

## SUPERCAPACITOR NANOCOMPOSITE USING rGO, MWNT AND PANI

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### ABSTRACT

There has been a lot of research on developing high performance Li-ion batteries and fuel cells but still the slow power capability and high maintenance cost is a barrier in using them for many applications. To solve this problem supercapacitors have been developed, which have long life cycle, high speed charge and discharge, high power density and no issues with short circuit. But they have low energy density. The objective of this paper is to explain how Graphene-based supercapacitors with high power density along with high energy density can be produced at low cost. These supercapacitors store energy as electric charge on porous materials. Graphene is a suitable material for making super capacitors because of its high surface area, chemical stability, lattice structure and most importantly, its appealing electrical properties. Theoretically a monolayer of  $sp^2$  bonded atoms can have a specific capacitance upto  $\sim 550$  F/g as well as a surface area of  $2475$  m<sup>2</sup>/g. There are many methods to synthesize graphene but the price and quality and viability do not come together. thus being a barrier in industrial applications. The porous graphene material reported in this thesis was synthesised by improved hummers method. It was mixed with a conducting polymer, Polyaniline (PANI) to make the supercapacitor electrode. XRD has a peak at  $24.34^\circ$  suggesting that the interlayer distance is  $3.64$  Å with absence of functional groups containing oxygen such as hydroxyl and carbonyl groups. FTIR peaks also have low intensity of oxygen related peaks, thus supporting the above statement. The resistivity test was conducted using the 4 probe method which showed that the sample containing both MWNT and rGO had the highest resistivity. For comparison electrodes were also prepared using MWNT-PANI and rGO-MWNT-PANI. For the electrochemical performance of the electrodes Cyclic Voltammetry (CV) test was done which showed PANI-RGO-MWNTs have a greater current density and higher specific capacitance of  $330$  F g<sup>-1</sup>.

**KEYWORDS:** Reduced Graphene Oxide, Graphene; Polyaniline, Cyclic Voltammetry, XRD, FTIR

### INTRODUCTION

The increasing demand for power to develop newer technologies has resulted in increased focus on scientific and industrial communities to find better sources of energy[1]. Considering the environmental effects of present energy sources, we need to have a better energy storage technique. In spite of a lot of research being done to develop Li-ion batteries and fuel cells having high performance characteristics [2-4], they require high maintenance and low capability acting as barrier from being used in major applications.

A capacitor is a passive electrical device which stores energy as charge in the electrical field between two conducting plates called electrodes. Capacitors generally can release the stored charge quite fast resulting in a high power, but cannot store much energy.

In a Conventional capacitors when external voltage is applied, charges get accumulated on the surfaces of the two electrodes which are separated by an insulating dielectric layer, thereby, an electric field is generated which allows the device to store energy.

Super capacitors electrodes have a much larger surface area and a much smaller separation between the electrodes because the charge is stored on the electrode. The electrode absorbs charge like a sponge. An electrode of graphene can theoretically have a surface area of  $2630 \text{ m}^2/\text{g}$  [5].

A super capacitor and an electrolytic capacitor have similar construction, except for the electrodes. The electrolytic capacitor is made of metal electrodes whereas the supercapacitor has highly porous electrodes. Electrolytic capacitors are made of aluminum, tantalum and ceramic where they use solid/liquid electrolytes with a separator between two symmetrical electrodes. Supercapacitor electrodes are made using nanomaterials because they have a very high surface area, thus increasing the charge density.

Super capacitors are basically classified into electrical double-layer capacitors (EDLCs) - (good electrical conductivity and long cycle life, but with a relative low specific capacitance )and pseudocapacitors (have high specific capacitances of poor stability and slow response during the charge/discharge cycling).[6, 7]. Hence, to overcome these barriers it is required to create a composite electrode having high energy density as well as power density thus having advantages of both pseudocapacitors & EDLCs.

Graphene has been called as wonder material by many researchers. it consists of a single layer of sp<sup>2</sup>-bonded carbon in a hexagonal lattice. It can be considered as a candidate for electroactive carbon electrode because of its high Thermal and electrical conductivities, mechanical strength, and specific surface area.[8, 9] Researchers have proved it to be a suitable material for solar cell electrodes,[10] secondary batteries[11] and ultracapacitors.[12] It is polymerized with polyaniline (PANI) which is a conducting polymer because of ease of availability, cheaper price, environmental stability, no special equipment required to handle it, and the multiple redox states which lead to specific pseudocapacitance of a high degree. [13]

A battery charges slowly but can have more charge, i.e. low energy density and high power density. A capacitor charges fast but can hold less charge, i.e. high energy density but low power density. The capacitances of electrolytic capacitors are in the range 0.1 to 10  $\mu\text{F}$  with a voltage profile of 25 to 50 V [14]. A supercapacitor combines the advantages of both battery and a capacitor, i.e. it has a high energy and power density. It holds more charge and charges faster (see table 1).

A super capacitor and an electrolytic capacitor have similar construction, except for the electrodes. The electrolytic capacitor is made of metal electrodes whereas the supercapacitor has highly porous electrodes. Electrolytic capacitors are made of aluminum, tantalum and ceramic where they use solid/liquid electrolytes with a separator between two symmetrical electrodes. The composite produced had a capacitance value of  $350 \text{ F g}^{-1}$  at  $0.5 \text{ A g}^{-1}$ , charge/discharge efficiency of 96.7%.

In electric double layer capacitor, also known as supercapacitor, the electrical charge stored at the metal/electrolyte interface.. charge in the order of  $\sim 10^6$  Farad can be stored in it(tabulate examples w.r.t materials used). They can be considered complementary to batteries because they can deliver low energy density & high power density. They also have a very long life cycles (see Table 0). Thus it combines the best parts of battery and capacitor and brings it

into a single hybrid charge storage device. [14].

The electrodes can be made with Graphene as it has a very high surface area, thereby more charge can be stored on it. Theoretically graphene has a surface area of 2475 m<sup>2</sup>/g. Graphene has such a high surface area because it is just a single layer of atoms and it has a very porous structure, thus allowing it to store more charge than any other material.

**Table 1: Comparison between Batteries, Super Capacitor and Electrolytic Capacitor [15]**

Parameter	Batteries	ECSC	Electrolytic Capacitors
Specific energy (Wh/kg)	10–100	1–10	<0.1
Charging time	1 < <i>t</i> < 5 h	1–30 s	10 <sup>-3</sup> < <i>t</i> < 10 <sup>-6</sup> s
Discharging time	<i>t</i> > 0.3 h	1–30 s	10 <sup>-3</sup> < <i>t</i> < 10 <sup>-6</sup> s
Lifetime	1000	10 <sup>6</sup>	10 <sup>6</sup>
Specific power (W/kg)	<1000	10,000	10 <sup>-6</sup>
Charge/discharge efficiency	0.7–0.85	0.85–0.98	>0.95

## MATERIAL FABRICATION PROCESS

### Preparation of Graphene Oxide (GO)

The schematic of synthesis process is shown in Figure 1. GO was prepared by oxidizing the graphite powder with modified Hummer's method[16]. The GO is heavily oxygenated with a basal plane mainly occupied by C=O, C-OH and COOH groups. 0.285 grams of exfoliated graphite was added to a conical flask 40 ml of H<sub>2</sub>SO<sub>4</sub> and 10ml of H<sub>3</sub>PO<sub>4</sub>. This mixture was stirred for an hour and then kept in ice bath. Then 0.4g of KMnO<sub>4</sub> solution was added to 30 ml water. This solution is added drop by drop to the solution in conical flask. It is added drop by drop so that the temperature of the solution does not go beyond 50 degrees, which can lead to formation of Mn<sub>2</sub>O<sub>7</sub>, which is an explosive compound. Thus it is preferable to keep temperature below 20 degrees. After the entire KMnO<sub>4</sub> solution is added we stir the solution for 3 days. After 3 days, few drops of H<sub>2</sub>O<sub>2</sub> are added to the solution. If there are any unoxidised metal ions the color changes to yellow. No color change occurs if there are no unoxidised metal ions. The solutions are then sonicated for 15 minutes and then centrifuged for about 20 minutes. Graphene is collected. Preparation of reduced graphene oxide (rGO) Graphene oxide is not a good conductor, so to overcome that fault we convert it to reduced graphene oxide[17]. For this 0.1 g of GO is taken in 50ml of Deionised water and 0.1 ml of Hydrazine Monohydrate is added to it. The solution is then heated to 95 degrees for 1 hour. Reduced graphene oxide is collected on a filter paper and washed repeatedly with DI water to remove excess hydrazine. The final product is dried in oven.

### Preparation of Polyaniline (PANI) – RGO (Reduced Graphene Oxide) Composite by Interfacial Polymerization[18]

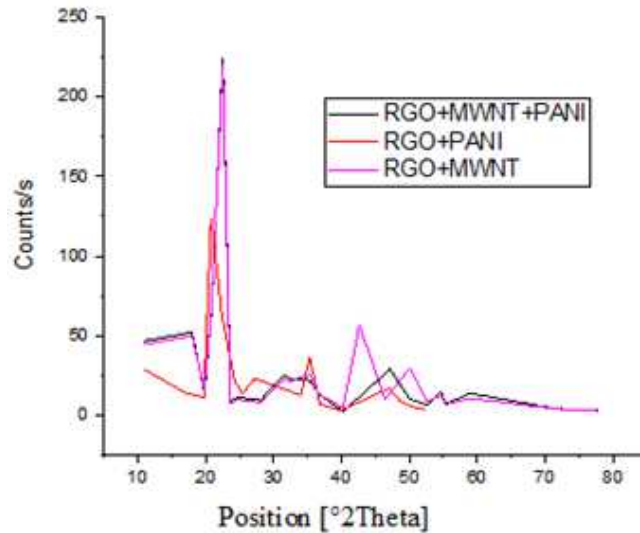
Aniline was polymerized using interfacial polymerization. Two solutions were used. In first solution 20 mL hydrochloric acid (1 M) with 4 mmole ammonium persulfate. The second solution contained 20 mL chloroform with 4 mmole aniline and the required nanoparticles. The solutions were stirred using a magnetic stirrer for one hour. Then the oxidant based solution was transferred to the first aniline based solution. The reaction took place almost instantly, polyaniline was synthesised at the interface of the solutions which were immiscible. The polyaniline nanofibers were green and filled the container over time. The polyaniline doped nanofibers were filtered and dried at room temperature for 24 hours. 3 types of nanoparticles were used to prepare 3 different composites: Reduced Graphene Oxide, Multiwalled nanotubes and a combination of both.

**Table 2: Ratio of MWNT and RGO in PANI**

Sample	Weight of RGO (grams)	Weight of MWNT (grams)
I	0.17	0.25
II	0.24	0.0
III	0.0	0.24

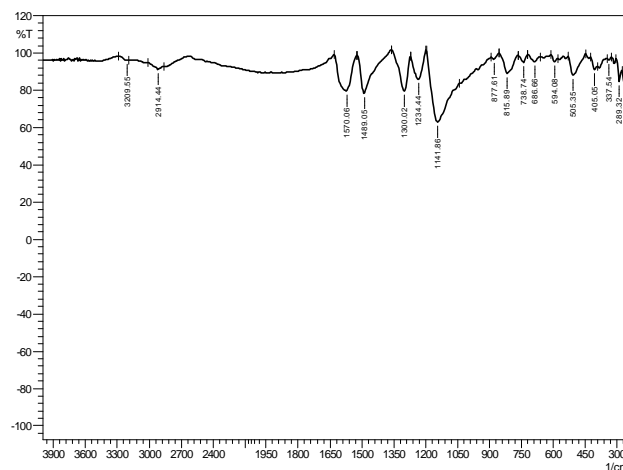
## EXPERIMENTAL RESULTS

### XRD

**Figure 1: XRD Pattern of RGO, RGO-MWNT and RGO-MWNT-PANI**

XRD has a peak at  $24.34^\circ$  suggesting that the interlayer distance is  $3.64 \text{ \AA}$  with absence of functional groups containing oxygen such as hydroxyl and carbonyl groups[19]. Also there is no peak at  $12^\circ$  which suggests that the micro scale Graphite is totally converted into reduced graphene oxide.

### FTIR

**Figure 2 FTIR Pattern of RGO-MWNT-PANI**

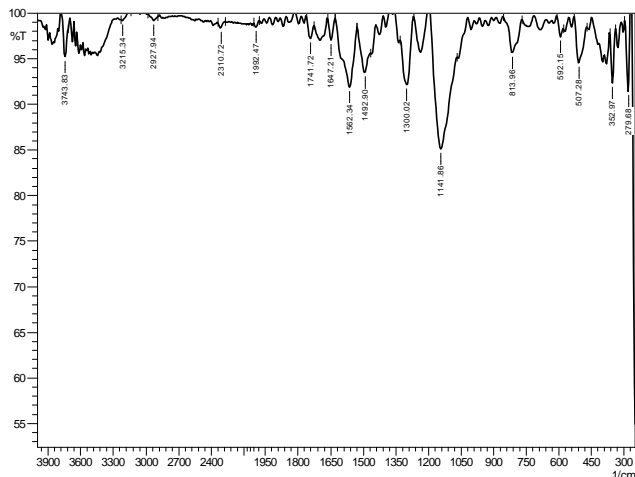


Figure 3 FTIR pattern of RGO- PANI

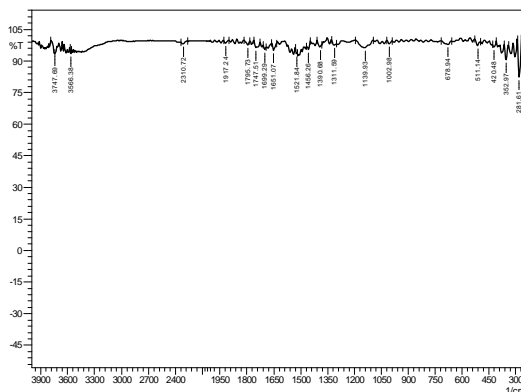


Figure 4 FTIR Pattern of MWNT-PANI

The bands at 1431 cm<sup>-1</sup> & 1558 represent to C=C stretching vibrations of benzenoid & quinoid rings, respectively. The bands of aromatic, C=N, C-N and C-H stretching vibration at 1240, 1298 and 1078 cm<sup>-1</sup> also can be clearly recognized, respectively[20].

This result indicates that PANI is in the proton doped emeraldine salt state.

**Cyclic Voltammetry Test**

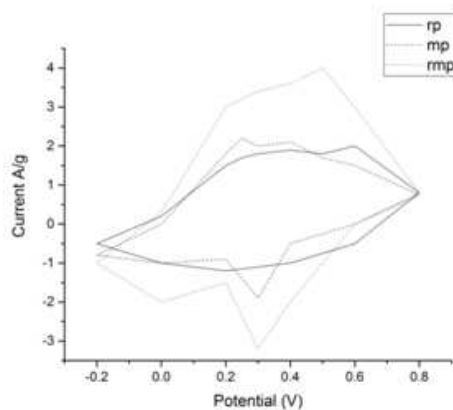


Figure 5: CV result at 10mV s<sup>-1</sup> of RGO-PANI (rp), MWNT-PANI(mp) and RGO-MWNT-PANI (rmp)

Cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS) was used to characterize the electrochemical performance of the samples. Fig. (5) presents the CV curves of all samples at a sweep rate of 10 mV s<sup>-1</sup> with a potential range from -0.2 to 0.8 V in 1 M H<sub>2</sub>SO<sub>4</sub> solution. For PANI–RGO–MWNTs and PANI–MWNTs electrodes, the two couples of redox peaks, i.e., C1/A1 and C2/A2, in CV curves result in the redox capacitance. The redox peak C1/A1 is attributed to the redox transition of PANI from leucoemeraldine (semiconducting state) to emeraldine form (conducting state), whereas C2/A2 is ascribed to the transformation from emeraldine to pernigraniline.[21,22] PANI–RGO–MWNTs sample exhibits a larger current density response compared to PANI–RGO and PANI–MWNTs electrodes at the same scan rate, suggesting that PANI-RGO-MWNTs have higher specific capacitance.

The specific capacitance can be calculated by  $sc=A/SV$

where A is area under the curve and sv is the scan voltage. The specific capacitance of the PANI– RGO is about 185 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup>. The specific capacitance of the PANI–MWNTs is about 169 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup>. The specific capacitance of the PANI– RGO–MWNTs is about 330 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup>. The enhanced specific capacitance is a result of the synergistic effect between MWNTs, RGO and PANI, in addition to the good electrical conductivity of the sample.

### Resistivity Measurement

Resistivity of the sample was measured using a 4 probe method. Resistivity is the inversely related to conductivity. Thus it can be concluded from this test that PANI-MWNT-RGO have the highest conductivity.

**Table 3: Resistivity test of MWNT and RGO in PANI**

S. no.	Name of the Sample	Resistivity (Ω )
1	PANI + MWNT + RGO	1034
2	PANI + RGO	698
3	PANI + MWNT	294

### CONCLUSIONS

In conclusion, Nanocomposite material for a super capacitor was prepared by using graphite as the raw material. Using improved hummers method it was converted into Graphene Oxide. This was later converted into Reduced Graphene Oxide for better conductivity. This Reduced Graphene Oxide was then polymerized with Aniline, which is a conducting polymer, to create the nanomaterial composite for the super capacitor. Multi walled nanotubes were also added to study its effect on properties of the nanocomposite. Cross sectional morphology, structure and phase studies of the synthesized composites were carried out by using a multitude of characterization techniques. These characterization techniques revealed that the material best suited for use as electrode is PANI-RGO-MWNT composite. The specific capacitance was calculated to be 350 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup>

Graphene is a wonder material which is useful in nearly all fields ranging from construction to a display. But there is a single reason why it isn't commercially popular; it is because producing high quality graphene at industrial level is still very expensive. But that barrier is decreasing as time passes.

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## REFERENCES

1. G. Wang, L. Zhang and J. Zhang, *Chem. Soc. Rev.*, 41, pp. 797-828, 2012.
2. M. Armand and J. M. Tarascon, *Building better batteries*, *Nature*, 451, pp. 652- 657, 2008.
3. H. Wu, G. Yu, L. Pan, N. Liu, M. T. McDowell, Z. Bao and Y. Cui, *Nature Communications*, 4, 1943, 2013.
4. C. M. Park, J. H. Kim, H. Kimc and H. J. Sohn, *Chem. Soc. Rev.*, 39, pp. 3115-3141, 2010
5. A. Peigney, C. Laurent, E. Flahaut, R. R. Bacsa, A. Rousset, *Carbon* 39 (2001) 507–514
6. G. P. Wang, L. Zhang and J. J. Zhang, *Chem. Soc. Rev.*, 2012, 41, 797.
7. Y. Zhai, Y. Dou, D. Zhao, P. F. Fulvio, R. T. Mayes and S. Dai, *Adv. Mater.*, 2011, 23, 4828.
8. A. Rudge, I. Raistrick, S. Gottesfeld and J. P. Ferraris, *Electrochim. Acta*, 1994, 39, 273.
9. X.-h. Yang, Y.-g. Wang, H.-m. Xiong and Y.-y. Xia, *Electrochim. Acta*, 2007, 53, 752.
10. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, 306, 666.
11. A. K. Geim, *Science*, 2009, 324, 1530.
12. J. Liu, Y. H. Xue, Y. X. Gao, D. S. Yu, M. Durstock and L. M. Dai, *Adv. Mater.*, 2012, 24,2228.
13. Y. Zhou, Z.-Y. Qin, L. Li, Y. Zhang, Y.-L. Wei, L.-F. Wang and M.-F. Zhu, *Electrochim. Acta*, 2010, 55, 3904.
14. M Jayalakshmi\*, K Balasubramanian, *Int. J. Electrochem. Sci.*, 3 (2008) 1196 - 1217
15. *Electrochemical Power Sources: Batteries, Fuel Cells, and Supercapacitors*, By Vladimir S. Bagotsky, Alexander M. Skundin, Yuriy M. Volkovich
16. Marcano et al. *ACS Nano*, 2010, 4 (8), pp 4806–4814, DOI: 10.1021/nn1006368
17. K. Zhang, L. L. Zhang, X. S. Zhao and J. Wu, *Chem. Mater.*, 2010, 22(4), 1392.
18. Ahmad Abdolahi et al, *Materials* 2012, 5, 1487-1494; doi:10.3390/ma5081487
19. P. Delhaes, *Graphite and Precursors*, CRC Press, Boca Raton, FL, 2001.
20. Li, Y.; Zhao, X.; Xu, Q.; Zhang, Q.; Chen, D. *Langmuir* 2011,27, 6458–6463
21. J. Wei, J. Zhang, Y. Liu, G. Xu, Z. Chen and Q. Xu, *RSC Adv.*, 2013, 3, 3957.
22. C. C. Hu and J. Y. Lin, *Electrochim. Acta*, 2002, 47, 4055.

