{C_\mathrm{d}}\left(\frac{\partial r_\theta}{\partial E}\right)_{\theta,\varphi} & \frac{1}{\Gamma_\mathrm{m}}\left(\frac{\partial r_\theta}{\partial \theta}\right)_{E,\varphi} - s & \frac{1}{\Gamma_\mathrm{m}}\left(\frac{\partial r_\theta}{\partial \varphi}\right)_{E,\theta} \\ -\frac{F}{C_\mathrm{d}}\left(\frac{\partial r_\varphi}{\partial E}\right)_{\theta,\varphi} & \frac{1}{\Gamma_\mathrm{m}}\left(\frac{\partial r_\varphi}{\partial \theta}\right)_{E,\varphi} & \frac{1}{\Gamma_\mathrm{m}}\left(\frac{\partial r_\varphi}{\partial \varphi}\right)_{E,\theta} - s \end{vmatrix}} \tag{4.24}$$

Expansion of the determinants leads to polynomials in s, so that we see that adsorption mechanisms give rise to *RLC* equivalent circuits, provided that they satisfy the PR conditions.

[6] We could have got rid of a lot of Γ_m quantities by defining our concentration variables in mol $\mathrm{m^{-2}}$, $\Gamma = \Gamma_\mathrm{m}\theta$ rather than θ, but it is more usual to formulate kinetics in terms of coverages.

It seems. looking at Eq. 4.24, that the impedance is a quadratic in s divided by a cubic in s. But we know we could have formulated the problem only in terms of θ and not both θ and φ

$$Z = -\frac{1}{C_\mathrm{d}} \frac{\frac{1}{\Gamma_\mathrm{m}} \left(\frac{\partial r_\theta}{\partial \theta}\right)_E - s}{\begin{vmatrix} -\frac{F}{C_\mathrm{d}} \left(\frac{\partial r_\mathrm{e}}{\partial E}\right)_\theta - s & \frac{1}{\Gamma_\mathrm{m}} \left(\frac{\partial r_\mathrm{e}}{\partial \theta}\right)_E \\ -\frac{F}{C_\mathrm{d}} \left(\frac{\partial r_\theta}{\partial E}\right)_\theta & \frac{1}{\Gamma_\mathrm{m}} \left(\frac{\partial r_\theta}{\partial \theta}\right)_E - s \end{vmatrix}} \tag{4.25}$$

which leads to a linear polynomial over a quadratic. This simplification originates in the fact that Eqs. (4.6) and (4.7) are not independent equations: $r_\theta = -r_\varphi$. Providing that no further simplification can occur, we can see what the equivalent circuit is for the HER. There are two poles, so two capacitors. There is (probably) no pole at zero, but there is a zero at infinity, so there will be (poles $+1$) $- 1 = 2$ resistors. We therefore find, choosing the Cauer 1 form, the well-known equivalent circuit for the HER (including the solution resistance, this is the circuit of Fig. 3.1a). Furthermore, we could deduce that C_d is in parallel to the rest of the circuit by noting that for large s, $Z \sim 1/sC_\mathrm{d}$; this is hardly surprising because we set it up this way.

The astute reader will have noticed that the impedance we derived for the HER could equally well have been derived for the H UPD reaction, since we have not specified the details of the partial derivatives. Yet we know that reaction has a different circuit, so some further simplification must be possible in that case. That case has a pole at zero, which means that the constant term in the denominator polynomial must be zero. A closer look at this shows that this arises because $r_\mathrm{e} = -r_\theta$; one electron is directly associated with one adsorbed species.

Returning again to the HER, we note that whether we omitted the third reaction or not, we would get the same expression. We might look for a further simplification on omitting the third reaction, but in this case we would not find it: *there is the same equivalent circuit despite the additional reaction step.* So how do we decide on whether a simplification such $r_\theta = -r_\varphi$ or $r_\mathrm{e} = -r_\theta$ occurs or not? This must depend on the stoichiometric coefficients in some way. Specifically it depends on a parameter I, the number of independent reactions[7]. Reactions are independent if none of them can be written as combinations of the others, in the sense of Hess's law. Because the external species are not important here, we omit them from consideration and write the HER as:

$$\begin{aligned} \mathrm{Pt(site)} + \mathrm{e^-} &\rightleftarrows \mathrm{PtH(ads)} \\ \mathrm{PtH(ads)} + \mathrm{e^-} &\rightleftarrows \mathrm{Pt(site)} \\ 2\mathrm{PtH(ads)} &\rightleftarrows 2\mathrm{Pt(site)} \end{aligned} \tag{4.26}$$

If we had step one alone (which is the H UPD case), then there is one independent reaction, $I = 1$. Adding step 2 gives a second independent reaction, since step 2 is not just a multiple (or backwards version) or step 1, i.e., $I = 2$. But adding the third step does not lead to an additional independent reaction, because step 3 can be written as step 2 minus step one:

$$\begin{array}{ll} \mathrm{PtH(ads)} \rightleftarrows \mathrm{Pt(site)} + \mathrm{e^-} & -1 \\ \underline{\mathrm{PtH(ads)} + \mathrm{e^-} \rightleftarrows \mathrm{Pt(site)}} & \underline{2} \\ 2\mathrm{PtH(ads)} \rightleftarrows 2\mathrm{Pt(site)} & 3 \end{array} \tag{4.27}$$

Likewise, the mechanism with only steps 1 and 3 also has $I = 2$, and so these different $I = 2$ cases cannot be distinguished just by looking at the form of the equivalent circuit.[8]

From the two parameters I and X, we can estimate the numbers of capacitors and resistors (assuming an RC circuit) and the number of bends in a Bode magnitude plot as

[7] Mathematically $I = \mathrm{rank}(\boldsymbol{N})$. The rank of $\boldsymbol{N}$ after the electron row is removed is $I - X/2$.

[8] A full analysis of the potential dependence of the circuit elements could distinguish these cases.

- Number of capacitors, including the double-layer capacitor: $I + 1 - X/2$.
- Number of resistors, including the solution resistance: $I + 1$
- Number of bends on a Bode magnitude plot of the total impedance (including C_d and R_s): $2I + 1 - X/2$

These numbers follow from the rules we had for the numbers of capacitors and resistors in a general *RC* circuit (though not that simply). We have assumed an *RC* circuit, but we expect that if inductive behavior applies, an inductor will replace a capacitor, and so the above number is for capacitors and inductors together. It is possible to show that inductors cannot occur at equilibrium. This rules remain an estimate because sometimes the circuit may look simpler than this. For example, at some potentials, poles and zeroes may coincide, leading to apparently simpler behavior. This type of simplification is more likely far from equilibrium, and so experiments at or near equilibrium are to be preferred. For example, in the case of the HER, the charge transfer resistance may reduce to a very small value at high overpotentials. Omitting it from the circuit, the double-layer and other capacitor combine in parallel and the resulting circuit is just a parallel *RC* combination.

4.1.1 Formulating Langmuir and Tafel Kinetics

We have deliberately left the impedance in terms of the partial derivatives, to emphasis that in many cases the type of equivalent circuit does not depend on the intimate details of the rate law. However, to answer some more specific questions, such as when inductive behavior arises, we need to specify the rate laws. We will do this for the case of mass action rate laws, which means that the reaction order of the species in an elementary reaction is just the absolute value of the stoichiometric coefficient:

$$3\mathrm{A} + 5\mathrm{B} \quad \rightleftarrows \quad 2\mathrm{C} + \mathrm{D} \tag{4.28}$$

$$v_1 = v_{1\mathrm{f}} - v_{1\mathrm{b}} \quad = \quad k_1 \theta_\mathrm{A}^3 \theta_\mathrm{B}^5 - k_{-1} \theta_\mathrm{C}^2 \theta_\mathrm{D} \tag{4.29}$$

where $v_{1\mathrm{f}}$ and $v_{1\mathrm{b}}$ are the forward and backward rates. If we include the reaction sites as distinct species, then mass-action kinetics and Langmuir kinetics are the same, so we assume that in this section. The partial derivatives with respect to the concentrations can be written in a particularly simple way for mass action kinetics, a fact that helps to give the impedance a fairly simple structure. For example,

$$\frac{\partial v_1}{\partial \theta_\mathrm{A}} \quad = \quad 3k_1 \theta_\mathrm{A}^2 \theta_\mathrm{B}^5 = \frac{3v_{1\mathrm{f}}}{\theta_\mathrm{A}} \tag{4.30}$$

$$\frac{\partial v_1}{\partial \theta_\mathrm{C}} \quad = \quad -2k_{-1} \theta_\mathrm{C} \theta_\mathrm{D} = \frac{-2v_{1\mathrm{b}}}{\theta_\mathrm{C}} \tag{4.31}$$

and we can generalize this to

$$\frac{\partial v_j}{\partial \theta_i} \quad = \quad \frac{-n_{ij} v_{j\mathrm{f}}}{\theta_i}, \text{ for reactant } i \tag{4.32}$$

$$\frac{\partial v_j}{\partial \theta_i} \quad = \quad \frac{-n_{ij} v_{j\mathrm{b}}}{\theta_i}, \text{ for product } i \tag{4.33}$$

where n_{ij} denotes the stoichiometric coefficient of species i in reaction j. With a bit of extra work, we can force the partial derivatives with respect to potential into this form if we assume

Tafel potential dependence, again associating potential and electrons.

$$-\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}}\frac{\partial v_j}{\partial E} = -\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}}\left[\frac{-\beta_j|n_{\mathrm{e}j}|F}{RT}v_{j\mathrm{f}} - \frac{(1-\beta_j)|n_{\mathrm{e}j}|F}{RT}v_{j\mathrm{b}}\right], \quad \text{step } j \text{ a reduction} \tag{4.34}$$

$$= -\frac{n_{\mathrm{e}j}F^2\Gamma_\mathrm{m}}{RTC_\mathrm{d}}\left[\beta_j v_{j\mathrm{f}} + (1-\beta_j)v_{j\mathrm{b}}\right] = \frac{-n_{\mathrm{e}j}v_{j\mathrm{e}}}{\theta_\mathrm{e}} \quad (n_{\mathrm{e}j} \text{ is negative}) \tag{4.35}$$

$$\text{where } v_{j\mathrm{e}} = \beta_j v_{j\mathrm{f}} + (1-\beta_j)v_{j\mathrm{b}},\ \theta_\mathrm{e} = RTC_\mathrm{d}/F^2\Gamma_\mathrm{m} \tag{4.36}$$

$$-\frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}}\frac{\partial v_j}{\partial E} = \frac{-n_{\mathrm{e}j}v_{j\mathrm{e}}}{\theta_\mathrm{e}}, \quad \text{step } j \text{ an oxidation } (n_{\mathrm{e}j} \text{ positive}) \tag{4.37}$$

$$\text{where } v_{j\mathrm{e}} = (1-\beta_j)v_{j\mathrm{f}} + \beta_j v_{j\mathrm{b}} \tag{4.38}$$

(Here $n_{\mathrm{e}j}$ means the stoichiometric coefficient of electrons in step j.)

Now we may use these expressions to simplify the impedance from the form in Eq. (4.24). The pattern of s on the main diagonal is the way that eigenvalues are defined, so that the roots of the denominator polynomial (which are the poles) are also the eigenvalues of a matrix $-\Gamma_\mathrm{m}^{-1}\boldsymbol{Q}$, where $\boldsymbol{Q}$ is a matrix of partial derivatives. Likewise, the numerator is a polynomial in s whose roots (the zeroes) are the eigenvalues of $-\Gamma_\mathrm{m}^{-1}\boldsymbol{Q}(1)$, where the notation (1) means that we have deleted the first row and column:

$$Z = -\frac{\left|-\Gamma_\mathrm{m}^{-1}\boldsymbol{Q}(1) - s\boldsymbol{I}\right|}{C_\mathrm{d}\left|-\Gamma_\mathrm{m}^{-1}\boldsymbol{Q} - s\boldsymbol{I}\right|} = \frac{\left|\Gamma_\mathrm{m}^{-1}\boldsymbol{Q}(1) + s\boldsymbol{I}\right|}{C_\mathrm{d}\left|\Gamma_\mathrm{m}^{-1}\boldsymbol{Q} + s\boldsymbol{I}\right|} \tag{4.39}$$

$$\boldsymbol{Q} = \begin{bmatrix} \frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}}\left(\frac{\partial r_\mathrm{e}}{\partial E}\right)_{\theta,\varphi} & -\left(\frac{\partial r_\mathrm{e}}{\partial \theta}\right)_{E,\varphi} & -\left(\frac{\partial r_\mathrm{e}}{\partial \varphi}\right)_{E,\theta} \\ \frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}\,\Gamma_\mathrm{m}}\left(\frac{\partial r_\theta}{\partial E}\right)_{\theta,\varphi} & -\left(\frac{\partial r_\theta}{\partial \theta}\right)_{E,\varphi} & -\left(\frac{\partial r_\theta}{\partial \varphi}\right)_{E,\theta} \\ \frac{F\Gamma_\mathrm{m}}{C_\mathrm{d}}\left(\frac{\partial r_\varphi}{\partial E}\right)_{\theta,\varphi} & -\left(\frac{\partial r_\varphi}{\partial \theta}\right)_{E,\varphi} & -\left(\frac{\partial r_\varphi}{\partial \varphi}\right)_{E,\theta} \end{bmatrix} \tag{4.40}$$

where $\boldsymbol{I}$ is an identity matrix of the appropriate size. We can separate $\boldsymbol{Q}$ into its contributions from each step, $\boldsymbol{Q} = \boldsymbol{A}_1 + \boldsymbol{A}_2 + \boldsymbol{A}_3$ where an "elementary" matrix is defined as a product of a column vector (a column of the stoichiometric matrix) times a row vector:

$$\boldsymbol{A}_j = \begin{bmatrix} n_{\mathrm{e}j} \\ n_{2j} \\ n_{3j} \end{bmatrix}\begin{bmatrix} n_{\mathrm{e}j}v_{j\mathrm{e}}/\theta_\mathrm{e} & n_{2j}v_{j\mathrm{fb}}/\theta & n_{3j}v_{j\mathrm{fb}}/\varphi \end{bmatrix} \tag{4.41}$$

where species 2 and 3 are the adsorbed H and the sites, and $v_{j\mathrm{fb}}$ means $v_{j\mathrm{f}}$ if the stoichiometric coeffient is negative (*reactants* drive the *forward* reaction) and means $v_{j\mathrm{b}}$ if the stoichiometric coeffient is positive (*products* drive the *backward* reaction) For the hydrogen evolution reaction we have

$$\boldsymbol{A}_1 = \begin{bmatrix} -1 \\ 1 \\ -1 \end{bmatrix}\begin{bmatrix} -v_{1\mathrm{e}}/\theta_\mathrm{e} & v_{1\mathrm{b}}/\theta & -v_{1\mathrm{f}}/\varphi \end{bmatrix} = \begin{bmatrix} v_{1\mathrm{e}}/\theta_\mathrm{e} & -v_{1\mathrm{b}}/\theta & v_{1\mathrm{f}}/\varphi \\ -v_{1\mathrm{e}}/\theta_\mathrm{e} & v_{1\mathrm{b}}/\theta & -v_{1\mathrm{f}}/\varphi \\ v_{1\mathrm{e}}/\theta_\mathrm{e} & -v_{1\mathrm{b}}/\theta & v_{1\mathrm{f}}/\varphi \end{bmatrix} \tag{4.42}$$

$$\boldsymbol{A}_2 = \begin{bmatrix} -1 \\ -1 \\ 1 \end{bmatrix}\begin{bmatrix} -v_{2\mathrm{e}}/\theta_\mathrm{e} & -v_{2\mathrm{f}}/\theta & v_{2\mathrm{b}}/\varphi \end{bmatrix} = \begin{bmatrix} v_{2\mathrm{e}}/\theta_\mathrm{e} & v_{2\mathrm{f}}/\theta & -v_{2\mathrm{b}}/\varphi \\ v_{2\mathrm{e}}/\theta_\mathrm{e} & v_{2\mathrm{f}}/\theta & -v_{2\mathrm{b}}/\varphi \\ -v_{2\mathrm{e}}/\theta_\mathrm{e} & -v_{2\mathrm{f}}/\theta & v_{2\mathrm{b}}/\varphi \end{bmatrix} \tag{4.43}$$

$$\boldsymbol{A}_3 = \begin{bmatrix} 0 \\ -2 \\ 2 \end{bmatrix}\begin{bmatrix} 0 & -2v_{2\mathrm{f}}/\theta & 2v_{2\mathrm{b}}/\varphi \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 4v_{2\mathrm{f}}/\theta & -4v_{2\mathrm{b}}/\varphi \\ 0 & -4v_{2\mathrm{f}}/\theta & 4v_{2\mathrm{b}}/\varphi \end{bmatrix} \tag{4.44}$$

The usual matrix multiplication rule (dive row down column) gives a 3×3 rank-1 matrix for each elementary matrix. We will not progress beyond writing out this form here, other than to note that since the eigenvalues of a sum of matrices ($\boldsymbol{Q}$) are not simply related to the eigenvalues of the individual matrices $\boldsymbol{A}_j$, the general problem of characterizing the poles and zeroes of the impedance is mathematically difficult.

4.1.2 Some Results for Langmuir and Tafel Kinetics

Without proof, we give some qualitative results about inductive behavior for mechanisms with Langmuir and Tafel kinetics. In fact we actually only require in the proofs that the signs of some partial derivatives have known values, so we can depart a bit from Langmuir kinetics and still find these things to be true; likewise we only require the potential dependence of the rate constants to be monotonic rather than Tafel. We also assume that all reactions are to some extent reversible (forward and backward rates are both non-zero) and we assume that the same species does not occur on both sides of a reaction. Then we may show that

1. At the equilibrium potential, the equivalent circuits are RC. Inductive behavior can only occur away from equilibrium.

2. A single reaction step cannot show inductive behavior.

3. For mechanisms with a single adsorbed species (and adsorption sites), inductive behavior requires the presence of a step that is oxidizing in the direction of adsorption (ODA) and a step that is reducing in the direction of adsorption (RDA). For example the first step of the HER is RDA and the second step is ODA (the direction of adsorption here is the backward direction, which is oxidizing), so the HER with steps 1 and 2 can show inductive behavior but the HER with only steps 1 and 3 cannot.

4. Mechanisms no more than a single adsorbed species or reaction site on the reactant or product side, without reaction cycles, and with only a single electron-transfer step gives an RC circuit.

5. We do not always need two electron-transfer steps to get inductive behavior.

Note that a mechanism that can show inductive behavior at some potentials may have an RC circuit at other potentials.

Chapter 5

Some Misconceptions

We have dealt with many misconceptions in the text so far, but there are some more that it is worth making explicit, even though it may now be obvious to the reader than they are false.

My potentiostat has only 20 kHz frequency response, so I can't make impedance measurements at 400 kHz.

If you have a two-channel measurement system (such as the Solartron) that measures the actual a.c. voltage across the working and reference electrodes and the actual a.c. current (through a resistor in series with the counter electrode), then you compensate for phase and amplitude shifts caused by poor potentiostat response. You should bypass the voltage and current measurements systems (V_{out} and I_{out}) of your potentiostat, since they can be a source of phase and amplitude error (the current measurement system especially). Note that the 5 mV potential amplitude you requested may be severely attenuated at 400 kHz, but may still be measurable. If it is not, you can request a large enough amplitude to actually get 5 mV at the cell; in fact all this attenuation may help by filtering out noise and distortions. There will be a big phase shift, but you are measuring what it is and correcting for it, the calculated impedance will be correct.

Each resistor in an equivalent circuit corresponds to a reaction step.

In general, there is no correspondence between reaction steps and equivalent circuit elements. For example, the charge transfer resistance in the HER equivalent circuit is a function of both electron-transfer steps and the other elements likewise depend on parameters from more than one reaction. In the literature, there are assertions that the two resistors correspond to "fast" and "slow" steps, but this is not correct.

Each adsorbed species has an associated adsorption pseudocapacitance.

The fact that in the simple adsorption reaction, the capacitor in the faradaic impedance is equal to the steady-state pseudocapacitance is unfortunate, since in general this relationship is not true. One cannot estimate surface coverages from integrating the capacitance in an equivalent circuit. Specifically the capacitance in the HER circuit is different from the steady-state adsorption pseudocapacitance, and even goes to infinity at high overpotentials, meaning that it cannot be integrated at all.

OK, OK, but a faradaic impedance of a mechanism with adsorption will at least have one capacitor in its equivalent circuit.

Nope. Consider the HER mechanism with adsorbed H, reaction sites, and diffusion of both H_2 and H^+ (to make H^+ influenced by diffusion the reaction could be carried out in a solvent such as acetonitrile). Then one can choose rate constants and diffusion constants to give an equivalent circuit containing only resistors and Warburgs, but no capacitors (except the double layer capacitor)[1]. This example relies on the diffusion coefficients being quite different which may make it unrealistic, but it does show that in principle there need not be a capacitor.

An inductor cannot occur in an equivalent circuit because electrochemical mechanisms do not involve storage of magnetic energy.

The equivalent circuit is only that, *equivalent,* to an electrochemical system; it does not really exist and so there is no implication that magnetic energy is involved in the electrochemical system. An inductor is simply an element that, in combination with the other elements, leads to the appropriate phase and amplitude in the current that the mechanism being measured actually exhibits.

The charge-transfer resistor results from electron-transfer steps.

This is usually true, but it is possible to find a mechanism with no electron-transfer steps at all that nonetheless has the same circuit as the UPD adsorption reaction. What significance should we therefore attach to this resistor? The most important aspect about a resistor is that it is an energy dissipating element. Whenever we have a process that dissipates energy (generates entropy) such as a chemical reaction, there will be an impedance with a positive real part, whose equivalent circuit usually has a resistor[2]. The act of crossing an activation barrier in a reaction will dissipate energy, so the charge-transfer resistor might better be termed an activation resistor.

My fuel cell equivalent circuit has some complicated porous mass-transport elements that are in series with the electrode impedance because the gas mass transport is adjacent to the region where the electrode reaction takes place.

Things are in series when the same current flows through them and the potential differences across them add. The fact that things are physically adjacent does not mean they have to be in series. In the above case, there is no potential difference across the mass-transport structure, and so it is not in series. This is seen already in the Randles circuit, where the diffusion occurs away from the electrode, but the double-layer capacitance spans the reaction resistor and the Warburg element. There is no potential drop across the diffusion layer – the electrode senses only the concentrations at the surface (though the flux-concentration relationship does reflect what is happening further out). Physical relationships need not be reflected in equivalent circuits; even in the Randles circuit the potential difference across the Warburg element doesn't have too much physical significance.

I added another element to my equivalent circuit and the fit improved, so I am justified in adding that element.

The fit (e.g, as measured by χ^2) always improves when you add a parameter. The real question is whether it improves enough to be statistically significant. There is a test for this, involving

[1] See Fig 2 in D.A. Harrington, J. Electroanal. Chem., 449 (1998) 9.

[2] PtP: Give an example of a circuit that dissipates power but has no resistor.

the F ratio:

$$F = \frac{\chi^2(n-1) - \chi^2(n)}{\chi^2(n)/(2N-n)} \tag{5.1}$$

Here $\chi^2(n-1)$ is the chi-squared goodness of fit (usually output by the fitting program) for the circuit with $n-1$ parameters, $\chi^2(n)$ is the value with the additional parameter, and N is the number of frequencies fitted. A better fit gives a smaller χ^2 and so a larger F value. The F test decides whether or not this F value could have arisen by chance. The F value is looked up in a table with 1 and $2N-n$ degrees of freedom to find the probability that the given F value could be exceeded by chance. For the degrees of freedom usually required in EIS, this probability may have to be calculated with some software, e.g., Maple. A small value of the probability (say $<1\%$) indicates that the addition of the parameter was reasonable. For equally-weighted data, the sum of squares is proportional to χ^2 and can be used in its place in the above test.

Appendix A

Exercises

Exercise 1 Show that the slope of a Bode magnitude plot is -1 for a capacitor.

Exercise 2 A 5 mV rms potential perturbation is applied to an electrochemical cell, and the a.c. current is found to be 0.69 mA rms with a phase, relative to the potential of 74.4°. The electrode area is 0.80 cm^2, and the frequency is 1 kHz. (a) Calculate the impedance (in Ω cm^2) at 1 kHz. Give your answer in both magnitude/phase form and real and imaginary part form. (b) The above measurement is made at a potential where no electrochemical reaction occurs. Estimate the double-layer capacitance and the solution resistance.

Exercise 3 Separate Eq. (2.34) into magnitude and phase parts to find the a.c. diffusion length, the length at which the a.c. magnitude drops to $1/e$ of its initial value.

Exercise 4 Derive Eq. (2.44).

Exercise 5 The impedance for a reaction $O(aq)+e^- \rightarrow R(aq)$ at 298 K is measured over a range of frequencies at $\eta = -0.10$ V and $\eta = -0.20$ V. Some data are given in Fig. A.1 (all in base SI units). Interpret these data, being as quantitative as you can.

Exercise 6 There is another case that could be added to Fig. 3.1. Give the pole-zero plot, a circuit, and the Bode plot for this case.

Exercise 7 Enumerate all distinct *RC* circuits with zero, one, or two capacitors and classify them in terms of their behavior at low and high frequencies.

Exercise 8 Show that the phase of an *RC* circuit is always non-positive. Hint: Consider the factored form of the impedance, Eq. (3.5), and then plot the poles and zeroes in the *s*-plane and consider their phase relationship to the point $\mathrm{j}\omega$.

Exercise 9 Show that for the finite diffusion case of the irreversible single-step reaction with diffusion (Sec. 2.4), the polarization resistance measured by impedance is equal to the inverse slope of the steady-state current-potential curve (which you'll first need to calculate). Note that $\lim_{x\rightarrow 0}(a/\sqrt{x})\tanh(b\sqrt{x}) = ab$ or $\lim_{x\rightarrow 0} a\sqrt{x}\coth(b\sqrt{x}) = a/b$.

Exercise 10 Evaluate the parameter X for each of the cases in Chapter 2, for the hydrogen evolution reaction with H^+ external and H_2 diffusing, and also for both H^+ and H_2 diffusing.

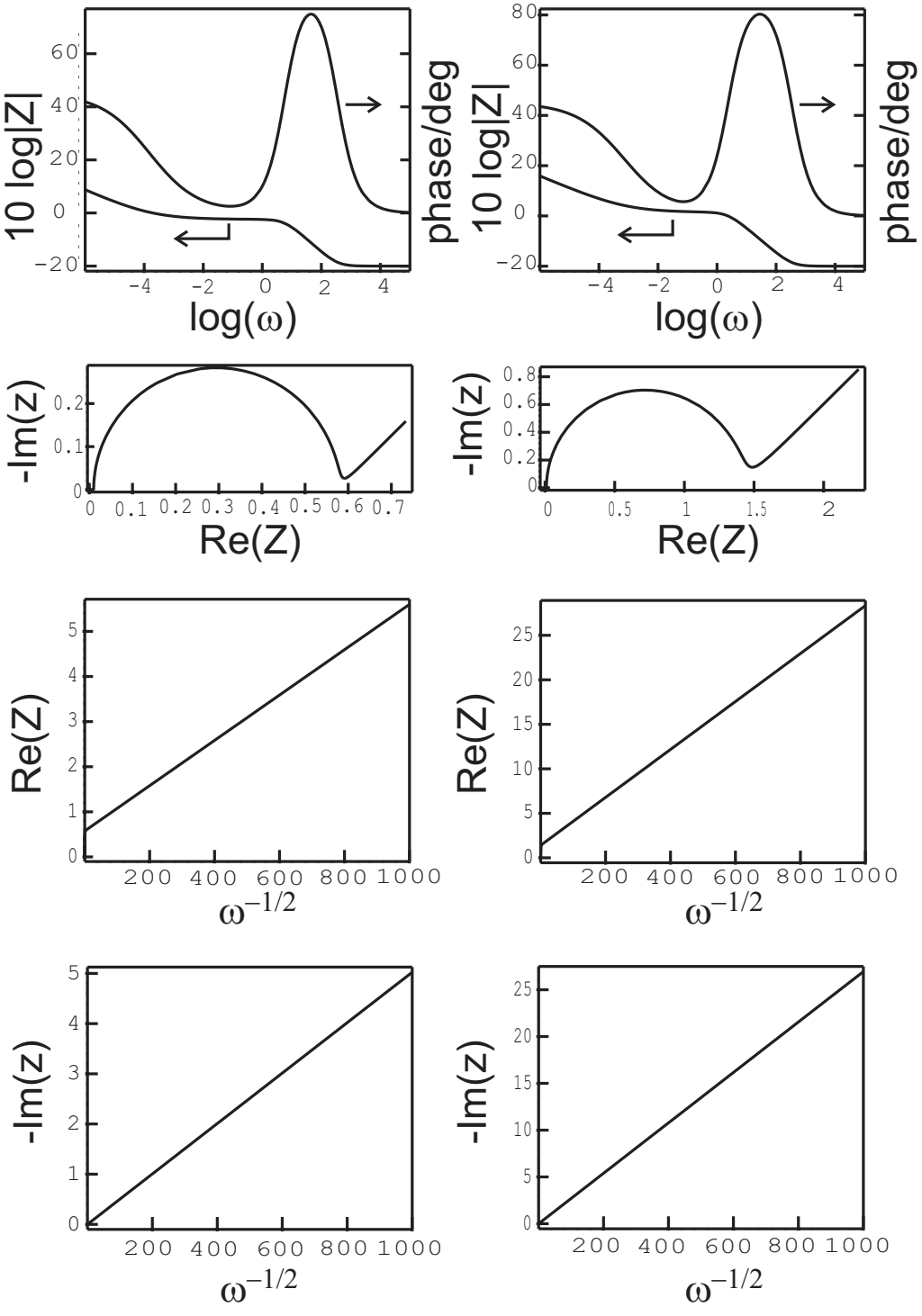


Figure A.1: Randles Exercise.

Appendix B

Cauer 1 Synthesis

The algorithm is:

1. Find the resistor $R = \lim_{s\to\infty} Z(s)$.

2. Subtract off the resistor to give a new impedance $Z(s) \longleftarrow Z(s) - R$.

3. Convert to admittance $Y(s) = 1/Z(s)$

4. Find the capacitor $C = \lim_{s\to\infty}(Y(s)/s)$.

5. Subtract of the capacitor to give a new admittance $Y(s) \longleftarrow Y(s) - sC$.

6. Convert to impedance $Z(s) = 1/Y(s)$.

7. Repeat steps 1.-6.

Step 1 gives zero if the numerator degree is less than the denominator degree in the impedance function, and gives the leading coefficient of the numerator otherwise. Step 4 gives the leading coefficient of the numerator of the admittance. Therefore the scheme can be implemented as a series of long divisions of polynomials, which we illustrate for the example of Eq. (3.13).

$$Z = \frac{2s^2 + \frac{17}{21}s + \frac{2}{35}}{s^2 + \frac{32}{105}s + \frac{1}{210}} \tag{B.1}$$

$$s^2 + \frac{32}{105}s + \frac{1}{210}\overline{)2s^2 + \frac{17}{21}s + \frac{2}{35}} \quad 2 \tag{B.2}$$

$$\underline{2s^2 + \frac{64}{105}s + \frac{2}{210}} \tag{B.3}$$

$$\frac{1}{5}s + \frac{1}{21} \quad \overline{)s^2 + \frac{32}{105}s + \frac{1}{210}} \quad 5s \tag{B.4}$$

$$\underline{s^2 + \frac{5}{21}s} \tag{B.5}$$

$$\frac{1}{15}s + \frac{1}{210}\overline{)\frac{1}{5}s + \frac{1}{21}} \quad 3 \tag{B.6}$$

$$\underline{\frac{1}{5}s + \frac{1}{70}} \tag{B.7}$$

$$\frac{1}{30}\overline{)\frac{1}{15}s + \frac{1}{210}} \quad 2s \tag{B.8}$$

$$\underline{\frac{1}{15}s} \tag{B.9}$$

$$\frac{1}{210}\overline{)\frac{1}{30}} \quad 7 \tag{B.10}$$

and we read the quotients off as the resistors and capacitors: $R = 2$, $C = 5$, $R = 3$, $C = 2$, $R = 7$.

Appendix C

Impedance Reading List

C.1 Books and Chapters

C.1.1 Review Articles

(focusing mainly on reaction mechanisms and kinetics)

1. A. Lasia, Electrochemical Impedance Spectroscopy and Its Applications, in Modern Aspects of Electrochemistry, B. E. Conway, J. Bockris, and R. White, Eds., Kluwer Academic/Plenum Publishers, New York, 1999, Vol. 32, pp. 143-248. (The best review article.)

2. J.R. Macdonald (Ed.), Impedance spectroscopy: emphasizing solid materials and systems, Wiley, NY 1987. (Not much on electrochemical mechanisms. Coming out in second edition soon.)

3. C. Gabrielli, Identification of Electrochemical Processes by Frequency Response Analysis, Solartron Instrumentation Group, 1980. (Good brief introduction to the subject. Used to be handed out freely by Solartron.)

4. C. Gabrielli, Electrochemical impedance spectroscopy: principles, instrumentation, and applications, in Physical electrochemistry: principles, methods, and applications, I. Rubinstein, Ed., Marcel Dekker, NY 1995, Ch 6, pp. 243-292 (Good survey chapter.)

5. D.E. Smith, AC polarography and related techniques: theory and practice, in Electroanalytical chemistry, A.J. Bard, Ed., Marcel Dekker, NY, 1966, Vol 1, pp 1-155.

6. M. Sluyters-Rehbach and J.H. Sluyters, Sine wave methods in the study of electrode processes, in Electroanalytical chemistry, A.J. Bard, Ed., Marcel Dekker, NY, 1970, Vol 4, pp 1-128.

7. M. Sluyters-Rehbach and J. Sluyters, A.C. techniques (for electrode kinetics), in Comprehensive Treatise of Electrochemistry, J.O'M. Bockris, Yu.A. Chizmadzhev, B.E. Conway, S.U.M. Khan, S. Sarangapani, S. Srinivasan, R.E. White, and E. Yeager, Eds., Plenum Press, NY, 1984. Vol. 9, pp 177-292.

8. M. Sluyters-Rehbach and J.H. Sluyters, Alternating current and pulse methods, in Comprehensive chemical kinetics, C.H. Bamford, C.F.H. Tipper, R.G. Compton, A. Hamnett, and G. Hancock, Eds.,Elsevier, NY, 1986, Vol. 26, pp 203-354.

9. M. Sluyters-Rehbach, Impedances of Electrochemical Systems: Terminology, Nomenclature and Representation, Pure and Applied Chem., 66 (1994) 1831-1891. (The IUPAC rules on impedance nomenclature; not intended as a review, but serves as one.)

C.1.2 Circuits and Impedance

1. G.C. Temes, J.W. LaPatra, Introduction to circuit synthesis and design, McGraw-Hill, 1977, TK454.2 T45. (Especially good on the different conditions for positive real functions.)

2. A. Budak, Passive and active network analysis and synthesis, Houghton Mifflin, Boston, 1974, TK454.2 B82 (Good on *RC* circuits, lots of examples.)

3. S. Seshu and N. Balabanian, Linear Network Analysis, Wiley, NY, 1959. TK3226S44. (The one to read if you're into all the topology and graph theory stuff)

4. B. Peikari, Fundamentals of Network Analysis and Synthesis, Prentice Hall, NJ, 1974, TK454.2 P43.(Quick, readable section on Brune and Bott-Duffin Synthesis; also has graph theory stuff.)

5. B.D.O. Anderson, S. Vongpanitlerd, Network Analysis and Synthesis; A Modern Systems Theory Approach, Prentice Hall, NJ, 1973, TK454.2 A5 (Hard going, but covers the state-space methods for network synthesis.)

C.2 Journal Articles

C.2.1 Equivalent Equivalent Circuits

1. S. Fletcher, Tables of Degenerate Electrical Networks for Use in the Equivalent-Circuit Analysis of Electrochemical Systems, J. Electrochem. Soc., 141 (1994) 1823-1826. (Equivalent equivalent circuits for cases of up to 6 elements. Has a conjecture at the end that could probably be answered.)

2. F. Berthier, J.-P. Diard, Distinguishability of equivalent circuits containing CPEs Part I. Theoretical Part. J. Electroanal. Chem. 510 (2001) 1-11.

C.2.2 Fitting Algorithms

1. R.H. Milocco, An iterative least squares method for the identification of electrochemical impedances, J. Electroanal. Chem., 273 (1989) 243-255. (Fit directly to a rational function. Uses iterations of linear least squares.)

2. T.J. VanderNoot, I. Abrahams, The use of genetic algorithms in the non-linear regression of immittance data, J. Electroanal. Chem. 448 (1988) 17-23.

3. M. Yang, X. Zhang, X. Li, X. Wu, A hybrid genetic algorithm for the fitting of models to electrochemical impedance data, J. Electroanal. Chem. 519 (2002) 1-8.

C.2.3 Measurement Models, Best ways to fit data, Ambiguities.

1. P. Agarwal, M. E. Orazem, L.H. Garcia-Rubio, Measurement Models for Impedance Spectroscopy. I. Demonstration of Applicability, J. Electrochem. Soc., 139 (1992) 1917. (The paper introducing the idea of measurement modelling in impedance. Use of the Voight circuit as a check of the Kramers-Kronig Relationship.)

2. P. Agarwal, O.D. Crisalle, M. E. Orazem, L.H. Garcia-Rubio, Application of Measurement Models to Impedance Spectroscopy. II. Determination of the Stochastic Contribution to the Error Structure, J. Electrochem. Soc., 139 (1992) 1917.

3. P. Zoltowski, A New Approach to Measurement Modelling in Electrochemical Impedance Spectroscopy, J. Electroanal. Chem., 375 (1994) 45-57. (Advocates the rational function plus double-layer capacitance as a good measurement model.)

4. P. Zoltowski, The Power of Reparametrization of Measurement Models in Electrochemical Impedance Spectroscopy, J. Electroanal. Chem., 424 (1997) 173-178. (Fitting to the rational function plus double layer capacitance gives less sensitivity on initial parameter estimates than equivalent circuit fitting. Differences in fitting Z or Y.)

5. F. Berthier, J.-P. Diard, C. Montella, L. Pronzato, E. Walter, Choice of Experimental Method Induced by Structural Properties of Mechanisms, J. Electroanal. Chem., 399 (1995) 1-6. A mechanism can give the same exptal data with different parameters sets. (first shown by Lasia's group for the V-H mechanism).

6. F. Berthier, J.-P. Diard, P. Landaud, C. Montella, Steady-state Investigation and Electrochemical Impedance Spectroscopy: Identifiability and Distinguishability of Metal Dissolution and Passivation Mechanisms, J. Electroanal. Chem. 362 (1993) 13-20. (Different mechanisms can give same data; different parameters for same mechanism can give same data.)

7. F. Berthier, J.-P. Diard, C. Montella, L. Pronzato, E. Walter, Sur L'indentifiabilité Structurelle de la réaction de Volmer-Heyrovsky, J. Chim. Phys. 90 (1993) 2069-2081.

C.2.4 Kramers-Kronig

1. P. Agarwal, M. E. Orazem, L.H. Garcia-Rubio, Measurement Models for Impedance Spectroscopy. I. Demonstration of Applicability, J. Electrochem. Soc., 139 (1992) 1917. (The paper introducing the idea of measurement modelling in impedance. Use of the Voight circuit as a check of the Kramers-Kronig Relationship)

2. P. Agarwal, M. E. Orazem, L.H. Garcia-Rubio, Application of Measurement Models to Impedance Spectroscopy. III. Evaluation of Consistency with the Kramers-Kronig Relations, J. Electrochem. Soc., 142 (1995) 4159.

3. J.M. Esteban, M.E. Orazem, On the Application of the Kramers-Kronig Relations to Evaluate the Consistency of Electrochemical Impedance Data, J. Electrochem. Soc., 138 (1991) 67

4. M. Urquidi-Macdonald, S. Real, D.D. Macdonald, Application of Kramers-Kronig Transforms in the Analysis of Electrochemical Impedance Data. III. Stability and Linearity, Electrochim. Acta 35 (1990) 1559-1566.

5. J.R. Macdonald, M.K. Beachman, Linear-System Integral Transform Relations, Rev. Mod. Phys. 28 (1956) 393. Everything you wanted to know about KK, Hilbert Transforms and more. Buried here somewhere is the equivalence ofthe PR and KK conditions.

C.2.5 CPE and Roughness

1. R. de Levie, The Influence of Surface Roughness of Solid Electrodes on Electrochemical Measurements, Electrochim. Acta, 10 (1965) 113-130. (The classic paper on roughness.)

2. W. Scheider, Theory of the Frequency Dispersion of Electrode Polarization. Topology of Networks with fractional Power Frequency Dependence, J. Phys. Chem. 79 (1975) 127-136. (The best paper as to the physical content of the CPE. Dissipative processes are in the electrolyte phase.)

3. G.J. Brug, A.L.G. van den Eeden, M. Sluyters-Rehbach and J.H. Sluyters, The analysis of electrode impedances complicated by the presence of a constant phase element, J. Electroanal. Chem. 176 (1984) 275-295.(Interprets the frequency dispersion as a distribution of time constant, independently of any particular physical model).

4. T, Pajkossy, L. Nyikos, Phys. Rev. B. 42 (1990) 709-719. (Various fractal models summarized and a general treatment given. Cell geometry and the counterelectrode matters. Sluyters (IUPAC article) claims that this paper (?) proves that dispersion behaviour always enters as $Y = aY^{\alpha}_{\rm ideal}$, but this doesn't seem obvious.)

5. W.H. Mulder and J.H. Sluyters, An Explanation of Depressed Semi-Circular Arcs in Impedance Plots for Irreversible Electrode Reactions, Electrochim. Acta, 33 (1988) 303-310. (Fractal Roughness gives CPE.)

6. J.C. Wang, Impedance of a Fractal Electrolyte-Electrode Interface, Electrochim. Acta 33 (1988) 707-711. (Disagree with Pykossy and Nyikos paper.)

7. W.H. Mulder, J.H. Sluyters, The admittance of smooth electrodes with a fractal carpet structure. J. Electroanal. Chem. 282 (1990) 27-32. (Fractal carpets, i.e., fractal blocking patterns on smooth electrodes) do not give CPE behaviour.)

8. W.H. Mulder, J.H. Sluyters, T, Pajkossy, L. Nyikos, Tafel Current at Fractal Electrodes, 285 (1990) 103-115. (Can extract exchange current even from fractal electrodes.)

9. J. Bisquert, G. Garcia-Belmonte, F. Fabregat-Santiago, P.R. Bueno, Theoretical Models of a.c. Impedance of Finite Diffusion Layers Exhibiting Low Frequency Dispersion, J. Electroanal. Chem. 475 (1999) 152-163. (Interesting paper. A different reason for frequency dispersion.)

10. Z. Kerner, T. Pajkossy, Impedance of Rough Capacitive Electrodes: the Role of Surface Disorder, J. Electroanal. Chem. 448 (1998) 139-142. (Exptal test that CPE is due to heterogeneities on the atomic scale rather than surface roughness. Not the final word on this topic.)

11. T. Pajkossy, T. Wandlowski, D.M. Kolb, Impedance Aspects of Anion Adsorption on Gold Single Crystal Electrodes, J. Electroanal. Chem. 414 (1996) 209-220. (Argues that specific adsorption is related to capacitance dispersion.)

12. F.H. von Heuveln, Analysis of Nonexponential Transient Response Due to a Constant Phase Element, J. Electrochem. Soc., 141 (1994) 3423. (Shows that get non-exponential time domain transients with CPE. Whole analysis is strictly incorrect since inverse Laplace is only done for the linearized system.)

13. P.H. Bottelberghs, G.H.J. Broers, Interfacial Impedance Behaviour of Polished and Paint Platinum Electrodes at Na2WO4-Na2MoO4 Solid Electrolytes. (Derives time domain response for current step. Similar problem to the above ref.)

14. P. Zoltowski, On the Electrical Capacitance of Interfaces Exhibiting Constant Phase Element Behaviour, J. Electroanal. Chem., 443 (1998) 149-154. (Argues CPE double-layer can't be ideally polarizable - see also next ref.)

15. G. Láng, K.E. Heusler, Remarks on the Energetics of Interfaces Exhibiting Constant Phase Element Behaviour, J. Electroanal. Chem., 457 (1998) 257-260. (Reply to the above. Discusses the power dissipation in relationship to CPE.)

16. B. Tribollet, paper at EIS 2004, (Compare presence of CPE in local EIS vs Global EIS. For some systems finds global CPE but not local; conclude the dispersion is 3-D rather than 2-D.)

C.2.6 Impedance and Stability, Multiple Steady States etc.

1. C. Gabrielli, Métaux Corrosion Industries, [Pt I, Ch I] 573 (1973) 171-184; [Ch II] 574 (1973) 223-244; [Pt II, Chs. III, II] 577 (1973) 309-327; [Pt II, Ch. V] 578 (1973) 356-369. (Gabrielli's thesis. The pioneering work in stability, impedance, etc.)

2. C.-N. Cao, On the Impedance Plane Displays for Irreversible Electrode Reactions Bases on the Stability Conditions of the Steady-State. I. One State Variable Besides Electrode Potential, Electrochim. Acta, 35 (1990) 831-836. (Conditions on the equivalent circuits or A, B, C parameters that must apply if the system is stable. Independent of the nature of the state variables.)

3. C.-N. Cao, On the Impedance Plane Displays for Irreversible Electrode Reactions Bases on the Stability Conditions of the Steady-State. II. Two State Variable Besides Electrode Potential, Electrochim. Acta, 35 (1990) 837.

4. M.T.M. Koper, Adv. Chem. Phys. 92 (1996) 161. (Stability and spectral shapes, Nyquist criteria.)

5. M.T.M. Koper, Stability Study and Categorization of Electrochemical Oscillators by Impedance Spectroscopy, J. Electroanal. Chem., 409 (1996) 175-182.

6. J. D. Campbell, D. A. Harrington, P. van den Driessche and J. Watmough, Stability of Surface Mechanisms with Three Species and Mass-Action Kinetics, J. Math. Chem., 32 (2002) 281-301.

C.2.7 Second Harmonic and Nonlinear Impedances.

1. D.A. Harrington, Theory of Electrochemical Impedance of Surface Reactions: Second Harmonic and Large-Amplitude Response, Can. J. Chem., 75 (1997) 1508-1517.

2. D.A. Brevnov and H.O. Finklea, Second harmonic ac voltammetry study of a fast faradaic process in the presence of the uncompensated resistance, J. Electroanal. Chem., 488 (2000) 133-139.

3. van Gheem, (Brussel's group), paper at EIS 2004 (random harmonic grid excitation. Enables separation of the non-linear stochastic noise)

4. Stoynov papers.

C.2.8 Harrington Theory Papers

1. D.A. Harrington and P. van den Driessche, Equivalent Circuits for Some Surface Electrochemical Mechanisms, J. Electroanal. Chem., 567 (2004) 153-166. (Tree graph mechanisms have RC circuits. Topological equivalent circuits.)

2. J. D. Campbell, D. A. Harrington, P. van den Driessche and J. Watmough, Stability of Surface Mechanisms with Three Species and Mass-Action Kinetics, J. Math. Chem., 32 (2002) 281-301. (Two adsorbed species plus sites but no electrons.)

3. D.A. Harrington and P. van den Driessche, Stability and Electrochemical Impedance of Mechanisms with a Single Adsorbed Species, J. Electroanal. Chem., 501 (2001) 222-234. (The RDA and ODA rules for inductive behavior; classifies all cases with a single adsorbed species.)

4. D.A. Harrington and P. van den Driessche, Impedance of Multistep Mechanisms: Equivalent Circuits at Equilibrium, Electrochim. Acta, 44 (1999) 4321-4329. (A cleaner formalism than earlier).

5. D.A. Harrington, Electrochemical Impedance of Multistep Mechanisms: Mechanisms with Static Species, J. Electroanal. Chem., 449 (1998) 29-37. (Has the exact relationships between partial derivatives with and without treating the sites as a distinct species.)

6. D.A. Harrington, Electrochemical Impedance of Multistep Mechanisms: A General Theory, J. Electroanal. Chem., 449 (1998) 9-28. (Proves things in all generality. Later treatments are simpler by ignoring static species).

7. D.A. Harrington, Electrochemical Impedance of Multistep Mechanisms: Mechanisms with Diffusing Species, J. Electroanal. Chem., 403 (1996) 11-24.

C.2.9 Other

1. A. Sadkowski, State Variable Approach to Electrochemical Systems, J. Electroanal. Chem., 454 (1998) 39-52.

2. C. Gabrielli and B. Tribollet, A Transfer Function Approach for a Generalized Electrochemical Impedance Spectroscopy, J. Electrochem. Soc., 141 (1994) 1147. (Has the state-space matrices. Also has that the low-freq. limit is slope of polarization curve generalized.)

3. R.D. Armstrong and M. Henderson, Impedance Display of a Reaction with an Adsorbed Intermediate, J. Electroanal. Chem., 39 (1972) 81-90. (Shows that impedance spectral shapes are isotherm independent.)