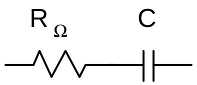
Ohmic drop: 3. Dynamic compensation with Autolab and GPES software

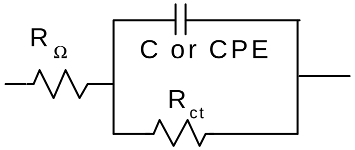
In some electrochemical systems, the ohmic resistance changes with time. In the GPES software (versions 4.8 and higher) Dynamic Ohmic Drop Compensation is available as an option in the Cyclic Voltammetry method and Chrono Methods. With this option, it is possible to measure a changing ohmic resistance and compensate for it during the measurement[1]. The method operates by applying a 10 kHz block wave for a short period at the end of each potential step, as shown in Figure 1.

Theory

In order to use this option one has to assume that the electrochemical system under study and upon applying a 10 kHz block wave behaves as a capacitance and resistance in series:



where, R is the ohmic resistance and C is the double layer capacitance. But as the following circuit is often used to represent an electrochemical system,



one has to make sure that the frequency of the block wave is such that the contribution of R_{ct} is negligible.

For a system consisting of a capacitor and a resistance in series the current response to an applied potential pulse can be described as:

$$I = \frac{V}{R} e^{\left(\frac{-t}{RC}\right)}$$

where, V is the amplitude of the applied potential pulse, R is the ohmic resistance, t is time and C is capacitance as shown in Figure 2.

The above equation has two unknowns, R and C that can be calculated by taking two points on the curve in the Figure 2, I_1 at t_1 and I_2 at t_2. This results in two equations with two unknowns:

$$I_1 = \frac{V}{R} e^{\left(\frac{-t_1}{RC}\right)}$$

$$I_2 = \frac{V}{R} e^{\left(\frac{-t_2}{RC}\right)}$$

From the above equation R can be calculated as:

$$R = \frac{V}{I_1 e^{\left(\frac{-t_1}{RC}\right)}}$$

and C can be calculated from

$$\ln\left(\frac{I_1}{I_2}\right) = \frac{(t_1 - t_2)}{RC}$$

The advantage of using a block wave is that both the positive (I^+) and negative (I^-) current response can be used for calculations. The absolute difference between those responses, given in the following equation will then be used in the calculations.

$$I_1 = I_1^+ - I_1^-$$

$$I_2 = I_2^+ - I_2^-$$

Limitations of the method

For systems where RC > 800 µs the values for I_1 and I_2 will be almost identical, meaning that an accurate calculation of R and C is impossible. The same holds for systems where RC < 25 µs, where the value for I_2 will be close to zero. This means that only systems that have RC times within these values will produce accurate results.

Another limitation of the method is due to the frequency of the block wave. Since this frequency is 10 kHz, only the current ranges above 100 µA can be used. It is advised to use the highest possible current range to prevent overload.

Results of measurement on a real cell

A cell was used with 1 mM of $K_3Fe(CN)_6$ in 1 M KNO_3. Working electrode was a Pt sheet, counter electrode a GC-rod and reference electrode an Ag/AgCl. A cyclic voltammogram was measured with simultaneous measurement of the ohmic resistance of the cell. The results shown in Figure 3 indicate that the ohmic resistance has a low value (as expected) and is stable during the measurement.

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[1] The method cannot be used with the standard Autolab potentiostats, a modification is needed in the hardware of the PGSTAT30.

Figure 1: Schematic representation of the application of a 10 kHz block wave and the end of each potential step during cyclic voltammetry.

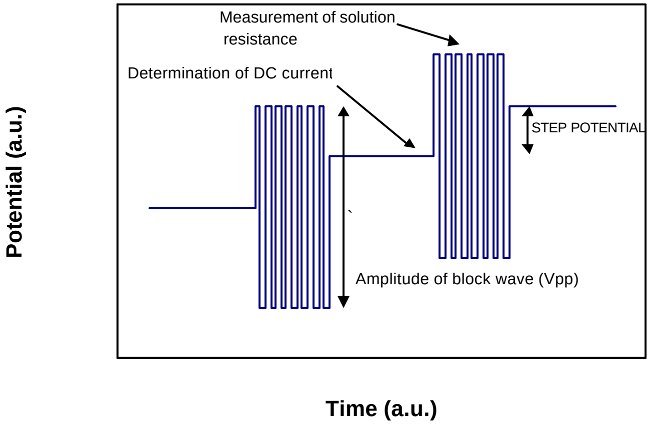

Figure 2: Current in response to the application of the block wave, as a function of time.

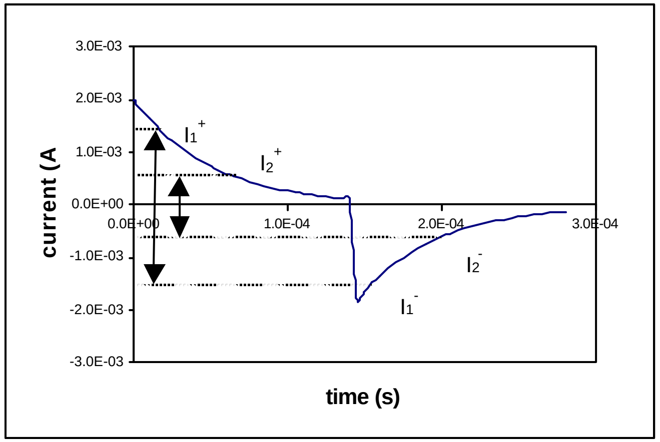

Figure 3: Cyclic voltammogram of Fe(II)/Fe(III) couple in KNO_3 solution, with dynamic ohmic drop compensation.