DOI: 10.24996/ ijs.2017.58.4A.7

Iraqi Journal of Science

ISSN: 0067-2904

Manufacture of Graphene-based Supercapacitors

Hend Kadhim Abdul-Rassol*, Adi Mahmoud Abdul-Hussein
Applied Physics Division, Applied Science Department, University of Technology, Baghdad, Iraq.

Abstract

A graphene-based supercapacitors (SC) were manufactured. The main objective of this research was to use as possible as environmentally, clean and natural materials for the SC electrodes, electrolytes and the separators. The SC consisted of a multi-layer graphene (MLG); as the electrode material, prepared by mixing graphene powder with water/acetone mixture, then the solution deposited on metal foils (aluminum and copper) by chemical spray technique, which is a simple and inexpensive technique to prepare the MLG films. The spraying time was (2 and 4 minutes) for making two MLG films with different thicknesses. The electrolytes were used is (lemon juice, table salt dissolved in water, and distillated water). The separators were a commercial materials; PTFE polymer and cellulose based parchment paper (PP), as these separators are commercial their dielectric constant was calculated. The thickness of the deposited MLG, the Al and Cu foils, and the separators was measured by optical microscope. The assembled SC was tested and measured the capacitance by LCR meter, the voltage across its electrodes was measured by digital multi-meter, the structural properties were tested by X-ray diffraction (XRD) for the MLG deposited on Al and Cu foils.

Keywords: Multi-layer graphene, Supercapacitors, Chemical spray technique.

تصنيع مكثفات فائقة بأقطاب من الكرافين

هند كاظم عبد الرسول*، عدي محمود عبد الحسين
فرع الفيزياء التطبيقية، قسم العلوم التطبيقية، الجامعة التكنولوجية، بغداد، العراق.

الخلاصة

تم تصنيع مكثفات فائقة ذات اقطاب من الكرافين. حيث كان الهدف الرئيسي من البحث هو استخدام مواد نظيفة صديقة للبيئة وطبيعية على قدر الامكان لأقطاب المتسعات الفائقة، الالكترولايت و المادة العازلة. تألفت هذه المكثفات من الكرافين متعدد–الطبقات (كمادة القطب)، حيث تم تحضيرها بخلط مسحوق الكرافين مع محلول من الماء المقطر والأسيتون، ومن ثم تم ترسيبه على رقائق معدنية من الألمنيوم والنحاس بواسطة تقنية الرش الكيميائي، وهي تقنية سهلة ورخيصة لتحضير رقائق الكرافين متعدد–الطبقات. وقت الرش كان (2 و 4 دقائق) للحصول على الكرافين متعدد–الطبقات بسمكين مختلفين. محاليل الالكتروليت المستخدمة هي (عصير الليمون، ملح الطعام المذاب في الماء، و الماء المقطر). وتم استخدام مواد عازلة وهي (بوليمر التفلون، وورق سيليلوزي)، وحيث ان هذه المواد هي مواد تجارية تم حساب ثابت العزل (السماحية النسبية) لكلٍ منها. تم قياس سمك الكرافين–متعدد الطبقات، رقائق الالمنيوم والنحاس، والمواد العازلة بواسطة المجهر البصري. تم اختبار المتسعات الفائقة اللوحية وقياس السعة لكل منها بواسطة مقياس (LCR)، قياس فرق الجهد بين لوحيها

*Email: h30.hend@gmail.com

بواسطة فولتميتر رقمي، و الخصائص التركيبية لطبقة الكرافين متعدد–الطبقات المرسبة على رقائق الالمنيوم والنحاس تم أختبارها بواسطة جهاز حيود الاشعة السينية (XRD).

Introduction

A massive amounts of energy is required in today's world, with the need of storing and delivering it at any time. Facing the excessive comprehensive use of fossil fuels with the finite access to them in the future, and the world's increasing energy demand, there is growing concerns for the development of clean portable energy storage devices.

Supercapacitors (SC) are now in the front line of electrochemical energy storage systems owing to their high power density and long life-time, therefore they are favorable for many applications. They also can be used to supplement batteries to extend the battery's life-time. However, due to their high costs; the use of SC is still limited, most commercially available SC contain expensive electrolytes and costly electrode materials [1].

Among the various electrode materials for SC, *graphene* has stand out. Since the first extraction of graphene material from graphite by K. Novoselov and A. Geim [2] via a micro-mechanical exfoliation (MME) method; in 2004, graphene has drawn great attention, due to its distinctive structure, outstanding properties and the fact that it is the thinnest material ever created by scientists.

Graphene is a single layer of carbon atoms packed in 2-D honeycomb lattice with atomic distance of (1.42 Å) [3], exhibit exceptionally remarkable physical properties like high electrical conductivity ($10^6\ \Omega^{-1}cm^{-1}$) [4], high intrinsic mobility limit of ($2\times10^5\ cm^2v^{-1}s^{-1}$) [5]. More importantly, the specific surface area (SSA) of graphene is theoretically up to ($2675\ m^2g^{-1}$), the intrinsic capacitance of graphene is ($21\mu F.cm^{-2}$), and its reasonable chemical stability made graphene a distinguished candidate for applications in flexible and stretchable electrode or SC [6].

The total performance of the SC substantially depends on all their cell components combined together, which is: the electrolytes, electrodes, separators and current collectors (CC). The capacitance, energy and power density of the SC are directly associated to the chemical and physical properties of the electrodes. The dielectric properties, conductivity of the electrodes, the breakdown voltage are responsible for SC energy density, power density. While the separator is responsible for preventing short-circuiting between the cathode and anode, also in charge of ions diffusion back and forth between the electrodes [7].

Experimental work

1. Solution Preparation

The solution required in the deposition process was prepared by adding (0.5gm) graphene powder in water/acetone mixture of (30ml) water and (140ml) acetone, and mixing the resulted solution in magnetic stirrer for 30 minutes, then it was put in ultrasonic cleaner for 3 hours to disperse the graphene particles in the solution; to obtain a stable dispersed solution.

2. Chemical Spray System

The chemical spray technique was used in preparing the films of MLG deposited on thin Cu and Al foils. Figure-1 shown the chemical spray system, where the whole system in the present work is homemade; which composed of the following parts:

1. Circular disc of Al, for placing the substrates or the samples.
2. Nozzle.
3. Solution bottle.
4. Tube connected to a compressor.
5. On/Off switch for the motor.
6. Motor, its speed (3 rpm).

Figure 1- The chemical spray system

3. Deposition Process:

The Al and Cu foils had been cleaned by distilled water for removing any dust or impurities that may be attached to it, then dried by cleaning paper preparing them for deposition. After preparation, the solution was placed in the bottle of the nozzle and the first foil was placed on the circular disc. The distance between the nozzle aperture and the disc was fixed to be (15 cm). After all these steps were done, starting the motor that circulates the circular disc, then solution was sprayed in vertical direction while the disc spinning, and making sure the droplets of the solution is falling in regular manner on the foil surface.

Four foils were prepared; two Cu foils and two Al. The spraying time of one Cu foil and one Al was fixed to be (2 min), the other two foils the deposition time was (4 min); for making two different thicknesses. After finishing the deposition the foils left to dry.

The thickness of the deposited layer of MLG were measured by optical microscope, the thickness of the separators and the Al and Cu foils were also measured. The structural properties of the MLG were tested by X-ray diffraction (XRD), the XRD spectra measurements have been done according to the JCPDS card (Joint Committee on Powder Diffraction Standards).

4. Supercapacitors Assembly:

The deposited foils were cut into (8.5cm×2.5cm dimensions) and gluing them on glass slides (7.5cm×2.5cm); one centimeter left longer from one longitude side for connecting the electric clips for wiring, after removing the deposited layer as diagrammatically demonstrated in Figure-2.

Applying the electrolyte to the surface of the electrodes by cotton pad to add enough amount of the solutions. Then, place a larger piece of the separator (10cm×3cm) between the two electrodes to avoid any contact between them, and tape the final SC to test it.

The capacitance was measured by LCR meter for the tablet SC and the voltage across its electrodes measured by digital multimeter.

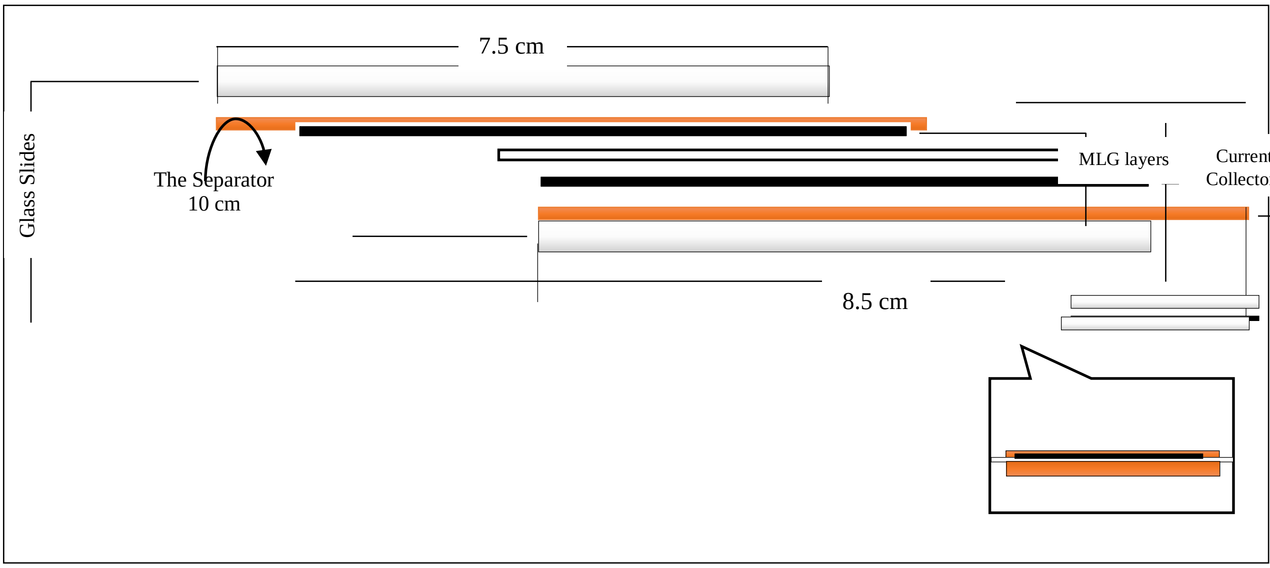

Figure 2- Illustrative image shows the parts of the assembled SC.

Results and discussion

1. Voltage measurements

The DC voltage across the electrodes of the assembled SC was measured by a digital multimeter as listed in Table -1.

Almost all the assembled SC had a good voltage readings (without charging it) despite its small dimensions. These measurements were done to figure out the best and most effective electrode and electrolyte as well as separator regarding their minimum voltages without charging.

Table 1- Voltage readings for the assembled SC.

Electrodes	**Separator**	**Voltage (mV)**		
		Lemon	Water & salt	Dis. water
Thin MLG on Al	PTFE	436	365	390
	PP	**625**	338	340
Thick MLG on Al	PTFE	128	31	75
	PP	85	33	127
Thin MLG on Cu	PTFE	334	432	192
	PP	208	380	310
Thick MLG on Cu	PTFE	63	250	196
	PP	**12**	223	73

2. LCR/ESR meter measurements:

In this research we used LCR/ESR meter (BK Precision 889B) to measure the capacitance of the assembled SC by differing the frequency; for various combination of electrode, electrolyte and separator materials, and make a chart comparison between the same electrodes/separator with different electrolyte solutions, and finding out the best material among them.

Now listing the capacitance vs frequency readings in Table-2, for each assembled SC and for all the possible combinations.

Table 2- LCR meter readings for the assembled SC.

Electrodes	CC	Separator	Electrolytes	Capacitance at 100Hz	Capacitance at 200kHz	Shown in figure
1.6 μm MLG	40 μm Al	PTFE	Lemon	1.6 μF	3.2 nF	Figure (3)
			Water & salt	1.2 μF	1.2 nF	
			Dis. water	**720.3 nF**	**849.2 pF**	
1.7 μm MLG	40 μm Al	PP	Lemon	15.8 μF	7.3 nF	Figure (3)
			Water & salt	1.4 μF	1.2 nF	
			Dis. water	1.4 μF	1.3 nF	
7.8 μm MLG (S.2)	40 μm Al	PTFE	Lemon	1.6 μF	4.4 nF	Figure-4
			Water & salt	2.5 μF	12.3 nF	
			Dis. water	1.2 μF	2.0 nF	
7.6 μm MLG	40 μm Al	PP	Lemon	5.2 μF	4.3 nF	Figure -4
			Water & salt	1.8 μF	7.9 nF	
			Dis. water	1.4 μF	3.1 nF	
1.4 μm MLG	36 μm Cu	PTFE	Lemon	3.4 μF	2.5 nF	Figure-5
			Water & salt	32.5 μF	231.8 nF	
			Dis. water	958.2 nF	858.4 pF	
1.5 μm MLG	36 μm Cu	PP	Lemon	7.1 μF	1.9 nF	Figure-5
			Water & salt	**235.1 μF**	**1.1 μF**	
			Dis. water	1.3 μF	1.3 nF	
11.5 μm MLG (S.1)	36 μm Cu	PTFE	Lemon	1.1 μF	1.8 nF	Figure-6
			Water & salt	3.1 μF	20.5 nF	
			Dis. water	2.8 μF	5.2 nF	
11.7 μm MLG	36 μm Cu	PP	Lemon	6.1 μF	4.4 nF	Figure-6
			Water & salt	10.6 μF	59.5 nF	
			Dis. water	3.5 μF	6.7 nF	

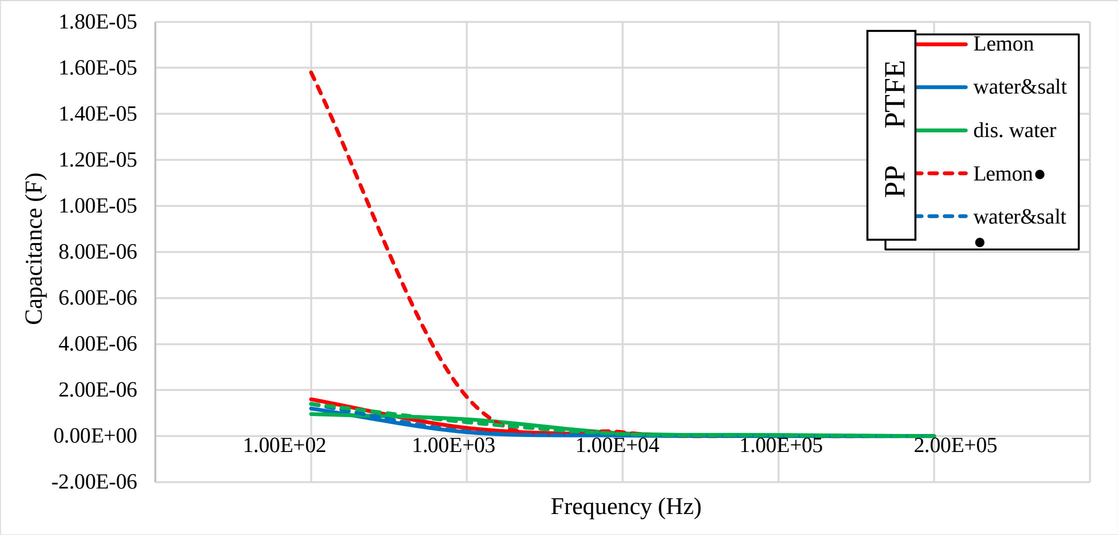

Figure 3-Cap. vs freq. readings for thin MLG deposited on Al, with PTFE and PP separators.

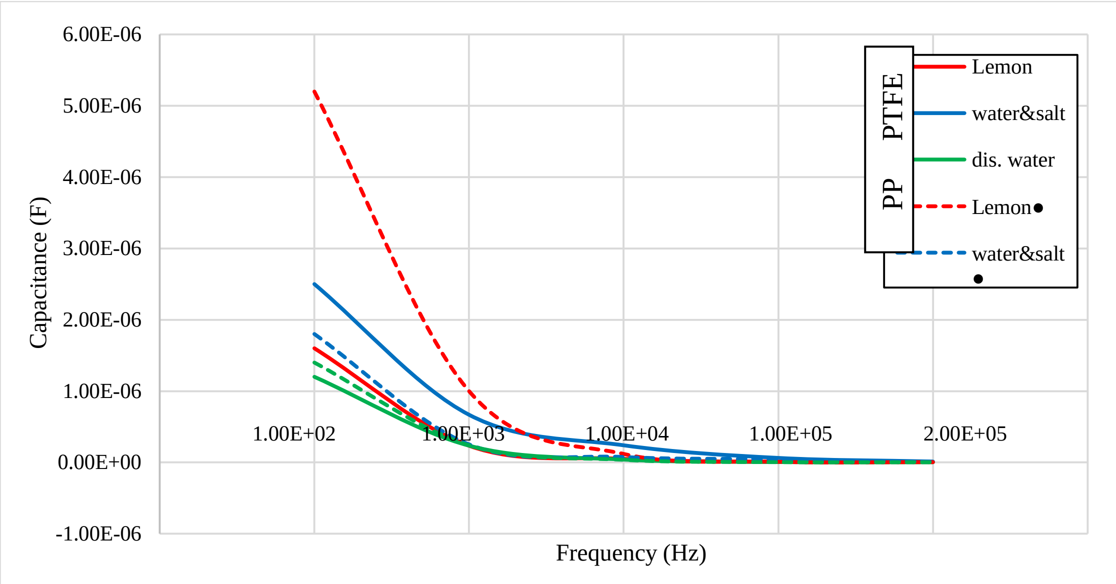

Figure 4-Cap. vs freq. readings for thick MLG deposited on Al, with PTFE and PP separators.

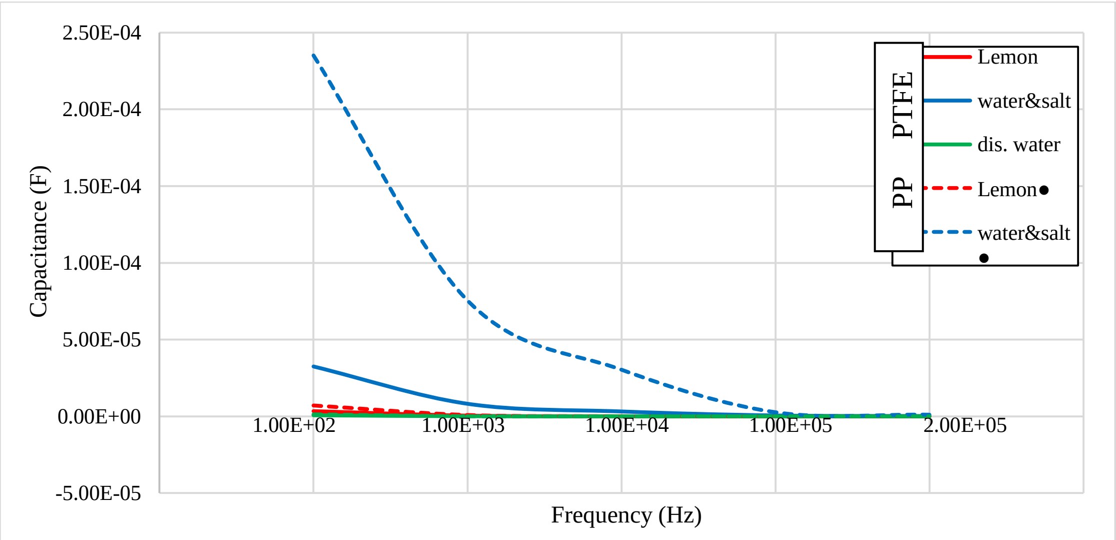

Figure 5- Cap. vs freq. readings for thin MLG deposited on Cu, with PTFE and PP separators.

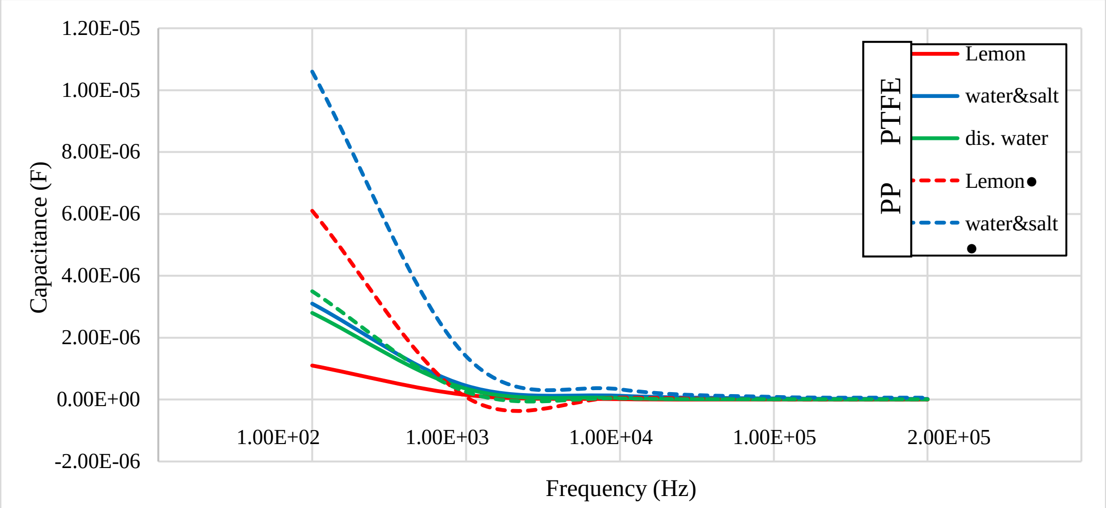

Figure 6- Cap. vs freq. readings for thick MLG deposited on Cu, with PTFE and PP separators.

***A*s a summary for the LCR capacitance readings and voltage measurements, we had:**

1. The highest capacitance was for thin layer of MLG deposited on thin Cu foil with water & salt electrolyte and PP separator.
2. Parchment paper is better separator than PTFE polymer for all the results, due to its higher dielectric constant as calculated.
3. MLG deposited on Cu foils are better than on Al foils, because Cu is a better electric connector than Al.
4. The thinner layer of MLG got the best results, due to the thinner MLG is approaching the properties of the single-layer graphene; which is the best.
5. The distilled water is the least effective electrolyte, because the only ions present is the H+ and OH- ions from the dissociation of H_2O and the ion formation is very low, and hence the conduction in solutions take place through ions therefore the only conduction happens due to the self-ionization of water.
6. The best was the water and salt mixture for the most combinations, because when sodium chloride (NaCl) is dissolved in water we find slightly H+ are attracted to Cl anions and slightly O- are attracted to Na cations. Anions and cations acts as charge carriers in solution. Subsequently, an aqueous NaCl solution will have dissolved ions that will conduct electricity which makes it a strong electrolytes.
7. Lemons contain acid that has both positive and negative ions, and serves as a reservoir for transferring electrons; to and from the electrodes. When two electrodes are suspended in the acidic lemon juice, the atomic structure of both the electrodes starts breaking, resulting in production of individual electrons. Both the electrodes are not in contact with each other and thus a flow of electrons is generated through the electrodes and electrolyte. That’s the reason why the lemon conduct electricity. But the NaCl dissolved in water is a better electrolyte because its higher ionization potential.
8. Lemon is better with MLG deposited on Al foils than on Cu foils. The lemon electrolyte wasn’t good with Cu foils, because it made a chemical oxidation with the reaction of oxygen, and formed a “patina” [which is an outer layer of copper oxide, that appears green in color], this layer of Cu oxide reduces the conductivity of the Cu, which made the reading containing those two a little bit lower than expected.

3. Relative Permittivity (Dielectric Constant) of the Separators:

The capacitance of the SC were measured by LCR meter, and by using equation.1 we calculated the dielectric constant of the PTFE and the PP separators [8]:

$$\boldsymbol{\varepsilon_r}' = {\boldsymbol{Ct}}/{\boldsymbol{\varepsilon_o A}} \quad \ldots\ldots\ldots\ldots \text{eq. 1}$$

- The dielectric constant $\boldsymbol{\varepsilon_r}'$ of ***PTFE polymer*** is: **2.22** at (100Hz).

- The dielectric constant $\varepsilon_r{}'$ of ***Parchment paper (PP)*** is: **4.03** at (100Hz).

4. X-Ray diffraction Analysis (for the deposited MLG):

The multi-layer graphene (MLG) deposited on Cu and Al foils by chemical spray system was characterized by X-Ray diffractometer, Figure- (7, 8) shows the XRD spectra for the samples (S.1 and S.2 shown in Table-2).

In Figure-7 for S.1; the (11.5 μm) MLG deposited on Cu foil, has the peak position corresponding to the (002) plan is almost identical to those in pristine graphite at (2θ = 26.49°) with interlayer distance (d =3.362Å). This suggests that the graphite lattice parameters persist and the crystalline structure is not destroyed and continued in the structure of the deposited MLG, but also; as a consequence, the intensity of the (002) peak is remarkably decreased compared to the pristine graphite, this reduction is associated with the interlayer distance; the graphite layers have separated due to the thermal exfoliation and subsequent sonication in acetone. Also the FWHM of the (002) peak is increased from 0.199° to 0.438° due to Scherrer broadening.

In addition, it has been known that the shock waves and shear force generated by ultra-sonication provoke cavitation bubbles, which can exfoliate pristine graphite into smaller and thinner flakes [9, 10].

The strong sharp peaks at (2θ = 43.56°, 50.3° and 73.92°) corresponding to (111), (200) and (220) plans of copper compared with the standard [JCPDS data card 04–0836] for copper [11].

Figure-8 XRD spectra for S.2, the MLG deposited on Al foil. The first peak at (2θ = 26.53°) with interlayer distance (d = 3.356Å) corresponding to (002) plan for MLG; having the same characterization of S.1.

Also observed that the intensity of the (002) peak for S.1 is slightly higher than the S.2, that's due to the thickness of the MLG deposited on the Al foil is thinner than the Cu foil; which is (7.8 μm and 11.5μm) respectively.

The four strong diffraction peaks at 2θ values of (38.38°, 45.23°, 65.39° and 78.62°) are characteristic of metallic aluminum [JCPDS no. 89-4037] [12].

The average crystalline size and the number of the layers calculated from equations (eq.2) and (eq.3) listed in the Table-3 [13], with results obtained from the XRD analysis.

$$D_g = \frac{K\lambda}{\beta\cos\theta} \quad \ldots\ldots\ldots\ldots \text{eq.2}$$

$$N = D_{g(hkl)}/d_{hkl} \quad \ldots\ldots\ldots\ldots \text{eq.3}$$

Table 3- The results obtained from the XRD analysis for S.1 and S.2.

Slide no.	(*hkl*) plan	2θ (deg.)	FWHM (deg.)	d (Å)	Dg (nm)	N*hkl*
S.1	G (002)	26.49	0.438	3.363	18.633	55.401
S.2	G (002)	26.53	0.472	3.356	17.292	51.527

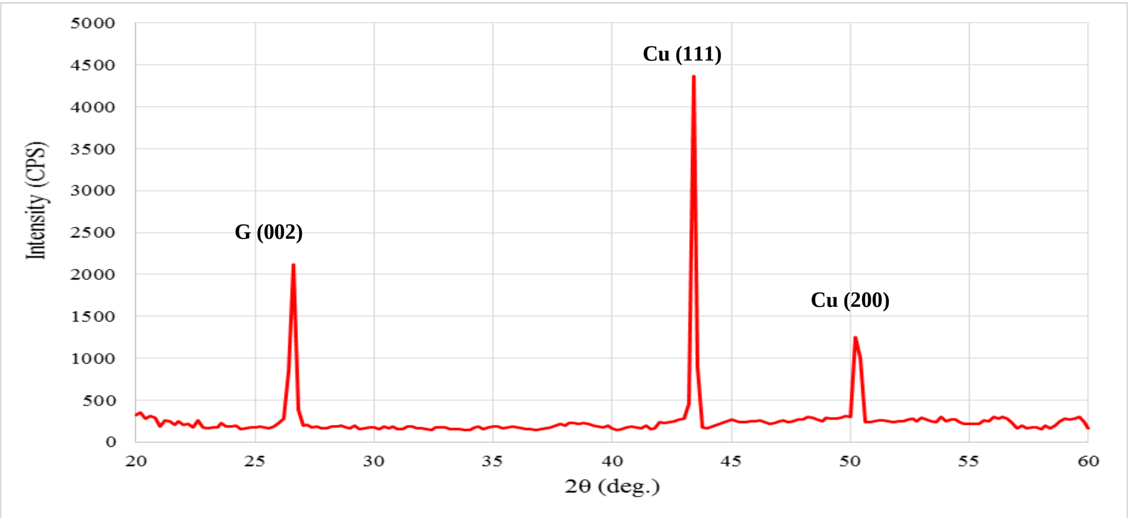

Figure 7- XRD spectra of S.1.

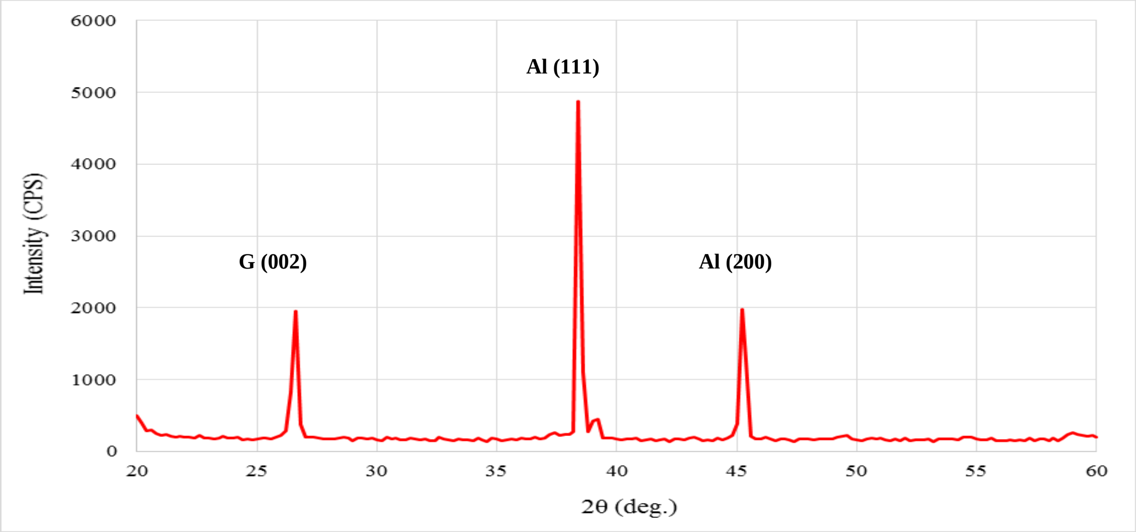

Figure 8-XRD spectra of S.2.

Conclusions

We can summarize the main conclusions to these remarked points:

1. The preparation of the solution (graphene + water/acetone) by mixing and ultra-sonicating gave a high dispersive and stable solution that worked very effectively in the chemical spray system which led to give a high regular, coordinator and smooth layer of MLG.
2. The capacitance results for the assembled SC had its maximum reading at (100Hz) with (235.1 μF) for the thin (1.5 μm) MLG deposited on thin Cu foil, with parchment paper separator and water and salt electrolyte. This reading is considered a very good capacitance reading considering the small dimensions of the SC.
3. The thinner the layer of MLG had better results because as the thickness decreasing; its properties became closer to those of single layer graphene.
4. An obvious results we had: A) The water and salt as the best electrolyte due to its high ionization potential. B) The parchment paper is better separator than PTFE due to its higher dielectric constant [as calculated]. C) The Cu is better than Al as current collectors due to its higher conductivity.
5. The crystallites size calculated by Sherrer equation from XRD spectra analysis for the MLG was (18.633nm) and (17.292nm), and the number of layers are (55.401) and (51.527) respectively.

References

1. Tarascon, J. M. and Armand, M. **2001**. Issues and challenges facing rechargeable lithium batteries. *Nature*, **414**: 359-67.
2. Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., and Firsov, A. A. **2004**. Electric Field Effect in Atomically Thin Carbon Films. *Science*, **306**(5696): 666–669.
3. Cooper, D. R., Benjamin, D., Ghattamaneni, N., Harack, B., Hilke, M., Horth, A., Majlis, N., Massicotte, M., Whiteway, E., Yu, V., and Vandsburger, L. **2012**. Experimental Review of Graphene. *ISRN Condensed Matter Physics: International Scholarly Research Network*, Article ID 501686, 56 pages.
4. Rani, L. and Singh, N. **2017**. Dynamical electrical conductivity of graphene. *Journal of Physics: Condensed Matter*, **29**(25).
5. Chen, J., Jang, C., Xiao, S., Ishigami, M., and Fuhrer M. S. 2008. Intrinsic and extrinsic performance limits of graphene devices on SiO2. *Nature Nanotechnology*, **3**: 206 – 209.
6. Ke, Q. and Wang, J. **2016**. Graphene-based materials for supercapacitor electrodes – A review. *Journal of Materiomics*, **2**(1): 37–54.
7. Hall, P. J. and Bain, E. J. **2008**. Energy-storage technologies and electricity generation. *Energy Policy*, **36**: 4352-4355.

8. Kasap, S. O. **2006**. *Principles of Electronic Materials and Devices*. 3rd ed. New York. McGraw-Hill©.

9. Yi, M., Shen, Z., Zhang, X., and Ma, S. **2013**. Achieving concentrated graphene dispersions in water/acetone mixtures by the strategy of tailoring Hansen solubility parameters." *Journal of Physics D: Applied Physics*, **46**(025301): 9pp.

10. Alam, S.N., Kumar, L. and Sharma, N. **2015**. Development of Cu-Exfoliated Graphite Nanoplatelets (xGnP) Metal Matrix Composite by Powder Metallurgy Route. *Graphene*, **4**: 91-111.

11. Theivasanthi, T. and Alagar, M. **2010**. X-Ray Diffraction Studies of Copper Nanopowder. *Archives of physics research*, **1**(2): 112-117.

12. Lei, X. and Ma, J. **2010**. Synthesis and Electrochemical Performance of Aluminum Based Composites. *Journal of the Brazilian Chemical Society*, **21**(2): 209-213.

13. Cullity, B. D. **1978**. *Elements of X-ray diffraction*. 2nd ed. Boston US. Addison-Wesley. 555 pages.