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CHEM-E4185 Electrochemical kinetics

Electrochemical methods - Impedance spectroscopy

1 Introduction

Electrochemical impedance spectroscopy (EIS) is a method that separates different processes in an electrochemical system based on their frequency dependency. The system is perturbed with a small-amplitude periodic signal (voltage or current), and the response is measured as a function of the frequency. With a single measurement, precise information of conductivity, reaction kinetics, electrode capacitance and diffusion is obtained. For example, facile charge transfer kinetics shows a response at high frequencies and mass transport is visible at low frequencies. However, careful consideration of the physical model of the system and reaction mechanism is required before the measurements can offer any meaningful information.

For the measurement to be successful, it has to fulfil four basic criteria: 1) The output results only from the input, i.e. no parasitic reactions take place in the system. 2) The input is moderate enough, so that the response is a linear function of the input. This depends on the form of the current-voltage plot but an amplitude of 10 mV, for example, can be used in most cases. 3) The system returns to its initial state after the input. 4) Impedance is finite and continuous.

2 Theory

The following chapter first introduces the concept of impedance, and then shows how the impedance of a simple electrochemical measurement is calculated.

2.1 Definition of impedance

An impedance measurement can be either potentiostatic or galvanostatic, depending on the input signal. In a potentiostatic EIS measurement, the cell is set to a defined dc potential, and a small amplitude sinusoidal potential signal is fed as an input. The potential signal creates a corresponding current response in the system, which might have some delay. The input and response are expressed in a complex form:

$$\begin{aligned} \text{input } E &= \hat{E}e^{j\omega t} \\ \text{response } I &= \hat{I}e^{j(\omega t + \phi)} \end{aligned} \quad (1)$$

where \hat{E} and \hat{I} are the amplitudes of the potential and current signals, respectively, j is the complex variable, ω is the angular frequency, t is time. The delay of the output is expressed with a phase shift ϕ . Impedance Z defined as the ratio of voltage E and current I , and it is a function of the frequency ω and the amplitude of the input signal.

$$Z \equiv \frac{E}{I} = \frac{\hat{E}}{\hat{I}}e^{-j\phi} \quad (2)$$

2.2 Calculating the impedance of a cell

When current flows in an electrochemical cell and the potential of the working electrode (WE) is measured against the reference electrode (RE), the impedance always has contributions from at least three factors. Firstly, the electrolyte resistance between the reference and the working electrode causes an ohmic drop, which depends on the current and the solution resistance R_s . Secondly, changing the potential of the working electrode causes charging of the electrode double layer capacitance. Thirdly, the actual reaction creates a faradic current in the system. The total current of the cell is a sum of the capacitive current and the faradic current:

$$i_{tot} = i_f + i_c \quad (3)$$

In terms of electrical circuit analogy, the faradic and capacitive processes thus occur in parallel. Therefore, the circuit form of an electrochemical cell consists of capacitive and faradic impedance elements of the working electrode connected in parallel, and in series with the impedance of the electrolyte (between WE and RE), shown in Figure 1.

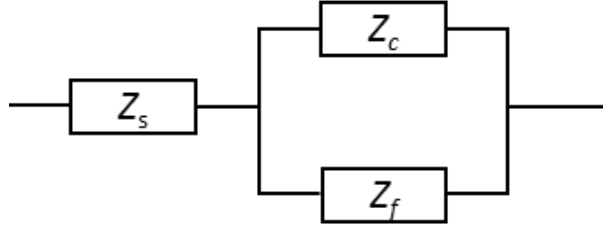


Figure 1. Impedance circuit of a cell.

The impedance of the electrolyte is simply $Z_s = E_s/i = R_s$. The impedance of a capacitor, Z_c , is easier to calculate in the Laplace domain:

$$\begin{aligned}
 i_c(t) &= C_{dl} \frac{dE(t)}{dt} \\
 \bar{i}_c(s) &= C_{dl} \bar{E}(s)s \\
 \bar{Z}_c(s) &= \frac{\bar{E}(s)}{\bar{i}_c(s)} = \frac{1}{s} \frac{1}{C_{dl}} = \frac{1}{j\omega} \frac{1}{C_{dl}}
 \end{aligned} \tag{4}$$

The actual faradic current is created by the redox-reaction



where n is number of transferred electrons in the reaction, and k_{red} and k_{ox} are the rate constants of the reduction and oxidation reactions, respectively. The flux j_k of a trace-ion k in the absence of convection is

$$j_k = -D_k \frac{dc_k}{dx} \tag{5}$$

where D_k is the diffusion coefficient. The mass balance of k leads to the Fick's 2nd law:

$$\frac{\partial c_k}{\partial t} = D_k \frac{d^2 c_k}{dx^2} \tag{6}$$

This partial differential equation is solved with the Laplace transform:

$$s\bar{c}_k - \bar{c}_{k,0} = D_k \frac{d^2 \bar{c}_k}{dx^2} \tag{7}$$

where the bar denotes the Laplace transform of the variable; $\bar{c}_{k,0}$ is the initial concentration of k . Equation (6) is thus transformed into an ordinary second order differential equation, which has a general solution¹

$$\bar{c}_k(s, x) = \frac{\bar{c}_{k,0}}{s} + A(s)e^{-\lambda_k x} + B(s)e^{\lambda_k x} \quad (8)$$

where $\lambda_k = \sqrt{s/D_k}$. The coefficients $A(s)$ and $B(s)$ can be determined with the boundary conditions

$$\frac{dc_k(t, 0)}{dx} = \frac{d\bar{c}_k(s, 0)}{dx} = -\frac{\bar{i}(s)}{D_k nF} \quad (9)$$

$$c_k(t, \infty) = \bar{c}_k(s, \infty) = c_k^b \quad (10)$$

and the initial condition

$$\bar{c}_k(0, x) = \bar{c}_{k,0} = c_k^b \quad (11)$$

where $\bar{i}(s)$ is the current in the Laplace domain, F is the Faraday constant and c_k^b the bulk concentration of k . The semi-infinite boundary condition (eq. 10) dictates that $B(s) = 0$, and the other boundary condition (eq. 9) determines the value of the coefficient $A(s)$. The final solution is

$$\bar{c}_k(s, x) = \frac{c_k^b}{s} \pm \frac{\bar{i}(s)}{nFD_k \lambda_k} e^{-\lambda_k x} \quad (12)$$

where the sign of the current depends on whether k is oxidized or reduced.

On the other hand, the Butler-Volmer equation for (ii) states that

$$\frac{i}{nF} = k_{ox}c_R^s - k_{red}c_O^s \quad (13)$$

where $k_{ox} = k^0 e^{(1-\alpha)f\eta}$ and $k_{red} = k^0 e^{\alpha f\eta}$, $f = nF/RT$, $\eta = E - E_{eq}$, and the subscript s represents electrode surface ($x = 0$). The linearization of eq. (13) yields

$$\frac{\Delta \bar{i}(s)}{nF} = k_{ox} \Delta c_R^s(s) - k_{red} \Delta c_O^s(s) + (1 - \alpha) f k_{ox} c_R^s \Delta \bar{E} + \alpha f k_{red} c_O^s \Delta \bar{E} \quad (14)$$

Calculating the surface concentration changes with eq. (12), and introducing them into eq. (14) leads to

¹ Use trial function $\bar{c}_k = e^{\lambda x}$ to the homogeneous form of the equation and determine the roots of the resulting characteristic equation. The solution is the sum of the homogeneous solution and the particular solution.

$$\frac{\Delta\bar{i}(s)}{nF} = -k_{ox} \frac{\Delta\bar{i}(s)}{nF\sqrt{sD_R}} - k_{red} \frac{\Delta\bar{i}(s)}{nF\sqrt{sD_O}} + [(1-\alpha)k_{ox}c_R^S + \alpha k_{red}c_O^S] \frac{nF}{RT} \Delta\bar{E} \quad (15)$$

Rearranging these terms shows us the equation for the faradic impedance:

$$Z_f(s) = \frac{\Delta\bar{E}(s)}{\Delta\bar{i}(s)} = \frac{RT}{n^2F^2A} \frac{1}{(1-\alpha)k_{ox}c_R^S + \alpha k_{red}c_O^S} \left(1 + \frac{k_{ox}}{\sqrt{sD_R}} + \frac{k_{red}}{\sqrt{sD_O}} \right) \quad (16)$$

The first term inside the brackets of eq. (16) is the charge transfer resistance. The second and third represent together the response from mass transfer, and the impedance element is named after the German scientist Emil Warburg (1846-1931). Thus, the faradic impedance consists two elements, charge transfer resistance and the Warburg element, connected in series. This circuit, known as the Randles circuit, is shown in Figure 2.

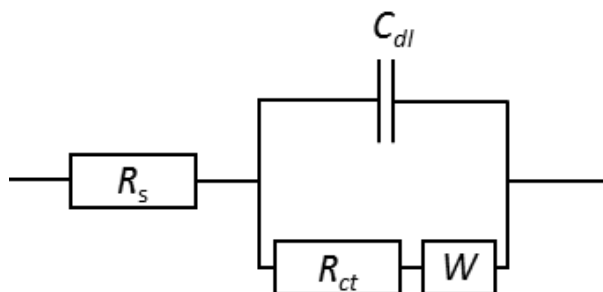


Figure 2. The Randles circuit.

3 Experimental

Again, we concentrate on the redox-reaction of iron (trace-ion)



which takes place on a glassy carbon electrode.

A solution of 2.5 mmol/L FeCl_3 and 2.5 mmol/L FeCl_2 in 0.5 mol/L HCl is prepared to a 100 mL volumetric flask. The cell is filled half-full with the solution, and a glassy carbon working electrode (GC, $d = 0.5$ cm), a Pt counter electrode, and a saturated

calomel reference electrode (SCE) are placed in the cell, and connected to a potentiostat according to the instructions of the assistant. N₂ gas purge is used to remove oxygen from the cell. The impedance is measured from 100 kHz to 1 Hz in different potentials (-0.16, -0.06, 0, 0.06, 0.16 V vs. E_{eq}).

4 Results

Use the Matlab script provided by the assistant to fit your results into an equivalent circuit. Show the measured impedance plots in a Nyquist form along with the fit results. Show how the relevant parameters in your equivalent circuit change with the potential. Compare your results with any literature values you can find.

Calculate the impedance of an EC circuit (Randles circuit without the Warburg element). In a Nyquist plot, what would it look like?

References

1. Gabrielli, Claude, Identification of electrochemical processes by frequency response analysis, Solartron Analytical Technical report number 004/83, Issue 3, 1998.