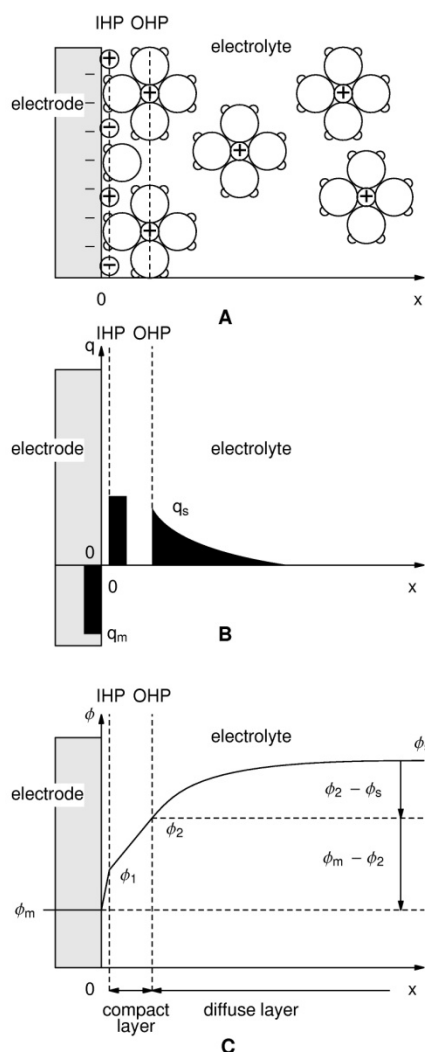


## Measurements of the double layer capacitance

### I – INTRODUCTION

All electrochemical processes take place at the electrode/electrolyte interface, *i.e.* the electrical double layer (Figure 1). Different models of this layer were stated by Helmholtz, Gouy-Chapman, Stern, or Grahame [1,2].



**Figure 1: Schematic of the electrical double layer according to the Grahame model (adapted from [2]). IHP: Inner Helmholtz Plane, OHP: Outer Helmholtz Plane. A: Electrode with an excess of negative charge; B: Localization of the charge in excess; C: Potential change versus distance towards the electrode /electrolyte interface.**

The structure of the double layer is similar to an electrical condenser constituted by two charged areas separated by a dielectric. The

dielectric thickness corresponds to the ionic radius, *i.e.* 50 nm.

In this note, the electrical double layer of the iron electrode in acidic conditions is investigated. For this purpose, two techniques are used to determine the value of the capacitance: the Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV).

### I – EXPERIMENTAL CONDITIONS

Investigations are performed by the VSP instrument driven by EC-Lab® software in a solution of HCl (0.1 M). The three-electrode set-up is used with:

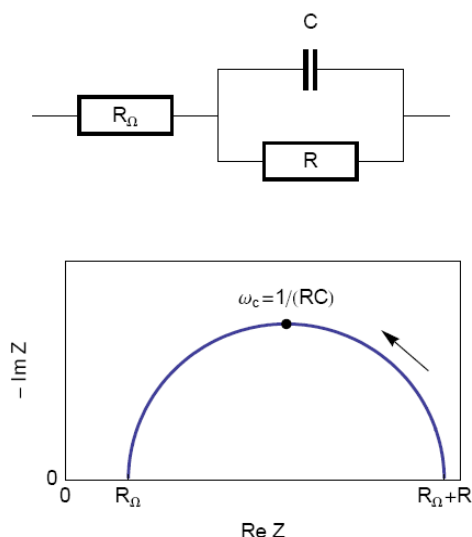
- a Rotating Disk Electrode (RDE) of iron as a working electrode with a surface area of 3.14 mm<sup>2</sup>,
- a platinum wire as a counter electrode,
- a Saturated Calomel Electrode (SCE) as a reference electrode.

For both techniques, experiments are carried out at the rotation speed of the electrode:  $\Omega = 800$  rpm (rotations per minute). For the CV experiment, the scan rate is 40 mV.s<sup>-1</sup>.

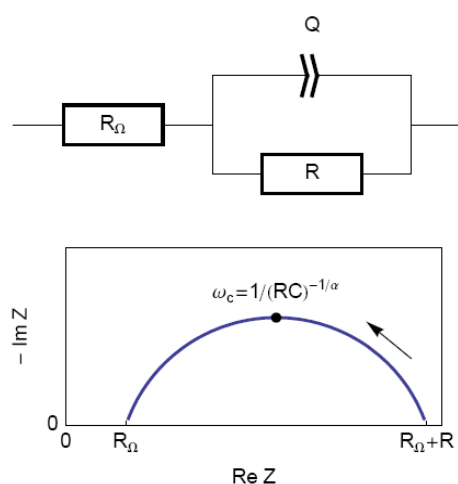
Data analysis for both techniques is also computed by EC-Lab® software.

### III – IMPEDANCE THEORY

The equivalent circuit, described in Figure 2, with a capacitance and a resistance in parallel and an additional resistance corresponding to the ohmic drop ( $R_1 + C/R_2$ ) should be a good model for the double layer. In this case, the resulting Nyquist diagram is close to a perfect semi-circle (Figure 2). However, for real systems, this is hardly ever the case. That's why, a constant phase element (CPE), noted  $Q$  in Figure 3, is introduced and used instead of the capacitance  $C$  in the  $R_1 + Q/R_2$  equivalent circuit [3,4]. Consequently, the resulting Nyquist diagram (Figure 3) corresponds to a depressed semi-circle in its upper-part.



**Figure 2: Equivalent electrical circuit  $R_{\Omega}+R/C$  (top) and corresponding Nyquist impedance diagram (bottom, arrow indicates increasing angular frequencies).**



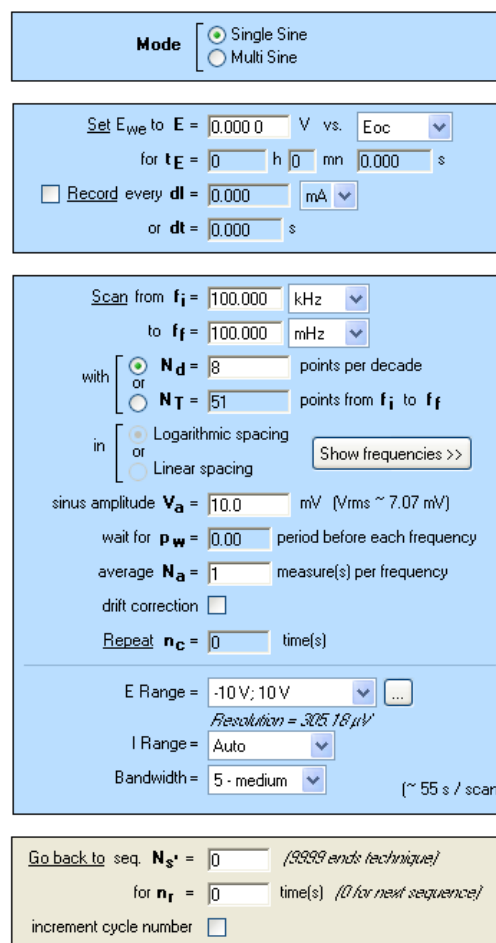
**Figure 3: Equivalent electrical circuit  $R_{\Omega}+R/Q$  (top) and corresponding Nyquist impedance diagram (bottom, arrow indicates increasing angular frequencies).**

Then, the analogy between the relationship described in Figs. 1 and 3 leads to Eq. 1. This equation gives the capacitance value at the frequency corresponding to the apex of the Nyquist diagram.

$$C_{dl} = Q(\omega_c)^{\alpha-1} \quad (1)$$

## IV – IMPEDANCE RESULTS AND ANALYSIS

The measurements are carried out with potentiostatic EIS (PEIS) techniques at open circuit voltage  $E_{oc}$  in the 100 kHz – 100 mHz frequency range and with a sinus amplitude ( $V_a$ ) of 10 mV. The settings of the impedance investigation are shown in Figure 4.



**Figure 4: Potentiostatic Impedance “Parameters Settings” window.**

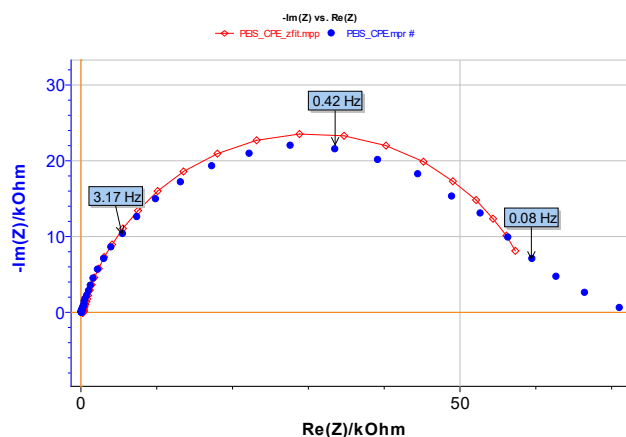
The points of the impedance diagram corresponding to lowest frequencies ( $Re(Z) \geq 55 \text{ k}\Omega$ ) clearly show that the system drifts with time, because of the time variant condition [5]. Therefore, these points are not taken into consideration (Figure 5).

As explained above, the fit is performed with the  $R1+R2/Q$  equivalent circuit (Fig. 6). First of all, the results show that the ohmic drop resistance ( $R1 = R_{\Omega} = 71 \Omega$ ) is insignificant before the charge transfer resistance

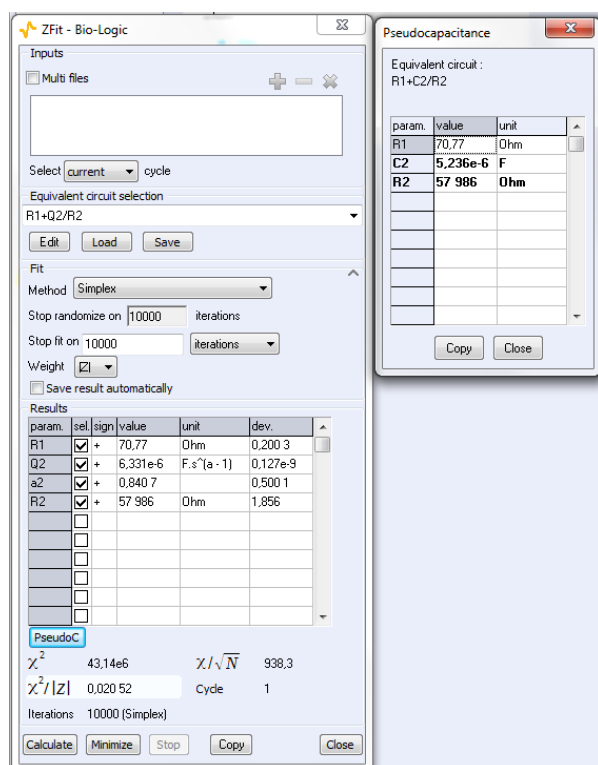
( $R_2 = R_t = 58 \text{ k}\Omega$ ). Moreover the value of  $Q$  is  $6.3 \mu\text{F}\cdot\text{s}^{\alpha-1}$  with  $\alpha$  equal to 0.84.

At this point, the capacitance of the system is computed with the “Pseudocapacitance” tool and the value of  $5.2 \mu\text{F}$  is determined for  $C_{dl}$  (Figure 6) [4].

It is possible to load the settings and the data files as PEIS\_CPE.mpr in the EC-Lab® Samples, Fundamental Electrochemistry folder.



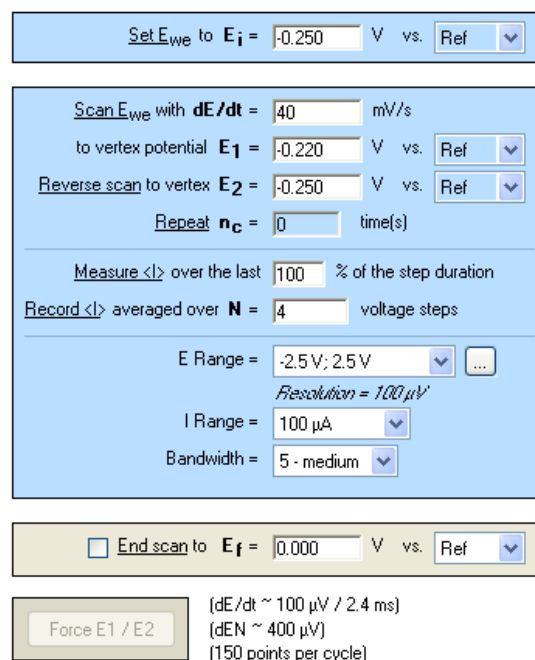
**Figure 5: Experimental (blue markers) and fitted (red curve) impedance diagram.**



**Figure 6: The “ZFit” and “Pseudocapacitance” results.**

## V – CYCLIC VOLTAMMETRY RESULTS AND ANALYSIS

$E_{oc}$  is determined before starting the CV experiment. The value is  $-0.235 \text{ V vs. SCE}$ . The parameters of the CV technique (Figure 7) are chosen accordingly, *i.e.* in a range of  $\pm 15 \text{ mV}$  around  $E_{oc}$  with a scan rate of  $40 \text{ mV}\cdot\text{s}^{-1}$ .



**Figure 7: Cyclic Voltammetry “Parameters Settings” window.**

As the ohmic drop can be neglected (see previous paragraph), the value of  $R_p$  can be determined by calculating the slope of the curve. The  $R_p$  values found for forward (Fig. 8) and backward sweeps of the potential are  $57 \text{ k}\Omega$  ( $= 1/17.673 \times 10^{-6}$ ) and  $61 \text{ k}\Omega$  respectively. Note that the  $R_p$  values determined by PEIS or CV techniques are in agreement. As the transport of the material does not limit the kinetics of the redox process, the following Eq. 2 is true [2]:

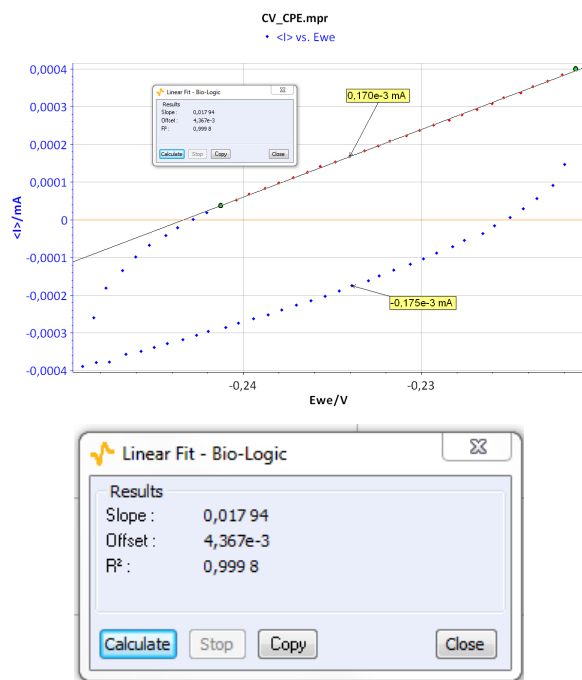
$$R_p = R_t \quad (2)$$

Assuming our system could be modeled by a real capacitance and a resistance in parallel; we can calculate the equations corresponding to the upper and lower part of the curve around the corrosion potential which is equal

to  $E_{oc}$ . From these equations, we extrapolated the two current values  $I_a$  and  $I_c$  corresponding to the corrosion potential for the anodic and the cathodic part of the curve, respectively, and were able to calculate the double layer capacitance with the following equation:

$$\frac{I_a - I_c}{2} = C_{dl} \frac{dE}{dt} \quad (3)$$

Finally, considering the values given in Figure 8 and Eq. 3, the capacitance,  $C_{dl}$ , is 4.3  $\mu\text{F}$ . It is possible to load the settings and the data files as CV\_CPE.mpr in the EC-Lab® Samples folder.



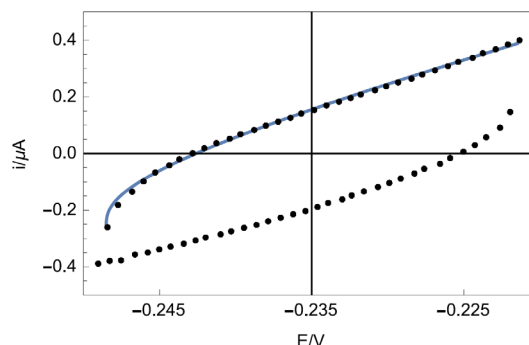
**Figure 8:** CV curve  $I$  vs.  $E_{we}$  for forward and backward voltage scan (top). “Linear Fit” tool for determining  $R_p$  (bottom).

It may be of interest to know it is possible to simulate the CV response of a circuit R/Q (Figure 3). For that purpose, the relationship Eq. (4), which expresses the current response of an R/Q circuit to a linear change of potential, is used:

$$I(t) = \frac{v_b t}{R2} + \frac{Q v_b t^{1-\alpha}}{\Gamma(2-\alpha)} \quad (4)$$

where  $v_b$  is the scan rate of the electrode potential,  $\Gamma$  the Euler gamma function,  $\alpha$  the dispersion parameter of the CPE and  $s$  the Laplace variable.

Figure 9 shows the experimental data points and the data simulated using Eq. 4. The results of the data fitting on the experimental points gives a value of 8.2  $\mu\text{F}\cdot\text{s}^{\alpha-1}$  with  $\alpha = 0.841$  determined by EIS.



**Figure 9:** Experimental points (dots) and Simulation (line) of the CV response of circuit R+R/Q (Figure 3) plotted by Mathematica software.

## VI – CONCLUSION

In this note, we have shown how to calculate capacitance values using EIS and CV. Firstly, it was assumed that the double layer was a true capacitance, and secondly it was a constant phase element (CPE). In this case, a pseudo capacitance was calculated and compared to the true capacitance value. The values given by all assumptions and all methods were all of the same order of magnitude.

**Table I: Summary**

EIS		CV	
$C_{dl}$ $C_{dl}/\mu\text{F}$	CPE $Q/\mu\text{F}\cdot\text{s}^{\alpha-1}$	$C_{dl}$ $C_{dl}/\mu\text{F}$	CPE $Q/\mu\text{F}\cdot\text{s}^{\alpha-1}$
5.2	6.3	4.3	8.2

Data files can be found in :  
C:\Users\xxx\Documents\EC-Lab\Data\Samples\Fundamental Electrochemistry\technique\_CPE

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- 1) A. J. Bard, L. R. Faulkner, *Electrochemical methods. Fundamentals and applications*, Wiley, Hoboken, (2001).
- 2) J.-P. Diard, B. Le Gorrec, C. Montella *Cinétique électrochimique*, Hermann, Paris, (1996).
- 3) E. Barsoukov, J.R. Macdonald, *Impedance Spectroscopy. Theory, experiment and applications.*, Wiley, Hoboken, (1987).
- 4) [Application Note #20](#) “Pseudo capacitance calculation”
- 5) [Application Note #55](#) “Interpretation problems of impedance measurements made on time variant systems”

*Revised in 08/2019*