Measurements of the double layer capacitance

I- Introduction

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

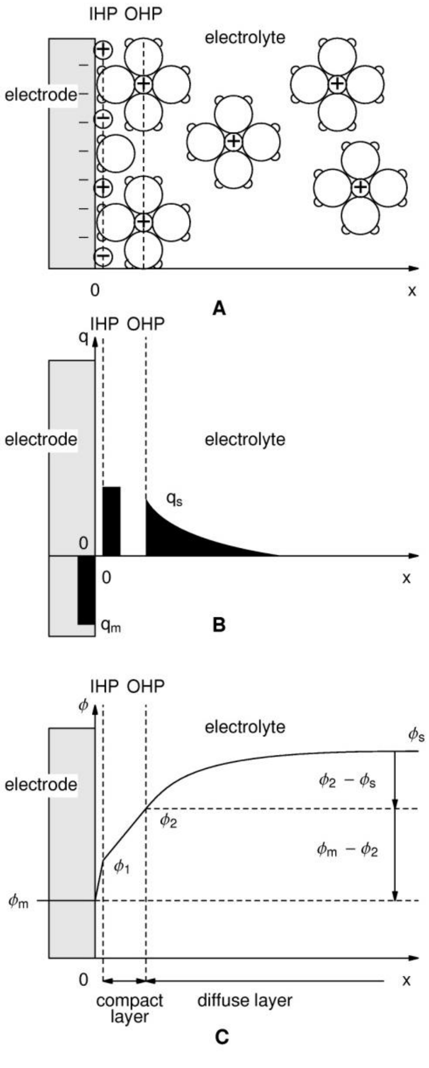

Fig. 1: Scheme of the electrical double layer according to the Grahame model (adapted from [2]). IHP: Inner Helmholtz Plane, OHP: Outer Helmholtz Plane. A: Electrode with an excess of negative charge; B: Localization of the charge in excess; C: Potential change versus distance towards the electrode/electrolyte 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. In this purpose, two techniques are used to determine the value of the capacitance: the Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV).

II- 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^2,
- a platinum wire as a counter electrode,
- and a Saturated Calomel Electrode (SCE) as a reference electrode.

For both techniques, experiments are carried out at the rotation speed of the electrode: Ω = 800 rpm (rotations per minute). For the CV experiment, the scan rate is 40 $mV.s^{-1}$.

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

III- Impedance theory

The equivalent circuit, described in Fig. 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 (Fig. 2). However, for real systems, it is hardly ever the case. That's why, a constant phase element (CPE), noted *Q* in Fig. 3, is introduced and used instead of the capacitance *C* in the R_1+Q/R_2 equivalent circuit [3,4]. Then, the resulting Nyquist diagram (Fig. 3) corresponds to a depressed semi-circle in its upper-part.

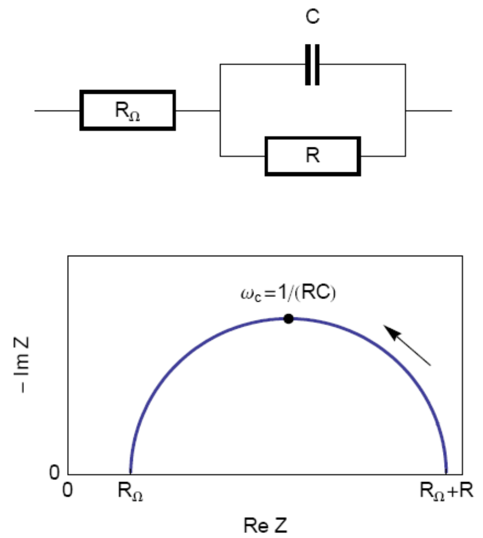

Fig. 2: Equivalent electrical circuit R_Ω+R/C (top) and corresponding Nyquist impedance diagram (bottom, arrow indicates increasing angular frequencies).

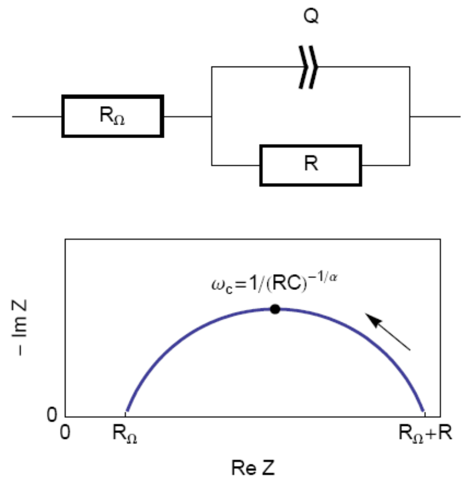

Fig. 3: Equivalent electrical circuit R_Ω+R/Q (top) and corresponding Nyquist impedance diagram (bottom, arrow indicates increasing angular frequencies).

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

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

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 Fig. 4.

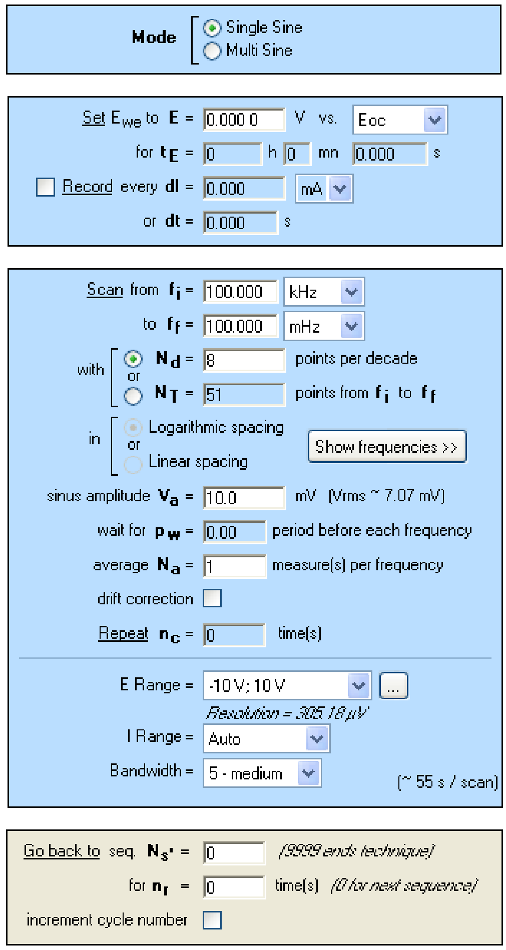

Fig. 4: Potentiostatic Impedance "Parameters Settings" window.

Points of the impedance diagram corresponding to lowest frequencies (Re(*Z*) ≥ 55 kΩ) clearly show that the system drifts with time, because of the non-stationary condition. Therefore, these points are not taken into consideration (Fig. 5).

As explained above, the fit is performed with the R_1+R_2/Q equivalent circuit (Fig. 6). First of all, the results show that the ohmic drop resistance ($R_1 = R_\Omega = 71\ \Omega$) is insignificant before the charge transfer resistance ($R_2 = R_t = 58$ kΩ). And the value of *Q* is 6.3 µF.$s^{\alpha-1}$ with α equal to 0.84.

Then, the capacitance of the system is computed with the "Pseudocapacitance" tool and the value of 5.2 µF is determined for C_{dl} (Fig. 6) [4].

It is possible to load the settings and the data files as PEIS_CPE.mpr in the EC-Lab® Samples folder.

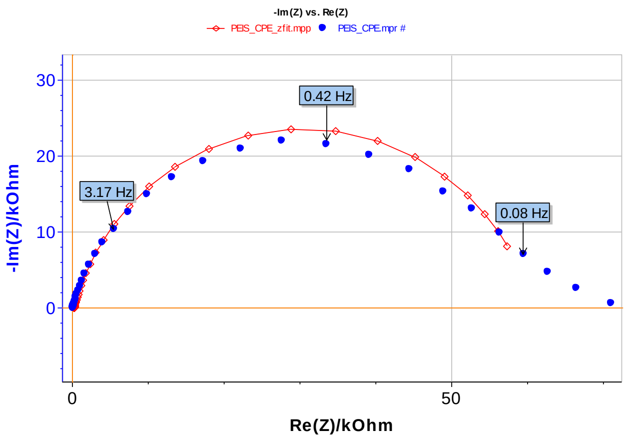

Fig. 5: Experimental (blue markers) and fitted (red curve) impedance diagram.

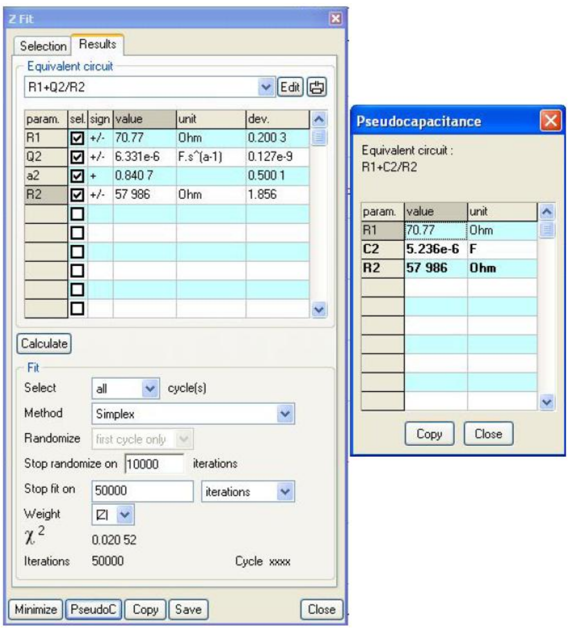

Fig. 6: The "Zfit" and "Pseudocapacitance" results.

V- Cyclic voltammetry results and analysis

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

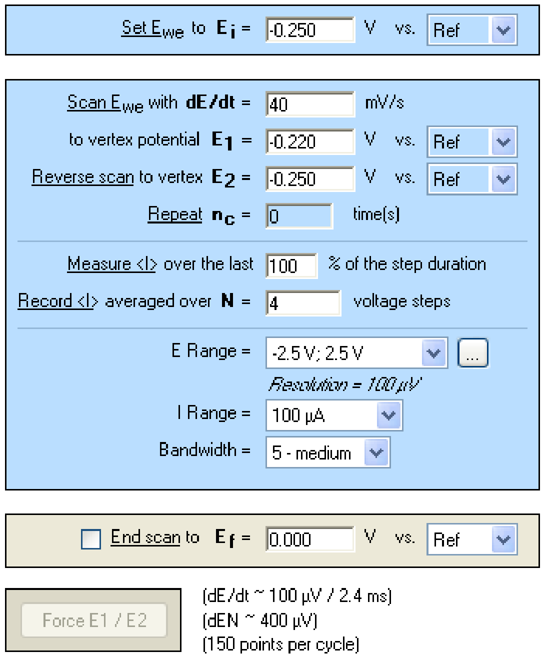

Fig. 7: Cyclic Voltammetry "Parameters Settings" window.

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 kΩ (= 1/17.673 x 10^{-6}) and 61 kΩ 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]:

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

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:

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

Finally, considering the values given in Fig. 8 and Eq. 3, the capacitance, C_{dl}, is 4.3 µF.

It is possible to load the settings and the data files as CV_CPE.mpr in the EC-Lab® Samples folder.

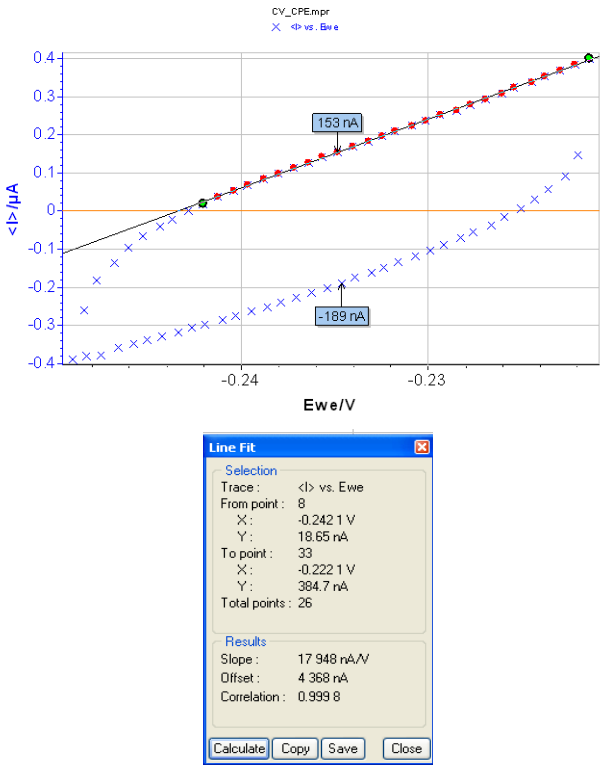

Fig. 8: Steady-state curve *I* vs. E_{WE} for forward and backward voltage scan (top). "Line Fit" tool for determining R_p (bottom).

By the way, it is possible to simulate the CV response of a circuit R/Q (Fig. 3). For that purpose, the relationship Eq. (4), in which the current response of a CPE is corresponds to a linear change of potential, is used:

$$I_Q(t) = L^{-1}\left[\frac{v_b}{s^2}\frac{1}{Qs^{\alpha}}\right] = \frac{v_b t^{1+\alpha}}{Q\Gamma(2+\alpha)} \qquad (4)$$

where v_b is the scan rate of the electrode potential, Γ the Euler gamma function, and *s* the Laplace variable.

Results of the simulation are shown in Fig. 9, using parameter values measured from EIS data. Measuring I_a, I_c and using Eq. (3) leads to C_{dl} = 5.2 x 10^{-6} F which corresponds to the value measured from EIS data.

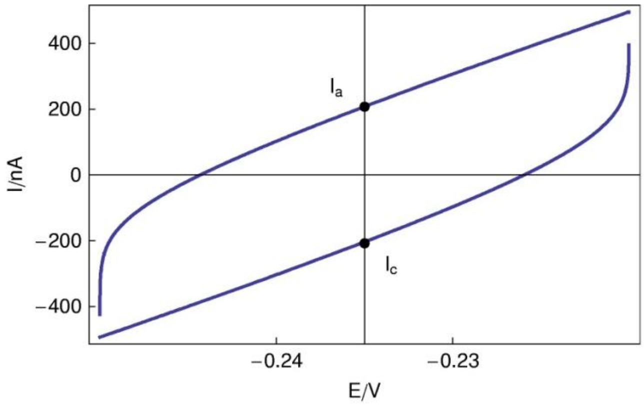

Fig. 9: Simulation of the CV response of circuit R+R/Q (Fig. 3) plotted by Mathematica software.

VI- Conclusion

Capacitance values determined by both techniques (EIS and CV) are summarized in Table 1. The magnitude of the capacitance (~ 5 µF) is the same.

However, in the case of the data obtained from CV investigation, the hypothesis of a true capacitance is assumed. But regarding the impedance result, this assumption is not verified and may explain the difference between the capacitance values.

Table 1: Summary

	Impedance	CV	
	(CPE hypothesis)	measured	simulated (CPE hypothesis)
C_{dl}/µF	5.2	4.3	5.2

References

[1] Electrochemical methods. Fundamentals and applications, A. J. Bard, L. R. Faulkner, ed. Wiley (Hoboken), 2001.

[2] Cinétique électrochimique, J.-P. Diard, B. Le Gorrec, C. Montella, ed., Hermann (Paris) 1996.

[3] Impedance Spectroscopy. Theory, experiment and applications. E. Barsoukov, J.R. Macdonald, ed. Wiley (Hoboken), 1987.

[4] Application Note #20, http://www.bio-logic.info/potentiostat/notes.html