Physical Electrochemistry & Equivalent Circuit Elements

Part 2

CORROSION

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Electrolyte Resistance

Solution resistance is often a significant factor in the impedance of an electrochemical cell. A modern three-electrode potentiostat compensates for the solution resistance between the counter and reference electrodes. However, any solution resistance between the reference electrode and the working electrode must be considered when you model your cell.

The resistance of an ionic solution depends on the ionic concentration, type of ions, temperature, and the geometry of the area in which current is carried. In a bounded area with area, A, and length, l, carrying a uniform current, the resistance is defined as,

1 $\quad R = \rho \dfrac{l}{A}$

ρ is the solution resistivity. The reciprocal of ρ (κ) is more commonly used. κ is called the conductivity of the solution and its relationship with solution resistance is:

2 $\quad R = \dfrac{1}{\kappa} \cdot \dfrac{l}{A} \rightarrow \kappa = \dfrac{l}{RA}$

Standard chemical handbooks will often list κ values for specific solutions. For other solutions, you can calculate κ from specific ion conductances. The units of κ is Siemens per meter (S/m). The Siemen is the reciprocal of the ohm, so 1 S = 1/ohm.

Unfortunately, most electrochemical cells do not have uniform current distribution through a definite electrolyte area. The major problem in calculating solution resistance therefore concerns determination of the current flow path and the geometry of the electrolyte that carries the current. A comprehensive discussion of the approaches used to calculate practical resistances from ionic conductances is well beyond the scope of this application note.

Fortunately, you usually don't calculate solution resistance from ionic conductances. Instead, you calculate it when you fit experimental EIS data to a model.

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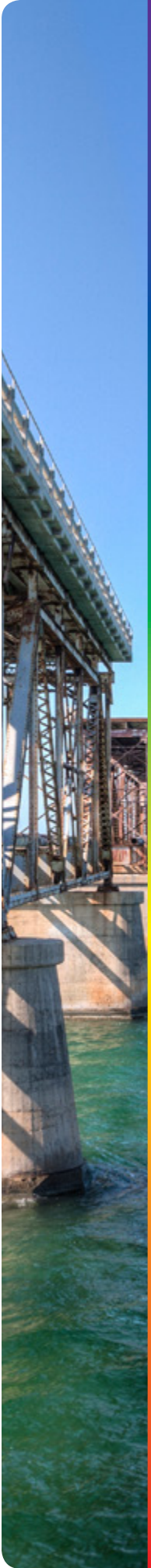
Double Layer Capacitance

An electrical double layer exists on the interface between an electrode and its surrounding electrolyte. This double layer is formed as ions from the solution adsorb onto the electrode surface. The charged electrode is separated from the charged ions by an insulating space, often on the order of angstroms. Charges separated by an insulator form a capacitor so a bare metal immersed in an electrolyte will be have like a capacitor. You can estimate that there will be 20 to 60 µF of capacitance for every 1 cm^2 of electrode area though the value of the double layer capacitance depends on many variables. Electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc. are all factors.

Polarization Resistance

Whenever the potential of an electrode is forced away from its value at open-circuit, that is referred to as "polarizing" the electrode. When an electrode is polarized, it can cause current to flow through electrochemical reactions that occur at the electrode surface. The amount of current is controlled by the kinetics of the reactions and the diffusion of reactants both towards and away from the electrode.

In cells where an electrode undergoes uniform corrosion at open circuit, the open circuit potential is controlled by the equilibrium between two different electrochemical reactions. One of the reactions generates cathodic current and the other generates anodic current. The open circuit potential equilibrates at the potential where the cathodic and anodic currents are equal. It is referred to as a mixed potential. If the electrode is actively corroding, the value of the current for either of the reactions is known as the corrosion current.

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Mixed potential control also occurs in cells where the electrode is not corroding. While this section discusses corrosion reactions, modification of the terminology makes it applicable in non-corrosion cases as well as seen in the next section.

When there are two, simple, kinetically-controlled reactions occurring, the potential of the cell is related to the current by the following equation 3.

$$\text{3} \quad I = I_{corr} \left(e^{\frac{2.303\,(E-Eoc)}{\beta a}} - e^{\frac{2.303\,(E-Eoc)}{\beta c}} \right)$$

where,

I = the measured cell current in amps,

I_{corr} = the corrosion current in amps,

E_{oc} = the open circuit potential in volts,

β_a = the anodic Beta coefficient in volts/decade,

β_c = the cathodic Beta coefficient in volts/decade.

If we apply a small signal approximation to equation 3, we get the following (equation 4):

$$\text{4} \quad I_{corr} = \frac{\beta_a \beta_c}{2.303\,(\beta_a + \beta_c)} \cdot \left(\frac{1}{R_p} \right)$$

which introduces a new parameter, Rp, the polarization resistance. As you might guess from its name, the polarization resistance behaves like a resistor.

If the Beta coefficients, also known as Tafel constants, are known you can calculate the Icorr from Rp using equation 5. Icorr in turn can be used to calculate a corrosion rate.

We will discuss the Rp parameter in more detail when we discuss cell models.

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Charge Transfer Resistance

A similar resistance is formed by a single, kinetically-controlled electrochemical reaction. In this case we do not have a mixed potential, but rather a single reaction at equilibrium.

Consider a metal substrate in contact with an electrolyte. The metal can electrolytically dissolve into the electrolyte, according to,

5 $\quad Me \longleftrightarrow Me^{n+} + ne^-$

or more generally

6 $\quad Red \longleftrightarrow Ox + ne^-$
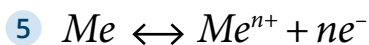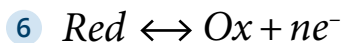
In the forward reaction in the first equation, electrons leave the metal and metal ions diffuse into the electrolyte. Charge is being transferred.

This charge transfer reaction has a certain speed. The speed depends on the kind of reaction, the temperature, the concentration of the reaction products and the potential.

The general relation between the potential and the current (which is directly related with the amount of electrons and so the charge transfer via Faradays law) is (equation):

7 $\quad i = i_o \left(\dfrac{C_o}{C^{*}_o} \exp\left(\dfrac{\alpha n F \eta}{RT}\right) - \left(\dfrac{C_R}{C^{*R}} \exp\left(\dfrac{-(1-\alpha)nF\eta}{RT}\right) \right) \right)$

with,

i_0 = exchange current density

C_O = concentration of oxidant at the electrode surface

C_O* = concentration of oxidant in the bulk

C_R = concentration of reductant at the electrode surface

η = overpotential ($E_{app} - E_{oc}$)

F = Faradays constant

T = temperature

R = gas constant

α = reaction order

n = number of electrons involved

When the concentration in the bulk is the same as at the electrode surface, $C_O = C_O$* and $C_R = C_R$*. This simplifies equation 7 into (equation 8):

8 $$i = i_0 \left(\exp(\alpha \, \frac{nF}{RT} \, \eta) - \exp(-(1-\alpha) \, \frac{nF}{RT} \, \eta) \right)$$

This equation is called the Butler-Volmer equation. It is applicable when the polarization depends only on the charge-transfer kinetics. Stirring the solution to minimize the diffusion layer thickness can help minimize concentration polarization.

When the overpotential, η, is very small and the electrochemical system is at equilibrium, the expression for the charge-transfer resistance changes to:

9 $$R_{ct} = \frac{RT}{nFi_0}$$

From this equation the exchange current density can be calculated when Rct is known.

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Diffusion

Diffusion also can create an impedance called a Warburg impedance. The impedance depends on the frequency of the potential perturbation. At high frequencies, the Warburg impedance is small since diffusing reactants don't have to move very far. At low frequencies, the reactants have to diffuse farther, increasing the Warburg-impedance.

10   $Z_W = \sigma(\omega)^{-\frac{1}{2}}(1\text{-}j)$

On a Nyquist Plot the Warburg impedance appears as a diagonal line with a slope of 45°. On a Bode Plot, the Warburg impedance exhibits a phase shift of 45°.

In equation 23, σ is the Warburg coefficient defined as:

11   $\sigma = \dfrac{RT}{n^2 F^2 A \sqrt{2}} \left(\dfrac{1}{C^{*0}\sqrt{D_O}} + \dfrac{1}{C^{*0}\sqrt{D_R}} \right)$

In which,

ω = radial frequency

D_O = diffusion coefficient of the oxidant

D_R = diffusion coefficient of the reductant

A = surface area of the electrode

n = number of electrons involved

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This form of the Warburg impedance is only valid if the diffusion layer has an infinite thickness. Quite often, however, this is not the case. If the diffusion layer is bounded (as in thin-layer cell or coated samples), the impedance at lower frequencies no longer obeys the equation above. Instead, we get the form:

12 $$Z_O = \sigma\,(\omega)^{-\frac{1}{2}}\,(1\text{-}j)\,\tanh(\delta\,\frac{j\omega}{D})^{\frac{1}{2}})$$

with,

δ = Nernst diffusion layer thickness

D = some average value of the diffusion coefficients of the diffusing species

This more general equation is called the "finite" Warburg. For high frequencies where $\omega\rightarrow\infty$, or for an infinite thickness of the diffusion layer where $\delta\rightarrow\infty$, $\tanh(\delta(j\omega/D)^{\frac{1}{2}})\rightarrow1$ and equation 23 simplifies to the infinite Warburg impedance. Sometimes these equations are written in terms of an admittance parameter, $Y_0=1/(\sigma\sqrt{2})$. See Table 3.

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Coating Capacitance

A capacitor is formed when two conducting plates are separated by a non-conducting media, called the dielectric. The value of the capacitance depends on the size of the plates, the distance between the plates and the properties of the dielectric. The relationship is,

(13) $$C = \frac{\varepsilon_o \, \varepsilon_r A}{d}$$

With,

ε_o = permittivity of free space (NIST defines it as it the "electric constant")

ε_r = dielectric constant (relative electrical permittivity)

A = surface of one plate

d = distances between two plates

Whereas the permittivity of free space is a physical constant, the dielectric constant depends on the material. Table 1 gives you some useful ε_r values.

Table 1. Typical Dielectric Constants

Material	ε_r
vacuum	1
water	80.1 (20°C)
organic coating	4 - 8

Notice the large difference between the dielectric constant of water and that of an organic coating. The capacitance of a coated substrate changes as it absorbs water. EIS can be used to measure that change.

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Constant Phase Element

Capacitors in EIS experiments often do not behave ideally. Instead, they act like a constant phase element as defined below.

The impedance of a capacitor can be expressed as:

$$\text{(14)} \quad Z_{CPE} = \frac{1}{(j\omega)^{\alpha}Y_0}$$

where,

$Y_0 = C = $ The capacitance

$\alpha = $ An exponent equaling 1 for a capacitor

For a constant phase element, the exponent α is less than one. The "double layer capacitor" on real cells often behaves like a CPE, not a capacitor. While several theories (surface roughness, "leaky" capacitor, non-uniform current distribution, etc.) have been proposed to account for the non-ideal behavior of the double layer, it is probably best to treat α as an empirical constant with no real physical basis.

Virtual Inductor

The impedance of an electrochemical cell sometimes also appears to be inductive. Some workers have ascribed inductive behavior to the formation of a surface layer, like a passive layer or fouling. Others have claimed that inductive behavior results from errors in the measurement, including potentiostat non-idealities.

Conclusion

This ends our section on Physical Electrochemistry and Equivalent Circuit elements. In the next chapter of our Introduction to Electrochemical Spectroscopy series we will discuss Common Equivalent Circuit Models. If you would like to view our library of application notes, please visit our website.

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