Characterization of a LIG-based parallel-plate supercapacitor

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Abstract: *Several samples of graphene-based electrodes were fabricated by laser-irradiation. Laser power and scanning speed were optimized, in order to favor the formation of nanostructured LIG electrodes. The analysis is performed by SEM, Raman spectroscopy, cyclic voltammetry and galvanostatic charge-discharge. With these optimized parameters, a parallel-plate supercapacitor is built and specific capacitance measurements are performed. Values up to* $(48 \pm 3) mF/cm^{-2}$ *for the sqared samples and* $(2,72 \pm 0.13)\ mF/cm^{-2}$ *for the supercapacitor device were obtained.*

I. INTRODUCTION

Graphene is a 2-dimensional allotrop of carbon known for its ellectrical and mechanical properties. Laser-Induced Graphene (LIG) is a fast, cheap and flexible method to produce porous graphene, interesting for its use in supercapacitor applications [1].

Supercapacitors differ from other types of capacitors for having a capacitance much higher than other capacitors, and let us dispense energy very fast for a short period of time. They use electrodes with high surface area separated by electrolytic dielectrics in order to do so [2].

In this study we will explore the LIG method to produce supercapacitors. A polyimide (PI) in form of Kapton film is irradiated by a CO_2 laser and is converted into a graphene compound.

We will focus the study on the synthesis of square electrodes by LIG by different values of the laser power and the laser scan rate. Then, the different samples will be analyzed by its bulk resistance, Raman spectroscopy, Scanning Electron Microscopy (SEM) and electrochemical characterization (cyclic voltammetry and charge-discharge cycles). After this analysis, optimum laser power and scan rate values are selected in order to apply in the fabrication of the supercapacitor device, and then proceed to the electrochemical analysis for the device determining the final specific capacity.

The experimentation will then consist of:

1. Fabrication of the square samples.
2. Characterization of the samples (Raman, SEM, CV, Charge-Discharge).
3. Selection of the optimized parammeters.
4. Fabrication of the supercapacitor device.
5. Characterization of the final device.

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II. EXPERIMENTAL PART

Before the fabrication of the supercapacitor, we are interested in fabricating the best graphene possible and maximizing the specific capacitance of the material. To do so, we are interested in studying the porosity of the LIG fabricated, as well as the number of layers and the number of defects present in the graphene structure. We also want to determine the capacitance of the electrodes.

We will use the SEM imaging to study the porosity of the material. With this method we can obtain a very good quality image with information about the topology of the sample.

In order to determine the density of defects and layer number of the graphene films, we can use Raman spectroscopy. This technique uses monochromatic light from a laser to get structural and chemical information of the sample. [3, 4]For the graphene, we get three main peaks in the spectra: the D band (around 1350 cm^{-1}), the G band (around 1580 cm^{-1}) and the 2D band (around 2700 cm^{-1}). The ratio between the intensity of the G band and the D band $\frac{I_G}{I_D}$ gives us information of the defects of the sample, and the ratio between the 2D and G bands $\frac{I_{2D}}{I_G}$ gives us information of the number of graphene layers [5].

Finally, we will perform an electrochemical characterization of the samples in order to determine the capacitance of the graphene samples by two methods: cyclic voltammetry (CV) and charge-discharge cycles. Three electrode configuration was used, with $Ag/AgCl$ $(3MKCl)$ as the reference electrode, Pt ring as the counter electrode and the LIG sample as the working electrode. For the complete device a two-electrode cell was used in a sandwich-like configuration using a quartz filter paper soaked in the electrolyte solution as the separator between two LIG electrodes. Cyclic voltammetry consists of measuring the current generated by a variable voltage. In our case, a positive voltage is applied until it

reaches 0.8V, and then decreases to 0V again. We can calculate the capacity through the formula:

$$C = \frac{Q}{\Delta V}, \tag{1}$$

The electric charge can be calculated from the area enclosed in the CV graph, and ΔV is the total potential window. We can also divide by the area of the sample to obtain the specific capacity.

$$C_S = \frac{\int I(V)dV}{\nu\ A\ \Delta V}, \tag{2}$$

Where we introduced $Q = \int \frac{I(V)}{\nu} dV$ and ν is now the voltage scan rate. We get the specific capacitance in units of $F\ cm^{-2}$. For our experiment we will have a scan rate of $2mV/s$, and a $1,6V$ potential window.

A. Fabrication of the graphene samples

For the fabrication of the graphene we are going to use a CO_2 K40 laser engraver, provided by the FEMAN laboratory of the UB. This laser has a maximum power of 40W, but the range of powers we can use for LIG is much narrower. If we use low power, it will not be enough to transform the PI into graphene, and if we use a high power we can burn the sample. 9 to 12% power (3,6 to 4,8 watts) is the range in which we will work.

We will make the design of the samples in a vector graphic format using the Inkscape program, and then pass it to the native software of the device, the K40 Whisperer, which will transform the file into numerical commands intelligible by the laser.

III. RESULTS AND DISCUSSION

Now we are going to discuss the details of the experimentation and its results.

A. First squared graphene samples and characterization

As mentioned before, there are mainly two parameters to tune when fabricating graphene by LIG; the laser scanning speed and the power. We are going to prepare samples at two different powers, 10% and 11% (4.0W and 4.4W), and at different scanning speeds for each. These are the prepared samples, with a size of 15x15mm each. We also added the bulk resistance value for each sample. The resistance measurement was taken with a multimeter, between the corners of the sample. This values are shown on Table I.

This resistance measurement serves as a first analysis, to see which samples are conductive and which are not. For example, sample number 5 gave a very high resistance value, in the order of $M\Omega$, as did sample number 6. The reason is different in the two samples: in sample 5 the speed was too high for that power and the polyimide was not evenly transformed into graphene, while in sample 6 the speed was too slow for that power and the sample burned.

TABLE I: Prepared samples, with laser power and scanning speed for each one

#	%Power	Scan. Speed ($mm\ s^{-1}$)	Resistance (Ω)
1	10	50	82
2	10	80	36
3	10	100	33
4	10	150	85
5	10	200	.....
6	11	100	.....
7	11	150	28
8	11	200	42

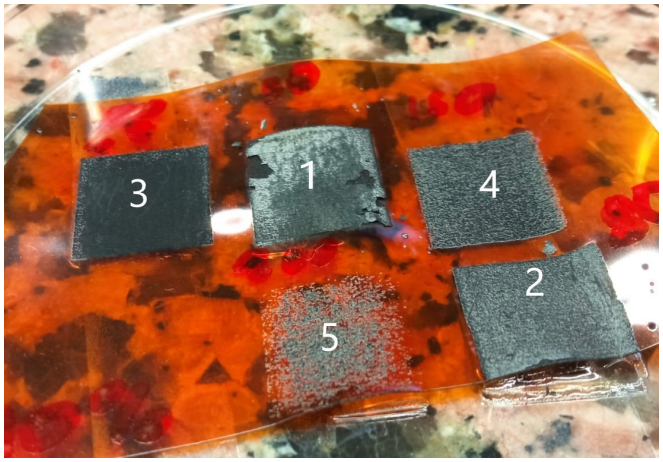
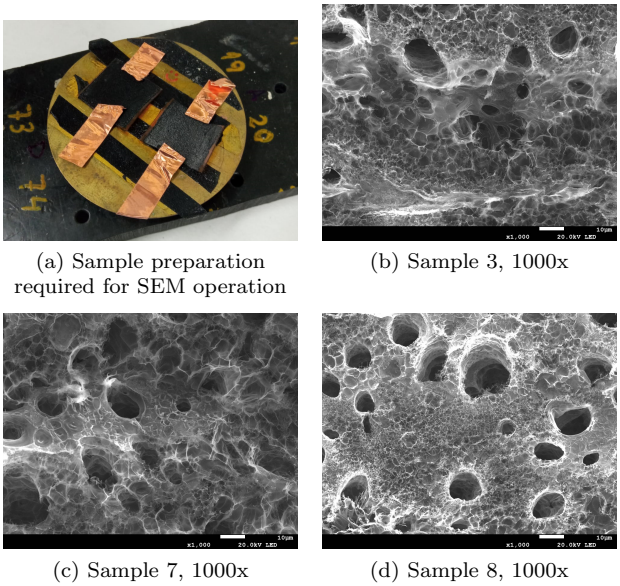


FIG. 1: Examples of some of the samples obtained for characterization. The numbers refer to Table. I

1. *SEM Imaging*

The first step we have done in the characterization is imaging by scanning electron microscope (SEM). Scanning electron microscopy provides us with topological information about the sample, in particular about its porosity, which is interesting in terms of sample capacity and charge storage. We used the microscope available at CCiTUB, and took images for the samples 3, 7 and 8; each one at 100x, 1000x and 5000x. In order to analyze the samples, we first need to prepare the for the



(a) Sample preparation required for SEM operation

(b) Sample 3, 1000x

(c) Sample 7, 1000x

(d) Sample 8, 1000x

FIG. 2: SEM images at 1000x for the samples 3, 7 and 8. We can appreciate the porosity of the LIG.

microscope, connecting them to the substrate with some copper tape. We can see the final assembly as well as some of the results in the Fig. 2.

2. *Raman spectroscopy*

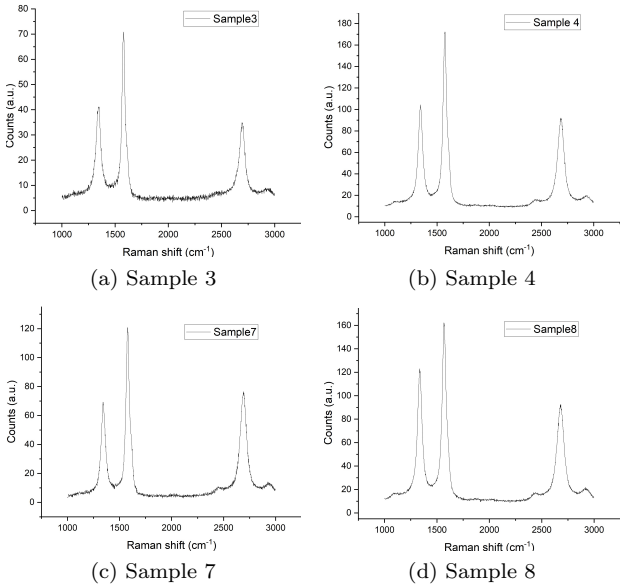
The next step will be the analysis of the samples by Raman spectroscopy. Specifically, we will use a 532nm laser at 50% power, provided by the CCiTUB facilities. In Raman spectroscopy, we can obtain structural information of graphene from the ratio between peaks, the position of the peaks, and the full width at half maximum (FWHM). We will analyze the ratio between the D and the G peak, which shows the number of defects in the sample, and the ratio between the 2D peak and the G peak, which gives us information of the number of graphene layers [4].

We are going to analyze 7 of the previous samples: Samples 1, 2, 3, 4, 7 and 8 referring to the numbering used in the Table I. On the following Table II you can see the ratio $\frac{I_G}{I_D}$ and the ratio $\frac{I_{2D}}{I_G}$ for each one of the samples. The uncertainty referred to the determination of the maximum in the spectrum is reflected as an uncertainty in the ratios between peaks in the Table II.

We could use previous work on Raman spectroscopy on graphene to estimate the number of layers present in the sample [5]. We can estimate our graphene samples in the range of 5-10 layers in this way, and with a more than acceptable level of defects.

TABLE II: Results of the Raman spectroscopy, ratios between the 3 main peaks of LIG-based graphene.

#	$\frac{I_G}{I_D}$	$\frac{I_{2D}}{I_G}$
1	1.87 ± 0.14	0.54 ± 0.04
2	1.50 ± 0.09	0.51 ± 0.04
3	1.72 ± 0.13	0.49 ± 0.04
4	1.65 ± 0.08	0.53 ± 0.03
7	1.74 ± 0.11	0.63 ± 0.04
8	1.32 ± 0.06	0.57 ± 0.03



(a) Sample 3

(b) Sample 4

(c) Sample 7

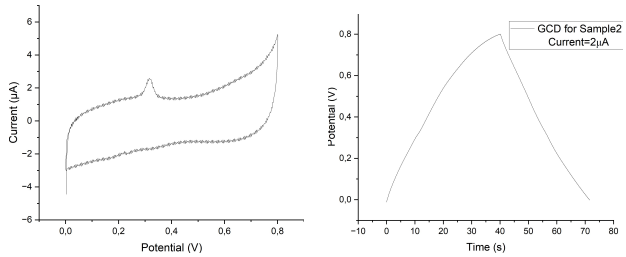
(d) Sample 8

FIG. 3: Raman spectroscopy spectra for the samples 2, 3, 7 and 8. We can see the main peaks for LIG graphene. Y axis is on arbitrary units.

3. *Electrochemical characterization*

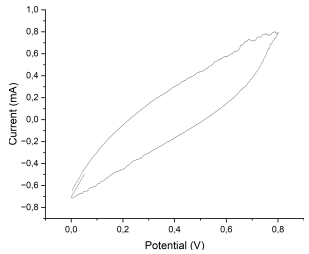
For the electrochemical characterization section we will perform two types of measurements: Cyclic Voltammetry (CV) and Galvanostatic Charge-Discharge (GCD). For this purpose, we will perform an assembly with an aqueous electrolyte solution, in our case $1MNaSO_4$.

The CV will consist on a measuring for the current for a cycled potential between two values $(0 - 0.8V)$, while the GCD consists of measuring the potential difference while applying a continuous current, so we can calculate the total charge of the graphene and therefore the capacitance of it. We performed this process for three of the samples, sample 2, sample 3 and sample 7. Samples 3 and 7 were very deteriorated due to the previous analysis and the preparation of several mounts with them, so it was decided to prepare new samples, this time larger (25 mm). These new samples gave in turn very good capacity results, close to those of some papers [6, 7]. Sample 2,

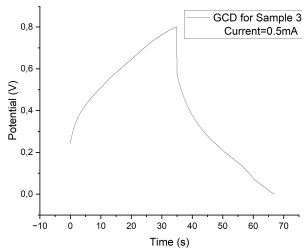


(a) CV for sample 2. Potential in V and Current in μA

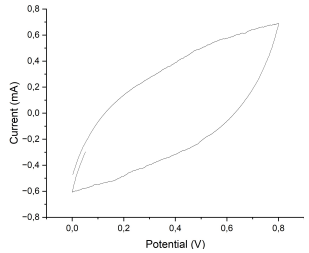
(b) GCD for sample 2. Current applied $2\mu A$



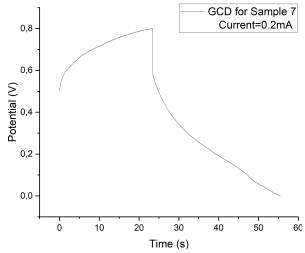
(c) CV for sample 3. Potential in V and Current in mA



(d) GCD for sample 3. Current applied $0.5mA$



(e) CV for sample 7. Potential in V and Current in mA



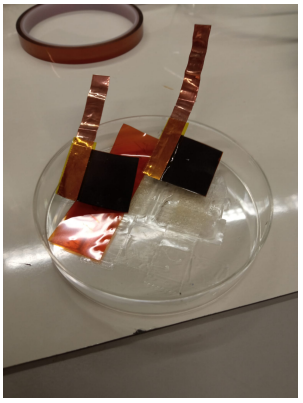
(f) GCD for sample 7. Current applied $0.2mA$

FIG. 4: CV and GCD graphs for samples 2, 3 and 7. We can see the GCD gave us some trouble on some of the samples.

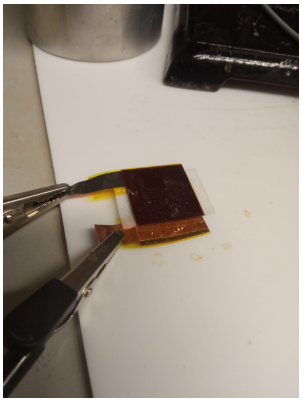
on the other hand, gives much worse results than these two samples, perhaps due to deterioration of the sample after previous analyses. You can also see in the Raman a higher amount of defects than in the other samples due to the lower I_G/I_D ratio. It can also be seen in the CV cycle that there is a small anomaly in this sample around 0.35V, another factor that shows the existence of impurities or defects. The sample area in the Table III is measured as the part of the sample that is in contact with the aqueous electrolyte solution.

TABLE III: Results of the calculation of the specific capacitance for the squared samples.

#	*Sample area*(cm^{-2})	$C_S(mF/cm^{-2})$
2	0.85 ± 0.08	0.80 ± 0.10
3	3.8 ± 0.2	48 ± 3
7	3.8 ± 0.2	41 ± 2



(a) LIG electrodes used in the construction of the supercapacitor.



(b) Final supercapacitor device

FIG. 5: Fabrication of the electrodes and the final supercapacitor device.

B. Construction and characterization of the supercapacitor device.

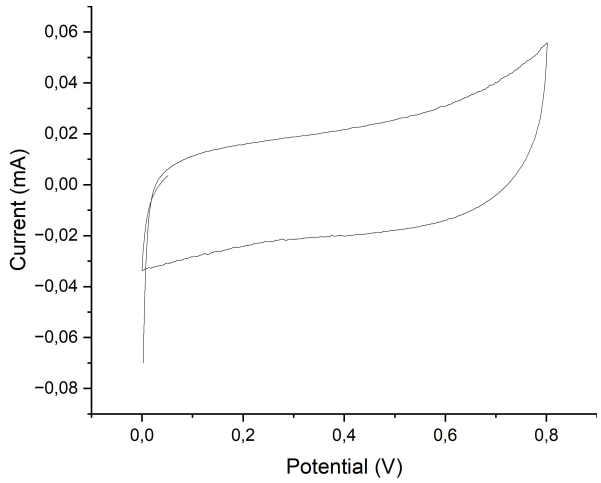
Now that we have characterized all the samples, we are in position for the construction of a parallel-plate supercapacitor using what we have done in the previous section.

For this purpose, we are going to build two electrodes using LIG, of 25mm each, based on sample number 7. This means that we will use 11% laser power and a scanning speed of $150mms^{-1}$. This sample has been chosen because it gives a good combination of results: good porosity index in SEM images, low level of defects and number of layers according to Raman spectroscopy measurements, and a high specific capacity calculated by electrochemical measurements. We could have also relied on sample number 3, which gave fairly similar results.

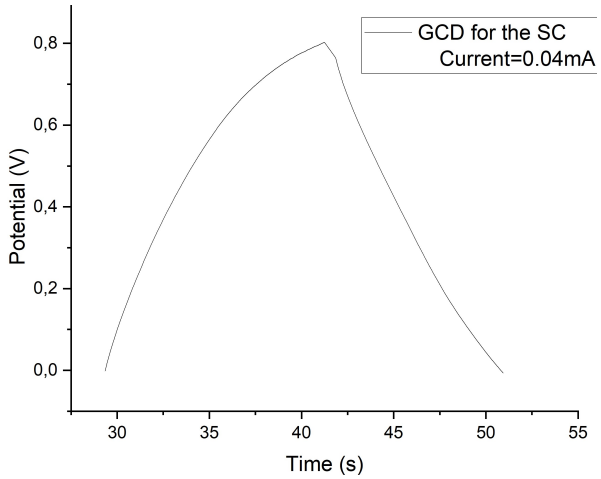
Once the electrodes have been manufactured, we will assemble the capacitor, applying copper tape to both in order to make the connections. In addition, we will place a quartz filter paper in between the electrodes, soaked in the aqueous electrolyte solution, which acts as a separator. We can see the electrodes and the final montage of the supercapacitor device on Fig. 5.

The next step is the electrochemical characterization of the supercapacitor. Analogously to the previous section, we will make the CV and GCD curves in order to calculate the specific capacitance of the supercapacitor. We can see the curves finally obtained for the device in Fig. 6.

We got a final specific capacitance for the supercapacitor of $(2,72 \pm 0.13)\ mF/cm^{-2}$. It is a good capaci-



(a) CV for the supercapacitor.



(b) GCD for the supercapacitor. Current applied $0.04mA$

FIG. 6: CV and GCD curves for the final supercapacitor device.

tance, but not in the $10 - 20\ mF/cm^{-2}$ specific capacitance range expected from the capacitance we got for the squared samples and previous papers [6, 7].

IV. CONCLUSIONS

- We have successfully fabricated multilayer graphene by LIG. We have analyzed the samples by Scanning Electron Microscopy (SEM), Raman spectroscopy measurements and calculated the specific capacitance of the fabricated graphene by electrochemical characterization measurements.
- Through this analysis we determined that the best samples were obtained for 11% laser power and 150 $mm\ s^{-1}$ scanning speed, or 10% power and 100 $mm\ s^{-1}$ scanning speed. We obtained good results for capacitance, comparable to those reported in the literature.
- We were able to fabricate a functional supercapacitor using electrodes fabricated by LIG. We obtained with it an acceptable capacity, although somewhat lower than expected.
- The fabrication process of the device could be improved and better values for the capacity could be tried to be obtained, but in any case it is demonstrated that the LIG is a good method for the fabrication of reliable multilayer graphene, with few resources and in a functional and fast way.

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