Supercapacitors investigations.
Part II: Time constant determination

I-Introduction

To complete the characterization performed on supercapacitor done in the application note #33 [1], it is interesting to know the time constant of supercapacitor.

In this note, the time constant of the supercapacitor will be determined by potentio-static/dynamic and Electrochemical Impedance Spectroscopy (EIS) techniques.

Note that in this note (if not indicated):

– the supercapacitor is modeled by a resistor and capacitor in series (Fig. 1).
– supercapacitor is considered as a capacitor and not as a Constant Phase Element [2].

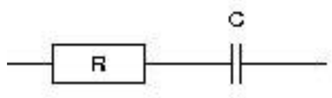

Fig. 1: Supercapacitor model

Noteworthy that time constant is similar in charge or in discharge.

N.B.: All settings and raw data files presented hereafter are available in the Data Sample folder of EC-Lab® Software with the following name: XXX_supercap.mpr.

II-Set-up description

Investigations are performed with a VMP3 equipped with a standard board. This board has EIS capability and is connected or not to 4A booster according to the measured current.

Characteristics of supercapacitor are the following:

- capacitance: 22 F ± 30%
- maximum operating voltage: 2.3 V
- mass of active material: ~10 g

Supercapacitor is connected to VMP3 *via* a standard 2-electrode connection.

III-Potentio technique

The potential pulse from 2.1 V to 2.3 V is carried out with Modular Potentiostatic technique (Fig. 2).

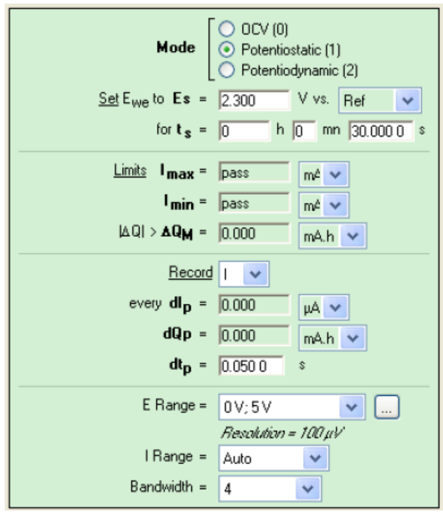

Fig. 2: Potentiostatic settings window.

The supercapacitor response to a potentio pulse follows the relationships:

$$i(t)=\frac{(\Delta E)}{R}\exp\left(\frac{-t}{\tau}\right);\ \tau=RC$$

where i is the current, ΔE is the potential step, R is the resistance in series, t is the time and τ is the time constant.

The equation of the current *vs* time is fitted with the Multi-Exponential Fit tool (Fig. 3). The time constant of the supercapacitor is 1.348 s.

Moreover, it is possible to calculate the value of the resistor in series of the capacitors. At t = 0, the equation is:

$E = R\, i$

so, R = 0.2 V / 4.54 A = 44.1 mΩ

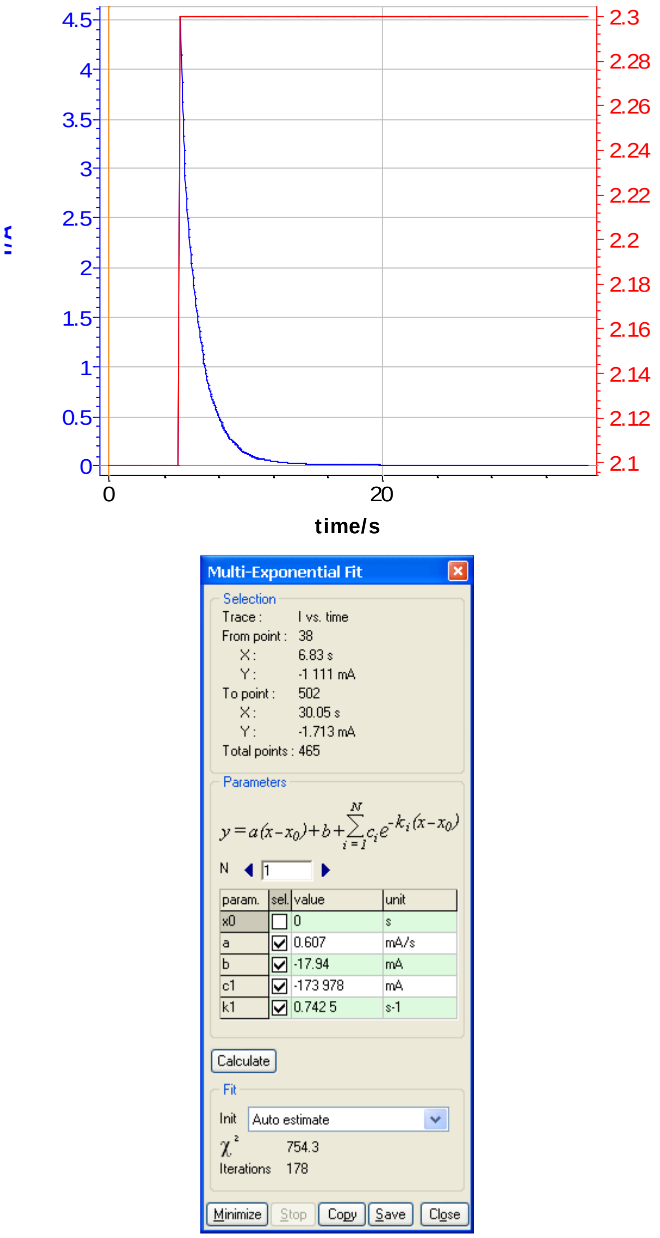

Fig. 3: *I vs t* curve.

The results of the previous potentiostatic technique can be completed by a potentiodynamic one. According to the relationship *I* = *C* d*E*/d*t*, it is indeed possible to determine the capacitance of the supercapacitor at different scan rates.

Potentiodynamic investigations are done at several potential scans 1, 3, 10, 50 and 150 mV/s between 0 to 2.3 V. These steps are performed within the same CVA technique with add of sequences (Fig. 4).

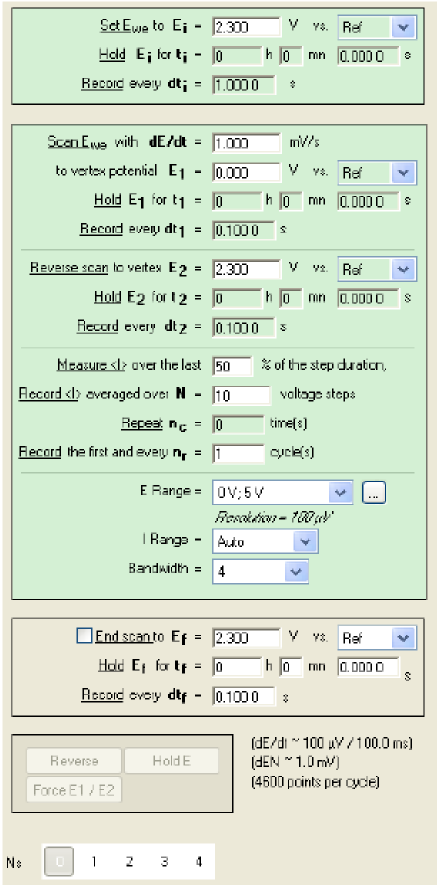

Fig. 4: Settings of CVA window.

The rectangular shape of the CV indicates reversible capacitive behavior (Fig. 5). When the scan rate increases, this shape evolves into a smoother rectangular shape [3,4].

The capacitance is summarized in Tab. 1. Capacitance decreases when scan rate increases. The capacitance value is in the range of 25-28 F in agreement with the specification given by the manufacturer.

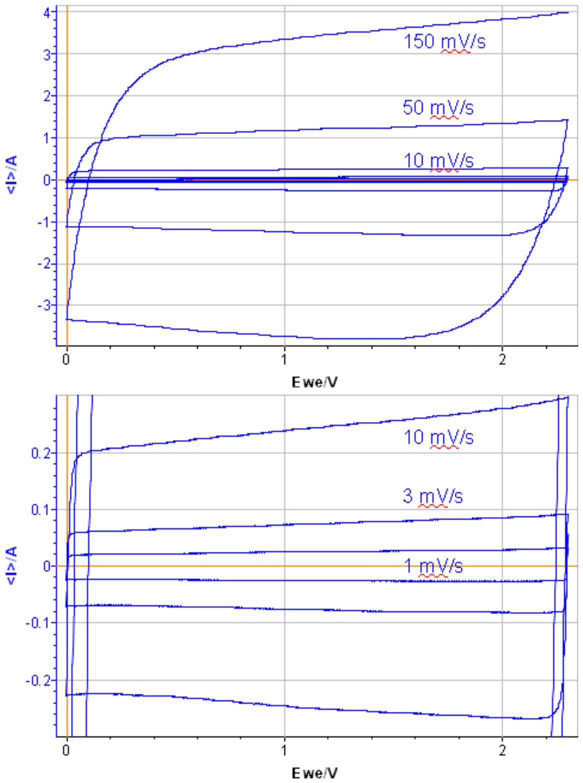

Fig. 5: Potentiodynamic curves of supercapacitor at scan rates of 1, 3, 10, 50 and 150 mV/s.

Tab. 1: Capacitance data.

d*E*/d*t*/ (mV.s^{-1})	**1**	**3**	**10**	**50**	**150**
Current/mA	28	80	262	1276	3772
C/F	28	27	26	26	25

IV-EIS investigations

Time constant can also be determined by EIS investigation. Eexperiements are carried out in similar conditions than previous paragraph *i.e.* the same range of potential. Measurements are done between 10 mHz to 200 kHz (Fig. 6) at several states of charge between 2.1 and 2.3 V.

Nyquist plot is shown in Fig. 7.

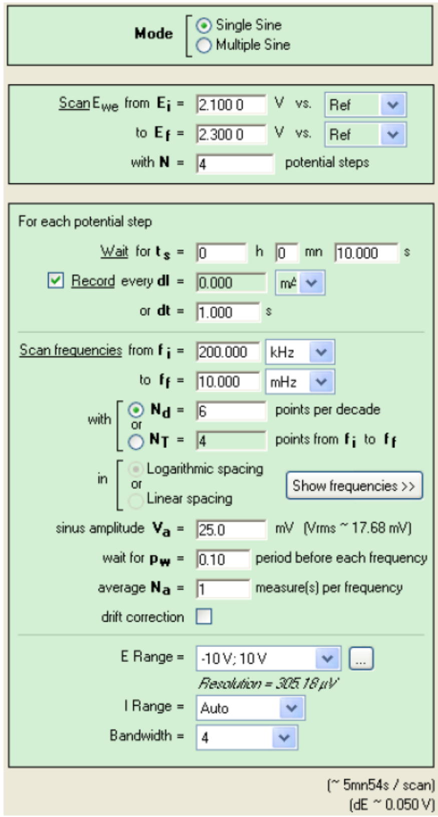

Fig. 6: EIS settings window.

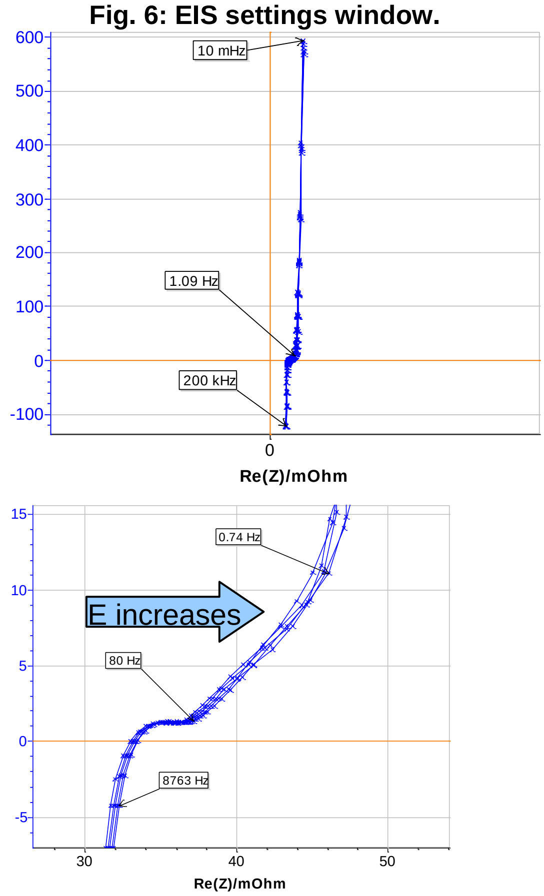

Fig. 7: EIS measurements. a (top): full diagram, b (bottom) zoom at high frequencies.

If the equivalent circuit is R + C and the fit is performed at low frequencies, Fig. 8 shows that R and C increase during the charge. Meaning that time constant increases. Refer to application note #45 to fit multiple EIS cycles and obtain data plot in Fig. 8.

For example, R is 52 mOhm at 2.1 V and C is 26.7 F, so τ is equal to 1.388 s. These values of R and τ are in agreement with the values previously determined by the potentio methods (Tab.2).

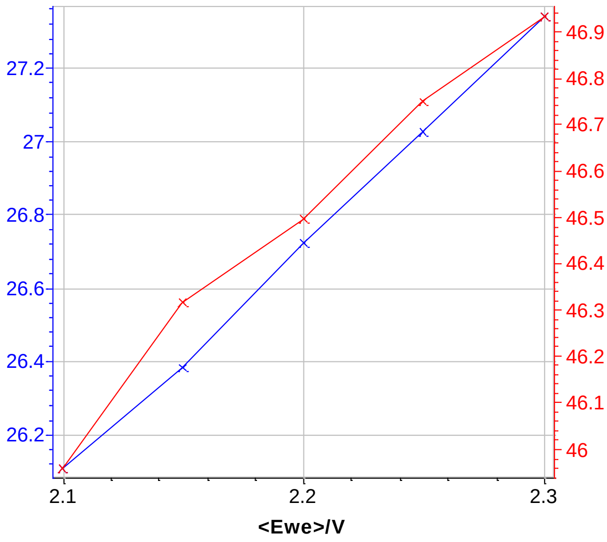

Fig. 8: Values of the fit at low frequencies.

R, C values and time constant determined by potentio method an EIS technique are in agreement.

Tab. 2: Capacitance measured by different methods.

	R/mOhm	C/F	τ/s
Potentio	44	25-28	1.348
EIS	52	26.7	1.388

At higher frequency, the simple model RC in series is no more relevant (Fig. 7b). Change of the signal from 45° to 90° is indeed observed at 1 Hz. This change was already described in the literature [5-7]. This behavior cannot be modeled by the simple R + C model in series but $R_1 + L_1 + C_2/(R_2+M_2)$ equivalent circuit (Fig. 9). In that circuit, R1 is the internal resistance, L1 inductance due to the connection, R2 is the charge transfer resistance and M is due to the matter transport in thin layer in linear symmetry. The resulting curve is plotted in Fig. 10. More information are available on the handbook of impedance [8].

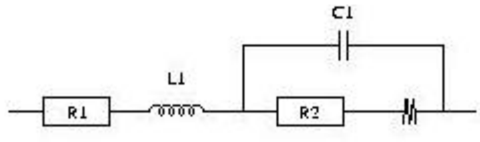

Fig. 9: model for higher frequencies.

For information, the fitted values are the following:

R_1 = 31.61 mOhm
L_1 = 98.45 nH
C_2 = 15.59 mF
R_2 = 4.23 mOhm
R_{d2} = 37.89 mOhm
τ_{d2} = 1.044 s

Note capacitance can be determined by the ratio of τ_{d2}/R_{d2} = 27.9 F.

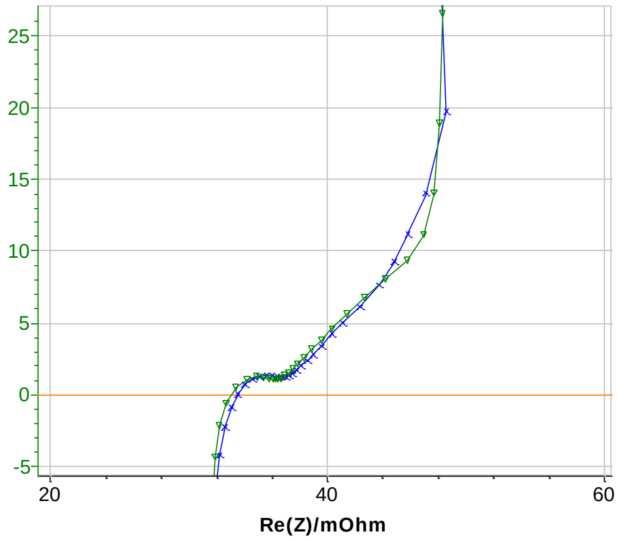

Fig. 10: Fit at high frequencies measured (x) and fitted (▼) curve.

Moreover, analysis of the higher frequencies data allows user to determine the diffusion coefficient thank to the following relationship where f_k is « knee » frequency and δ_D is the thickness between the two electrodes [8]:

$$2\pi f_k = \frac{3.88}{\left(\frac{\delta_D^2}{D}\right)}$$

V-Conclusion

This note shows how to determine the time constant by potentio and EIS techniques. The EIS method is more powerful because additional information are available at high frequencies.

References

[1] Supercapacitors investigations. Part I: charge/discharge cycling, Application note 33, http://www.bio-logic.info/potentiostat/notes.html

[2] CPE, Application note 21, http://www.bio-logic.info/potentiostat/notes.html

[3] Transparent electrochemical capacitor based on electrodeposited MnO_2 thin film electrodes and gel-type electrolyte. F. Moser, L. Athouël, O. Crosnier, F. Favier, D. Bélanger, T. Brousse, Electrochem. Communications, 2009, 11, 1259-1261.

[4] Synthesis and characterization of nano-MnO_2 for electrochemical supercapacitor studies. P. Ragupathy, H. N. Vasan, N. Munichandraiah, J. Electrochem. Soc. 2008, 155, A34-A40.

[5] Effect of specific surface area on capacity in asymmetric carbon/α-MnO_2 supercapacitors. A. J. Roberts, R. C.T. Slade, Electrochimica Acat, 2010, doi:10.1016/j.elctracta.2010.01.004.

[6] An activated carbon monolith as an electrode material for supercapacitors. V. Ruiz, C. Blanco, R. Santamaria, J. M. Ramos-Fernandes, M. Martinez-Escandell, S. Sepulveda-Escribano, F. Rodriguez-Reinoso, Carbon, 2009, 47, 195-200.

[7] Electrochemcial Characteristics and impedance spectroscopy studies of carbon-carbon supercapacitors. P. L. Taberna, P. Simon, J. F. Fauvarque, J. Electrochem. Soc. 2003, 150, A292-A300.

[8] Handbook of EIS – Diffusion impedances – http://www.bio-logic.info/potentiostat/notes.html