



CARBON-BASED MICRO-SUPERCAPACITORS ELABORATION

Fabrication process

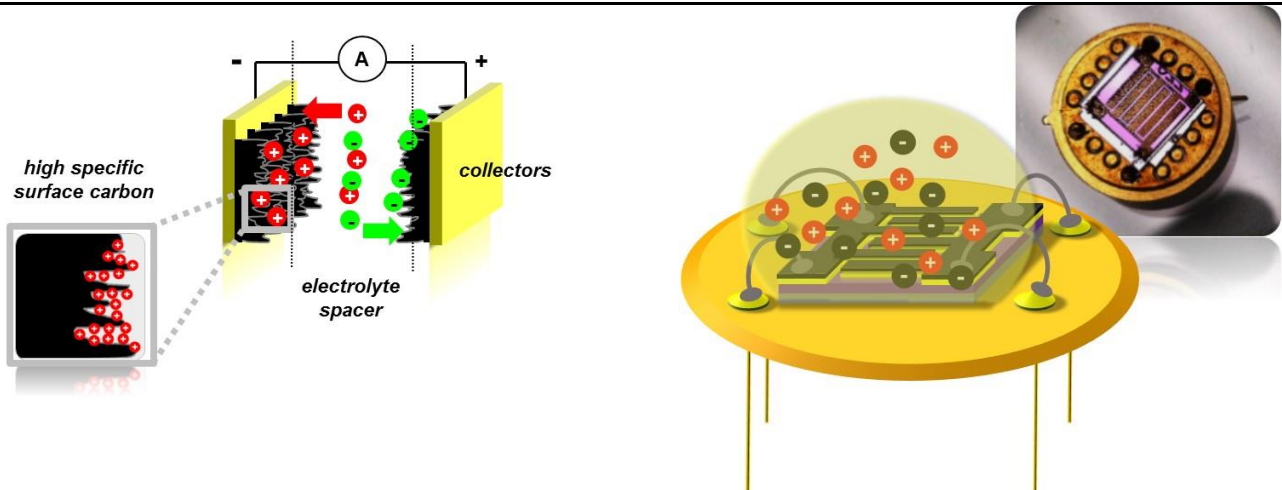


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EVACUATION INSTRUCTIONS

Instructions dedicated to supervisors

REMINDER: Teachers are responsible of the evacuation of all students he has in charge during an alert.

▶ **CLEAN ROOM N°1 AND N°3:**

Evacuate all persons present by emergency exits which lead directly into the entrance hall.

Do not pass through the airlock, do not undress.

▶ **CLEAN ROOM N°2 AND N°4 :**

Evacuate the students by the emergency exit which lead to the observation gallery and then to the back lawn.

Gather all students in front of the entrance of A.I.M.E.

Conduct a census.

**Do not go back in the building without the consent of the firemen or the director
(Or the technical manager present).**

EVACUATION INSTRUCTIONS FOR TEACHERS

REMINDER : Each teacher is responsible for the orderly and calm evacuation of all students under his care at the time of the incident.

IN THE MAIN CLEAN ROOM:

- ⇒ Evacuate the students by the emergency exit which leads directly into the hall.
- ⇒ Do not go through the airlock again; do not undress.
- ⇒ Exit through the main entrance of AIME.

IN THE PHOTOLITHOGRAPHY ROOM:

- ⇒ Evacuate the students by the emergency exit which leads directly into the corridor.
- ⇒ Do not go through the airlock again; do not undress.
- ⇒ Exit through the main entrance of AIME.

IN ASSEMBLY OR CHARACTERIZATION ROOMS:

- ⇒ Evacuate the students through the emergency exit leading to the green space behind the AIME.
- ⇒ Do not go through the airlock again; do not undress.
- ⇒ Take a tour of AIME.

GATHER ALL STUDENTS AT THE GATHERING POINT IN FRONT OF AIME.

TAKE A CENSUS.

**DO NOT REINSTATE THE PREMISES WITHOUT THE ADVICE OF THE PERSONNEL
IN CHARGE OF EVACUATION**

SECURITY INSTRUCTIONS

LOCATE THE SAFETY EQUIPMENT:

- emergency exits
- security showers
- fire extinguishers
- self-contained breathing equipment

WEAR PROTECTIVE GLASSES IS MANDATORY FOR:

- CHEMICAL CLEANING (RCA AND $H_2SO_4-H_2O_2$)
- ALL WET ATTACKS

TRAINEES ARE **FORBIDDEN** TO TRANSPORT CHEMICALS FROM ONE WORKSTATION TO ANOTHER.

Keep in mind that:

- gloves are compulsory but they do not provide sufficient protection against high temperatures or corrosive products,
- some baths give off noxious vapors, normally drawn in by laminar flow hoods,
- overshoes sometimes make the floor very slippery.

HANDLING INSTRUCTIONS

- Throughout the duration of the process, the quality control of each step must be a permanent concern if we want to achieve a final component in working order, as well as a good performance on the whole. For this purpose, we will use in parallel with the "components" wafer, a control/test wafer ("witness") which will characterize each step carried out.
 - Warning: the wafers boxes must be opened by turning the cover clockwise
 - For handling a wafer with a tweezer :
 - take advantage of the flat if the wafer is in the box
 - pinch at least 5mm from the edge of the wafer to reduce the risk of breakage.
- Any wafer coming out of a wet treatment must at the end undergo a rinsing with D.I. water and mechanical drying before being stored in its box.**
- A good rinsing must include a change of tweezer, it is necessary to have a second one available and clean all tweezers.
 - The tips of the pliers must not be wiped (neither on the gown, nor on paper), they must be rinsed with water and dried with nitrogen.
 - The function of the gloves is to protect the components from contamination. Contamination of gloves should also be avoided. They are absolutely not an effective protection against acids.
 - The plastic of the boxes cannot withstand temperatures above 250 ° C. In particular, cool down the wafers coming out from oven, for about 20 seconds in the open air.
 - Paper is a source of contamination, make minimal use of it.

CLEANROOM ENTRY PROCEDURE

- Leave street clothes and bags in the seminar room.
- Six lockers, lockable, can be used in the SAS for valuables.
- No more than 4 people in the airlock at the same time

Clean room entry:

Lab coat: white: permanent staff
blue: trainees
green: visitors

Overshoes: place the seam inside.

Do not put your foot in the clean part until you have put on your overshoes.

Mob caps: Provision in the wall dispenser.

Gloves: Provision in the wall dispenser. 2 sizes available.

Exit of clean room:

Lab coat/mob caps/goggles: place them in your personal box

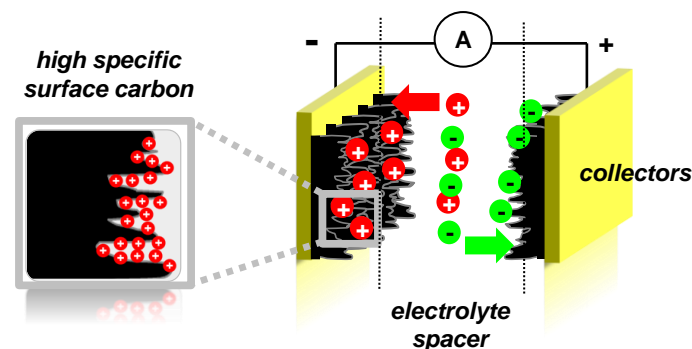
Overshoes/gloves: throw them in dedicated trashes.

Recommendations:

- Be careful not to enter the airlock with muddy or wet dress shoes (use the doormat at the entrance of the AIME).
- Limit the number of objects and documents entering the Clean Room (**carbon pencil prohibited**).

Micro-supercapacitors

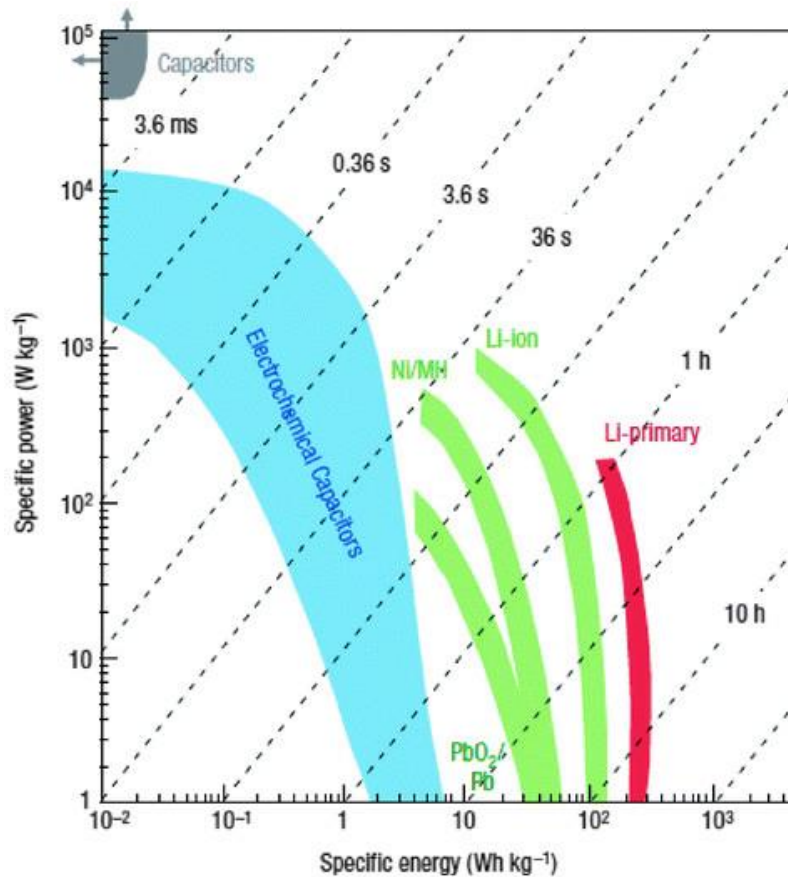
The continuous development of micro-electronic components brings new needs in terms of miniaturized high performance energy storage systems. While batteries suffer from limited power capabilities and cyclability, owing to the faradic nature of the storage mechanisms involved, electrochemical double layer supercapacitors (or so called EDLCs) can handle energy delivery and harvesting with fast charge and discharge (seconds to minutes). Indeed, EDLCs mostly store energy via reversible adsorption of ions from an electrolyte at the surface of high-surface-area carbons.



Several carbon materials are currently studied in order to improve the capacitance delivered by carbon based supercapacitors. Here is a list that described the most important ones:

- **Onion-like carbons (OLC):** 0-dimensional carbon materials which consist in spherical nanoparticles (5-10 nm) and have the particularity to exhibit a non-porous structure. High conductivity and moderate specific surface area ($500 \text{ m}^2 \cdot \text{g}^{-1}$).
- **Carbon nanotubes (CNT):** 1-D materials of about $1000 \text{ m}^2 \cdot \text{g}^{-1}$. Low density ($0.3 \text{ g} \cdot \text{cm}^{-3}$).
- **Graphene:** 2-D material which originated from the exfoliation of graphite; very conductive and high specific surface area
- **Activated carbons (AC):** 3-D carbon materials containing a high volume of micropores and mesopores, offering high surface area value (up to $3000 \text{ m}^2 \cdot \text{g}^{-1}$).
- **Carbide-derived carbons:** 3-D carbon materials with a narrow pore size distribution which can be fine tuned to the nanometer scale by controlling the synthesis parameters; high specific surface area (from 1000 to $3000 \text{ m}^2 \cdot \text{g}^{-1}$).

The simple electrostatic mechanism involved during the energy storage in supercapacitors provides high power densities (up to $15 \text{ kW} \cdot \text{kg}^{-1}$) and very long cycle life (more than 1,000,000 cycles), while comparing to batteries which store energy via redox reactions with slower kinetics. Below is a Ragone Plot resuming the performance of different energy storage systems :



Therefore, supercapacitors have already been used in broad range of applications in power electronics such as power buffer or memory back-up for toys, cameras, or mobile phones. EDLCs are also used in transportation to recover braking energy in tramways, hybrid electric vehicles and buses.

However, standard electrode preparation consisting in mixing the carbon with a polymer binder, is not compatible with micro-fabrication processes. Therefore, the miniaturization of supercapacitors has attracted much interest for the past five years. Some researchers focused on laser-writing techniques while other groups used ink-jet printing to make flexible micro-supercapacitors. But the capacitance values delivered are still limited. Recently, nanoporous carbide derived carbon films were integrated on silicon chips and exhibited interesting performance. Today, you are comparing the performance of your micro-supercapacitors prepared by electrophoretic deposition of activated carbon on silicon substrate to these devices.

PROCESS

PROCESS

I- SUBSTRATE CHARACTERIZATION

The substrate is a 2" p-type silicon (Si) wafer (doped by boron) with <100> orientation. The first step of the process is to determine the physical parameters of the substrate, **before any processing** (see the following table below).

Characterization	Parameters value
<input type="checkbox"/> 1° wafer thickness	$e =$ μm
<input type="checkbox"/> 2° 4-point probe	$V/I =$ Ω
<input type="checkbox"/> 3° sheet resistance	$R_{\square} =$ Ω/\square
<input type="checkbox"/> 4° resistivity calculation	$\rho_s =$ $\Omega.\text{cm}$
<input type="checkbox"/> 5° doping concentration	$N_A =$ at.cm^{-3}

II- MASKING OXIDE

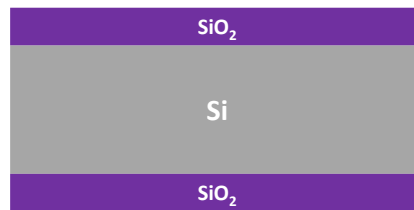
This step is usually performed by AIME staff. The goal is to obtain a thick silicon dioxide layer (SiO_2) which will protect the whole Si wafer. This oxide layer has many utilities such as the creation of windows (combined with photolithography), but it can also play the role of electrical insulator between components and the Si wafer.

1- Cleaning before Oxidation:

Operations	Conditions
<input type="checkbox"/> 1° Degreasing	Acetone
<input type="checkbox"/> 2° Rinsing	DI water
<input type="checkbox"/> 3° Chemical Oxidation	$\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ (1/1) - 2 min
<input type="checkbox"/> 4° Rinsing	DI water
<input type="checkbox"/> 5° SiO_2 etching	BOE HF - 30 s
<input type="checkbox"/> 6° Rinsing	DI water
<input type="checkbox"/> 7° Drying	Spin dryer
<input type="checkbox"/> 8° Washing - Drying	Washer dryer

2- Wet thermal Oxidation: This operation is performed inside oven N° 2-2

Conditions		
☐ process also test-wafer 1 and 2		
Temperature	Duration	Flow rates
☐ from 800°C to 1100°C	25 min	N ₂ = 1 l/min
☐ 1100°C	35 min	H ₂ = 2,3 l/min - O ₂ = 1,5 l/min
☐ 1100°C	30 min	O ₂ = 2,2 l/min
☐ 1100°C	5 min	Ar = 1,5 l/min
☐ from 1100°C to 800°C	60 min	N ₂ = 1 l/min



Remark: the wafer obtained at the end of this step is oxidized on both sides.

III- COLLECTORS FABRICATION:

This step provides the fabrication of interdigitated gold (Au) electrodes which will collect the current flowing through the micro-supercapacitor. Gold is used in order to avoid undesired electrochemical responses coming from the collectors.

Two different techniques can be applied: the collectors will be obtained whether by a conventional etching of a gold layer (see part **III-A**) or by a lift-off procedure (see part **III-B**). Since, the same mask will be used in both methods (see Annex), the first process (gold etching) will involve a positive resist while the second a reversible resist.

III-A/ Photoetching 1

This process is mainly composed of three consecutive steps. Briefly, a gold layer is first deposited by thermal evaporation (**metallization**). Second, a **photolithography** is performed on the Au-layer (subsequent operations of resist coating, UV exposure through the mask and resist development). The final step consists in a **wet etching** of the Au-layer.

All required operations are listed in the following parts:

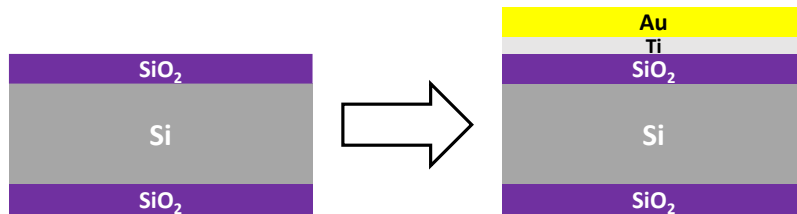
A-1/ Metallization:

This step is performed in order to obtain a layer of Au (~ 250 nm). Prior to this, a thin layer of Ti (~50 nm) is first deposited on the wafer as a seed layer.

Both depositions are performed under high vacuum using a thermal evaporation chamber which guarantees highly pure deposited layers.

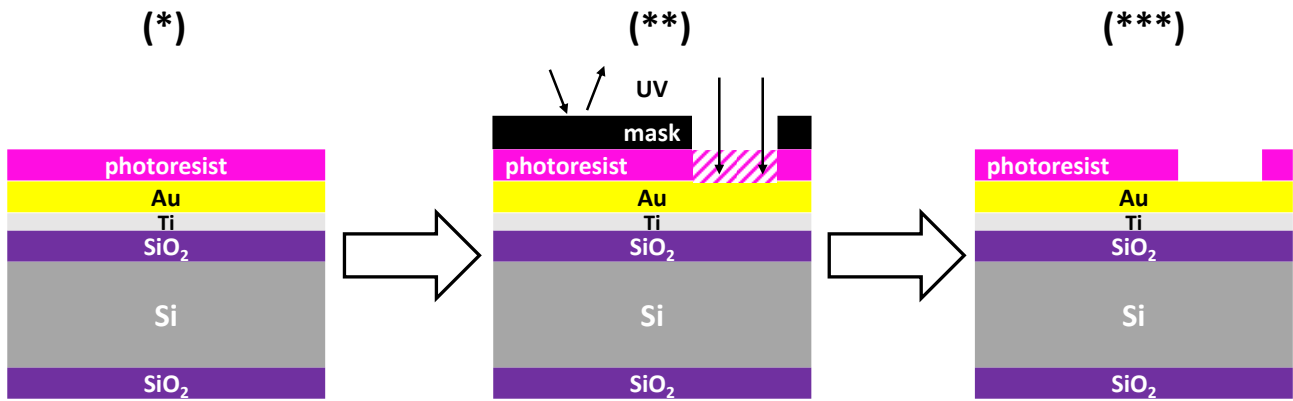
→ Fill all blank spaces with the conditions applied during the deposition:

Operations	Conditions
<input type="checkbox"/> 1°) pumping	duration =min
<input type="checkbox"/> 2°) deposition	pressure deposition =mbar rate (Ti) =nm/s duration (Ti) =min
	pressure deposition =mbar rate (Au) =nm/s duration (Au)=min



A-2/ Photolithography:

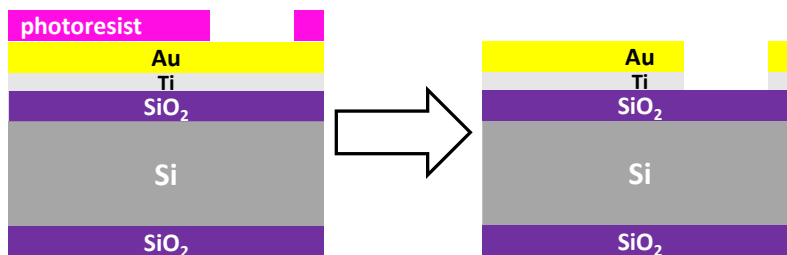
Supervisor's visa for the continuation of Operations		▼
Operations	Conditions	
<input type="checkbox"/> 1°) Drying	Hot plate 120°C – 2 min	
<input type="checkbox"/> 2°) Positive photoresist deposit	Resist Shipley S1813 Spin coater 4000 rpm - 30 s	
<input type="checkbox"/> 3°) 1st annealing	Hot plate 100°C – 60 s	
<input type="checkbox"/> 4°) Alignment - Insolation	Mask n°1 – 5 s	
<input type="checkbox"/> 5°) Development	Bath at 20 °C - 15 s	
<input type="checkbox"/> 6°) Rinsing	DI water	
<input type="checkbox"/> 7°) Drying	Spin dryer	
<input type="checkbox"/> 8°) Observation	Optical microscope	
<input type="checkbox"/> 9°) 2nd annealing	Hot plate 120° C - 45 s	



A-3/ Wet etching of Au layer:

The goal of this step is to etch parts of the Au/Ti layers which are not protected by the photoresist. This leads to delimited areas of Au, namely the collectors. This etching process is realized in a bath composed of [KII₂ + DI-H₂O] (**wet etching**). The etching is optically monitored and stopped when the underneath SiO₂ layer reappears. Finally, another wet etching composed of dilute [HF + H₂O₂ + DI-H₂O] is performed for removing the thin Ti layer.

	Supervisor's visa for the continuation of Operations	▼
Operations	Conditions	
<input type="checkbox"/> 1°) Au etching	KII ₂ + DI-H ₂ O – 50°C – optical monitoring	
<input type="checkbox"/> 2°) rinsing	DI-H ₂ O	
<input type="checkbox"/> 3°) drying	Spin dryer	
<input type="checkbox"/> 4°) control	Optical microscope – (return to step 1°/ if necessary)	
<input type="checkbox"/> 5°) Ti etching	HF + H ₂ O ₂ + DI-H ₂ O – (~ 30 s)	
<input type="checkbox"/> 6°) rinsing	DI-H ₂ O	
<input type="checkbox"/> 7°) resist removing	Acetone	
<input type="checkbox"/> 8°) rinsing	DI-H ₂ O	
<input type="checkbox"/> 9°) drying	Eau DI	



If you have chosen the photoetching process, go directly to part **IV**.

III-B/ Lift-off:

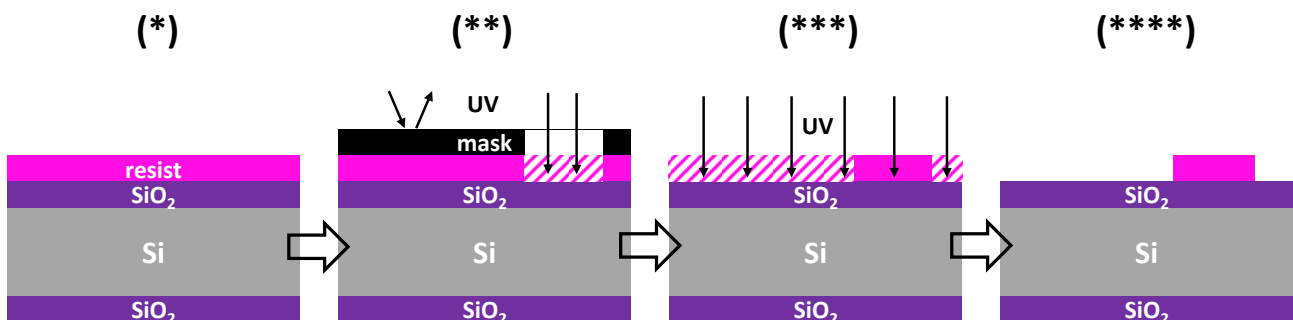
This process is also composed of three main steps. However, unlike the photoetching described previously, a **photolithography** is firstly performed on the wafer (subsequent operations of resist coating, UV exposure through the mask and resist development). The **metallization** (Au layer deposit) is then realized. The final step consists in removing the Au areas deposited on top of the resist using acetone, which leads to the gold collectors.

Since the mask used for the photolithography is the same as the one used for the photoetching, a **reversible photoresist** will be used. Therefore, two UV exposure will be done, one using the mask and the last one without.

All required operations are listed in the following parts:

B-1/ Photolithography:

	Supervisor's visa for the continuation of Operations	▼
Operations	Conditions	
<input type="checkbox"/> 1°) drying	Hotplate 120 °C – 2 min	
<input type="checkbox"/> 2°) adhesion promoter	HMDS 4 droplets (4000 rpm - 36s)	
<input type="checkbox"/> 3°) resist coating (*)	AZ5214 10 droplets (1000 rpm - 36s)	
<input type="checkbox"/> 4°) 1 st annealing	Hotplate 105 °C – 55s	
<input type="checkbox"/> 5°) trimming (edge of the wafer)	Syringe/acetone (4000 rpm - 36s)	
<input type="checkbox"/> 6°) alignment – exposure (**)	4 s	
<input type="checkbox"/> 7°) 2 nd annealing	Hotplate 105 °C – 55s	
<input type="checkbox"/> 8°) 2 nd exposure (without mask) (***)	28 s	
<input type="checkbox"/> 9°) development (****)	bath 20 °C – 35 s	
<input type="checkbox"/> 10°) rinsing	DI water	
<input type="checkbox"/> 11°) drying	Spin dryer	
<input type="checkbox"/> 12°) observation	Optical microscope	



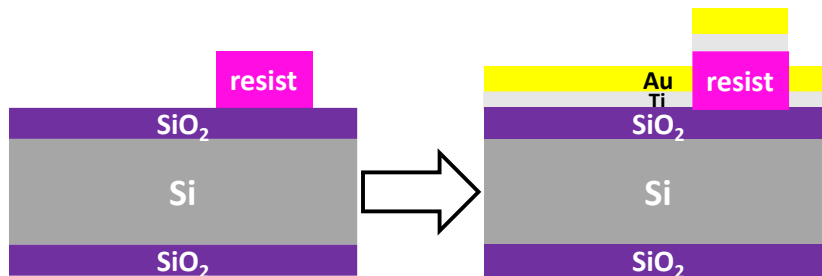
B-2/ Metallization:

This step is performed in order to obtain a layer of Au (~ 250 nm). Prior to this, a thin layer of Ti (~50 nm) is first deposited on the wafer as a seed layer.

Both depositions are performed under high vacuum using a thermal evaporation chamber which guarantees highly pure deposited layers.

→ Fill all blank spaces with the conditions applied during the deposition:

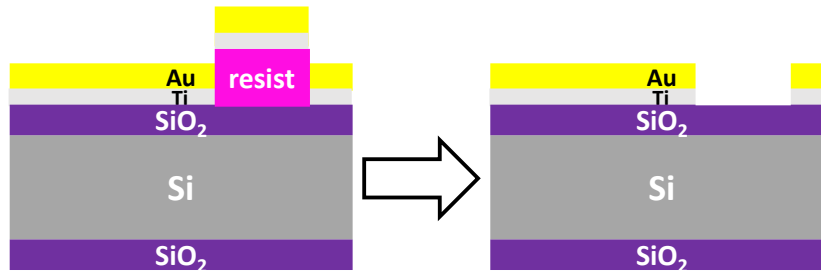
Operations	Conditions
<input type="checkbox"/> 1°) pumping	duration =min
<input type="checkbox"/> 2°) deposition	pressure deposition =mbar
	rate (Ti) =nm/s
	duration (Ti) =min
	pressure deposition =mbar
	rate (Au) =nm/s
	duration (Au)=min



B-3/ Resist removing:

In this step, the wafer is immersed in a bath of acetone. This operation leads to the removing of the resist which also involves the lift-off of the Au/Ti layers. Further annealing under N₂/H₂ atmosphere is finally performed at 250°C for 20 min to improve the thermal and mechanical properties of the deposit.

		Supervisor's visa for the continuation of Operations	▼
Operations	Conditions		
<input type="checkbox"/> 1°) lift-off	Acetone – optical monitoring		
<input type="checkbox"/> 2°) rinsing	DI-H ₂ O		
<input type="checkbox"/> 3°) drying	Spin dryer		
<input type="checkbox"/> 3°) annealing	250°C for 20 min under N ₂ /H ₂		



IV. ASSEMBLING:

The current collectors are now fabricated. In this step, the 2" wafer will be cut and connected onto TO8 socket for packaging.

Remark: Step 1 and 3 are performed by AIME staff.

1- Dicing:

A numerically controlled diamond-coated saw is used to dice the wafers into individual chips. Check and choose a chip which is **not short-circuited** (Multimeter test).

2- Mounting:

The chips are mounted on TO8 socket.

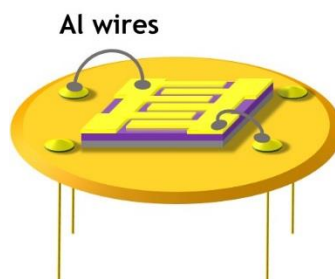
They must be glued on 2 pieces of silicon wafer using an epoxy adhesive. Then, annealing is performed at 120°C for 10 min.

3- Piranha:

In order to improve the adherence of the carbon particles after electrophoretic deposition, the chips are immersed in a mixture of $\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$ (1:1 vol) and rinsed before drying at 120°C for 10 min.

4- Micro-bonding:

The gold collectors are connected to the TO8 pins using a wedge-bonding technique (room temperature). The aluminum wires used are welded using ultrasonic energy to interconnect the chip to the package.



V. ACTIVATED CARBON DEPOSITION:

This step is dedicated to the deposition of the active electrodes. We choose a commercial powder of activated carbon (YP-50F from Kuraray Company). This material is a good candidate for supercapacitor applications due to its high specific surface area (high densities of nanopores displaying a diameter < 2 nm).

The active electrodes deposition is performed in solution which is composed of the activated carbon diluted in DI-H₂O, ethanol and MgCl₂. The Mg²⁺ ions have two utilities. First, when adsorbed to the carbon surface, Mg²⁺ ions facilitate the migration of carbon towards the cathode. Second, they enhance the adhesion between the gold collectors and the carbon electrodes.

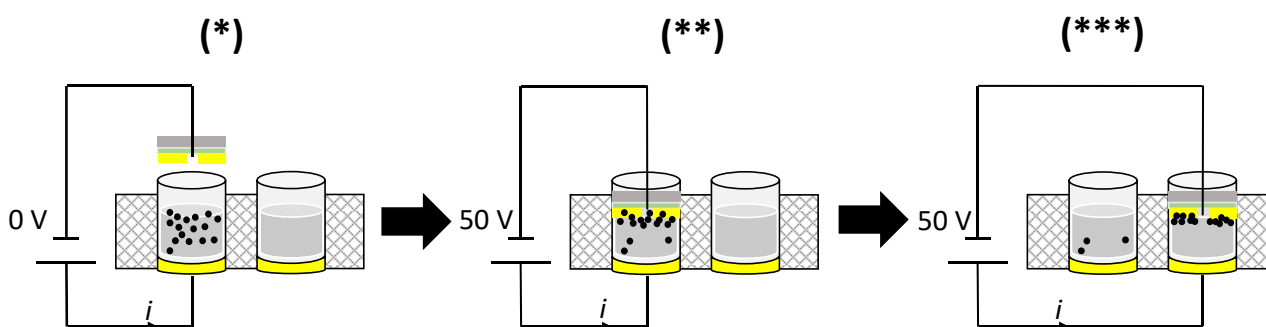
All steps of the carbon deposition described below are performed using a homemade setup.

1- TO8 mounting:

Mount the TO8 on the sample holder in Teflon. Cut the unused pins of the TO8 if necessary.

2- Carbon deposition:

The setup is composed of two containers which are connected to the positive terminal of a DC voltage generator. The TO8 is connected to the negative terminal (same potential for both collectors). The chip is then dipped in the first container which is filled with the carbon solution. Thereafter, a DC voltage is applied, generating an electrical field between the collectors and the containers. **Electrophoretic** forces will induce a motion of the carbon which will flow toward the gold collectors. The TO8 is finally dipped into the second container filled with acetone, the **DC voltage** being **still applied**. This step ensures to remove the carbon which might be deposited in between the collectors (short-circuit of the capacitor).



Operations	Conditions
<input type="checkbox"/> 1° electrical connection (*)	Negative (TO8) positive (containers) terminal
<input type="checkbox"/> 2° dipping in 1 st container	Carbon + DI-H ₂ O+MgCl ₂
<input type="checkbox"/> 3° deposition (**)	50 V – 15 s
<input type="checkbox"/> 4° dipping in 2 nd container (***)	50 V – 15 s
<input type="checkbox"/> 5° withdraw TO8	0 V
<input type="checkbox"/> 6° electrical test	Multimeter – if short-circuit, return to step 4°)

Remark: make sure to turn off the DC source before retrieving your TO8.

3- Annealing:

The final step of the deposition process is the annealing of the nanoporous carbon layer which enhances the adhesion to the gold collectors.

Operations	Conditions
□ 1°) annealing	Oven – 250 °C, 4 h

Remark: At this stage, the fabrication of the micro-supercapacitor is not complete yet. In fact, only the collectors and the active materials (nanoporous carbon) have been processed. For obtaining the final device and operating the micro-supercapacitor, an electrolyte (charges reservoir) must be added.

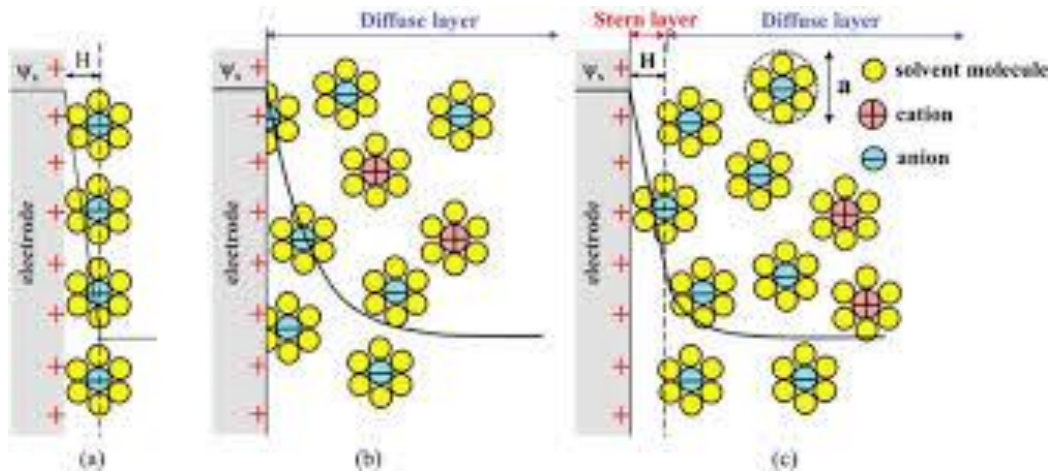
CHARACTERIZATIONS

CHARACTERIZATIONS

VI. ELECTROCHEMICAL DOUBLE LAYER

1- Helmholtz model:

The simplest model to describe the electrochemical double layer is the Helmholtz model (a).



Briefly, it assumes that the EDL part which originates from the electrolyte consists in a compact layer of counterions that counterbalance the surface layer of charges on the electrode. Thus, this two layer structure reminds the conventional parallel-plate capacitor configuration, and the capacitance of the EDL is given by the same relation:

$$C_H = \frac{\epsilon_0 \epsilon_r A}{d}$$

Where ϵ_r is the dielectric constant inside the EDL, ϵ_0 the vacuum permittivity, A the electrode surface area and d the distance between the surface charge layer and the counterion layer.

2- Diffuse layer:

The electrolyte still contains a large amount of ions that do not participate to the EDL formation according to this model. Nevertheless, the assumption that the electrode surface charges are completely screened by the counterion charges of the Helmholtz layer is not realistic. Therefore, a diffuse layer (b) is also taking into account, leading to the more sophisticated Gouy-Chapman-Stern model (c). The capacitance of the diffuse layer is described as follows :

$$C_{diff} = \frac{\epsilon_0 \epsilon_r A}{\lambda_D} \times f(T)$$

Where λ_D is the characteristic Debye length, which represents how far the electrostatic interactions between the electrode and the ions persists in the electrolyte:

$$\lambda_D = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{2e^2 C}}$$

In this formula, k_B the Boltzmann constant, T the absolute temperature, e the electron charge and C the bulk electrolyte concentration.

From these assumptions, the EDL capacitance is equivalent to :

$$\frac{1}{C_{DL}} = \frac{1}{C_H} + \frac{1}{C_{diff}}$$

→ Answer the following questions to be prepared for the electrochemical characterization session:

a) While using concentrated electrolytes, how does the capacitance of the diffuse layer evolve ?

.....
.....

b) In this case, where does the double layer capacitance mainly come from ?

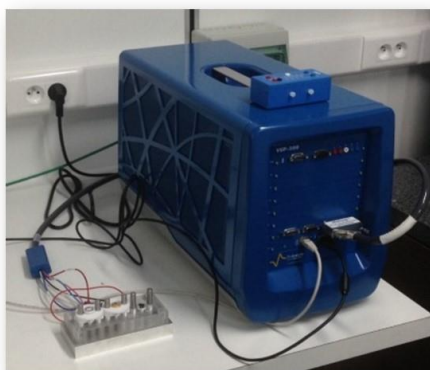
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IX. CHARACTERIZATION OF SUPERCAPACITORS

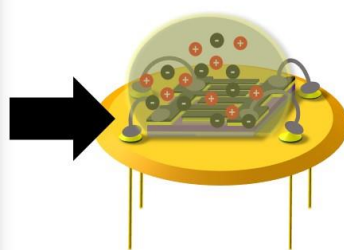
1- Experimental setup and procedure:

- To evaluate the capacitive behavior and performance of supercapacitors, several techniques are carried out with electrochemical workstations. Recent workstations are composed of a signal waveform generator, a potentiostat/galvanostat and a computer. Here, the characterizations are performed using a potentiostat VSP-300 (Bio-logic Instruments). In order to test an electrochemical cell, both two-electrode and three-electrode configurations can be built. The reference (REF, white wire) is needed as it exhibits a nonpolarizable behavior, thus allowing to measure accurately the WE voltage. However, while testing a device, the current flows through the counter electrode (CE, blue wires) and the working electrode (WE, red wires), and the voltage of the cell is measured since the reference electrode is shorted with the CE.
- Mount the TO8 on the Teflon sample holder and connect the two terminal (positive and negative) of the amplifiatory to the sample holder. The measurements are done using a 2-probes technique, *i.e* without electrode of reference.
- Spatter 50 μL of the electrolyte on the chip. The electrolyte is composed of a $[\text{NEt}_4\text{BF}_4]$ (1M) salt diluted in an organic solvent (propylene carbonate [PC]).
- Start characterizations requested in the following part.

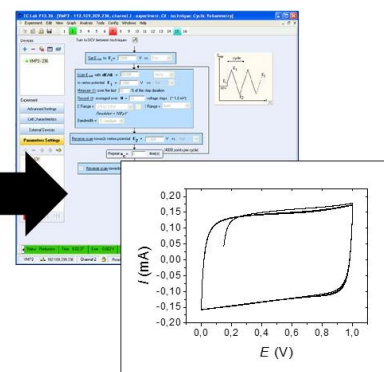
Experimental setup



μ -supercapacitor
(electrolyte deposit)



Measurements &
data analysis



2- Cyclic voltammetry:

The cyclic voltammetry is very useful to study the capacitive behavior, the reversibility of the charge and discharge of the cell, the cyclability and the nature of the mechanisms involved. The current is measured as a function of the potential applied at a constant scan rate:

$$U = U_0 + vt$$

With U the electrode potential, U_0 the OCV, v the scan rate and t the time.

Then the capacitance is deduced from the area obtained under the curve during the discharge:

$$C = \frac{\int_{E_2}^{E_1} IdV}{v \cdot \Delta V}$$

Where E_1 and E_2 are the limits applied during the voltage sweep, and ΔV the potential window.

→ Answer the following questions to be prepared for the electrochemical characterization session:

h) What becomes this relation while considering that the current is kept constant during the potential sweep? Deduce the shape of the cyclic voltammogram expected for an ideal supercapacitor.

.....

Then, the energy (in Joules) and power (in Watts) densities delivered are calculated as :

$$E = \frac{1}{2} C \cdot V^2$$

$$P = \frac{E}{\Delta t}$$

With C the capacitance (Farads), V the potential window (Volts) and Δt the duration of the discharge (seconds).

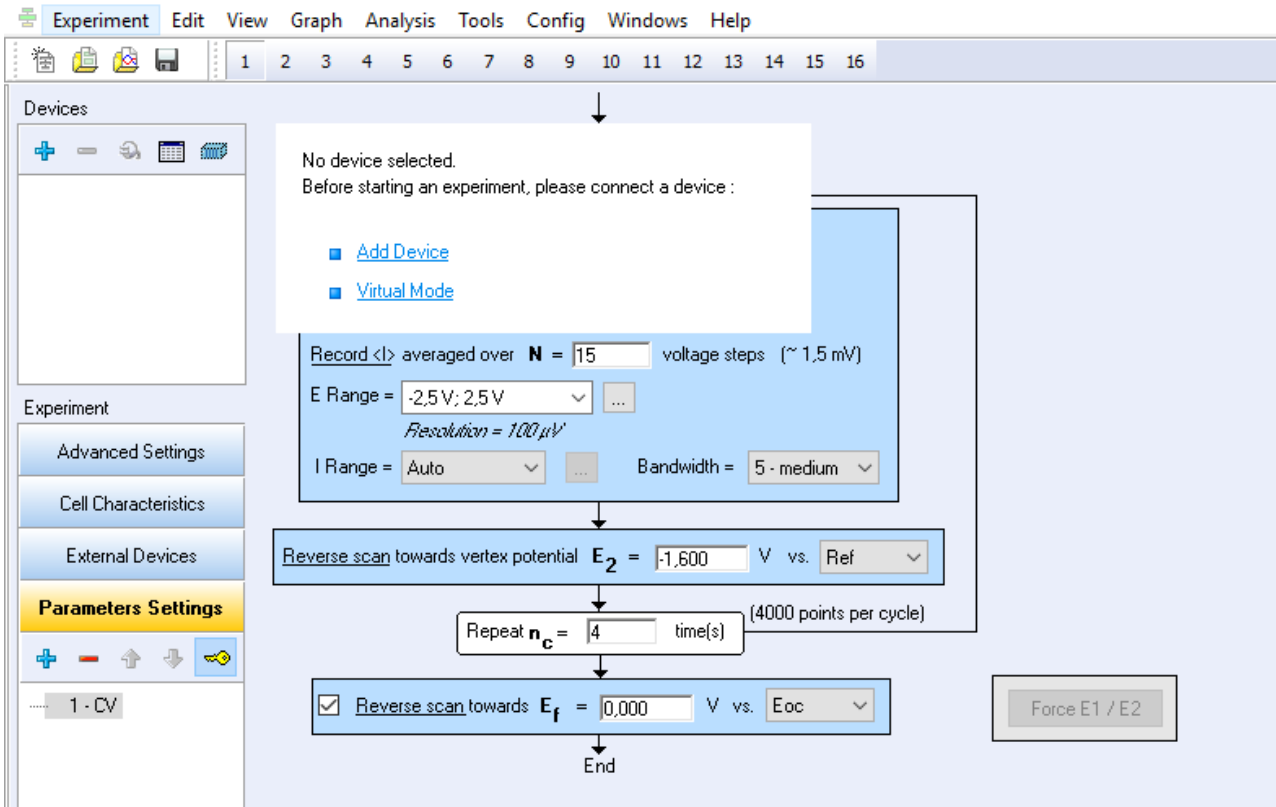
Remark: You have to divide by 3600 to convert the energy density in Wh.cm⁻².

Insert a new technique in Parameters settings and select Cyclic Voltammetry.

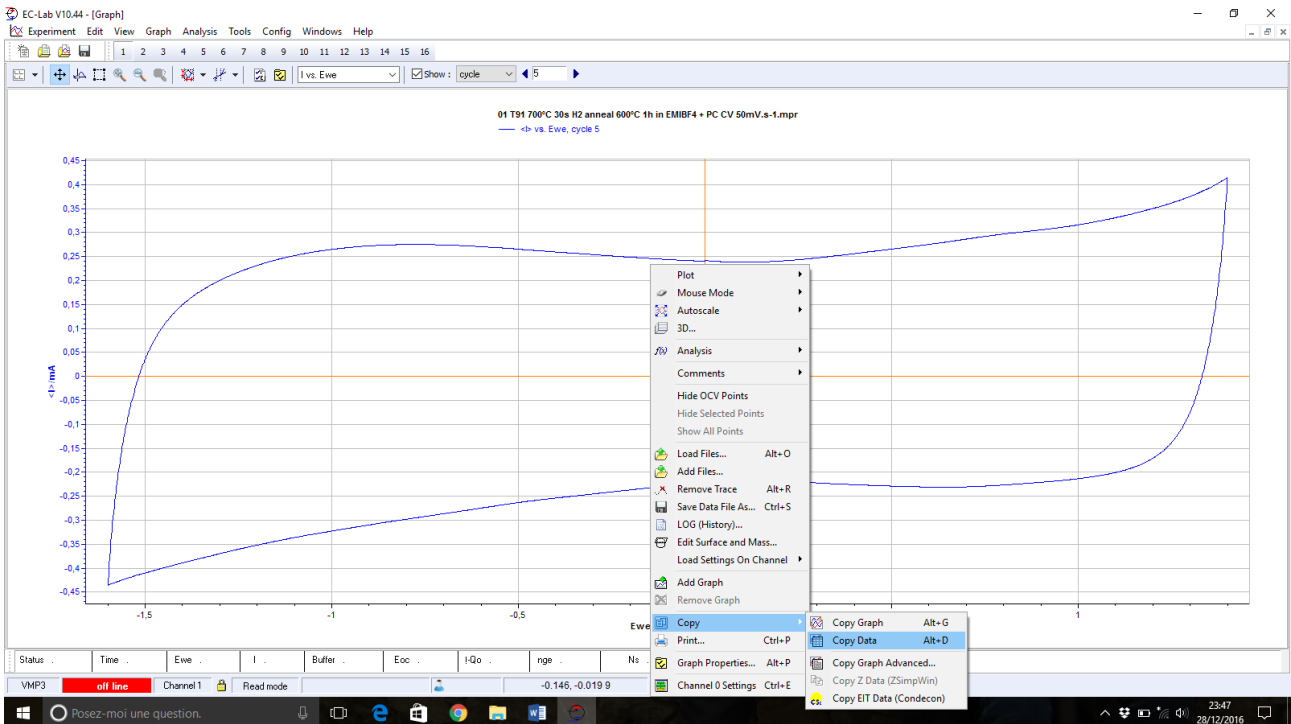
Make sure the experiment starts from the OCV. Set the potential limits $E_1 = 1$ V and $E_2 = 0$ V, and the scan rate at 100 mV.s⁻¹. The potential range will be restricted to [-1;1] to optimize the resolution.

Play on the N value to measure about 4000 points per cycle. Repeat the measurement for several cycles. Check "smooth on" in Advance settings and enter 100 as number of points. Add the electrolyte on your device and press the green arrow to run the experiment.

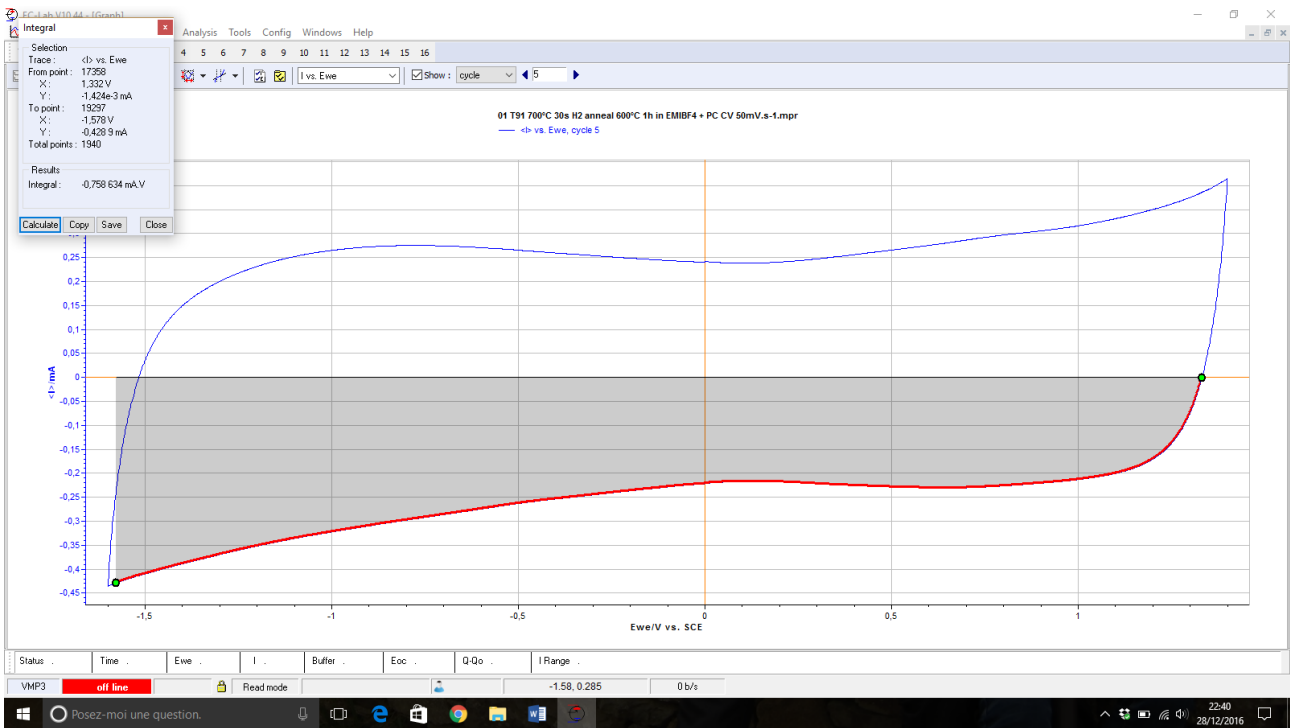
EC-Lab V10.44 - [VMP3 -, channel 1 - experiment: <no name> - technique: Cyclic Voltammetry]



Check the option “show cycle” to display one specific cycle, and right click on the graph to select “copy data”. Paste the datas in an Excel sheet to plot the curve.



Check the box “show” and choose one cycle. In Analysis, go to Math and Integral to calculate the capacitance of the micro-supercapacitor from the discharge current. Run another CV at 1 V.s^{-1} .



i) Does the signal have the shape expected?

.....

j) How does the CV shape evolve? Report the capacitance values obtained at 20, 50, 100, 200, 500 mV.s⁻¹ and 1 V.s⁻¹ in the table.

.....

Technique	Capacitance (mF.cm ⁻²)	Energy (μWh.cm ⁻²)	Power (mW.cm ⁻²)
□2°) CV	At 20mV.s ⁻¹ :		
	At 50mV.s ⁻¹ :		
	At 100mV.s ⁻¹ :		
	At 200mV.s ⁻¹ :		
	At 500mV.s ⁻¹ :		
	At 1 V.s ⁻¹ :		

4- Galvanostatic charge and discharge:

Another strategy to evaluate the performance of a device is to apply a current density and study the change of the measured potential. Thus, the capacitance is deduced from the slope of the discharge curve:

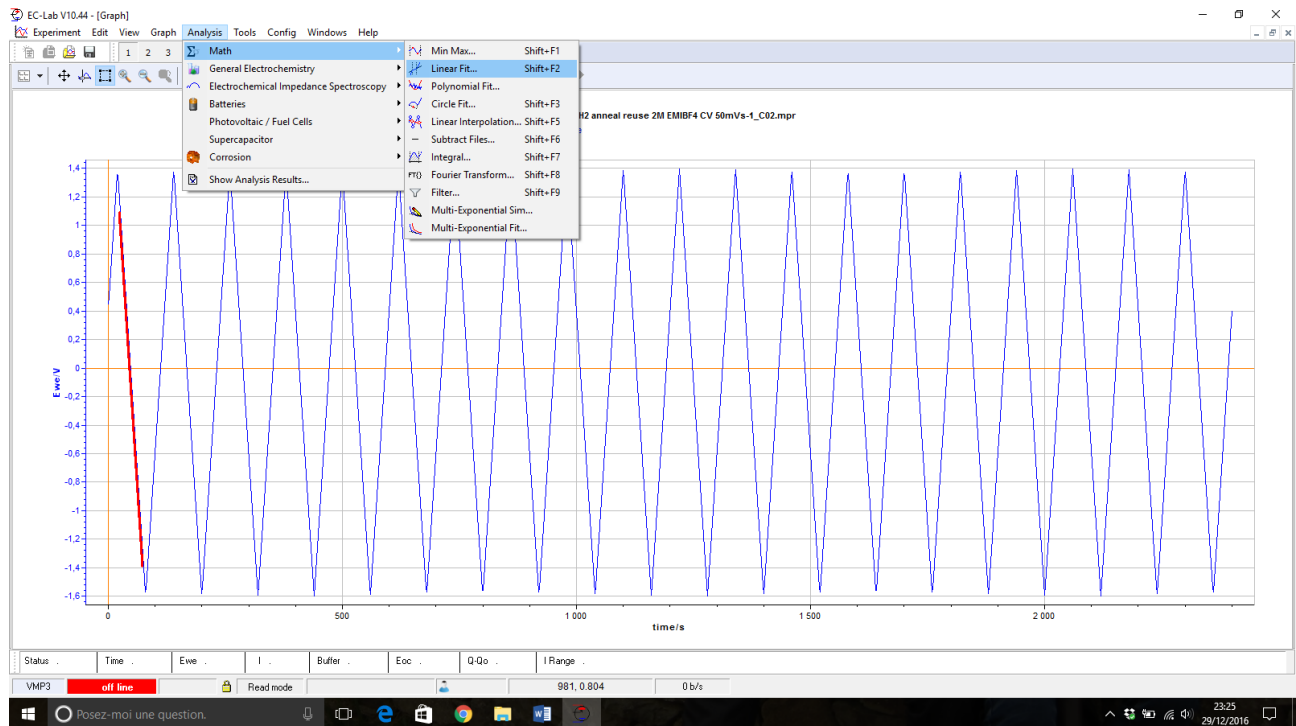
$$C = I \frac{dt}{dV}$$

Where I is the current density applied, and dV/dt the slope of the curve.

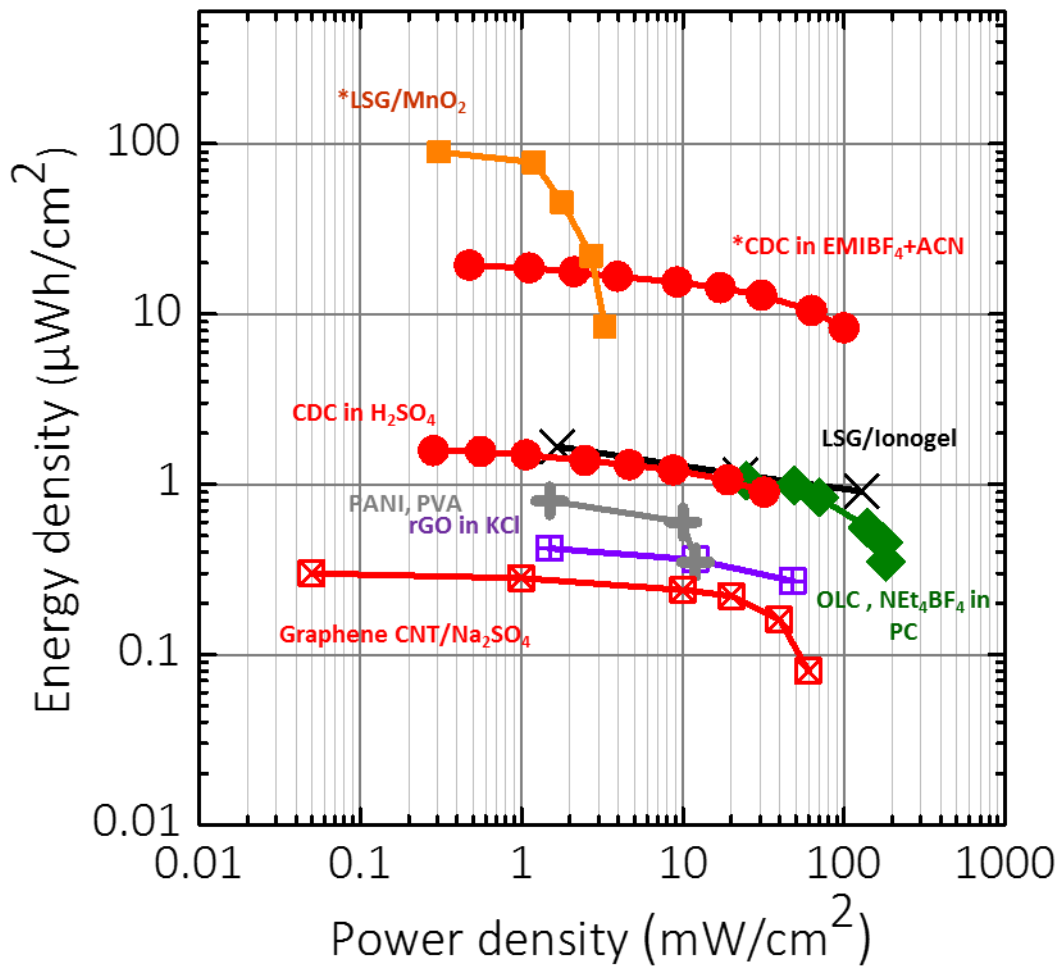
Run a chronopotentiometry. Press “+” to add a second sequence. Apply the average current obtained during CV tests as positive current during sequence N_s' = 0 and set the duration accordingly.

Limit the working potential to 1 V and go to sequence 1.
 Apply the same current (negative value) during sequence $N_s' = 1$ with the same duration.
 Limit the working potential to 0 V and go to sequence 0 for several cycles. From the obtained feature, apply a linear fit on the linear part of the discharge curve in Analysis/Linear fit to estimate the capacitance value.

k) Compare with the capacitance value obtained from CV tests.



l) Finally, calculate the different energy and power densities delivered for each scan rate and plot the results on the following Ragone Plot.



Learning more about electrochemical characterization techniques : (this part is given as information)

This technique consists in measuring the frequency response of a system under perturbation. It allows to understand of behave the electrons (high frequencies) and ions (low frequencies) in your system, thus giving a first quantification of the cell resistance and capacitance. Usually, a sinusoidal variation of potential is applied:

$$U(t) = U_{max} + \Delta U \sin(\omega t)$$

Where U_{max} is the potential at which the impedance is carried out, ΔU the amplitude of the signal, ω the pulsation of the signal. Then the response to this perturbation is a sinusoidal current with a phase shift :

$$I(t) = I_{max} + \Delta I \sin(\omega t + \varphi)$$

Where I_{max} is the initial current of the cell, ΔI the amplitude of the current, ω the pulsation and ϕ the phase shift. For calculation considerations, these relations are given in their complex form :

$$\Delta U(\omega) = U_{max} \exp j(\omega t)$$

$$\Delta I(\omega) = I_{max} \exp j(\omega t + \varphi)$$

The electrochemical impedance is defined as :

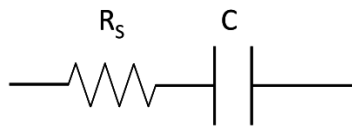
$$Z(\omega) = \frac{\Delta U}{\Delta I} = \frac{U_{max}}{I_{max}} \exp(-j\varphi) = |Z(\omega)| \exp(-j\varphi)$$

Which can be rearrange into :

$$Z(\omega) = Z' + jZ''$$

Where Z' is the real part and Z'' is the imaginary part of the impedance.

One of the simplest way to represent the supercapacitor frequency behavior is to associate a resistance R and a capacitance C in serie.



→ Answer the following questions to be prepared for the electrochemical characterization session:

c) Write the impedance expression related to this circuit

.....

d) Which part corresponds to the real part Z' ? The imaginary part Z'' ?

.....

The response of an electrochemical system is often given in a Nyquist Plot where the opposite of the imaginary part Z'' is represented vs the real part Z' .

e) What is the dominant factor at very high frequencies? At very low frequencies?

.....

Therefore, a vertical line is observed at low frequencies, while the curve crosses the Z' axe at high frequencies (sometimes exhibiting a semi-circle because of the contact resistance involved between the current collector and the active material). A transition region is also observed at medium frequencies with a curve slope close to 45° corresponding to the ions transport into the porous network of the electrode. A knee frequency is estimated at the intersection between these middle frequency and low frequency regions.

Finally, it is also interesting to consider the capacitance as a complex capacitance with a real and imaginary part. From the formula of the impedance of a capacitance (no resistance), the capacitance $C(\omega)$ can be written as a function of Z' , Z'' and the impedance modulus $|Z(\omega)|$, giving :

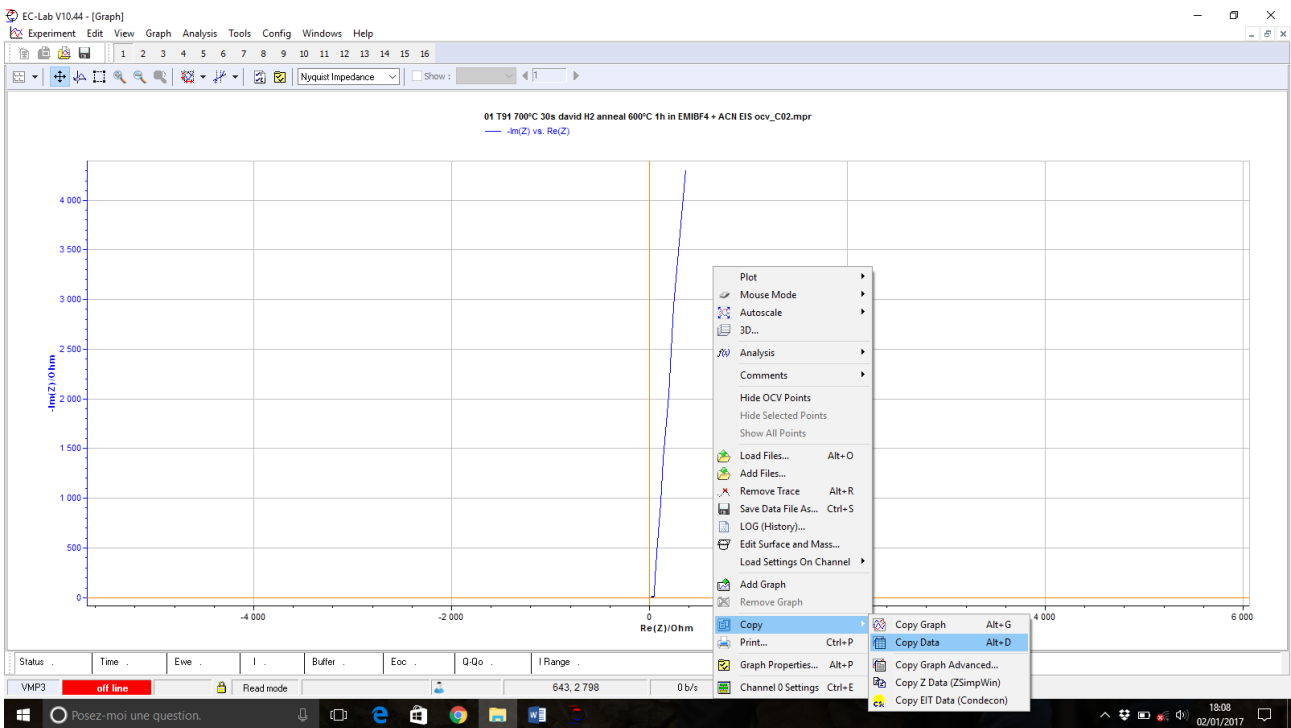
$$C(\omega) = C'(\omega) + C''(\omega)$$

With

$$C'(\omega) = \frac{-Z''(\omega)}{\omega|Z(\omega)|^2}$$

$$C''(\omega) = \frac{Z'(\omega)}{\omega|Z(\omega)|^2}$$

Thus the capacitance of the cell is given by C' at very low frequency. Another important value, the time constant τ of the cell, is estimated from the plot of C'' vs frequency as the inverse of the frequency at which C'' reaches a maximum. This constant is the time needed to deliver the energy with a 50% efficiency.



Technique	Cell characteristic
□ 1°) EIS	Cell resistance (ESR) =Ω.cm ⁻² Knee frequency =Hz Capacitance C' =mF.cm ⁻² Time constant τ =s

ANNEX

