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Graphite Paper-based Device for Energy Storage Application

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Graphite Paper-based Device for Energy Storage Application

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Abstract. The demand for versatile flexible energy storage device has arisen due to their potential, application in wearable and portable electronic product. This study presents the characterization of graphite paper-based capacitor and supercapacitor that are produced utilising commercially available pencils to draw a design by developing cheap, green, and reliable low profile electrical electrodes. The objectives of this study are to design graphite paper-based electrodes for energy storage application, characterize the physical properties of the electrodes and electrical properties of the device. Material characterization have been performed including morphology analysis of the electrodes using field emission scanning electron microscope (FESEM), compositional structures by using Energy dispersive X-ray spectroscopy (EDX) and chemical properties of the graphitic electrodes using Raman spectroscopy. Next, the electrical performance of the pencil drawn capacitor and supercapacitor have been performed. It is found that the Acidic G/PANI-Paper supercapacitor sample shows the best electrical performance in terms of lowest resistance with 0.59 MΩ, 1.12 MΩ, 1.8 MΩ and highest capacitance with 27.5 μF, 38.1 μF, 55.25 μF for respective 6 cm^2, 8 cm^2 and 10 cm^2 area size. These characteristics show that the graphite-paper based device has a great potential in flexible energy storage applications.

1. Introduction

The present trends indicate that the need for energy storage will increase with high production and demand, necessitating energy storage for many days or weeks or even months in the future. Next, the increasing awareness of nature for taking advantage of energy, various sources of energy were identified and put to versatile uses [1]. The demand for energy storage applications has increased to optimize cost, efficiency, reliability, and lifetime whilst meeting the performance requirements of the application. Besides, the industrial need for new energy technologies which provide clean and environmentally friendly solutions is also crucial to meet end user requirements and easier fabrication techniques for energy storage application.

An increasing demand for versatile flexible energy storage device also has arisen due to their potential, application in wearable and portable electronic product [2]. Cellulose is the most abundant biopolymer on Earth and has long been used as a sustainable building block of conventional paper [3]. Moreover, the advantages of cellulose or paper substrate are unexpensive and environmentally friendly, using simple fabrication techniques and promising candidates for the future of “green” and renewable electronics.

Paper now is the cheapest flexible substrate, and it has been widely used as an energy storage device [4-6]. Next, Carbon materials such as graphene could be absorbed into cellulose paper, rendering its conductivity and even electrochemical activity [1, 7]. Therefore, the main goal of this research is to study the characteristics and performance of the fabricated graphite paper-based device towards energy storage application, using capacitor and supercapacitor design structure.

2. Methodology

The steps involved in this study include preparation of the electrode using pencil drawing technique, material characterization, fabrication of the supercapacitor and analysis of graphite paper-based capacitor and supercapacitor electrical properties. Figure 1 illustrates the experimental process to fabricate the supercapacitor.

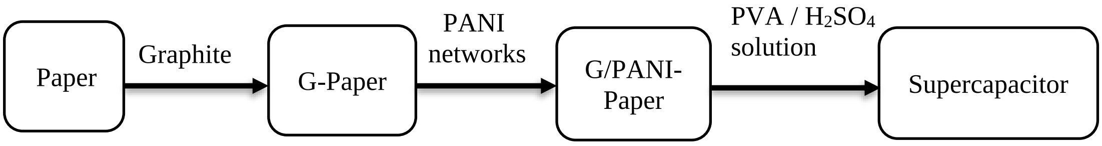
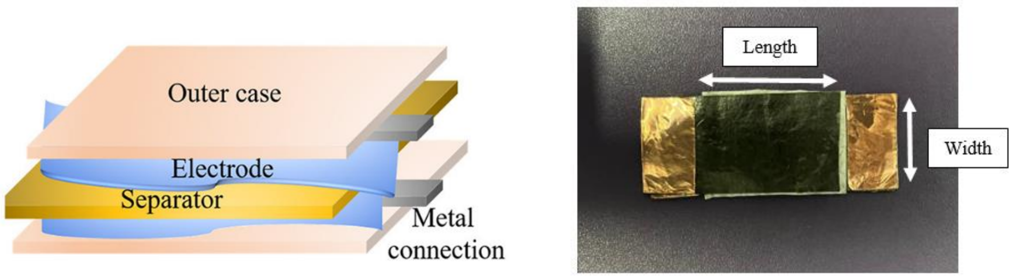


Figure 1. Experimental step of supercapacitor.

2.1. Device design structure

The solid-state structure of the capacitor and supercapacitor device consists of electrode, separator, metal connection and outer case as shown in Figure 2(a). Figure 2(b) shows an example of the assembled graphite paper-based device structure in this study.



(a) (b)

Figure 2. (a) Device structure and (b) Example of assembled sample.

Table 1 summarizes the elements of G-Paper capacitor and G/PANI-Paper supercapacitor samples in this study. The difference between the supercapacitor was the electrodes that were used to fabricate the devices. The cellulose membrane is used as a separator. The main function of a separator is to keep the two electrodes apart to prevent electrical short circuits while also allowing the transport of ionic charge carriers.

Table 1. Device structure's elements.

Device structure	G-Paper	G/PANI-Paper
Outer case	70 gsm A4 paper	70 gsm A4 paper
Electrode	G-Paper (Pencil drawing using Staedtler Mars Lumograph 8B Pencil)	- G/PANI (pencil drawing using 8B pencil followed by electrodeposition of PANI networks) - Acidic immersion mixture: PVA/ H_2SO_4 solution
Separator	Cellulose membrane	Cellulose membrane
Metal connection	Copper tape	Copper tape

The type of samples namely as G-Paper capacitor, Non-acidic G/PANI-Paper supercapacitor and Acidic G/PANI-Paper supercapacitor was designed by using the same width and varying the different length as shown in Table 2. Acidic and Non-acidic naming refers to treated or non-treated conditions for acidic immersion applied to the samples.

Table 2. Size of the samples.

Sample	Width (cm)	Length (cm)	Area (cm^2)
G-Paper 1	2	3	6
Non-acidic G/PANI-Paper 1	2	3	6
Acidic G/PANI-Paper 1	2	3	6
G-Paper 2	2	4	8
Non-acidic G/PANI-Paper 2	2	4	8
Acidic G/PANI-Paper 2	2	4	8
G-Paper 3	2	5	10
Non-acidic G/PANI-Paper 3	2	5	10
Acidic G/PANI-Paper 3	2	5	10

2.2. Formation of G-Paper and G/PANI-Paper
For the preparation of the G-paper electrode, a piece of A4 paper (70 gsm) was used. Then a common 8B pencil was used to draw on the A4 paper for forming a uniform graphite layer. Ruler guided drawing in orthogonal directions was repeated three times to form a stripe of uniform coating as shown in Figure 3. Basically, each pencil type with a different hardness has a different percentage of graphite. The lower percentage of graphite is the hardest [8].

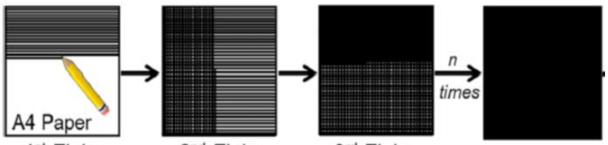


Figure 3. Pencil drawing method for the electrodes.

For the preparation of the G/PANI-paper electrode, a piece of standard A4 printing paper (70 gsm) was immersed in a 0.3 M hydrochloric acid (HCl) aqueous solution for about 10 min, then washed with deionized water thoroughly to eliminate any foaming compositions like carbonate and dried in a fume hood at room temperature. Then a common 8B pencil was used to draw on the acid-treated paper three times to form a uniform graphite layer. The PANI nanowire networks were synthesized by oxidation of 0.3 M aniline in 1 M HCl aqueous solution through a conventional two electrode system. The seeding layer of PANI was nucleated at a potential of 0.8 V and the PANI networks were grown under constant current density of 0.5 mA cm^{-2} for 10 min at room temperature.

For acidic immersion, Polyvinyl alcohol (PVA)/sulfuric acid (H_2SO_4) electrolyte was prepared by adding 6 g PVA power into 60 ml 1.0 M H_2SO_4 aqueous solution and into 60 ml deionized water. The entire mixture was heated to 85 °C with vigorous stirring until the solution became clear, then maintained at 85 °C for about 1 hour without stirring. After cooling down, two G-Paper and G/PANI-Paper electrodes were immersed into the PVA / H_2SO_4 electrolyte for 5 min and then were assembled into a supercapacitor by sandwiching a cellulose membrane as a separator between them. Then the devices were left in an electrical oven at 45 °C for about 4 h to vaporize the excess water.

2.3. Sample characterization
For material analysis, the samples were observed using Hitachi Field Emission Electron Microscopy - Energy Dispersive X-Ray Analysis (FESEM-EDX) and HORIBA Xplora Plus Raman microscope (source of visible light and 532 nm Nd Yag laser wavelength). For electrical analysis, measurement consists of capacitance value, resistance value and charging–discharging time.

3. Results and Discussion
The experimental results of the graphite paper-based capacitor and supercapacitor were analyzed and discussed as follows:

3.1. Raman Spectroscopy
The main features in the Raman spectra of carbons are called G and D peaks which corresponds to the edges and defects of the sp^2 domains as well as the E_{2g} mode for sp^2 carbon domains of graphite [9]. The 2D band is the second order of the D band, sometimes referred to as an overtone of the D band. The 1350 cm^{-1} band of graphite is known as the D band. The 1582 cm^{-1} band of graphite is known as the G band. The 2690 cm^{-1} band of graphite is known as the 2D band.

Based on spectra shown in Figure 4, it is found that the ratio of I_D/I_G is ranging between 0.12 to 0.21 while the ratio of the I_{2D}/I_G is from 0.42 to 0.64 for all samples. Thus, it can be predicted that carbon layer properties (from graphite pencil source) might composed the multi-layer graphene [10, 11]. Based on I_D/I_G and I_{2D}/I_G ratio, both agrees well with the concluded number of layers. The acidic treatment and PANI electrodeposition seem to be not able to change the carbon properties. The samples remained as multi-layer graphene based on this finding.

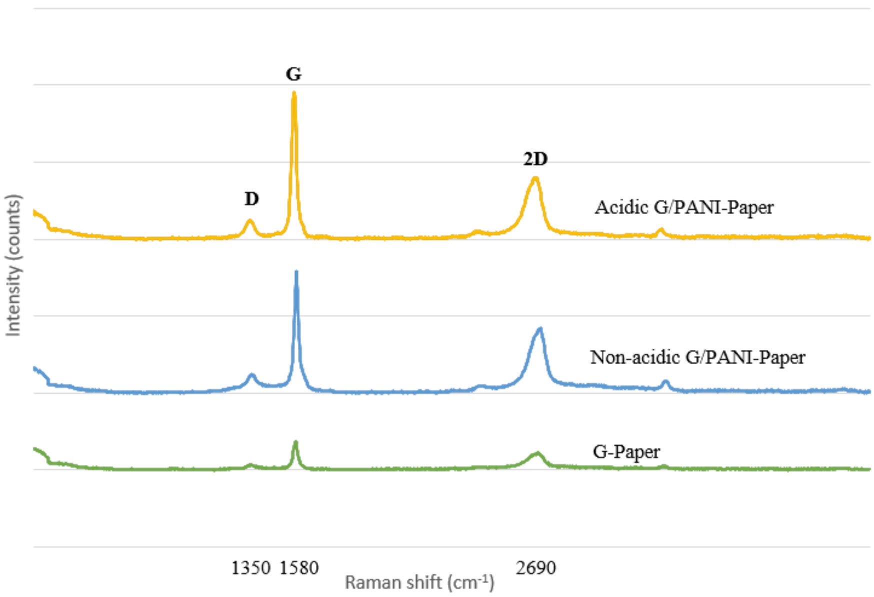


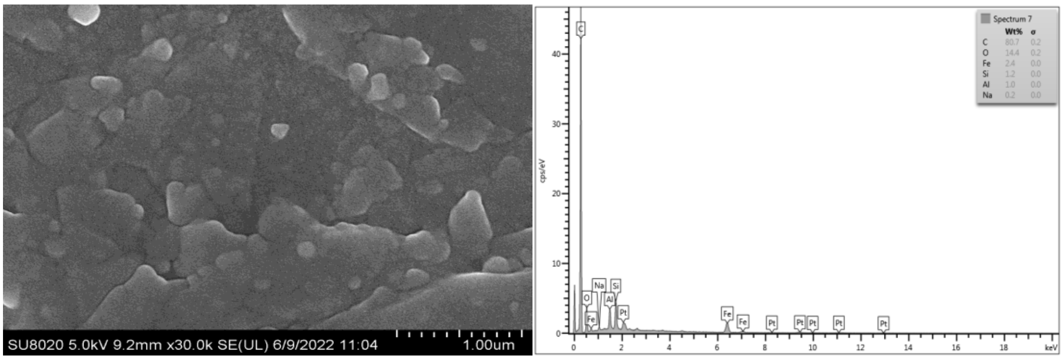
Figure 4. Raman spectra for different samples.

Based on the Raman data as well, full width at half maximum (FWHM) analysis had been perform as reported by Childres et al. on the width of the Raman spectra. The larger width will indicate the higher defect of graphene layers in crystal lattice [10]. From Table 3, there are no significant difference except at the D band which had a larger width probably had a higher defect compared to G band and 2D band [10].

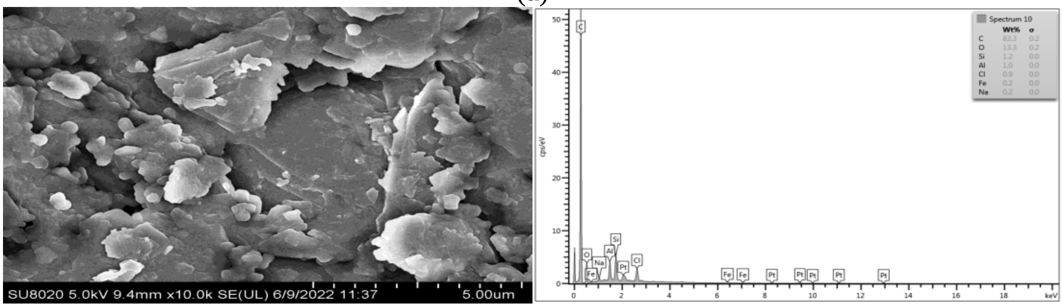
Table 3. FWHM in Raman band.

Sample type	D	G	2D
G-Paper	78	26	86
Non-acidic G/PANI-Paper	94	26	83
Acidic G/PANI-Paper	69	34	92

3.2. FESEM-EDX
Figure 5 shows FESEM images and EDX spectra for respective samples type in this study. There are random structures deposited all over the sample surface. There is no specific microstructure found on the surface of the sample and it mostly appeared like a flake-grain shape. There are no significant differences in terms of elemental presents on the surface substrate for this study because the weight percentage of the carbon are in similar range which is 80%-85%.



(a)



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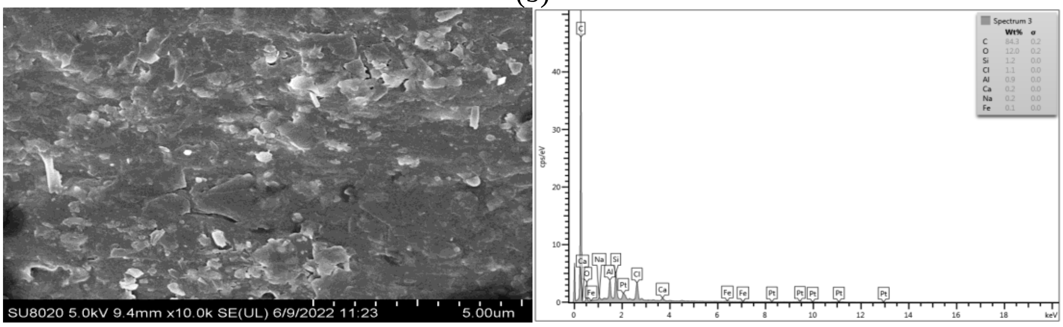

(c)

Figure 5. FESEM-EDX images of (a) G-Paper, (b) Non-acidic G/PANI-Paper, and (c) Acidic G/PANI-Paper.

3.3. Electrical characterization

In this analysis, the resistance and capacitance of the three types of samples with difference size of electrodes were observed. The size of electrodes was 6 cm^2, 8 cm^2 and 10 cm^2. As can be seen in Figure 6 and 7, the size of the electrodes effects the electrical properties of the capacitor and supercapacitor. As the area of the capacitor and supercapacitor increase, the capacitance and resistance value of the capacitor and supercapacitor increase. The capacitance is directly proportional to the area of capacitor and supercapacitor. The result satisfied the following equation:

$$C = \varepsilon A/d \qquad (1)$$

where C is capacitance, $\varepsilon = 3.6$ is dielectric constant of paper [12], A is area of electrode and d is a diameter of electrode.

From Figure 6, the Acidic G/PANI-Paper supercapacitor showed the highest capacitance value with 27.5 µF, 38.1 µF and 55.25 µF followed by Non-Acidic G/PANI-Paper supercapacitor and G-Paper capacitor. For the resistance value, the Acidic G/PANI-Paper showed the lowest resistance value with 1.82 MΩ, 6.25 MΩ and 10.5 MΩ compared than the Non-Acidic G/PANI-Paper supercapacitor and G-Paper capacitor as shown in Figure 7. The Acidic G/PANI-paper supercapacitor has achieved the highest capacitance and lowest resistance because of the HCL treatment and electrodeposition of PANI networks. This enhanced the electrical performance of the device. In terms of applications, higher capacitance and lower resistance is targeted. The Acidic G/PANI-Paper supercapacitor have the best electrical properties for this study.

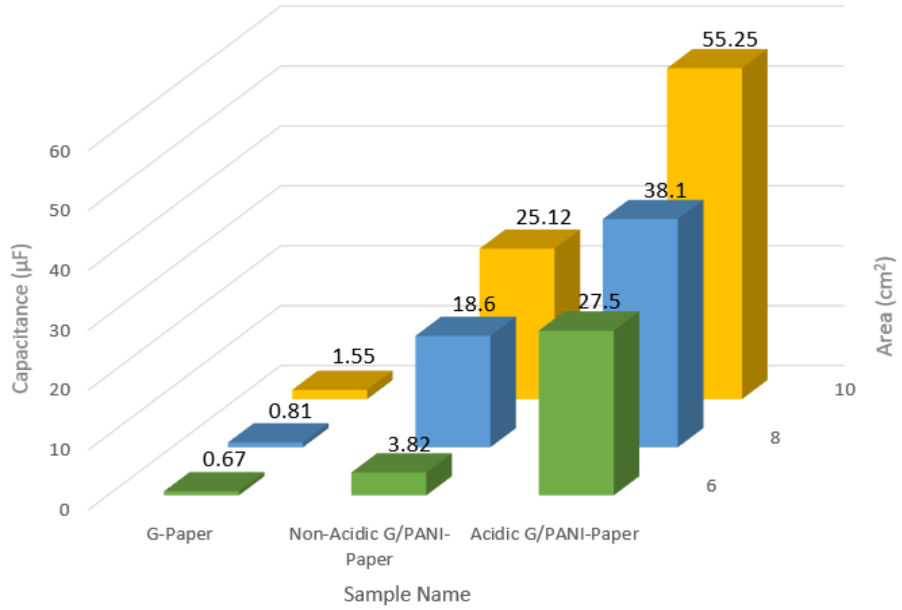

Figure 6. The measured capacitance of the graphite paper-based capacitor and supercapacitor.

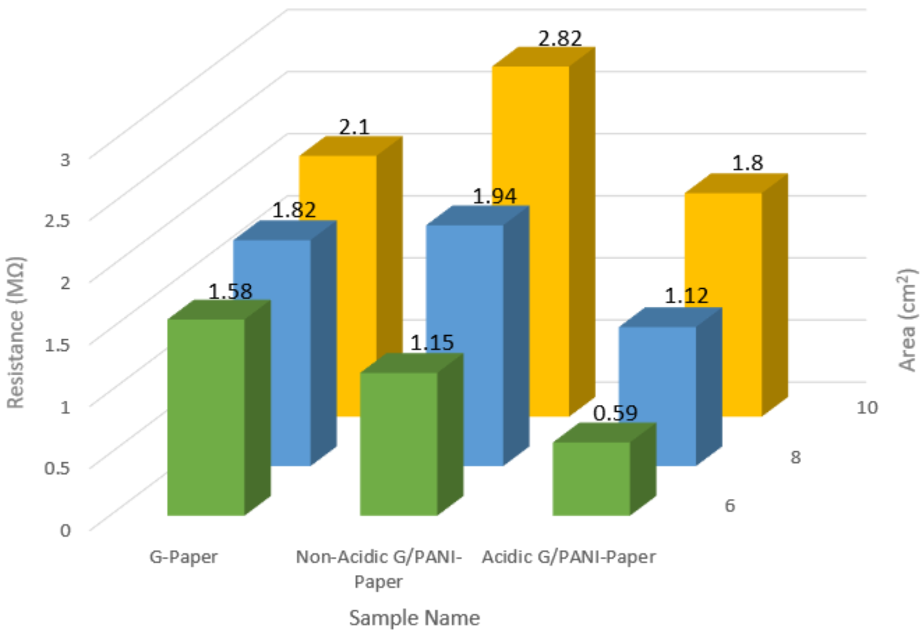

Figure 7. The measured resistance of the graphite paper-based capacitor and supercapacitor.

For the structure of capacitor and supercapacitor, the supercapacitor structure has better electrical properties than the capacitor structure in terms of electrical performance. In this study, this result satisfied the theoretical result. The supercapacitor was able to perform better because of the electrolytic solution on its electrodes. Based on this finding, acidic treatment and PANI electrodeposition for the supercapacitor enhance the electrical performance of the electrodes. With this characteristic, it is suitable for flexible device application.

Table 4. Charging–discharging time of capacitor by using 9 V battery.

Sample Name	G-Paper	Non-acidic G/PANI-paper	Acidic G/PANI-Paper
Maximum voltage (V)	0.19	0.62	0.80
Charging time (min)	1	1	1
Discharging time for the voltage to become 0 (min)	1	50	80

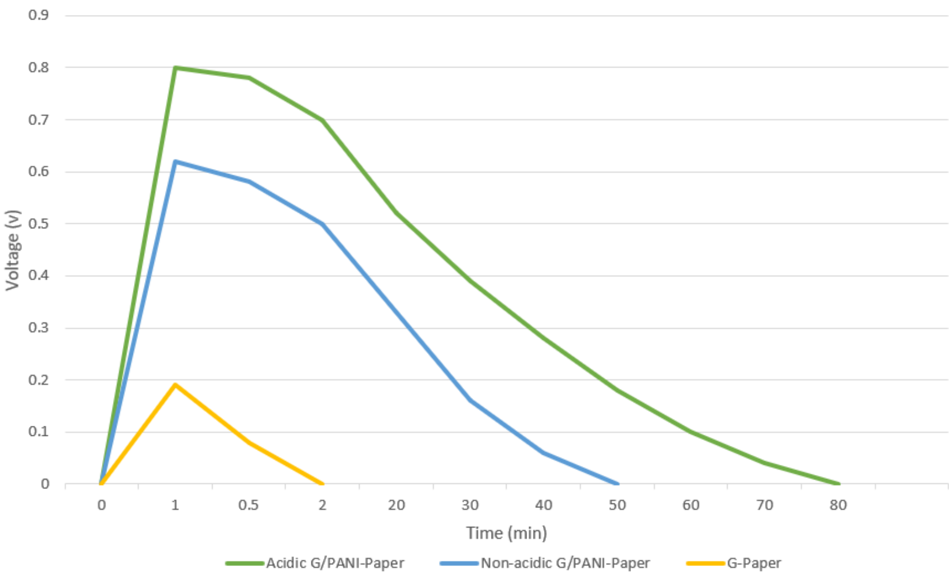

Figure 8. Charging-discharging curves of the capacitor and supercapacitor by using 9 V battery.

The charging-discharging time of the capacitor and supercapacitor with 8 cm^2 size area had been recorded using 9 V battery as shown in Table 4. Based on the result, when the area of the capacitor and supercapacitor increase, the maximum voltage and discharging time for the voltage to become 0 V also increase. Based on Figure 8, the Acidic G/PANI-paper shows the highest maximum voltage and discharging time followed by Non-acidic G/PANI-paper and G-paper. In terms of application, the longer discharging time was targeted, which indicated that the longer the capacitor and supercapacitor can create an electron flow in the circuit and act as a voltage source [13]. The acidic G/PANI-paper have the best discharging time for this study.

4. Conclusion

A simple pencil drawing technique was taken on A4 printing paper to make it conductive followed by electrodeposition of PANI networks on it to enhance the conductivity. The supercapacitors assembled by two Acidic G/PANI-Paper electrodes showed a higher capacitance and resistance value compared to the G-Paper and Non-acidic G/PANI-Paper. It was also shown that increasing the area of the electrode, improving the resistance and capacitance of the electrode. From this finding, the graphite paper-based supercapacitor has better device performance than the graphite paper-based capacitor in terms of electrical performance. This method is very low cost, environmental-friendly, easy to scale up and can be used for energy storage applications.

There is improvement recommendation have been identified based current work. Basically, the defect of the graphene layers would affect the electrical performance of the proposed devices. Therefore, the device optimization possibly able to reduce the defect of the graphene layers and thus enhance the overall performance. Besides, the better use of measurable method in applying pencil-drawn technique is required to keep produce the device structures uniformly and consistently.

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