# Fabrication of Supercapacitor Based on Graphene and Polyaniline for Energy Storage Applications

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**ABSTRACT**: In this paper, a proposed supercapacitorwas fabricated using an electrode of graphene layer covered with polyaniline layer. Uniform polyaniline layer was deposited using spraying technique. Characterizations were performed using scanning electron microscope (SEM) and UV-visible spectroscopy. The electrochemical measurements were assessed using cyclic voltammetry (CV), electrical impedance spectroscopy (EIS), and charge-discharge measurements. The results indicated that graphene/PANI double layers exhibited high porosity and large surface area. Polyaniline/graphenesupercapacitor had a specific capacitance as high as 915.78 F/g at scan rate of 5 mV/s in the scanning potential window from - 0.8 to 0.8 V with 4 mg active material. The fabricated supercapacitor prototype has provided an energy density of 127.19 Wh/kg at potential difference of 1V using aqueous electrolyte of 6M potassium hydroxide. The effect of temperature on supercapacitor performance was investigated and it was found that the influence of temperature on specific capacitance was insignificant. It was observed that an improvement in the specific capacitance with about 1% in temperature range between 25 ˚C and 70 ˚C.

**KEYWORDS:** Graphene, Polyaniline,Supercapacitors, Energy storage.

## I.INTRODUCTION

With the fast depletion of fossil energy sources and increasingly severe pollution from fossil fuels, there is a growing demand for the development of new energy conversion and storage devices. Great attentions have been focused on developing high performance, low cost and environmentally benign energy systems. Supercapacitors, as the energy storage devices between secondary batteries and traditional capacitors, have attracted increasing interests due to their high power density, longer cycle life, and low maintenance compared to conventional batteries [3-5]. Electronically conducting polymers as polypyrrole, polyaniline (PANI), polythiophene and poly[3,4 ethylenedioxythiophene] can store and release charges through redox processes associated with the π-conjugated polymer chains [6–]. When oxidation occurs (also referred to as p-doping), ions from the electrolyte were transferred to the polymer backbone and, on reduction (''undoping''), they were released back into the solution. Generally p-dopable polymers were more stable than n-dopable ones. The doping/dedoping process takes place throughout the bulk of the electrodes, offering the opportunity to achieve high values of specific capacitance. Among the conducting polymers, polyaniline (PANI) has attracted much attention because of their low cost, environmental stability, controllable electrical conductivity, and easy process ability [8].Combined PANI with various robust carbon materials such as graphite oxide, graphene, carbon nanotubes (CNTs), carbon fiber and mesoporous carbon, seems a promising way for the enhanced electrochemical properties [10-11]. In addition, the stability, electrical conductivity, and redox behavior of PANI could be greatly improved when incorporated with conductive carbon materials. For example, Meng et al. prepared paper-like flexible CNT/PANI composite, which exhibited a maximum specific capacitance of 424 F/g [12]. Zhao and co-workers developed and characterized high performance supercapacitor electrodes (hollow carbon spheres/PANI) synthesized via in situ polymerization process and the electrode displayed a maximum specific capacitance of 525 F /g [12]. As an intriguing two dimensional carbon material, graphene exhibits numerous unique and attractive physical, chemical, mechanical and electrical properties, such as high theoretical specific surface area, extraordinarily high electrical conductivity and excellent mechanical flexibility. The incorporation of graphene with PANI not only reinforces the stability and conductivity of PANI, but also significantly improves its electrochemical performance.

The main objective of this work is to fabricate a supercapacitor based on double layers of graphene and polyaniline electrode. The performance of supercapacitor as a function of temperature in the range between 25°C and 75 °Cis investigated. This supercapacitor introduces a high specific capacitance and good electrochemical properties due to a synergistic effect between graphene and plyaniline layers. The supercapacitor performance was assessed using cyclic voltammetry (CV), electrical impedance spectroscopy (EIS), and charge-discharge measurements.

## LITEARTURE SURVEY

Severalstudies have reported the properties of graphene for supercapacitorapplications. For example, it has been found that the specificcapacitance of graphene-basedsupercapacitors can reach 135,99 and 75 F $g^{-1}$ in aqueous, organic and ionic liquid electrolyte,respectively [1].In addition, nowadaysa good many of efforts have been centered on the combinationof graphene with conducting polymers for supercapacitorapplications in order to increase the capacitance. Conductingpolymers such as polyaniline (PANI) are particularly promisingsince they have advantageous properties including high specificcapacitance, low cost, mild synthetic condition and relativelyhigh conductivity .Accordingly, many graphene compositeswith PANI for supercapacitors have been developed [2].It has been proved that the stability of PANI is improved andthe capacitance value is significantly increased by thecombination.
Nevertheless, the specific capacitance of these compositesis still low for actual applications. For instance, Wang et al. [2]reported that the capacitance of the graphene/PANI composite isonly 233 F $g^{-1}$.

## II.MATERIALS

Graphite powder was purchased from Fischer Scientific. Sulphuric acid (98 wt.%), nitric acid (70 wt.%), hydrazine hydrate (65 wt.%), potassium permanganate and sodium nitrite were purchased from Sigma-Aldrich Ltd. Barium chloride (99%) was purchased from ALEC. Potassium hydroxide, silver chloride, sodium hydroxide and hydrogen peroxide (30 wt.%) were obtained from local chemical companies. Aniline (99%) was purchased from CDH. Ammonium persulphate (98.5%) was purchased from WINLAB. Hydrochloric acid (37%) and camphor sulfonic acid were purchased fromMereck.

## III. EXPERIMENTAL WORK

### 1. Graphene Oxide Preparation

Graphene oxide was prepared by a modified Hummers method [17-21]. Typically, 4.0 g natural graphite powder and 2 g sodium nitrate were mixed with 92 mL sulfuric acid in a 2000 mL flask place in an ice bath. The obtained solution was stirred with slowly addition of 12 g potassium permanganate, the stirring was continued for 2 h. The mixture solution was transferred to a 35 °C water bath and stirred for 30 min. After that, 184 mL of deionized water was slowly added into the solution and the solution temperature monitored was about 98 °C. The mixture solution was maintained at this temperature by heating for 30 min. Then, 560 mL deionized water and 40 mL of hydrogen peroxide was added sequentially to the mixture solution to terminate the reaction. The observed color of mixture was dark yellow. The resulting product was filtered and rinsed with 5% HCl solution to remove sulfate groups checked by barium chloride and repeated till no white precipitate exist, followed by distilled water (to remove HCl) checked with silver chloride for several times till no white color exists in the solution. The graphite oxide powder was obtained after drying in vacuum at 60°C overnight. The powder was then dispersed in distilled water to make concentration of 0.5 mg/mL, and exfoliated by ultrasonication for 1 h to obtain graphene oxide (GO). Finally, the stable suspension of brown graphene oxide was obtained. Graphene oxide was filtered and dried in an oven at 60°C for 12h.

### 2. Polyaniline preparation

Aniline (0.2 M) was added to 0.2 M HCl then kept for 1 h at room temperature. Ammonium persulfate (APS) in 20 mL distilled water was then slowly added to the suspension under stirring. The molar ratio of aniline, hydrochloric acid and APS was 1:1:1. The reaction was conducted by the in situ polymerization method in ice bath for 1 h then left at rest to polymerize for 24 hours at room temperature. The prepared mixture was filtered, rinsed with distilled water [20-22]. PANI was simultaneously dedoped by 25 mL 8 M sodium hydroxide at 95 °C for 20 h. The emeraldine salt was dried in air and then at 60ºC for 24h. PANI was doped with camphor sulfonic acid (CSA) and dissolved in chloroform.

3. Fabrication of Supercapacitor

Graphene oxide was deposited on the Stainless steel 304 current collector and reduced using filter paper soaked in hydrazine hydrate for 72h. A layer of polyanilinewas sprayed over graphene layer. The separator was a filter paper soaked in aqueous potassium hydroxide  (6  M). Supercapacitorwas assembled by stacking two fabricated electrodes with a separator. The fabricated supercapacitor as shown in Figure1 was sealed by laminating it with plastic foil and fixing the layer together by two clamps.
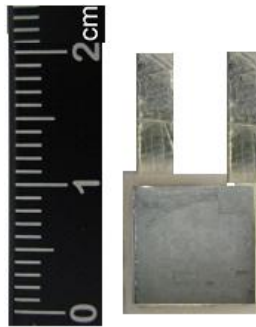


Fig. 1 Simulation Assembled supercapacitor

## IV. ELECTROCHEMICAL MEASUREMENTS

The electrochemical performance was analyzed for supercapacitor electrodes in a two-electrode system by CV and EIS using Potentiostat/Galvanostat/ZRE Gamry G750 instrument, and the galvanostatic charge-discharge was carried out with a Gamry  3000. The CV response of the electrodes was measured at different scan rates varying from 1 mV/s to 100 mV/s. EIS measurements were carried out with no dc bias with sinusoidal signal of 5 mA over the frequency range from 0.05 Hz to 1MHz.Performance of supercapacitor as a function of temperature was studied from in the range 25°C to 75 °C.The specific capacitance of the electrode was calculated from the CV curves according to the following  equation [25]:

$$C = \int \frac{idV}{(\Delta V * \upsilon * m)} \tag{1}$$

where C is the specific capacitance (F/g), i is the positive/negative scan current (A), V is the corresponding voltage (V), $\upsilon$ is the scan rate (V/s), $\Delta V$ is the potential differences (V) and m is the weight of the graphene film  (g).The energy  density and power density of  the  electrode  were  calculated according to  the  following equations [25]:

$$E = \frac{1}{2} * C * V^2 * \frac{1000}{3600} \tag{2}$$

$$P = \frac{E}{t} \tag{3}$$

where E is the energy density (Wh/Kg), C is the  specific capacitance  (F/g) , V is the cell  voltage  (V) , P is the average power density (W/Kg) and t is the discharge time (h).

## V. RESULTS AND DISCUSSION

In the fig 2, it shows the UV-visible spectra of GO, graphene and PANI doped with CSA. Spectrum  of  GOhas  a typical absorption peak at 233 nm with a  shoulder around  300 nm, which are ascribed to π-π* transition of

aromatic rings and n–π* transition of C=O, respectively [25].Spectrum of graphenehas  absorption peak at 270 nm , which  was  ascribe  to  π-π* transition  of  aromatic due to reduction to 72h.  From the spectrum of the PANI, the absorption peaked at ~350 nm due to $\pi$-$\pi^*$transition of the benzenoid rings and at ~430 nm (inconspicuous) and ~780 nm due to polaron- $\pi^*$transition and $\pi$-polaron transition are observed [24].
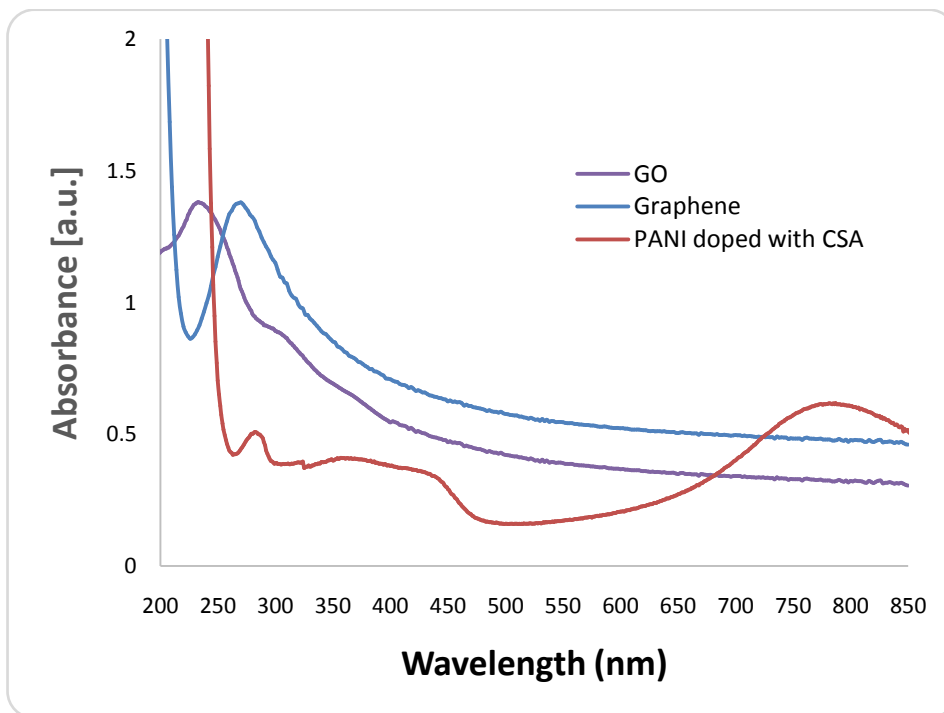


Fig. 2 UV-visible spectra of GO, Graphene and PANI doped with CSA

In the fig 3, it shows the SEM images of graphene and PANI doped with CSA layers. Figure (3a,b) shows the morphology of graphene at different magnifications that has a needle or fibrillar structure with a diameter size of about 120 nm due to reduction of graphene oxide after deposited on the stainless steel substrate**.** Figure (3c,d) shows the morphology of PANI doped with CSA layer at different magnifications that is uniformly coated on the surface of the graphene due to the use of spray coating method. PANI doped with CSA exhibits three phases of nanowire, coagulated granular and nanosheetstructures.The nanowires with an average diameter size of about 150 nm and nanosheets of PANI havean average width of about 1 um are formed and spread [23, 27].
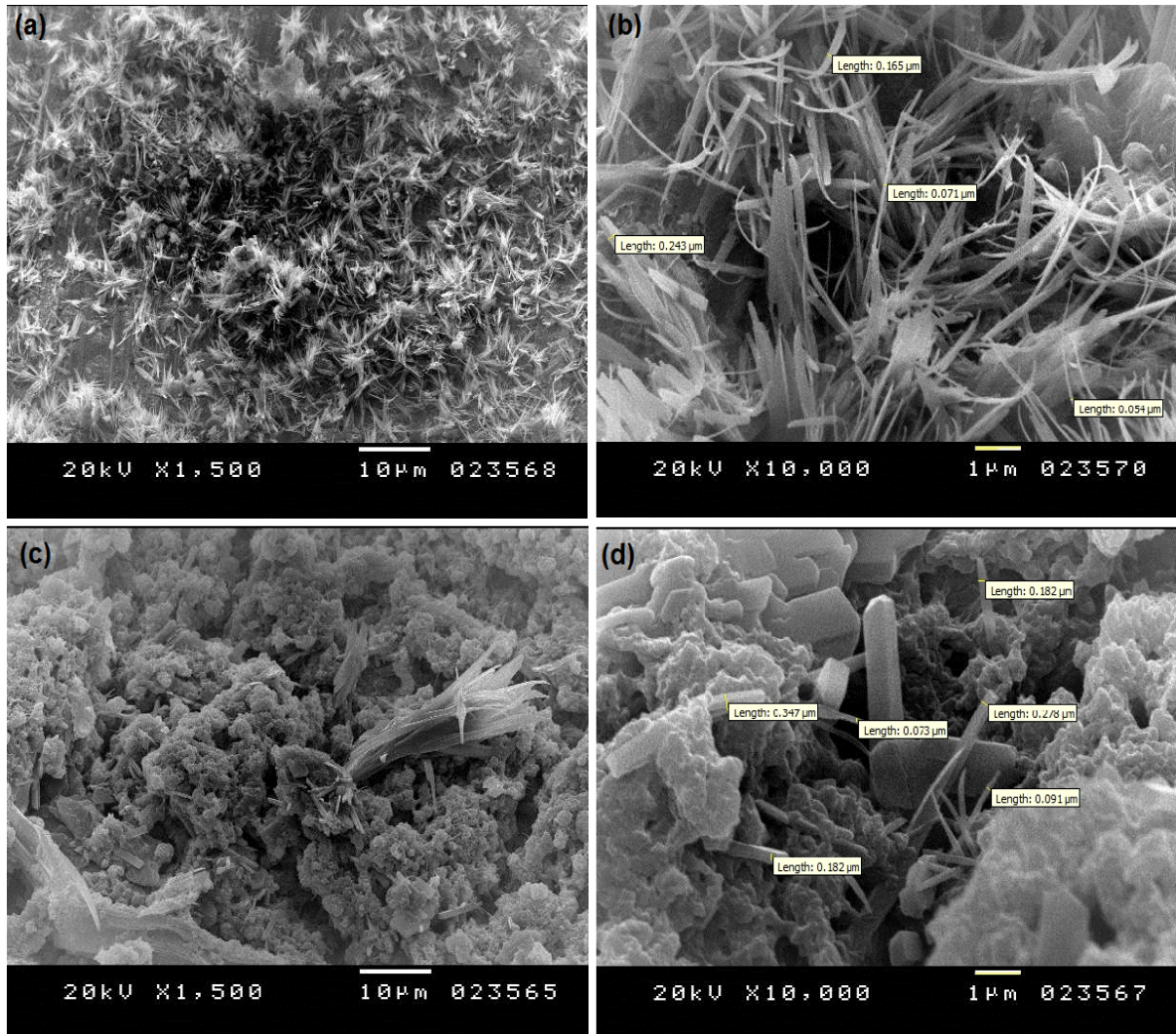
Fig. 3  SEM images of (a, b) graphene layer, (c, d) PANI doped with CSA layer

In the fig 4, it shows the CV of graphene/PANI double layers using two probes connection at differe scan rate from 1 mV/s to 100 mV/s with scanning potential window between - 0.8 and 0.8V. The CV curve area is gradually enlarged with the increase of the scan rate. The slight deviation from the standard rectangular shape, especially at a relatively high scan rate, could be attributed to the distributed charge storage, which is a classical porous electrode behavior. At a low scan rate, there is sufficient time for electrolyte ions migration to the inner part of the electrode [27]. The calculated specific capacitance was 915.78 F/g at scan rate of 5 mV/s and the weight of active material was 4 mg. The fabricated supercapacitor has an increased energy density of 127.19 Wh/kg at potential difference of 1V [26].
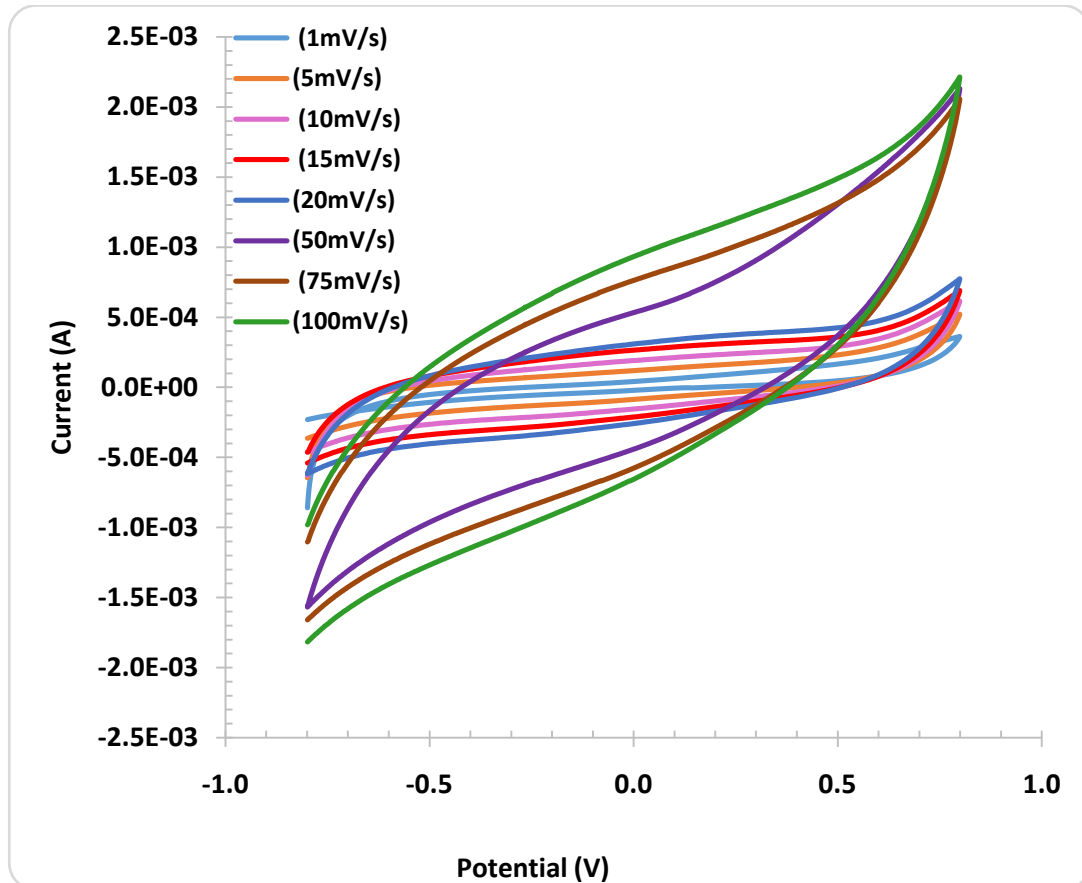
Fig. 4 CV curves of graphene/PANI -6 M KOH-graphene/PANI supercapacitor

In the fig 5, it shows the Nyquist plot of graphene/PANI -6 M KOH-graphene/PANIsupercapacitor. Nyquist plot shows a line in the low frequency region and a semicircle in the high frequency region. The semicircle corresponds to charge transfer resistance ($R_{ct}$). The value of charge transfer resistance is found to be 139.6 Ω. The intersection of the curve at the x-axis represents the internal or equivalent series resistance (ESR). ESR is the sum of the electrolyte resistance, the intrinsic resistance of the active electrode material and the contact resistance at the interface of the active material and the current collector. The value of equivalent series resistance is found to be 2.8 Ω. This resistance determines the rate of the charge and discharge and consequently the power capability of the supercapacitor. The slope of the 45° portion of the curve is called the Warburg resistance and is a result of the frequency dependence of ion diffusion/transport in the electrolyte [30, 3].
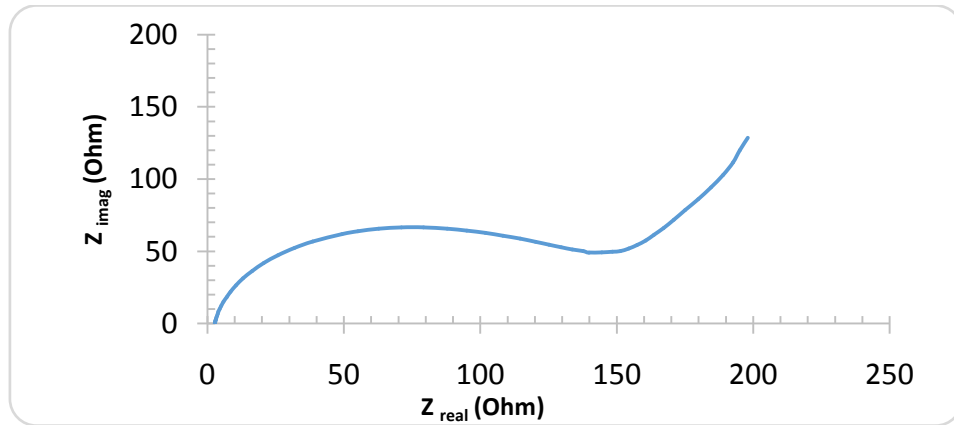
Fig. 5  Nyquist plot of graphene/PANI -6 M KOH-graphene/PANI supercapacitor

In the fig 6, it depicts the Bode plot of graphene/PANI-6 M KOH-graphene/PANIsupercapacitor. It contains the data plotted in a magnitude and phase versus frequency format. The impedance in the Bode plot decreases with the frequency increase while the phase angle decreases with the frequency increase until 476 Hz then increases rapidly with the frequency increase. For the current work, the knee frequency of the fabricated supercapacitor using KOH electrolyte is 476 Hz and phase angle is nearly -70˚. The significance of the so-called knee frequency in the bode plot is the critical frequency where all surface area is accessed, i.e., saturated [19, 30].
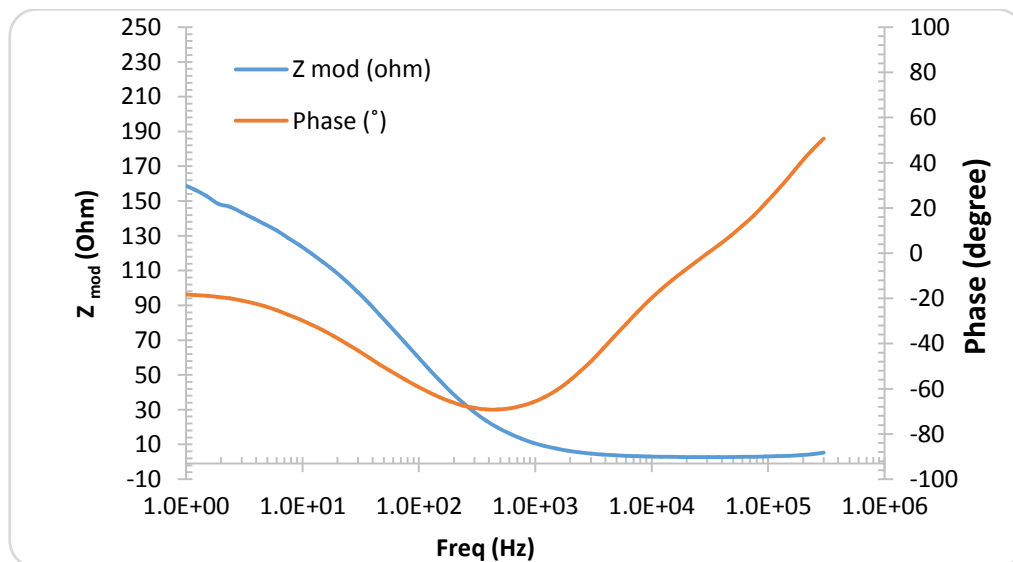


Fig. 6  Bode plot of graphene/PANI -6 M KOH-graphene/PANI supercapacitor

In the fig 7, it presents the galvanostatic charge-discharge curves of graphene/PANI double layers supercapacitor. Supercapacitor was charged and discharged at constant current of 4.58 $Ag^{-1}$ and 9 $Ag^{-1}$ in potential range from 0 to 1V. The graphene/PANI supercapacitor exhibited semi triangular shape charge-discharge curves due to synergetic effect between graphene and PANI layers. The deviation to linearity was typical of pseudocapacitive contribution, which demonstrated that the capacitances of  PANI layer mainly originate from pseudo-capacitance plus electric double layer capacitance of graphene layer. The charge–discharge time for graphene/PANI supercapacitor was 400 s at 4.58$Ag^{-1}$ and 200 s at 9$Ag^{-1}$, which was indicative of good capacitive behavior achieved [28].
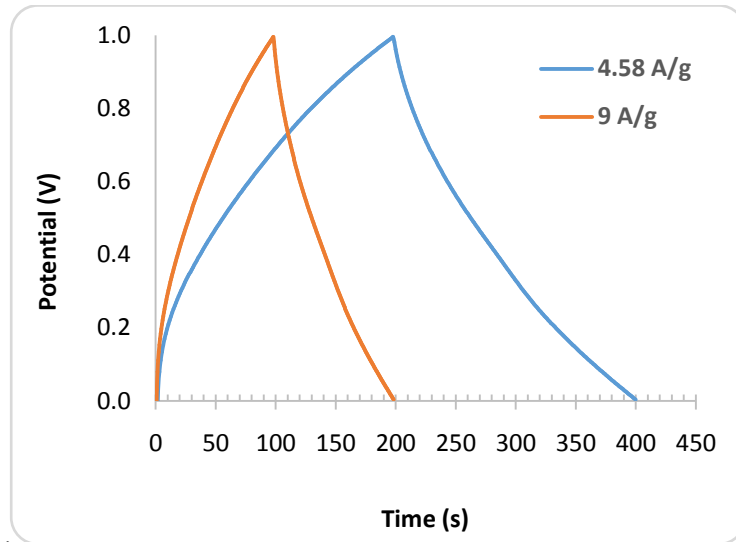
Fig. 7 Charge and discharge curves of graphene/PANI -6 M KOH-graphene/PANI supercapacitor at constant current of 4.58Ag$^{-1}$ and 9Ag$^{-1}$

In the fig 8, it represents the specific capacitance of graphene/PANI -6 M KOH-graphene/PANI supercapacitor as a function of temperature of 25˚C to 75 ˚C. The influence of temperature on specific capacitance is insignificant. Improvement in Specific capacitance was slightly for about 1% in the temperature range between 25˚C and 70 ˚C. Increasing the temperature have the main effect of reduce the electrolyte viscosity and enhance the accessibility of the surface for the ions. Interestingly, the specific capacitance decreases slightly when the temperature exceeds 70 ˚C. This observation can be explained by the increasing thickness of the Helmholtz layer (charge separation distance) caused by Brownian motion of the ions at high temperature.The capacitance is inversely proportional to the charge separation distance [10, 31].
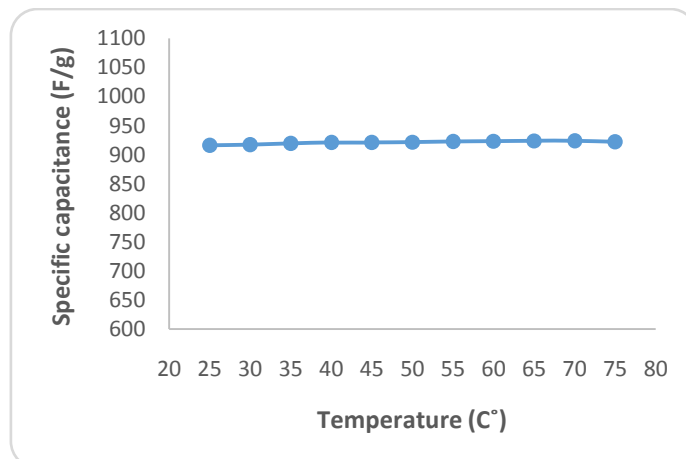


Fig. 8 Specific capacitance of graphene/PANI -6 M KOH-graphene/PANI supercapacitor as a function of temperature of 25˚C to 75 ˚C

## VI.CONCLUSION

Supercapacitors with graphene/PANI electrodes and filter paper separator were fabricated. The results indicated that graphene/PANI double layers exhibited high porosity and large surface area. The fabricated supercapacitor provided an increased specific capacitance of 915.78 F/g, energy density of 127.9 Wh/kg and power density of 4.58 kW/kg. The high value of the power density was suitable for surge power applications. Supercapacitor performance was stable in temperature range between 25 ˚C and 70 ˚C.

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