

# The Comparative Study Analysis Of The Electrochemical Performance Of Reduced Graphene Oxide Based Super-Capacitor With Polyaniline (Pani) And Without Pani, Synthesized Using Tour's Method.

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## Abstract:

This research focused on the comparative analysis of the electrochemical Performance of Reduced graphene oxide-based capacitor with polyaniline (PANI) and without PANI. The graphene (purified natural graphite flake) was synthesized to obtain the graphene oxide using the modified Hummers method also known as the Tour's method which is one of the oldest techniques but the most suitable methods for the formation of bulk graphene oxide. The graphene oxide was reduced to Reduced graphene oxide (RGO) by using ascorbic acid as a reducing agent. The Reduced graphene oxide (RGO) composite was synthesized by continuous in situ polymerization-hydrothermal reduction process using Isopropanol and water as a microenvironment adjusting agent for in situ polymerization of PANI and the RGO control composite was also fabricated without PANI for comparative study analysis of its electrochemical performance. The characterization to analyze the electrochemical performance of the Reduced graphene Oxide based super capacitor with PANI and without PANI was done using the Cyclic voltammetry.

**Keywords:** Natural flake Graphite (NFG), Graphene oxide (GO), Reduced graphene oxide (RGO), PANI (polyaniline), Tour's method, cyclic voltammetry (CV)

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## I. Introduction

The graphene Oxide has a similar layered structure like that of graphite but the plane of carbon atoms in Graphene Oxide is heavily decorated by oxygen-containing groups, which not only expand the interlayer distance but also makes the atomic-thick layers hydrophilic. As a result, these oxidized layers can be exfoliated under moderate ultra-sonication. The exfoliated sheets containing only one or few layers of carbon atoms like graphene, are known as graphene oxide (GO) and in this paper, Graphene oxide was reduced using ascorbic acid as a reducing agent to obtain reduced graphene oxide (RGO).

The graphene oxide has important applications in areas related to transparent conductive film, composite materials, solar energy and biomedical applications. The main properties of graphene Oxide are hygroscopicity and dispersibility. **Figure 1(a)** shows the structure of a single layer graphene and **Figure 1(b)** shows the structure of graphene oxide. Graphene Oxide sheet can also be considered as the combined structure of oxygen-containing functional groups, such as C-O, C=O and -OH that has been supported on the surface of a single layer graphene. As a result of the addition of oxygen-containing functional groups both the structure and the properties of Graphene Oxide changes. The oxidation process produces structural defects which shifts the physical properties of Graphene Oxide away from that of pure graphene. However, the presence of the oxygen-containing functional groups also makes graphene Oxide strongly hydrophilic as a result of which GO can be dispersed in several solvents like water.

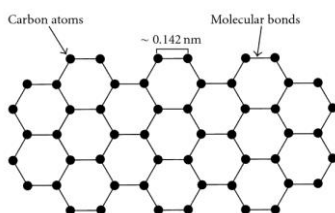
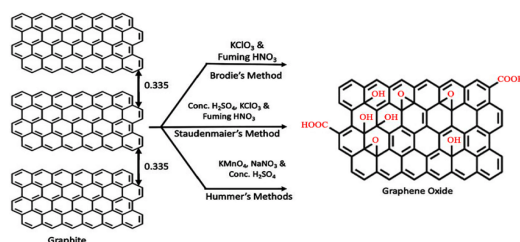


Figure 1a: Schematic structure of a single graphene



**Figure 1b: Schematic structure of graphene oxide**

Graphene can be easily synthesized by the oxidation of the natural flake graphite (NFG) powder, which is the most easily accessible source of graphite and is seriously gaining popularity due to its low cost, availability and its known ability to be converted to graphene oxide and also reduced to Reduced graphene oxide (RGO). This Flake graphite is a naturally occurring mineral that is purified by removing the hetero atomic contamination. This was first demonstrated in the synthesis of Graphene Oxide in 1859 by British Chemist Brodie who added a portion of potassium chlorate to slurry of graphite in fuming nitric acid (Brodie, B.C. 1859). Then In 1898, Staudenmaier L. improved on this method by using a mixture of concentrated sulfuric acid and fuming nitric acid and finally added chlorate to the reaction mixture gradually. This improved procedure provided an improved protocol for the production of highly oxidized Graphene Oxide (Staudenmaier, L. 1898)

In this study, the oxidation of graphene (flake graphite) to graphene oxide was done using the Tour's method which is highly efficient and less hazardous, instead of using hydrazine or hydrazine hydrate in the chemical reduction of graphene oxide which is known to be very poisonous and could easily cause explosion, the Ascorbic acid was deployed as a primary reductant and is a new approach for reducing graphene oxide to Reduced graphene oxide (RGO) under mild conditions. Ascorbic acid has a mild reductive ability and also a higher chemical stability with water in comparison with sodium borohydride,  $\text{NaBH}_4$  and other reductants like hydrazine because the ascorbic acid is eco-friendly. The Graphene oxide reduced by vitamin C could achieve a carbon to oxygen ratio of about 12:5 and a conductivity of 77 S/cm which is better in comparison to those produced by hydrazine and other various kinds of conducting polymers in a parallel experiment as revealed by Fernandez-Merino et al.

Polyaniline (PANI) is considered as the most promising electrode material and has been widely investigated due to its ease of synthesis, environmental stability, simple acid-doping/base-de-doping chemistry. The outstanding properties of graphene and the advantages of PANI have gained great research interest in the preparation of graphene/PANI composites and also Reduced graphene oxide/PANI Nano-fiber composite which can be prepared by in situ polymerization of polyaniline in the presence of Reduced graphene oxide (RGO) and followed by a continuous process of reduction (using hydrazine), re-oxidation and re-protonation. The RGO/PANI composites has microstructures of which are not very uniform and contains defects such as cracks, voids and dislocation which also reduces the electrochemical properties of the resulting materials.

The effect of solvents on the polymerization process is a key factor for the formation of a uniform and stable polymeric structure. In most cases, water is used as a solvent because of its availability and promotes the dispersion of RGO. However, as a strong polar solvent, water is not conducive to the dissolution and dispersion of PANI. The dielectric constant of water is much larger than that of PANI which makes it difficult for PANI to break through the molecular cages of water and diffuse to the surface of graphene to form a homogeneous solution, which then hinders the formation of homogeneous composites. It has been known from previous research, that those weak polar solvents such as chloroform, dimethyl sulfoxide, acetone, toluene, tetrahydrofuran etc. can enhance the solubility of polyaniline and PANI which is helpful to form a homogeneous structure and improve performance capacity, however, these solvents are known to be very toxic hence it's very difficult to promote their applications. Some eco-friendly organic solvents such as alcohols was researched in this paper and may also achieve the similar effect because Isopropanol has a more appropriate polarity to PANI in comparison with water. The dielectric constants are 80.1, 20.18, and 7.06 for water, isopropanol and polyaniline, respectively, which allows it to promote the PANI in situ polymerization by providing a more comfortable microscopic chemical environment.

In this paper, we have researched a simple and convenient method to synthesize high performance Reduced graphene oxide/PANI and RGO electrode materials by a continuous in situ polymerization-hydrothermal reduction process using Isopropanol and water as a microenvironment adjusting agent for in situ polymerization of PANI. Considering the solubility of graphene, the mixture of isopropanol and water as solvents was used instead of pure isopropanol because of the increase in solubility, the polymerization process resulted in a homogeneous structure and the PANI backbone structure is also optimized and contributed to the improvement of the electrochemical performance. The electrochemical results showed that the composite with the introduction of isopropanol not only delivers a higher specific capacitance but also exhibited a better cyclic performance.

## II. Materials:

Natural Graphite flakes (sigma Aldrich), phosphoric acid (Merck), Potassium permanganate (Sigma Aldrich), Polyaniline (Sigma Aldrich), Ammonium Persulphate (Sigma Aldrich), Hydrochloric acid (Merck), Barium Chloride BaCl<sub>2</sub> (MERCK), Concentrated Tetra-oxo-sulphate VI acid [H<sub>2</sub>SO<sub>4</sub>] (Sigma Aldrich), Ascorbic Acid (Bristol scientific company), Hydrogen Peroxide [H<sub>2</sub>O<sub>2</sub>] (MERCK), Ethanol and Isopropanol (Sigma Aldrich). All chemicals were used without further purification.

## III. Methodology:

### Synthesis of graphene oxide from graphite powder (Graphene) using Tour's method:

In synthesizing graphene oxide, the mixture of 90mL of concentrated H<sub>2</sub>SO<sub>4</sub> (Sulfuric acid) in (9:1 (v/v) ratio) was prepared and poured into the mixture of 0.50 g natural flake graphite powder and 4.5 g of KMnO<sub>4</sub> (potassium permanganate) and it resulted in temperature change of 40°C. The mixture was then heated to 50°C using a temperature-controlled water bath and stirred for 12 hours and as the reaction time was increased, it turned out to be a paste. After the 12 hours duration, the mixture was cooled to room temperature and then 250 mL of distilled water was added to the mixture to stop the reaction. Then, 10 mL of 30 wt.% H<sub>2</sub>O<sub>2</sub> was added to reduce manganese ion to soluble manganese sulfate and manganese oxides and also reduce residual KMnO<sub>4</sub> to soluble manganese sulfate (MnSO<sub>4</sub>) in an acidic medium, as described in the following reaction:



Then 30 wt.% H<sub>2</sub>O<sub>2</sub> was added and bubbling occurred and a bright yellow color was observed indicating a high level of oxidation. The filter paper was used to filter the solution to remove the metal sulfate and a graphite oxide (GTO) and a filter cake was produced. The yellow cake was washed with 5% HCl aqueous solution until the sulfate ions were removed completely. The removal of the metal sulfate ions was confirmed using Barium chloride, BaCl<sub>2</sub> solution. The washing process was carried out repeatedly by centrifugation at 4000 rpm for 4 hours, until the supernatant was decanted away. The pH of the collected material was checked using a universal indicator. The collected material (GTO) was stirred in distilled water at 60°C for 12 hours in a water bath. This process is called exfoliation.

### Reduction of Graphene Oxide (RGO):

The Graphene oxide was reduced through the following processes- the exfoliation and reduction using the reducing agent as detailed below:

(i) Exfoliation: The single layer graphene oxide which was formed after been dispersed into distilled water and was heated with magnetic stirrer for 12 hours at 60°C in a water bath. The black paste formed was collected by filtration followed by centrifugation and dried at 60°C for 24 hours.

(ii) Reduction: the graphene oxide obtained from stage (i) is then dispersed and 4 g of ascorbic acid (AA) was added to this solution and stirred with a magnetic stirrer for 30 min at 60°C; the reduced product was centrifuged at 4000 r/s for 40 min to remove the supernatant. Then, excess 30 wt.% H<sub>2</sub>O<sub>2</sub> was added to the black paste to oxidize the remaining ascorbic acid by stirring for 30 min at 60°C. After stirring, the resultant black product was collected by centrifugation at 4000 r/s, washed with ethanol and distilled water 3 times respectively and dried at 120°C for 24 hours so as to get a thick good film in the shortest possible time.

### Preparation of polymerized RGO/PANI and RGO Composite:

In the preparation process of RGO/PANI, 4.5mg of RGO, 7.5mL water and 10mL isopropanol were added into a 100mL beaker. Followed by 15min sonication and then 0.685mL of polyaniline was added into the above solution. After an additional 15min sonication, the reaction system was transferred to an ice bath with a strong magnetic stirring, 0.610mL concentrated phosphoric acid (85%), and 0.500mL concentrated hydrochloric acid (10M) was added into the above mixture. After a further 15min stirring, 0.429g of ammonium persulfate (APS) was added into the mixture to initiate the polymerization of polyaniline. The stirring was continued for 6 hours and the reaction temperature was kept running at 0-5 °C and then the resulting dark green mixture was transferred into an 80mL Teflon-lined stainless-steel autoclave and heated at 100°C for 5hours. When the autoclave was naturally cooled down to room temperature, the RGO/PANI-1 was obtained by vacuum filtration. Additionally, RGO/PANI-2 was fabricated following the same process as preparing RGO/PANI-1 using pure water, without adding isopropanol. A pure RGO was fabricated as a control composite according to the same process as preparing RGO/PANI-1 in the absence of PANI.

### Preparation of the Graphene based super-capacitor from the RGO/PANI and RGO Composite:

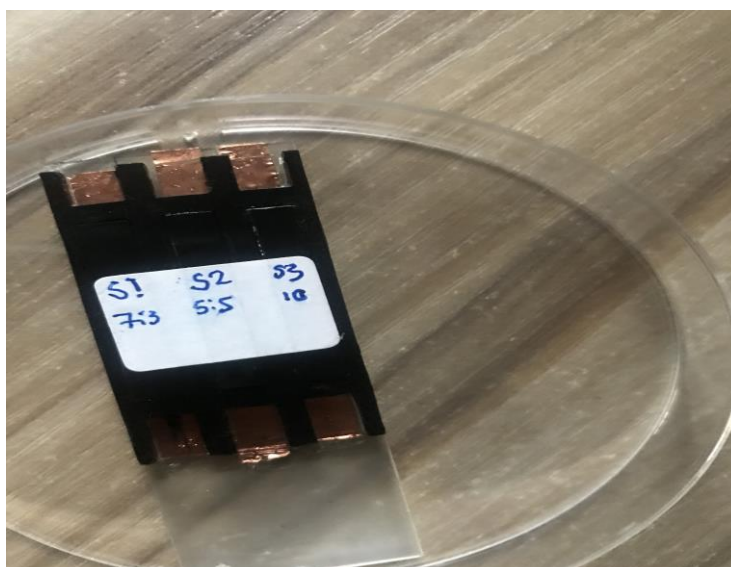
The graphene based Super-capacitor was prepared by stacking the RGO/PANI-1 and RGO/PANI-2 and RGO Composite which was processed into electrodes by rolling a mixture with 5 % wt. PTFE and 5 % wt. carbon

black into 250 µm thick films. Discs of 8 mm in diameter and carbon loading ~ 15 mg/cm<sup>2</sup> were punched out. The picture of the stacked of super-capacitor components with a glassy fibrous paper as a separator which was later attached to a two-electrode cell is as seen in Fig 2a. The separator is a filter paper which was soaked in aqueous potassium hydroxide (c=7.5 M). The Silver or graphite foil were used as charge collectors. The stack was sealed by inserting the stack between two microscope glasses, held together by two small clamps. A compact stacking is necessary to ensure a stable connection between all components. The specific capacitance C<sub>s</sub> of a super-capacitor was calculated from the curves of the cyclic voltammetry using the formula stated below:

$$C_p = A / 2kmAv$$

Where C<sub>p</sub>= the specific Capacitance in F/g  
 A= the surface area of the curve (AV) on the graph  
 K= the Scan rate Mvs<sup>-1</sup>  
 M= Active Mass (Mg)

The capacitance per weight for just one electrode was obtained by further multiplication by four. The factor 4 was derived from the electrical double layer at the electrode interface forming one capacitor on each electrode (Atkins, De Paula 2006).



**Figure 2(a) The picture of the stacked RGO PANI/RGO super-capacitor components**

**Method of Characterization of the Reduced Graphene oxide super capacitor:**

The electrochemical properties were determined and measured by characterization using the cyclic voltammetry.

**Cyclic Voltammetry (CV):**

This is an electrochemical technique in which the current that develops in an electrochemical cell under conditions where voltage is in excess of that predicted by the Nernst equation. CV is performed by cycling the potential of a working electrode and measuring the resulting current CV which yields basic information about a capacitive electrochemical cell including: Voltage window, Capacitance and Cycle life. The testing of packaged capacitors requires two-electrode connections as all potentiostats can operate with two-electrode connections. Both the reference electrode and the counter electrode leading to one side of the capacitor are connected. When the working electrodes lead to the other side is connected, a voltage sweep applied to an ideal capacitor creates a current given by:

$$I = \frac{dQ}{dt} = C \frac{dV}{dt} \dots\dots\dots (Eq.1)$$

Where I is current in amperes, and  $\frac{dV}{dt}$  is the scan rate of the voltage ramp.

The Voltage scan rates for the super-capacitor testing was between 0.1 mV/s and 1 mV/s. The Scan rates at the lower end of this range allow slow processes to occur but takes a lot of testing time. Fast scan rates often

show lower capacitance than slower scan rate hence on high-value capacitors may require more current than the instrument can put out or measure. The maximum allowed scan rate is:

$$\left(\frac{dV}{dT}\right)_{max} = \frac{I_{max}}{C} \dots\dots\dots (Eq. 2)$$

where  $I_{max}$  is the instrument's maximum current in amperes.

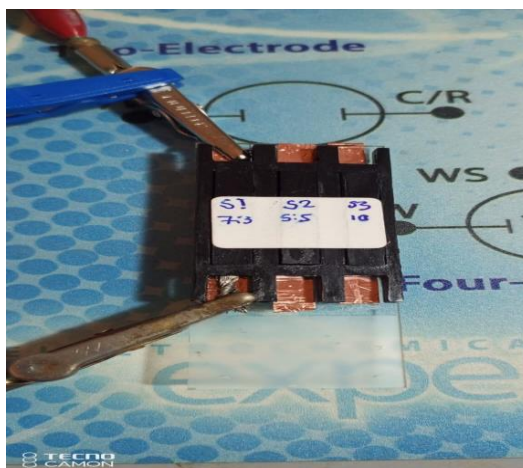
#### IV. Results and Discussion

##### Electrochemical performance analysis:

The electrochemical performance of the electrode materials was analyzed using cyclic voltammetry (CV) with a two-electrode system and a scanning potential range of 0.0V-1.0V and Figures 4(a-h) showed the CV curves of the RGO/PANI-1, RGO/PANI-2 and RGO composites at scanning rates of 10mVs<sup>-1</sup>, 50mVs<sup>-1</sup> and 100mVs<sup>-1</sup>. The response current density of RGO/PANI-1 is noticeably higher than that of RGO/PANI-2 which indicated that RGO/PANI-1 has a higher specific capacitance which could be attributed to the higher doping level and higher electron conductivity as shown in **Table 1**.

SUPERCAPACITOR	SPECIFIC CAPACITANCE Fg <sup>-1</sup>	SCAN RATES mVs <sup>-1</sup>
RGO/PANI-1	8.033x10 <sup>-3</sup>	100
RGO/PANI-2	2.487x10 <sup>-4</sup>	50
RGO/PANI-2	2.750x10 <sup>-4</sup>	100
RGO	4.104x10 <sup>-4</sup>	10
RGO	3.052x10 <sup>-5</sup>	100

**Table 1: The Specific capacitance of the RGO/PANI and RGO**



**Figure 2b The Electrode attachment of RGO/PANI and RGO capacitor cells for the cyclic voltammetry.**



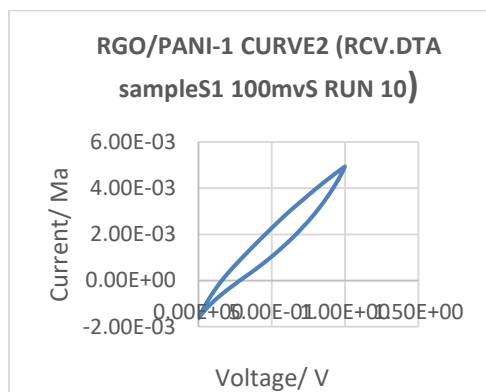
**Figure 2d: Laboratory Sessions**

**Curve Analysis:**

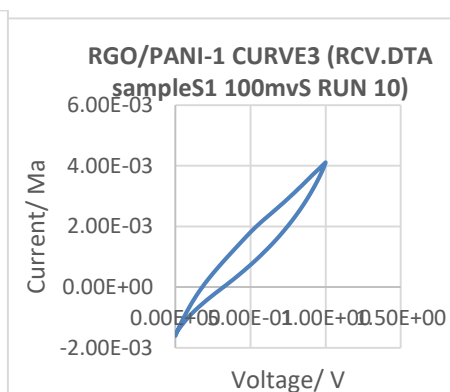
The CV shape RGO/PANI-1 composite showed the high current density response as it is noted that the cathodic peaks shift positively and the anodic peaks shift negatively with the increase of potential scan rates from 10 mVs<sup>-1</sup> to 100mVs<sup>-1</sup> which is mainly due to the resistance of the electrode which indicated higher specific capacitance than that of RGO and this originated from its unique microstructure. The dispersion of nanoscale PANI on RGO reduced the diffusion and migration length of the electrolyte ions during the fast charge/discharge process and increased the electrochemical utilization of PANI. We found the sample of RGO/PANI-1 composite has better electroconductive performance in comparison with RGO/PANI-2 and RGO control composite. Furthermore, the obvious increase of response current with increased scan rates indicated a good electroconductivity for RGO/PANI-2 composite electrode.

The CV shape of the RGO control composite showed a relatively long circular graph with an obvious redox peak and a low current response to voltage reversal at each end potential, which indicated that RGO mainly possess electrical double-layer capacitance and the specific capacitance is poor in comparison with RGO/PANI-1 synthesized in Isopropanol and water but much better than RGO/PANI-2 synthesized in pure water. RGO as control composite also provided a good electron transfer path due to its excellent capacitance.

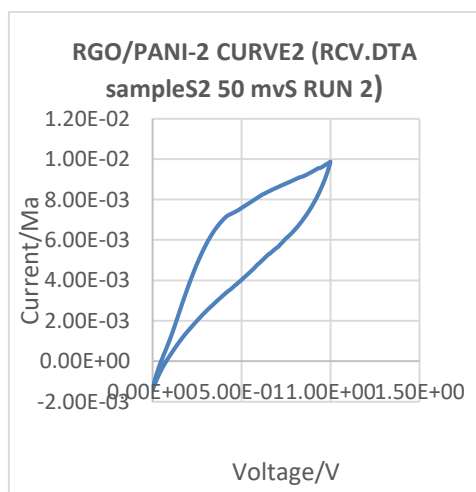
In Summary, all the results confirmed that the RGO/PANI composites exhibited excellent capacitance characteristic and good scan rate which can be attributed to these four factors: (I) The polyaniline polymerization by this method has a high doping and oxidation level which brought out the good conductivity and also exhibited a high specific capacitance. (ii) The Reduced Graphene oxide is intercalated by the surface polymerization of PANI which prevented the graphene sheets from stacking and aggregation and also enhanced the performance. (iii) The effects of the synergy between graphene and PANI aids overcoming the deficiencies of each other which caused higher specific capacitance of RGO/PANI-1 composite than RGO composite (iv) In addition, the introduction of isopropanol also allowed the doping and structural optimization of PANI which resulted in improved electrochemical performance enhancements. The RGO/PANI-1 and RGO/PANI-2 composite electrodes showed a pair of redox peaks in **Figures 4a-4h**, which can be ascribed to a comprehensive effect of the changes in PANI structures and the remaining oxygenated groups of the graphene-based nanosheets results in the redox capacitance.



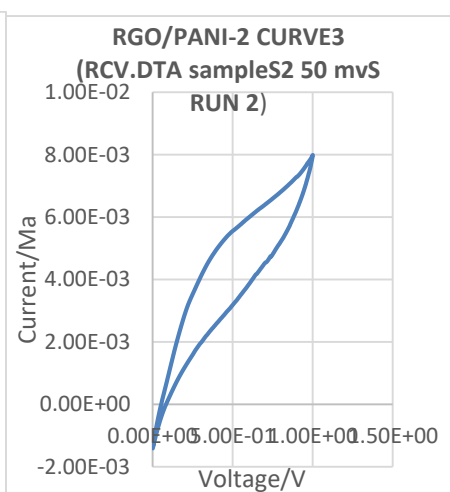
**Figure 4a**



**figure 4b**



**Figure 4c**



**Figure 4d**

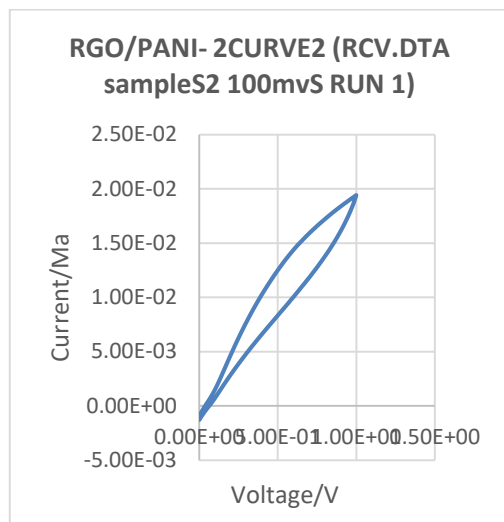


Figure 4e

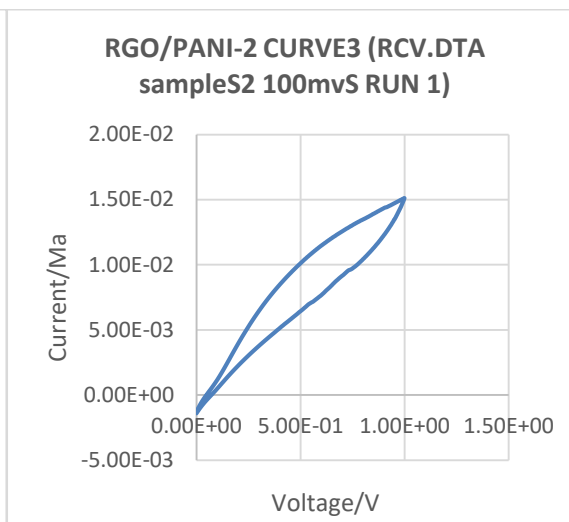


Figure 4f

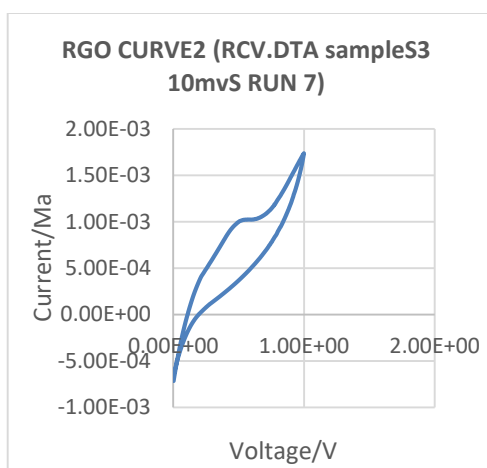


Figure 4g

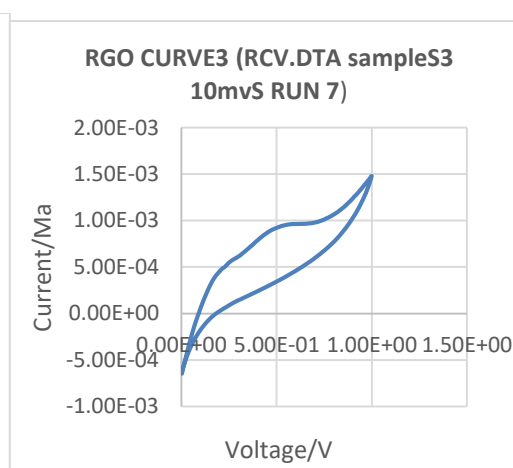


Figure 4h

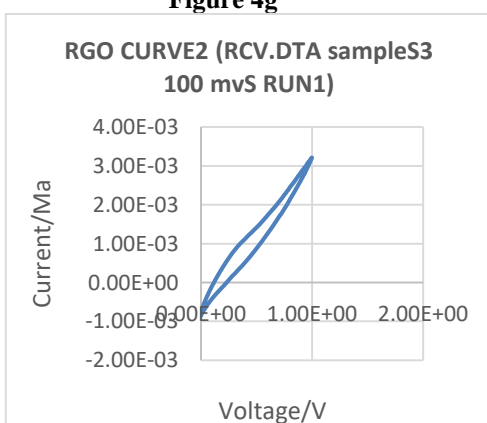


Figure 4g

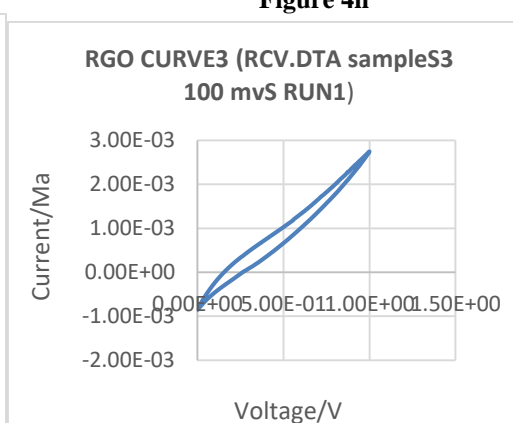


Figure 4h

Figures 4i-4p showed that PANI/RGO-1/RGO and RGO/PANI-2/RGO illustrated a triangular-shape charge/discharge curve, reflecting that its specific capacitance primarily originated from electric double layer capacitance. Meanwhile, it can be noted that the charge voltage becomes higher while the discharge voltage becomes lower after RGO nanosheets are incorporated with the PANI and this indicated that the energy consumed by the internal resistance is reduced, consequently, the effective energy storage is improved. This improvement is probably evident because the inner resistance of the electrode is reduced when RGO nanosheets are present. In

summary, the specific capacitances calculated from CV curves of PANI/RGO-1 is  $8.033 \times 10^{-5}$  F/G at scan rate of  $100\text{mVs}^{-1}$  and is higher than that of PANI/RGO-2 which is calculated at  $2.750 \times 10^{-4}$  at scan rate of  $100\text{mVs}^{-1}$  which is due to the higher doping level and higher electron conductivity as mentioned in **Table 1** above while the specific capacitance of the RGO control composite calculated from the CV Curve at scan rate of  $100\text{mVs}^{-1}$  is  $3.052 \times 10^{-5}$ .

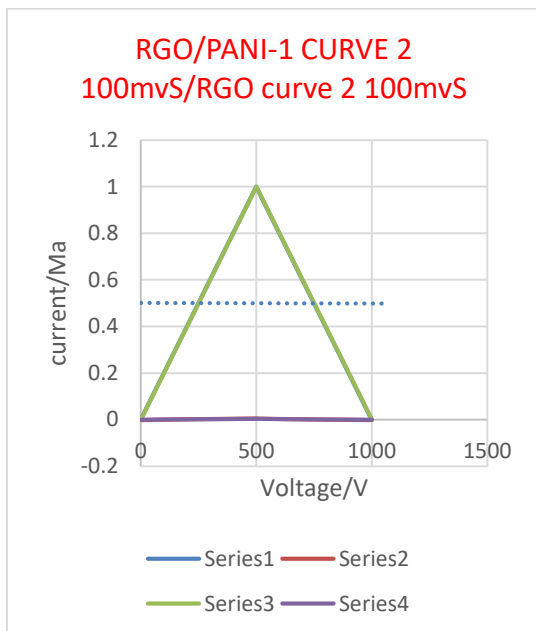


Figure 4i

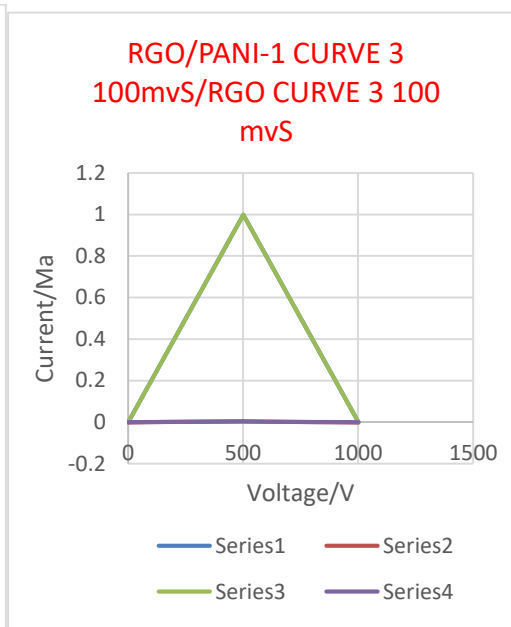


Figure 4j

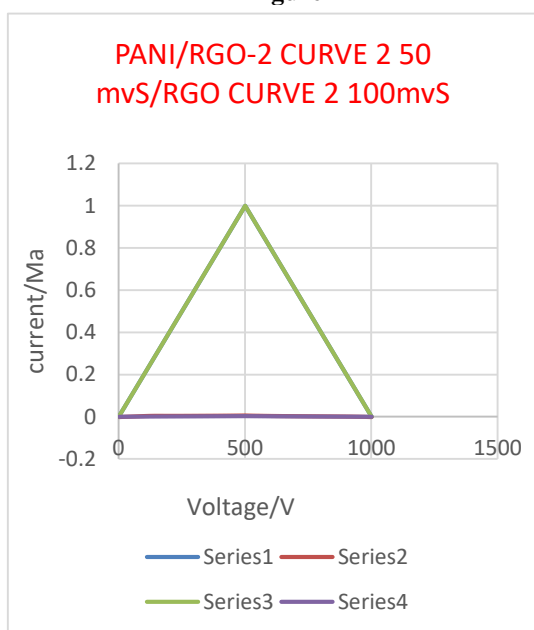


Figure 4k

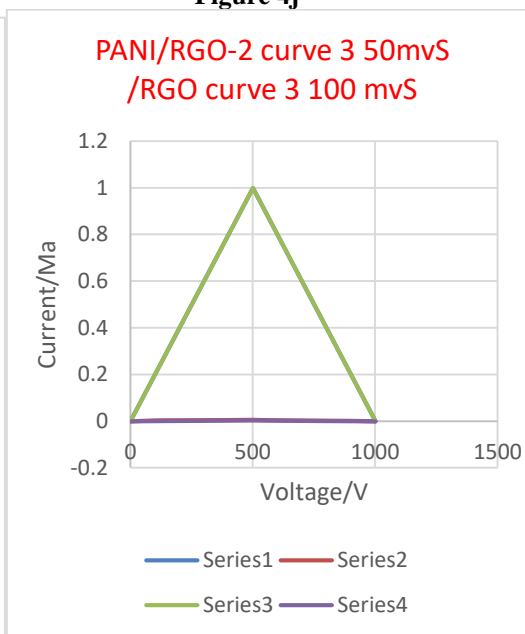


figure 4l



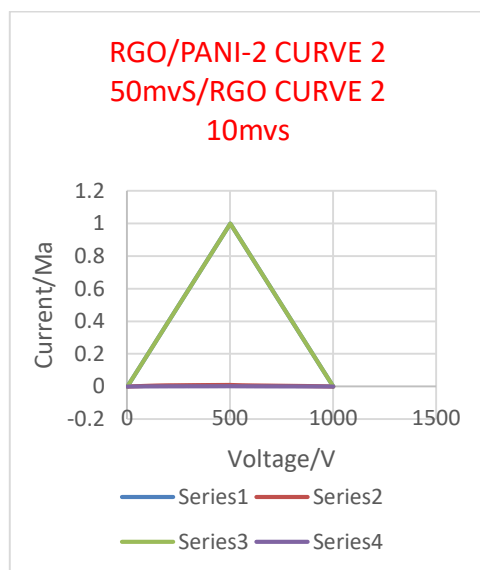


Figure 4m

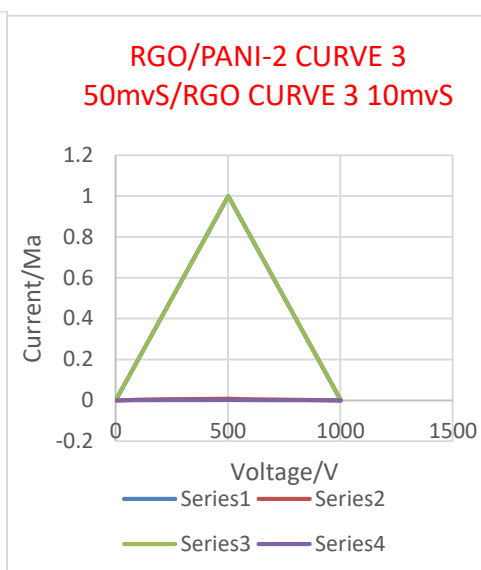


Figure 4n

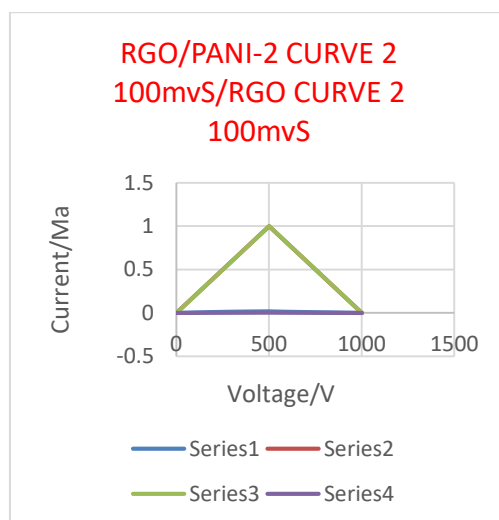


Figure 4o

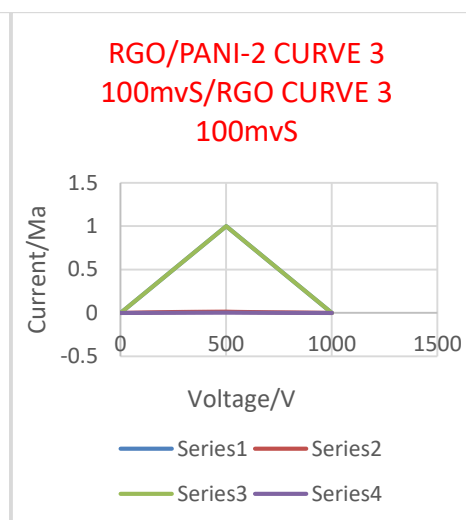


Figure 4p

## V. Conclusion:

In this paper, Natural flake graphite was synthesized to graphene oxide using Tour's method and reduced to Reduced graphene Oxide (RGO) using Ascorbic acid. The RGO/PANI composites were synthesized using a continuous in situ polymerization-hydrothermal reduction process in various modified solvent conditions. The introduction of PANI in the composite provided high conductivity as well as a relatively large area on which to deposit the PANI and it effectively reduced the kinetic difficulties for both charge transfer and ion transport throughout the electrode. The As-prepared RGO/PANI-1 composites synthesized in isopropanol and water exhibited excellent electrochemical performance and good Scan rate because isopropanol helped the dissolution of polyaniline and further enhanced the uniform distribution of the polymer within the RGO sheets. The specific capacitance calculated from the CV curve of RGO/PANI-1 composite was  $8.033 \times 10^{-5} \text{ F/G}$  at a charge-discharge current density of  $0.5 \text{ A}$  which is greater than that of PANI/RGO-2 prepared in pure water solution calculated at  $2.750 \times 10^{-4} \text{ Fg}^{-1}$  and that of the RGO control composite calculated at  $3.052 \times 10^{-5} \text{ Fg}^{-1}$ .

The greatly improved specific capacitance is due to the synergistic effect between RGO and PANI. In addition, the introduction of isopropanol also leads to the doping and structural optimization of PANI, resulting in additional electroconductive performance enhancements. This intriguing feature made it a suitable method in consideration of enhancement of electroconductive performance of RGO/PANI composites for electrochemical supercapacitors. The comparison of the conductivity of the reduced graphene oxide/polyaniline based super capacitor and RGO capacitor (as control composite) characterization using the Cyclic voltammetry has also shown the increase in the electrical conductivity of the RGO/PANI and RGO Super capacitors which are known as energy storage devices that stores energy electrochemically in conducting materials, in the presence of a suitable

electrolyte, by two different mechanisms, namely, the electrostatic adsorption of ions (charges) on a polarized surface and the reversible redox reactions of surface electro-active species, which will probably inform the replacement of batteries or boost batteries in multiple applications in the nearest future for their widespread utilization and commercialization and also to create the market demand of reduction in their cost and an enhancement of their energy density.

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