SYNTHESIS AND CHARACTERIZATION OF REDUCED GRAPHENE OXIDE FOR SUPERCAPACITORS

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Degree of Master of Science

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This Dissertation submitted in partial fulfillment of the requirements for the Degree of Master of Science in Material Science.

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DECLARATION

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The above candidate has carried out research for the partial fulfilment of the requirements for the Degree of Master of Science in Material Science under my supervision.

Project Supervisor: Prof.S. U. Adikary

 Date: 23/06/2020

Abstract

The main focus of this investigation was to add value to high purity Sri Lankan graphite. Reduced graphene oxide(rGO) was synthesized using locally available graphite from Kahatagaha mines and purity was recorded as 99%. Modified Hummers method was used to synthesize rGO. Synthesized rGO was characterized using Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) and X-ray Diffraction Spectroscopy(XRD). The specific capacitance was recorded as $0.45Fg^{-1}$ in rGO. The specific capacitance of the capacitor was calculated using cyclic voltammetry testing at $10mVs^{-1}$. SEM analysis shows the rGO surface character, larger surface area and warped morphology of rGO.

In this research, we were able to develop rGO material from locally available graphite for capacitor applications without surface activation. Numerous research projects are ongoing in this field with ultra-pure (99.99%) graphite materials but the purity of locally sourced graphite recorded as 90% to 99% without value addition. Therefore, the usability of local graphite to develop rGO seen prospective for its super capacitance performance, however, future improvement is needed.

Key words: Graphene, Supercapacitors, reduced graphene oxide.

ACKNOWLEDGMENTS

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LIST OF ABBREVIATIONS

EDLC   Electrically Double Layer Capacitor

rGO   reduced Graphene Oxide

GO   Graphene oxide

CMG   Chemically modified graphene

FTIR   Fourier transform infrared

SEM   Scanning Electron Microscope

XRD   X-Ray diffraction

CV   Cycle voltammetry

1. INTRODUCTION.

1.1 Sri Lankan graphite.

Graphite is well known vulgar make up crystalline polymer of carbon. A name often functional to graphite, "Miniran" in Sinhala language and as well called "plumbago" (Latin -"acts like lead") where it is popularly called "black-lead." Amorphous, Flake and Vain are the three principal varieties of graphite and vain graphite is widely available graphite form present in Sri Lanka. Due to its elevated purity, large mineralization and limited presence, vein type graphite deposits are considered as a specific natural outcome of graphite. Four structural well-defined graphite varieties obtaining by vein graphite(Balasooriya et al., 2006,2007). Size/shape of the vein, cooling conditions, nucleation conditions, composition of the origins, intensity and frequency of the hydrothermal activities are depend on structural varieties of graphite crystals(Hewathilake et al.,2015). Graphite with 90% to 99% of carbon and other minerals depending on the mode of occurrences, mode of processing and nature of graphite vein. Minerals in graphite are mainly related to the graphite surface and some are intercalated between graphite inter layers. According to chemical analysis, resulting that Fe, Ca, Mg, Si, Al and Na are the abundant trace elements present in vein graphite surfaces(Dissanayake et al., 1988).

Sri Lanka has a respectable history of graphite mining and supplying in early 1800s. Earnest mining and commercialism of Sri Lanka graphite began about 1824s(Lanka Graphite Limited,2016).

There are two traditions of manufacturing graphite in Sri Lanka today; as Kahatagaha Graphite Lanka Ltd., hold by the Government of Sri Lanka which was produced 915 M.T. Per year,2010 and Bogala Graphite Ltd., a 90%-owned secondary of Germany's Graphit Kropfmuhl AG which was produced 6000 M.T per year, 2012. Today, China is well known as the world largest graphite supplier.

Sri Lankan vein graphite are mainly ranging in thickness of less than 1 mm thick to veins over 1 m thick.
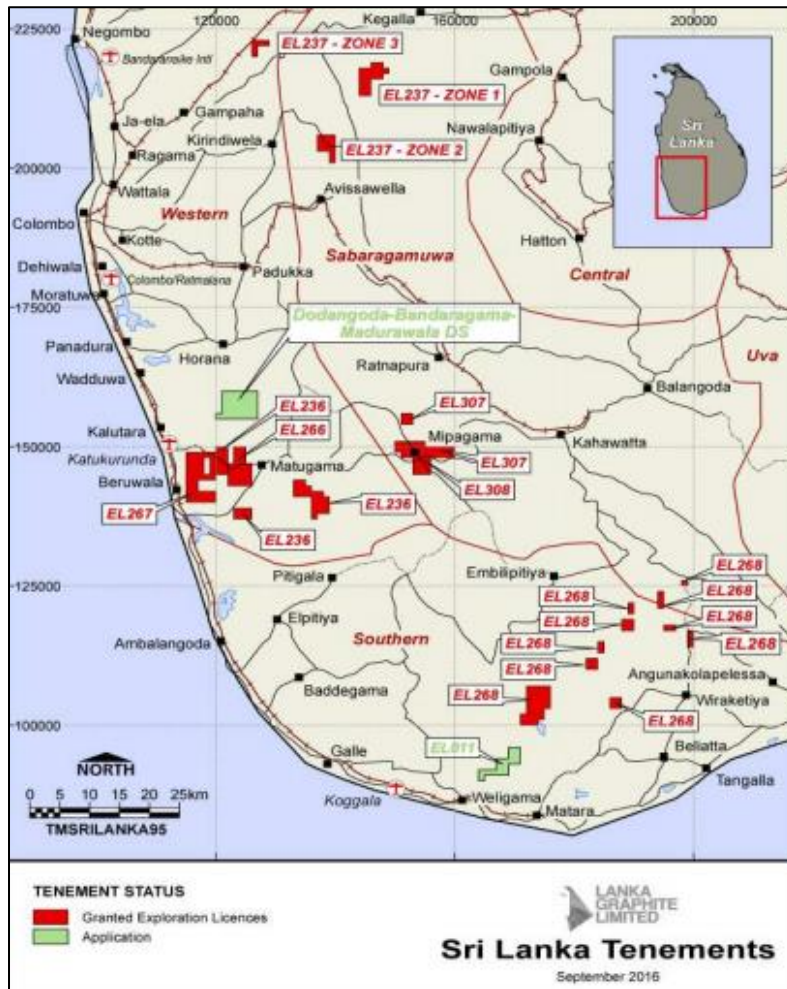
Figure 1.1. Distribution of graphite deposit in Sri Lanka

Loading plumbago barrels into bullock-carts for shipping #IMG544

Workers sorting and packing graphite into barrels for export near Colombo #IMG613

PLUMBAGO or Graphite Preparation IMG0216
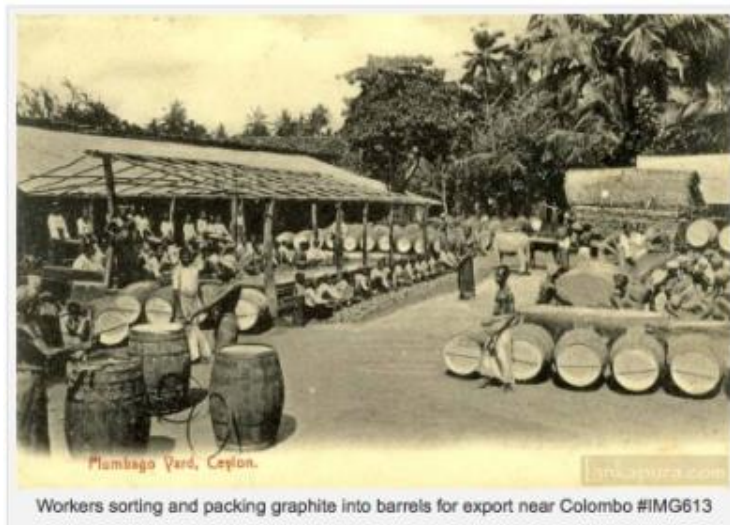
Figure 1.2. Graphite mines in early days.

1.2 Graphene, Graphene oxide and reduced Graphene oxide(rGO).

Graphene is a layer of hexagonal carbon with the thickness of one carbon atom. Carbon is a chemical element with atomic number 6, atomic mass about 12.0107 u, atomic radius of 170 pm and belongs to group 14 of the periodic table. The first looking at invention of graphene and a revolution in the field lead by Andre Geim and Kostya Novoselov in 2004. They were awarded the Nobel Price in physics for this invention in 2010. They started with graphite and produced a single sheet through a top-down approach called "micro-mechanical cleavage" method. Nowadays the most effective way of producing graphene is "Chemical Vapor Deposition and Chemical Etching" Technique. Not only the reference methods but also there are several methods to producing graphene in laboratory level as well as commercial level. The inter layer distance of two graphene sheet is recorded as 0.335nm and carbon atom separation is 0.141nm. The representative distance for two inter planes are agglomerating based on weak Van-der Waals/London forces (Andres et al,2013). Based on the characterization, graphene can be consider as two dimensional material with elevated properties such as mechanical, electronic, optical, thermal and functional material (Geim et al,2007).
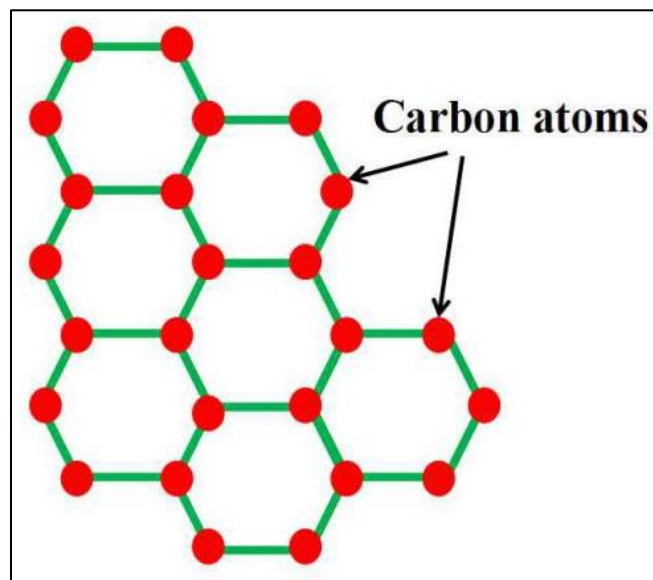
Figure 1.3. Carbon structure of graphite layers.

Probable applications may include solar cells, transparent electrodes and electronic devices, composites, water purification applications, absorbent material and energy storage devices sensors etc. Graphene is stronger than diamond, light weight and flexible. It shows much fast electrons flows respect to another conductor/semi conductor materials such as silicon. Therefore, many industries will affect by its numerical quantity.

Recently many researchers are interesting to produce graphene by reduction of graphene oxide and engaging other chemical synthesis methods. Deposition of single layer graphene on silicon substrate named as "chemical vapour deposition" at elevated temperatures requires advance technologies. Mass production of graphene using this technology.

Chemical adaptation/modification of graphite to graphene oxide, which is started by graphene oxide through chemically modified graphene substrates. Graphene oxide hold an reactive oxygen functional groups. But both graphene and graphene oxide show electrically insulating behaviour due to distressed electron flow, but most vital reactions of graphene oxide are its reduction to graphene/ rGO/ chemically reduced graphene. Graphene oxide material incorporate with oxide functionalists (alcohols and epoxides) but hold the shape structure comparable to graphite (Bielawski et al,2009). The surface functionality sharply decreases the layer to layer interactions because of its hydrophilic behaviour due to water intercalation among layers. Ultra-sonication/ sonication in water or polar organic solvent media may causes significant damage to the graphene oxide layers (Tascon et al,2008). The oxidation process also originates the breaking of the graphite structure into several component parts (Zhang et al,2009). Ceiling dispersibility of graphite/graphene oxide in solution is very crucial for further processing for new derivations. The dispersity depends on solvent and surface properties of graphite/graphene oxide during oxidation process. The dispersibility is proportional to the surface polarity.

Hydrazine monohydrate is used to prepare reduce graphene oxide from graphene oxide because strong reductors show a high reaction with water unless graphene oxide recognized as hydrophilic portion.

Characterizing the properties of the graphene oxide and resulting, the surface area is a measurement of the BET is measured as 466 m^2 g^{-1} throughout hydrazine reduction and theoretical value to be 2620 m^2 g^{-1} (Rouff et al,2009). The conductivity of the rGO sample was measured to be 2400 S m^{-1}, 0.021 S m^{-1} for graphene oxide and 2500 S m^{-1} for graphite (Stankovich et al,2007).

Strong chemical oxidants can be worn for the synthesis of graphene oxide when graphite using as starting material. The most important alteration of GO is reduction to graphene/rGO like resources. This can be achieved with strong reductants for example hydrazine(N_2H_4) or sodium borohydride ($NaBH_4$).

Reduced graphene oxide can produce by graphene oxide by several methods such as chemical, thermal etc. As above mentioning chemical procedures directed by strong reductants and seem few pros and cons. Thermal reducing methods are still seeking by researches and expose graphene oxide to elevated temperatures such as 1500K in inert environment. This research work also produced rGO through thermal puff method.

1.3 Graphene and Graphene composites.

Graphene sheets are producing with specific nature of them and it is very essential to combined with other elements, functional groups or polymers to enhance its elevated properties. Those combinations can be considered as likely nano scale segments of new composites. In general composites are consisting two phases called matrix and constituent phase. Graphene composites shows the metal parts are surrounded by graphene sheets. General approach for synthesis of graphene-metal nano composites in water-ethylene gycol medium and graphene oxide as a precursor and transition metal oxides or hydroxides as nano particles. These transition metal

nano particles are embedded among graphene oxide sheets and catalytic reduction of graphene oxide with reducing agents in ethylene glycol and resulting product is graphene-metal nano composite. When combination of graphene with polymers exhibit enhance performance, which are not only the purpose of reinforce but also to introducing new elevated electronic properties. Novel composites are making through various methods such as polymerization with nano particles, colloidal dispersion and electrochemical encapsulation etc.

1.4 Capacitors and supercapacitors.

Electrochemical capacitors are exhibiting respectable attraction due to their elevated power density with abbreviated charging time and enhanced cycling efficiency. They are exhibiting long lifetime with respected to batteries. When compare with traditional dielectric capacitors, this sort of capacitors has advanced energy density. Hence supercapacitors/ultracapacitors are most common energy storage devices and power supply devices for massive engineering applications as well as electronic applications. But their energy densities are still lower than the batteries and researcher are developing nano scale films/platelets to tackle this issue.

Electric double layer capacitors in terms of supercapacitors/ultracapacitor are devices with elevated capacitance values which are greater than other kind of capacitors available today. The most significant advantage of supercapacitors is ability to withstanding with out degrade like batteries on charge-discharge process. This is the main reason to combination of batteries and supercapacitors during engineering applications. Those kind of capacitors can be charge and discharge rapidly and release the large amount of energy while short period of time to the system since are required.

Mainly supercapacitors are based on carbon(activated carbon, carbon nano tube, graphene, etc) technology with large surface area in very tiny separation distance. This containing two metal electrodes those are separate by a dielectric material.
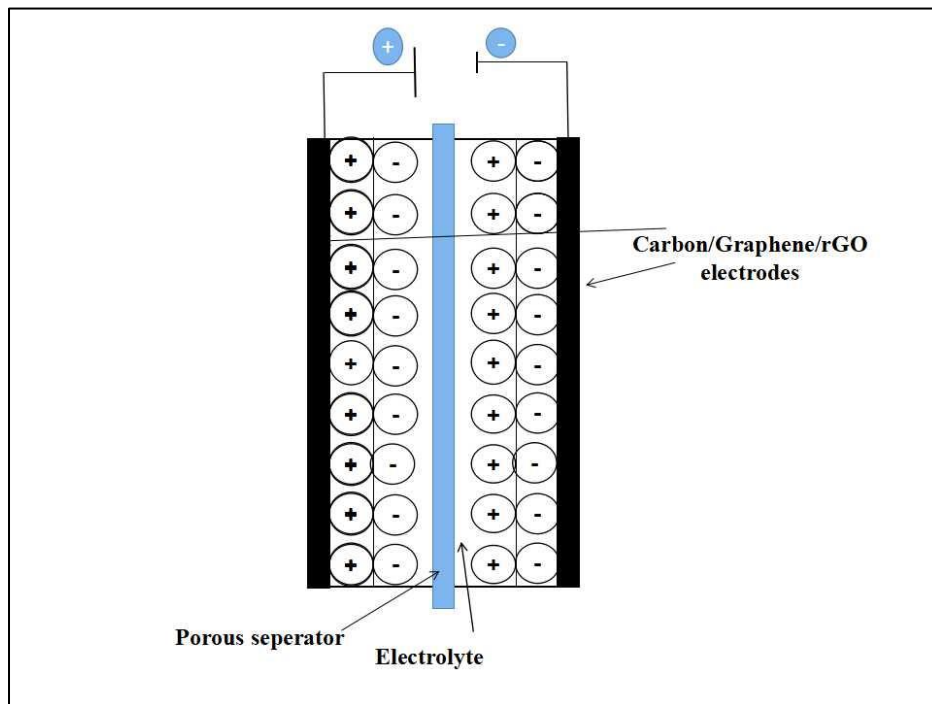
Figure 1.4.1 The schematic diagram of Supercapacitors.

Electrically double layer capacitors(EDLC) are consisting two porous electrodes which can be made by carbon, activated carbon, graphene, rGO etc. Those two electrodes are separated by porous separator and immersed in aqueous electrolyte and porous separator might be permeable for ion electrolyte. For this kind of capacitors, each electrode-electrolyte interface represents a separate capacitor therefore, entire cell can be consider an two capacitors. The plane area of the electrodes and the thickness of electrical double layer is proportional and inverse proportional to the double layer capacitance respectively. Therefore, this kind of capacitors for combination with large surface area and extremely small double layer thickness are responsible for their extra ordinary high capacitance values.

In electronic devices can find various kinds of fixed capacitors. Those are basically divided for two main categories. Those are Polarize capacitors and Non polarize capacitors.

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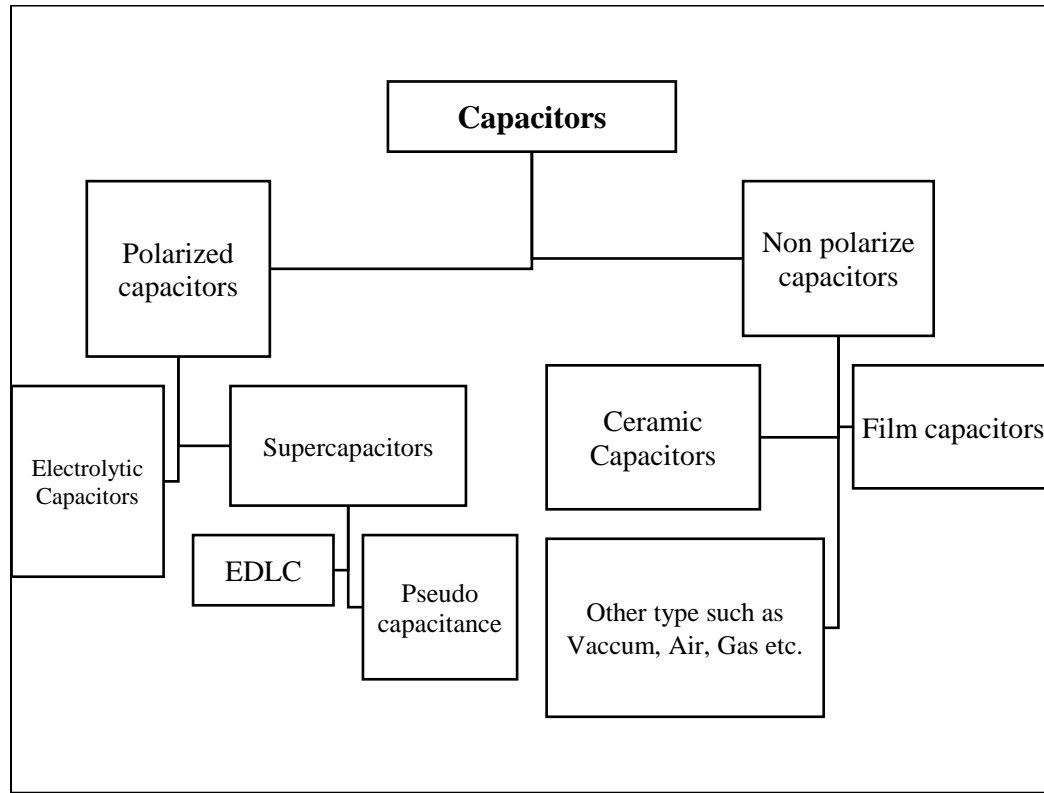
Figure 1.4.2 Schematic representation of Capacitor type

Supercapacitors are basically divided to two categories those are electrically double layer capacitance and pseudo capacitance. EDLC are followed under physical process of the Helmholtz double layer phenomena and Pseudo-capacitors are capable for hoard electric energy via electro chemically with reversible faradaic charge transfer progression. The combination of both EDLC and pseudo capacitors to increase power density and they called as "Hybrid Capacitors".

1.5 Research Justification.

Reduced graphene oxide supercapacitors are developing by many researchers in many years. This research project also dealing with similar practices but with utilizing Sri Lankan natural graphite source as core active material. The main objective is value adding to Sri Lankan available natural resources.

1.6 Objectives.

Therefore, this research project was conducted to:

I.   To understand the novelty of smart materials and their current trend in the world.

II. Synthesis and characterization of rGO.

III. Validate the rGO supercapacitor with the aid of many spectroscopic methods.

2.LITERATURE REVIEW

2.1 Carbon and carbon based materials for capacitor/super capacitor applications.

Carbon based materials are considering as potential electrode material for lot of industrial engineering electronic applications. Due to their low cost, high process-ability, large surface area, lack of toxicity, elevated electronic conductivity and excellent stability are making it as the most popular selection to date. Usually carbon can store charges based on electro chemical double layer formed at the electrode-electrolyte interface than dynamic material. Hence, the capacitance is affected on the plane area of the electrodes (Zhang et al,2009). Carbon materials such as graphene, rGO, activate carbon, carbon nanotubes/fibers etc are broadly using to fabricating electrodes for capacitors/supercapacitors owing to their high plane area. The recorded specific capacitance of carbon and its derivatives are with the ranges of 50-175 Fg^{-1} for aqueous electrolyes and 30-100 Fg^{-1} for organic electrolytes respectively (Wang et al,2012). The specific surface area is important for electrical double layer capacitors because of more sites/active sites are readily available for ions accumulation by electrostatic interactions to improve capacitance. Many researchers are interesting to enhance the specific surface area by several methods such as heat/alkaline treatment, steam treatment, CO_2 activation etc to obtaining high class capacitive performances (Zhu et al,2011).

Although, the definite capacitance is not always unswervingly proportional to the surface area due to pore volume of electrode. Carbon materials are consisting pores with wide ranges and those are categorized as three main types based on aspect of its diameters such as micropores (<2 nm), mesopores (2-50 nm) and macropores (>50 nm) respectively(Frackowiak et al,2002).

Micropores are the important constituent for electrical double layer capacitors than mesopores and macropores due to ultimate utilization of porous surface area. The presence of mesopores are important to smooth transfer of electrolyte ions to active material to across the micropores. Micropores are consisting the almost same dimension of ions. Therefore, capacitance values are depending on all three kind of pore sizes and the presence of mesopores on the surface (Ghosh et

al, 2012). many researcher are noted the relationship between pore size and ion size of electrolyte can affected to enhancement of EDLC performance with respected to large pores (Chamiola et al,2006). Hence the distribution of pore size among the surface is necessary factor to achieving maximum capacitive performance.

When look at all available resources, the electrochemical performance of capacitor is depending on many parameters for example specific surface area of electrode material, pore size and distribution, nature of porosity, ion diameter of electrolyte and conductivity of electrode material. The activation of pores in carbon material may lead to large surface area and resulting outcome will high performance electronic devices(Zhang et al,2009).

The wettability of carbon surface functioning by surface functional groups or hetero atoms absorbed by carbon pores. This may cause for faradaic redox reactions. Boron, nitrogen, oxygen and sulphur can recognize as hetero atoms (Largeot et al, 2008). oxygen containing acidic groups can affected for electrolyte decomposition for organic electrolyes. Therefore, aqueous electrolyes may recommended for electrolyte solution for surface impure electrode material. Further more another adverse effect by hetero atoms is increasing electrical resistance because of higher reactivity obtaining bonded hetero atoms. This will be acting as barriers for electron transfer.

2.2 Graphene as carbon material

A single layer of graphite with close-pack conjugate hexagonal lattice named as "Graphene" which can consider as the fundamental element of all kind of graphite base materials such as fullerene. Nano tubes and stacked graphite(Geim et al,2007).
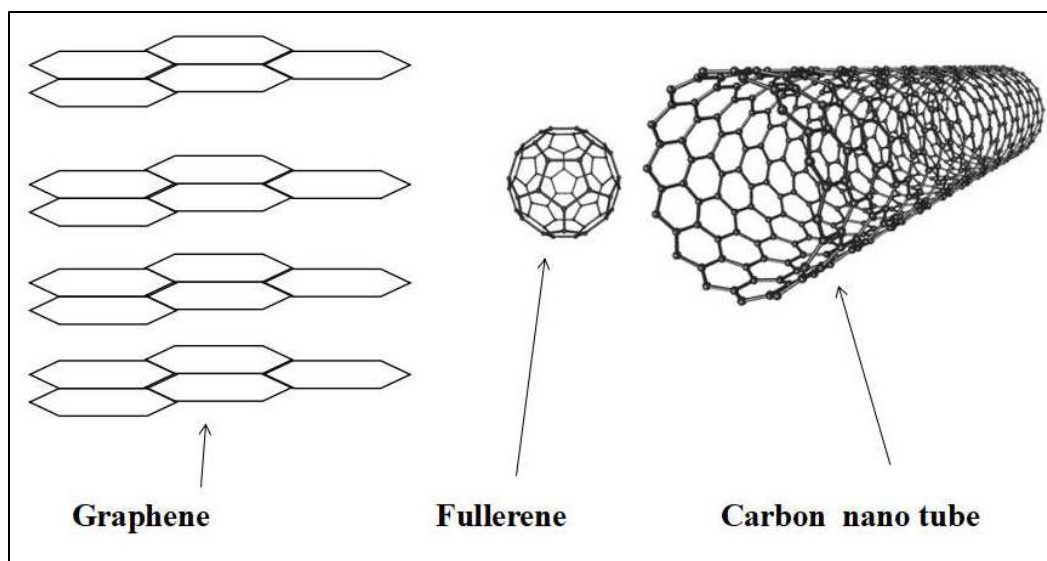
Figure 2.2.1 schematic representation of Graphene, fullerene and Carbon nano tube.

Nowadays, many researchers are highly interesting on graphene due to its elevated carrier mobility (200 000 $cm^2V^{-1}s^{-1}$)(Geim et al,2007), thermal conductivity (5000 W m^{-1} K^{-1}) (Balandin et al,2011), optical transmittance (98%) (meyer et al,2007), conjectural specific surface area (2650 m^2g^{-1}), and smart mechanical strength(Coleman et al, 2010).

Graphene/ graphene based materials such as reduced graphene oxide be able to synthesized by top-down approach and bottom-up approach. Top-down approaches means started with bulk material/graphite decomposition to graphene material. Bottom-up approach consign to the synthesis of graphene by hydrocarbon gas or aromatic hydrocarbon molecules.

Many researches are interesting to trying numerous physical and chemical methods to fabricate graphene/CMG.

The physical methods summarized as micromechanical exfoliation(Novoselow et al,2004), growth on electrically insulating surfaces(Berger et al,2006), chemical vapour deposition (Li X et al,2009) and etching on a silicon substrate(Jiao et al,2009). The main drawbacks of above mentioned method are it requires high temperatures exceeding 1100 ℃ and low or ultrahigh vacuum conditions(Li X et al,2009).

The chemical methods consist of oxidation, exfoliation and reduction of graphite(Park et al,2009), direct exfoliating graphite through sonication(Hernandez et al,2008), intercalation approach(Li X et al,2008), quenching(Tang et al,2009), electrochemical synthesis of graphene by electrochemical reduction of graphene oxide(Guo et al,2009), electrolytic exfoliation(Liu et al, 2008) and carbon nanotubes for graphene nanoribbon by chemical oxidation(Kosynkin et al,2009).

Another methods such as arc discharge approach(Wang et al,2010), substrate-free gas-phase synthesis approach(Dato et al, 2009), the ball milling approach(Fan et al,2010) and solvent-assisted exfoliation approach(Coleman et al,2012) also involving to producing of graphene in large scales.

Chemical reduction approach can be consider as individual most proficient methods for squat cost and extensive creation of graphene. Other methods are considering as high cost low yield and limited processability in bulk production(Guo et al,2011). This advance involves oxidation of graphite to GO and it is highly oxygenated with hydroxyl, epoxide, carbony and carboxyl functional groups. Which may cause for strong hydrophilic nature.This graphite transformation traditionally called intercalation and reduction of exfoliated graphene sheets to graphene conceded by using reducing chemicals(hydrazine), photocatalytic reduction, electrochemical, hydro thermal, solvothermal and thermal reduction(Chen et al,2010).

But this reduction of GO from graphene indicate irreversible agglomeration then this can effect inversely for further processing (Wallace et al,2012). At higher pH range, reduced graphene oxide can be prepared by chemical reduction without using polymeric or surfactant stabilizer(Li D et al,2008). This kind of stabilizers enhancing the solubility of graphene(Patil et al,2009). Another major drawback of this reduction method described as hydrazene and $NaBH_4$ are

toxic/explosive to some degree and then reduction of GO desirable to carried on green chemical approach such as ascorbic acid, reducing metal powders and suger etc(Zhang et al,2011).

Novel methods of reduction/dehydration process also shows an effective way of graphene producing among many researches. By a simple heating of GO suspension in a strong alkaline medium at moderate temperatures(50-90 ^{o}C) can prepared a stable graphene sol(Fan X et al,2008). This method is very much famous among many researchers due to plain, unsoiled and controlled way to adapt Go to rGO. With the aid of photocatalyst, graphene can produced by UV-irradiated photo chemical reduction approach(Salas et al,2010).

2.3 Graphene based materials for supercapacitors/EDLC

Graphene based materials are most commonly exhibiting wonderful performances as electrode materials in ultra/supercapacitors. Chemically modified graphene (CMG) are exhibiting elevated specific capacitance of 135 Fg^{-1} and 99 Fg^{-1} in aqueous and organic electrolytes, respectively(Stoller et al,2008). Another interesting approach to prepare self accumulate graphene hydrogel via a psudo-hydrothermal method. This approach shows much greater capacitance records than previously commented method such as 175 Fg^{-1} and 152 Fg^{-1} under at scan rates of 10 and 20 mV s^{-1} respectively(Xu Y et al,2010). Under same conditions which was about 50% greater than graphene agglomerate particles. Solvothermal reduction of graphene oxide may lead to self assemble graphene organogel with 3D macrostructures also recently interested among many researchers. This shows high capacitance as 140 Fg^{-1} at discharge current density of 1 Ag^{-1} n a extensive voltage array of 0-3 V. The highest energy density of the self assembled graphene based supercapacitor was recorded to be 43.5 Wh kg^{-1} (Sun Y et al,2011). The energy density and power density of the supercapacitors are recorded as 15.4 Wh kg^{-1} and 16 300 W kg^{-1} respectively at high discharge current density of 30 Ag^{-1}(Fan Z et al,2010). The maximum specific capacitance was recorded as 385 Fg^{-1} on 3D graphene sandwich structures due to fast transportation of the electrolyte at a scan rate of 10 mVs^{-1} in 6 M KOH solution.

Single electrode capacitors exhibiting much higher capacitance such as 220 and 135 Fg^{-1} for reduced graphene oxide untimely and late annealing at a current density of 0.2 A g-1(Kim T et al,2010). The best way to prepare reduced graphene oxide from GO, using urea as reducing agent to removing oxygen containing groups(Lei Z et al,2012)

2.4 Graphene based materials for pseudo-capacitors.

Pseudo-capacitors exhibiting elevated specific capacitance with respect to EDLCs but lower operating voltage. Another drawback is pathetic durability due to electrodes undertake physical changes throughout charge/discharge because of mechanical degradation. Transition metal oxides(d and f block) and conducting polymers are the most suitable material for pseudo-capacitors(Mao Lu et al,2013). Even so, the conductivity of metal oxides and conducting polymers are much lower than graphene. The electrochemical reaction will takes place at the interface of the electrode materials which may resulting idle consumption of the dynamic material.

2.5 Effect of surface area and capacitance performance.

Surface area of graphene/rGO can be enhance by chemical activation methods. The enhanced specific surface area was recorded as 3100 m2g-1 through chemical activation of exfoliated graphene oxide and it was exhibit elevated electrical conductivity under short oxygen and hydrogen content(Zhu Y et al,2011). An energy density of 70 Wh kg^{-1} was reach at a current density of 5.7 A g^{-1} in organic electrolyte contained by working voltage of 3.5 V(Zhang L et al,2012). The advantages of chemical activation can be describe as elevated conductive performance, higher cycle lifetime due to high stable nature and free standing/flexible porous carbon thin films for super capacitor applications. The specific capacitance of flexible graphene thin films exhibiting 120 Fg-1, 26 Wh kg-1 as an energy density, 5880 S m-1 of in-plane electrical conductivity and 2400 m2 g-1 of specific surface area, shows elevated performances(Zhang L et al,2012).

2.6 Graphene-metal oxide/hydroxide composites for capacitors/supercapacitors.

To achieving the structural elasticity and stable high specific capacitance, transition metal oxides are the well-known ingredient for supercapacitors with their various oxidation numbers such as RuO_2, MnO_2, V_2O_5, NiO, and CoO. Due to high specific capacitance and constitutional reversibility, ruthenium oxides(RuO_2) is most famous transition metal oxide for supercapacitor along with many researchers(Simon et al,2008) exhibiting 570 Fg^{-1} as specific capacitance value for 38.3 wt.% Ru weight and electrochemical stability recorded as 98% retention after 1000 cycles with the energy density of 20 Wh kg^{-1}(Wu et al,2010). The composite electrode(graphene-RuO_2) exhibiting elevated specific capacitance than either untainted graphene or RuO_2 electrode. But primary drawback is high cost of RuO_2 than other transition metals.

Another most interesting metal oxide recognized as manganese oxide(MnO_2) due to its low cost, non toxic, most plenty and elevated energy density(Toupin et al,2004). Self-limiting depositing approach is the most effective way of nano scale synthesis of MnO_2 on the graphene surface beneath microwave irradiation(Yan et al,2010). The specific capacitance of 310 F g^{-1} at 2 mV s^{-1} was recorded for 78 wt.% MnO_2-graphene composite electrode(Mao et al,2013). Some researchers are developing graphene-MnO_2 composite as the optimistic electrode and activated carbon as the depressing electrode and called asymmetric electrochemical capacitors(Fan et al,2013).

Cobalt hydroxide($Co(OH)_2$) and nickel hydroxide are also combined with graphene to establish composite electrode material for supercapacitors(Wang et al,2010). ($Ni(OH)_2$)-graphene composite electrode supercapacitors are exhibiting the pecific capacitance of 1335 Fg $^{-1}$, current density as 2.8 A g^{-1}(Chen et al,2010).

There are several positive consequence observe in two electrode systems of graphene-metal oxide composites for EDLCs as well as pseudo-capacitors. Main advantage is long cycle life time with out corrupting its own capacitive performances.
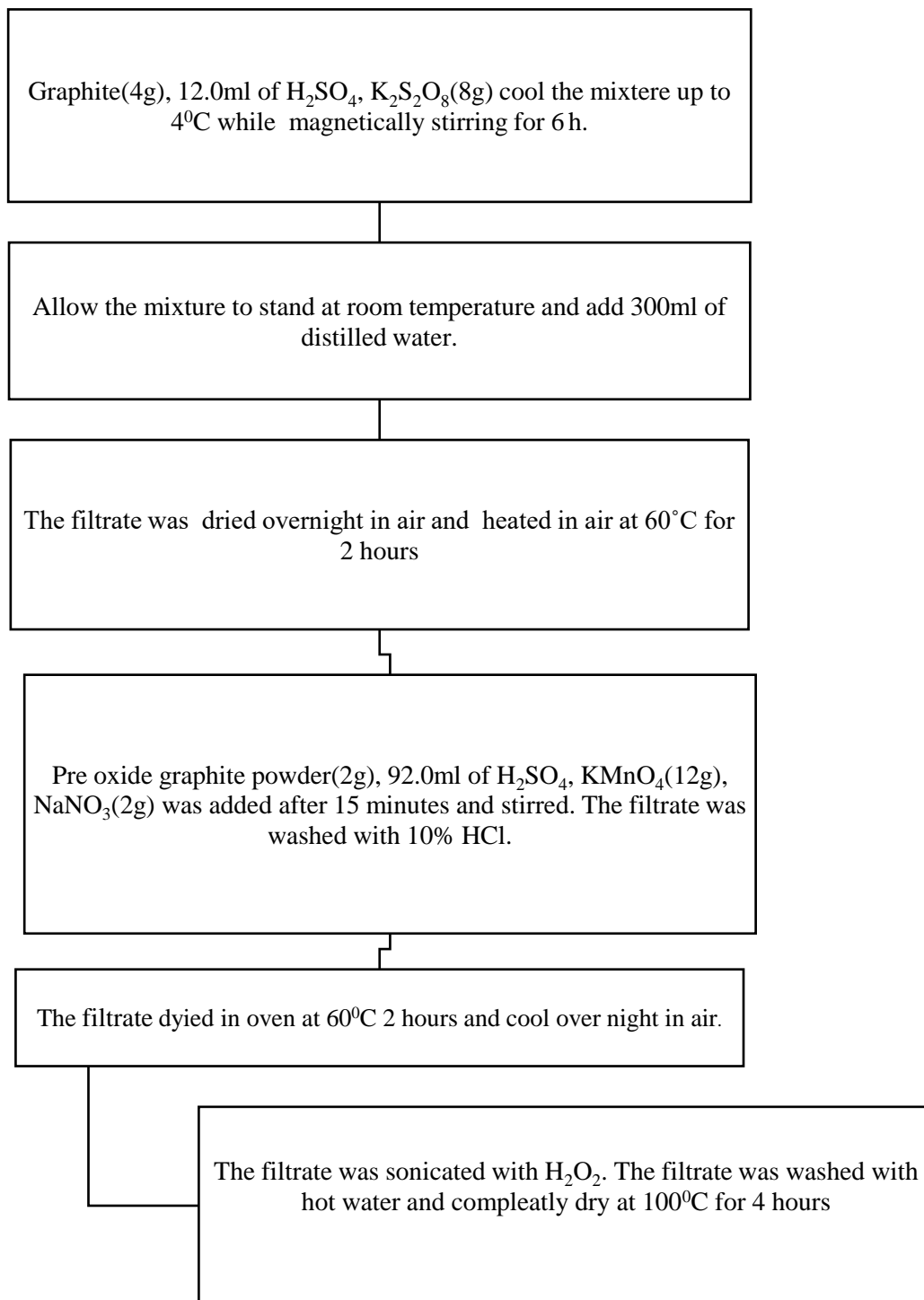
2.7 Supercapacitors and their energy storage mechanism.

Ultracapacitors are electrochemical energy storeroom devices and those can be describe as two categories depend on the way of energy storing. Electrical double layer capacitors are exhibiting capacitance from electrostatic charge amassing take place at the electrode/electrolyte interface.

Pseudo-capacitors are exhibiting rapid and reversible redox process at typical latent due to electro active substances.

Formal electrostatic capacitors are consisting of two electrical conductive electrodes separated by ion permeable porous material and electrical charge amass inside the electrolyte field in among two conductive electrode plates. Traditional capacitors are store very small energy due to limited plate area. But supercapacitors such as EDLC are able to lay up much large energy because of the great inter face area and the atomic range charge separation distance.

3.RESEARCH METHODOLOGY.

Graphite(4g), 12.0ml of H_2SO_4, $K_2S_2O_8$(8g) cool the mixtere up to 4^0C while magnetically stirring for 6 h.

Allow the mixture to stand at room temperature and add 300ml of distilled water.

The filtrate was dried overnight in air and heated in air at 60˚C for 2 hours

Pre oxide graphite powder(2g), 92.0ml of H_2SO_4, $KMnO_4$(12g), $NaNO_3$(2g) was added after 15 minutes and stirred. The filtrate was washed with 10% HCl.

The filtrate dyied in oven at 60^0C 2 hours and cool over night in air.

The filtrate was sonicated with H_2O_2. The filtrate was washed with hot water and compleatly dry at 100^0C for 4 hours

3.1 Synthesis of reduced graphene oxide.

Graphite sourced from Kahatagaha graphite lanka(pvt) ltd with 99% purity was used. Analytical grade reagents and chemicals such as H_2SO_4, H_3PO_4, $KMnO_4$, H_2O_2, P_2O_5, $K_2S_2O_8$, HCl, absolute ethanol and ether supplied by Sigma-Aldrich Co., USA were used. The synthesis of graphene oxide was done by using "Modified Hummer's Method". The method was summarized as below. To reduced the graphene oxide to reduced graphene oxide, graphene oxide was expose to 400^0C for 5 minutes through the puff method.

Figure 3.1.1 photograph of synthesis procedure

3.2 Construction of capacitor.

Reduced graphene oxide electrode was fabricated on top of a stainless steel conductor, and used binder was Polytetrafluoroethylene (mass ratio 80:20). The fabricated (7 x 4 cm^2) stain less steel electrode was dried in a vaccume oven at 100^0C. A polyester separator soaked in 1M H_3PO_4

solution was placed in between two electrodes. The capacitor assembled in an inert environment where a glove box(Mbraum,Unilab,Germany) was used for this purpose.

Figure 3.2.1 schematic representation of capacitor component

Figure 3.2.2 Applying adhesive solution on the stainless steel plate

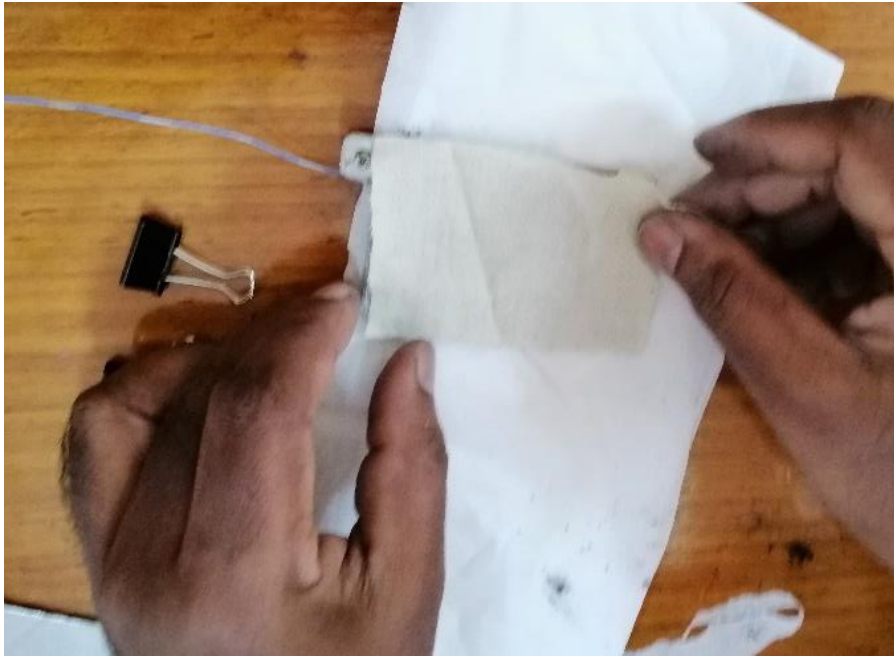Figure 3.2.3 Applying rGO on the adhesive

Figure 3.2.4 Insert Porous separator in between two electrons

Figure 3.2.5 Inject electrolyte solution on the porous separator

Figure 3.2.6 construction of super capacitor

3.3 Material Characterization.

The structural possessions of materials were characterized by using XRD, FTIR, Galvanostat/potentiostat and analytical methods. Electrochemical measurements were performed with a Galvanostat/potentiostat tester (Biologic 150). The capacitor had a arrangement with a stainless steel plate as the counter electrode. A modified carbon/rGO and Cu-rGO working electrode 4cm x 7cm was used as a current collector.

4.RESULTS AND DISCUSSION

Fourier transform infrared (FTIR) spectrometer was used to study the communication of a particular beam of near IR radiation with sample evaluate frequencies at which the sample absorbs the radiation and the intensities of the absorptions. At specific frequencies, chemical functional groups are recognized to absorb beam. Hence, the chemical structure can be determined from the recorded frequencies. FTIR spectra were recorded on a FTIR-ATR spectrometer (Tensor 27). FTIR done in rGO, graphene oxide and raw graphite. The board peak ranging from 3000 to 3700 cm^{-1} high frequency area in graphene oxide was attribute to O-H stretching and vibrations of absorbed water molecules and structural OH groups are well-known indicating high inclusion and/ or attachment of water to the GO structure, which doesn't allow any distinction between C-OH and H_2O peaks. The characteristic peak for GO was observed at $1735cm^{-1}$ for carboxyl C=O group. This characteristic peak was seen much lower in reduced graphene oxide sample. Aromatic C=C group can see in GO and rGO samples at $1573cm^{-1}$. The peak at $1630cm^{-1}$ assign to the stretching vibration of C=C. O-H vibrations of water was noted at the low frequency reagan close to 1600 cm^{-1}. It was found that different types of oxygen were present in reduced graphene oxide including sp2 hybridized C=C peak of reduced graphene at the band 1750 cm^{-1}.

According to FTIR analysis, thermal treatment can be recognized as an effective way of producing rGO by reducing GO due to low intensities of oxygen related functional peaks.
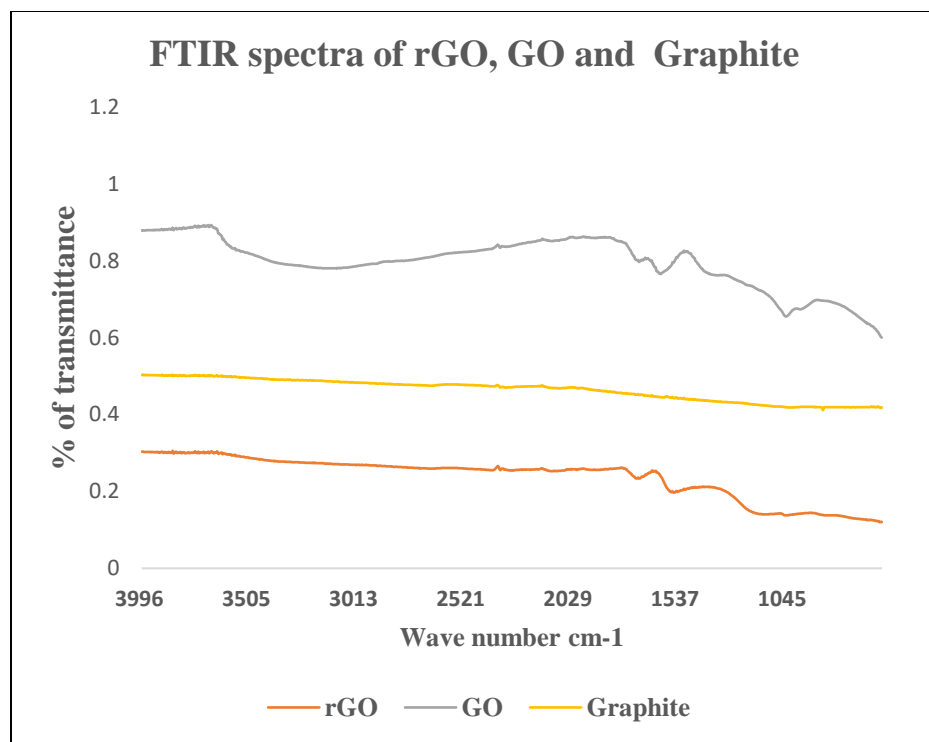
Figure 4.1. FTIR diagram of rGO, GO and Graphite.

Electric double layer capacitor properties were strongly depends on physico-chemical properties for example specific surface area, pore size of semi conductor material(Qiao et al,2002). SEM shows that the porosity of rGO material. SEM employed was a Carl Zeiss ECO D8 instrument.
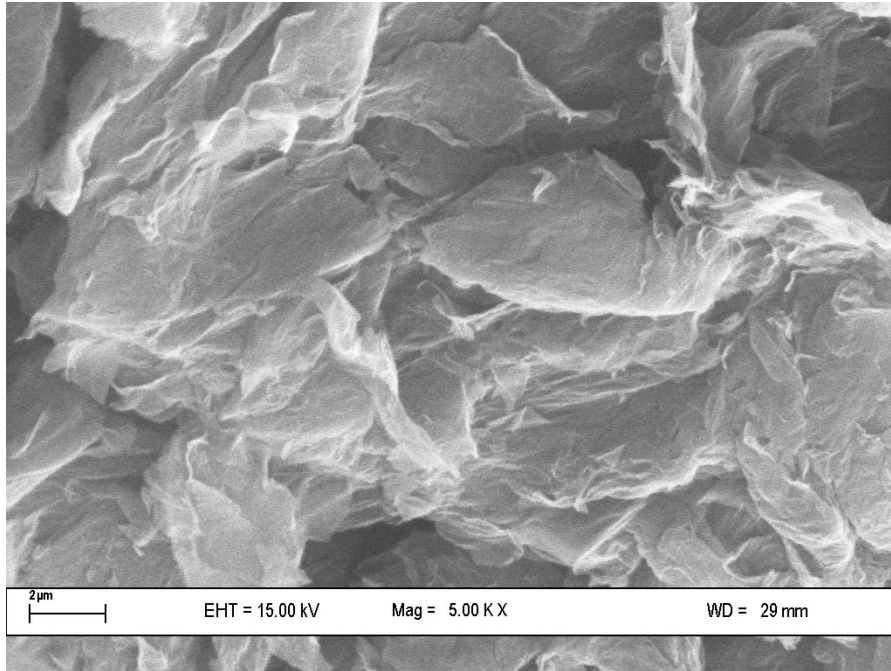
Figure 4.2 - SEM Micrograph of rGO.

The rGO sheets were ultrathin, smooth and representative the single layer or the minority layer rGO sheets in fig.4.2. The rGO nanosheets were layer structured, irregular and folding, as shown in the SEM image of fig.4.3. each individual layers were bound with each other. Resulted shaped of parallel ridges and channels so as to give added rigidity and strength suggested the intrinsic nature of graphene, because the 2D membrane structure(Fu et al,2013). The involvement of faradic phenomena was also approving the large reversible capacity, as well as the larger surface area and warped morphology of rGO(Hidayah et al,2017). The single GO sheets are exhibiting larger thickness (>2 µm) than rGO films. The large thickness is due to oxygen containing functional groups(Alam et al,2017). It can be seen in GO sheets are thicker at the edge than rGO. Therefore, SEM micrograph of GO is proving the rigid structure and it was did not bend.
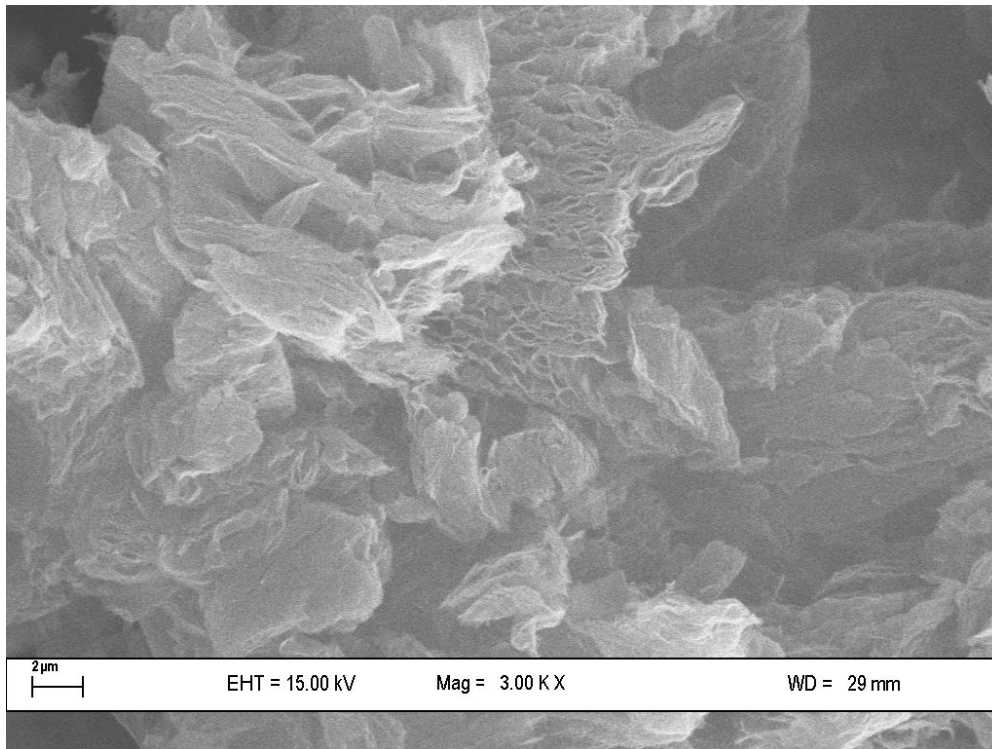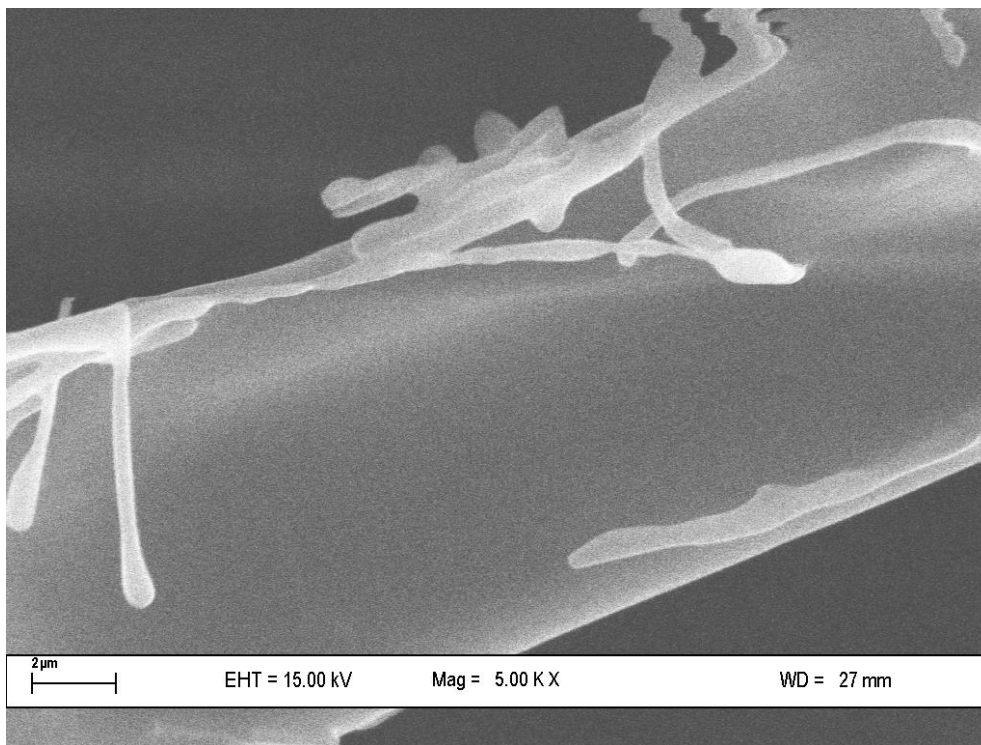
Figure 4.3.The rGO nanosheets

Figure 4.4 SEM images of GO

The SEM micro graphs of graphene oxide through "Modified Hummer's Method" clearly shows the 2D sheet-like structure. This is an evidence for GO has sandwich layered structure and possibility of withstand as individual sheets.

Go can reduced to graphene/rGO through several methods. The SEM images of rGO are showing presence the ultra thin sheets via thermal reduction of GO. The SEM images of rGO at under 35.23K magnification suggested that possibility of synthesis rGO with the thickness is less than 200 nm.
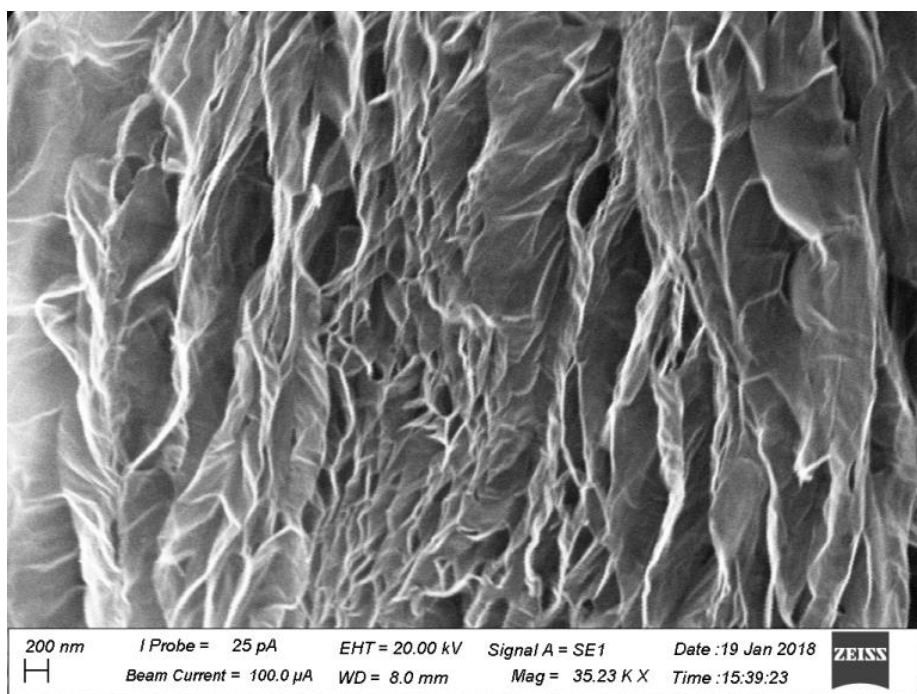

Figure 4.4. SEM image of rGO

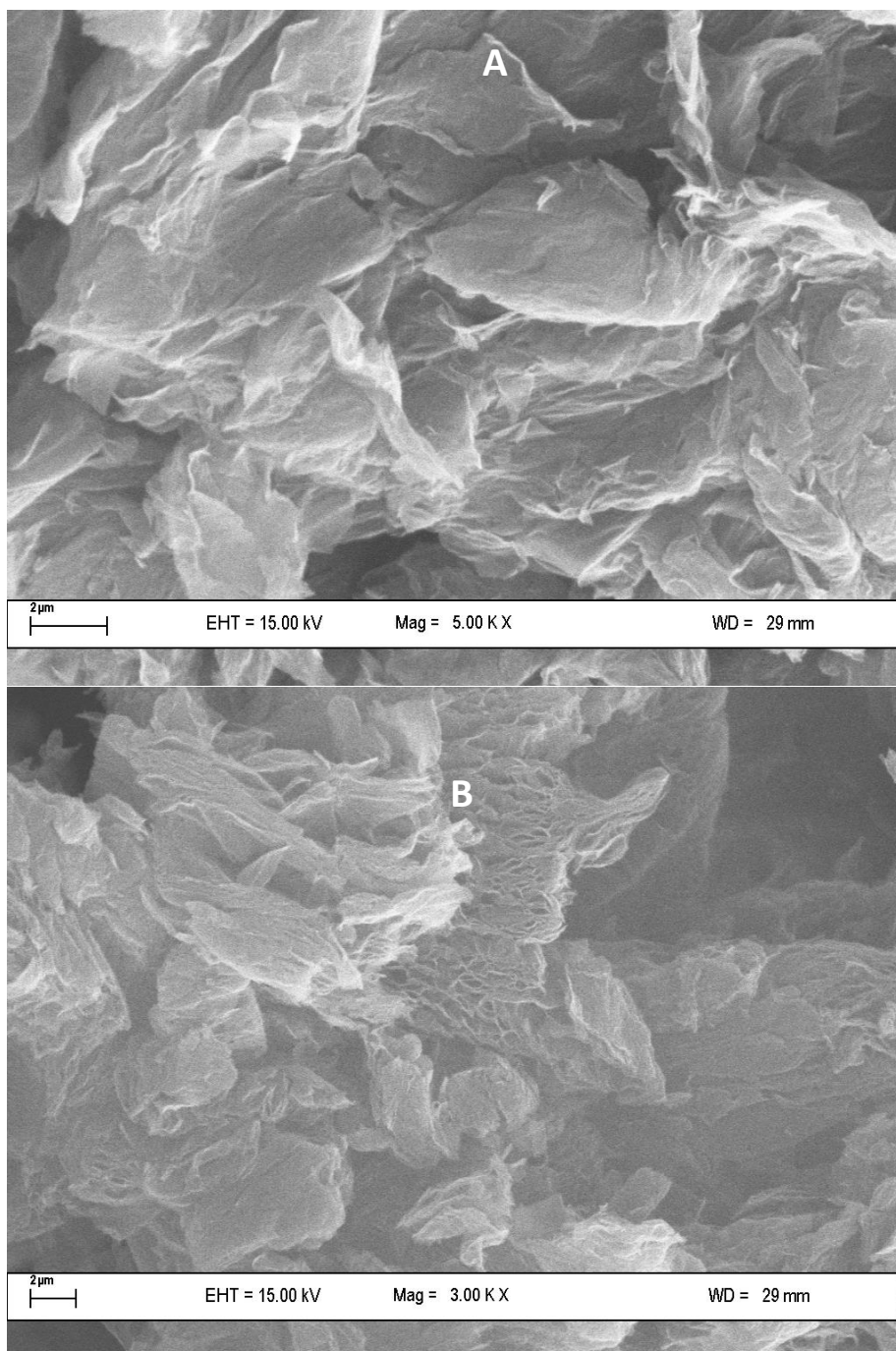The figure 4.A and figure 4.B of rGO clearly suggested the both consisting of stacked layers.

Figure 4.A and 4.B. Stacked layers of rGO.

X-ray diffraction (XRD) acquire compensation of the scattering of x-ray by crystalline materials to obtain a wide range of crystallographic in order. The samples were characterized by using XRD on a (Bruker Eco D8) using Cu Kα1 radiation.
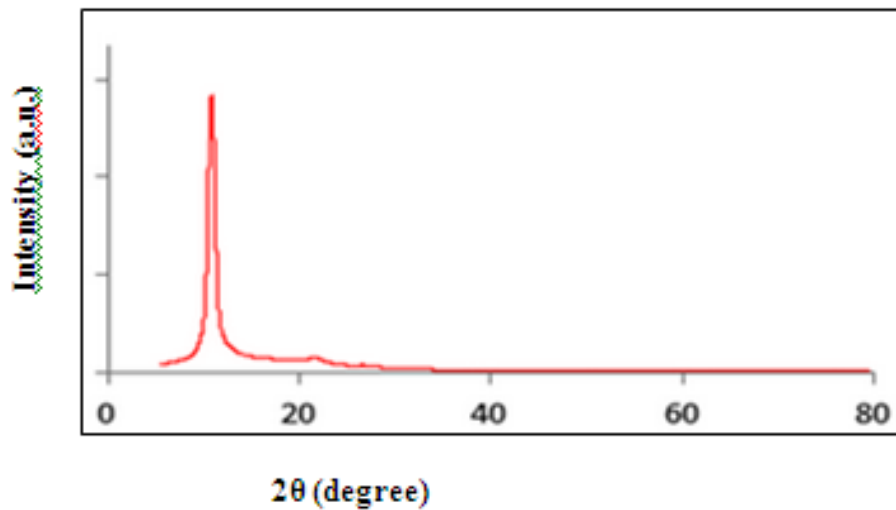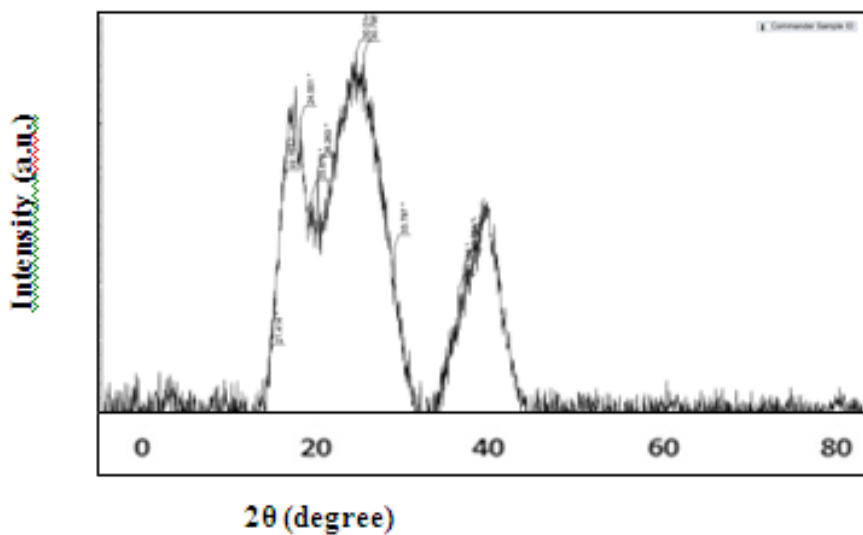
Figure. 4.5. XRD patterns of the GO.

Figure. 4.6. XRD patterns of the rGO.

The XRD pattern of rGO was shown in fig.4.6 and GO shows in fig. 4.5. The representative peak of GO and rGO is at 9.03° and 27.60 (Wang et al,2015) respectively. rGO shows sign of the

intensity and broadness of the peak at 2θ = 26.2630 and the fig.4.5 XRD pattern of GO has the sharp peak at 2θ = 11.7°. the conversion of GO to rGO can be observed from the desertion of the characteristic peak of GO at 2θ = 11.7°and appearing of the peak for rGO at 2θ = 26.2630.

The capacitive performance was study by using the charge/discharge technique, and the discharged results are shown in Figure 4.7.
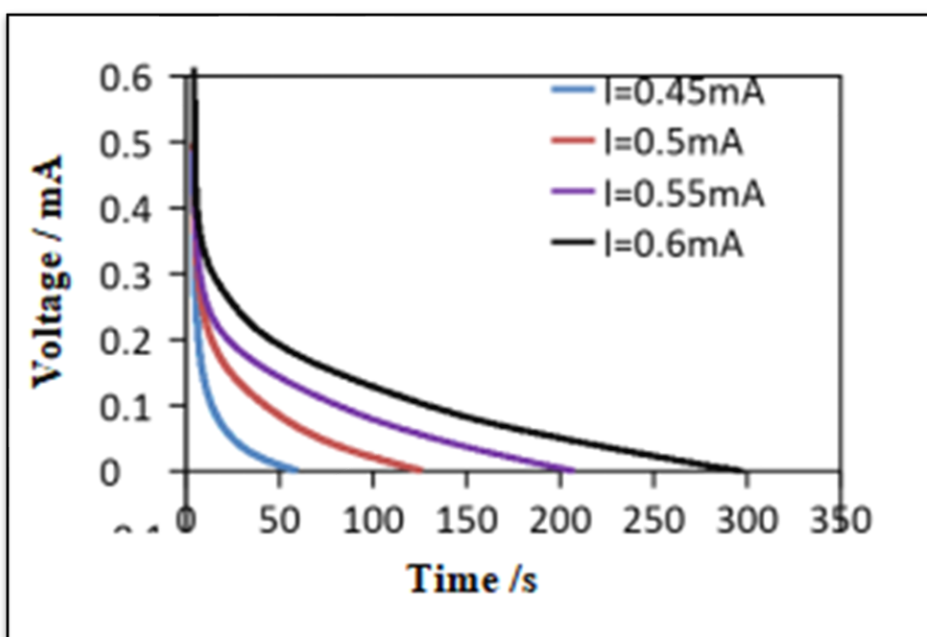

Figure 4.7 - Discharge curves of rGO relative to 0.45, 0.5, 0.55 and 0.6 mA constant current rates.

It is seen that the discharge profiles of the capacitor exhibit improved shapes at an applied charging current 1mA and discharge with different rates of constant current namely 0.45, 0.5, 0.55 and 0.6 mA respectively. Hence it was observed that the maximum retention of charges calculated for 300 s therefore 0.6 mA was indicating the improved discharge time.
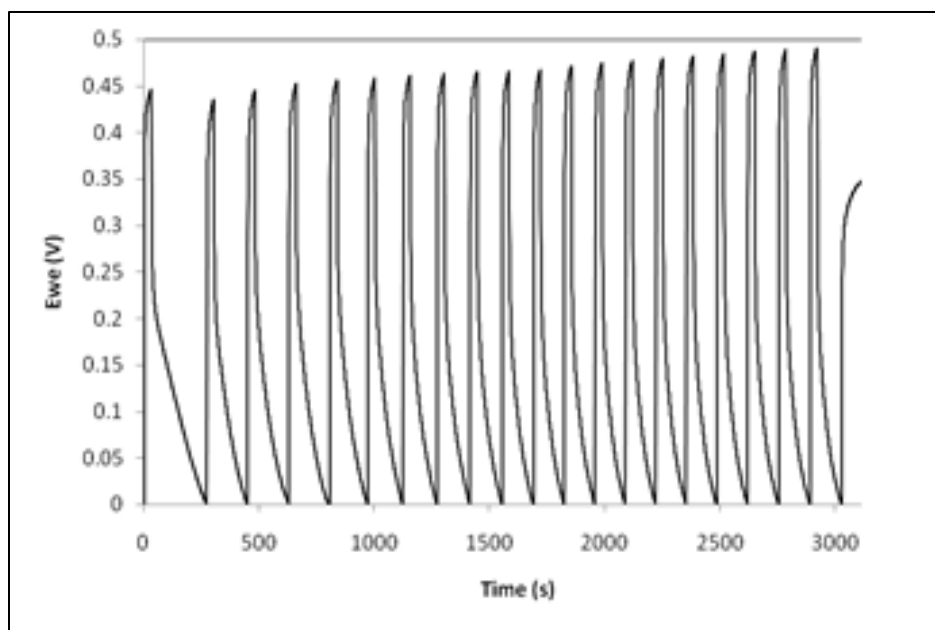
Figure. 4.8. Charge/ discharge curves of rGO capacitor.

Figure 4.8 shows 20 charges/discharge cycles tested for the developed capacitor. At the initial no load stage, the reported voltage was 0.253 V.

The charge applied was 0.1mA with an applied time duration of 1 minute and was compelled to draw the current till it reached zero volts. After performing 20 charges/discharge cycles, the load was eliminated to observed the open circuit voltage, and it was reported at 0.35 V.

When considering the values of initial and final open circuit voltages, it can be seen the ability to perform further without any deterioration. When considering the upper edges of the train, it was observed with the gradual increase which depicts in the potential of re-usability.

Usually, electric double layer capacitor has advantages such as quick charge-discharge rate, elevated power-density in discharging and recharging, exceptional cycle lives on the order of 105 to 106 [8]. Exceptional specific surface area and surface active carbon/graphene material are suitable for the EDLC devices. Fig.4.8. Indicating that rGO based supercapacitor exhibited stable charge/discharge cycling performance.

The capacitive performances of EDLC were considered by using cycle voltammetry (CV). The cyclic voltammograms of rGO are shown in fig. 4.9 and fig. 4.10. The cyclic voltammograms of

rGO electrode were measured in -25 to +15 at the scan rates of 0.1V/s, respectively. The CV curves fig.4.9 shows nearly oblong shapes, indicating the electrochemical capacitive performance.
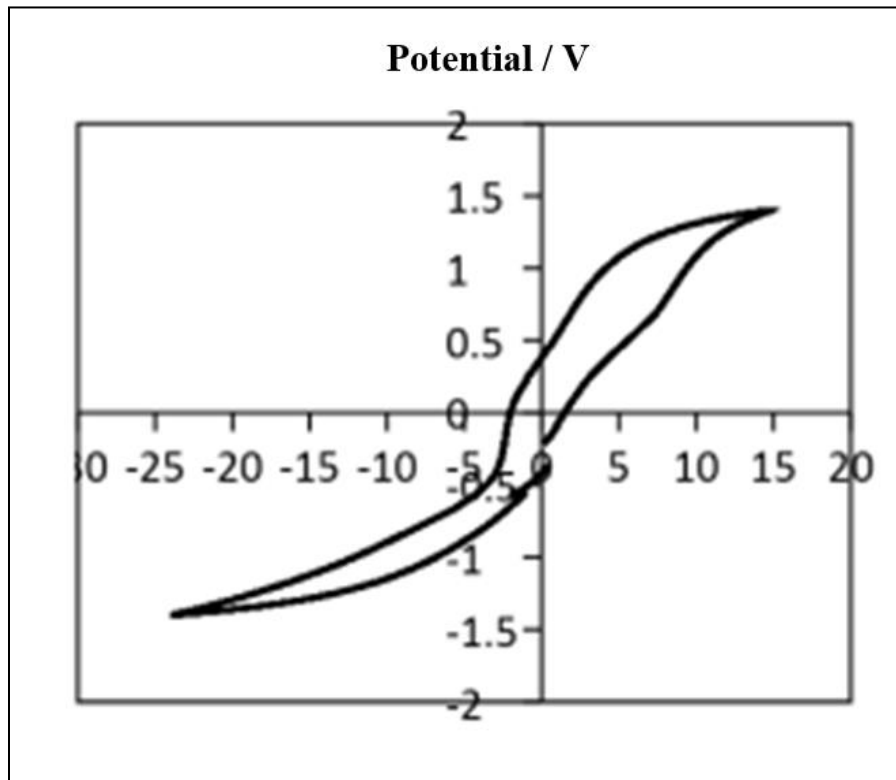
Potential / V

Figure 4.9. - Cyclic voltametry of rGO capacitor.

Margins shall be 20 mm all around and an additional binding gutter of 10 mm on the appropriate edge (Mirror Margins). The width of a text column shall be 75 mm with a space of 10 mm in between.
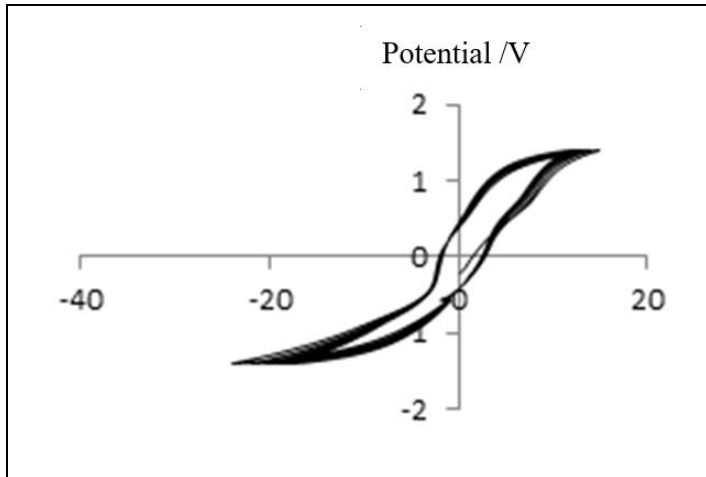
Figure 4.10. - Repeated cycles of cyclic voltammetry.

Cyclic voltammetry was not only used for capacitive performances but also agreed to test the electrochemical performance of EDLC. Figure 4.10 shows cyclic voltammetry diagrams attain with rGO electrode under the same scan rate of 0.1V/s. A chain of CV tests were carried out to study the mechanism of the electron transfer. At the electrode, both anodic and cathodic peak currents remaining constant with the constant scan rate and are linear with the square root of the scan rate in the range of -25 to +15 indicating a diffusion controlled feature of the redox process of the capacitor. There was no apparent difference between the repeated cycles, further confirmed the expected reversibility of this kind of rGO supercapacitors.
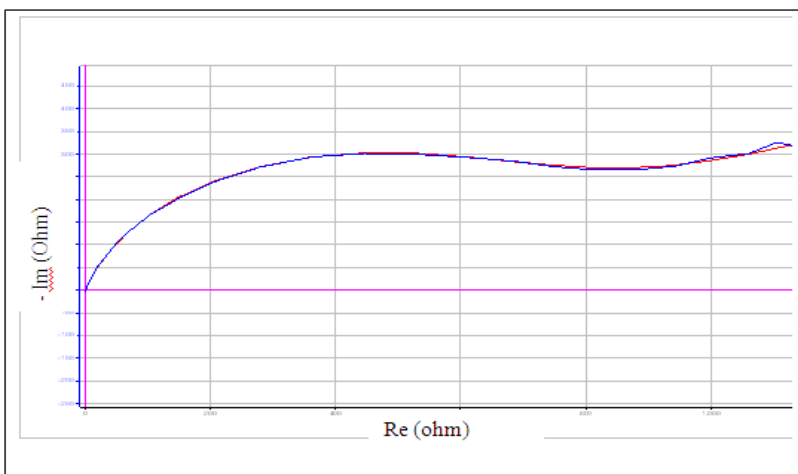

Figure 4.11. - Impedance spectroscopy(blue clour) and curve fit (red colour) of rGO capacitor.
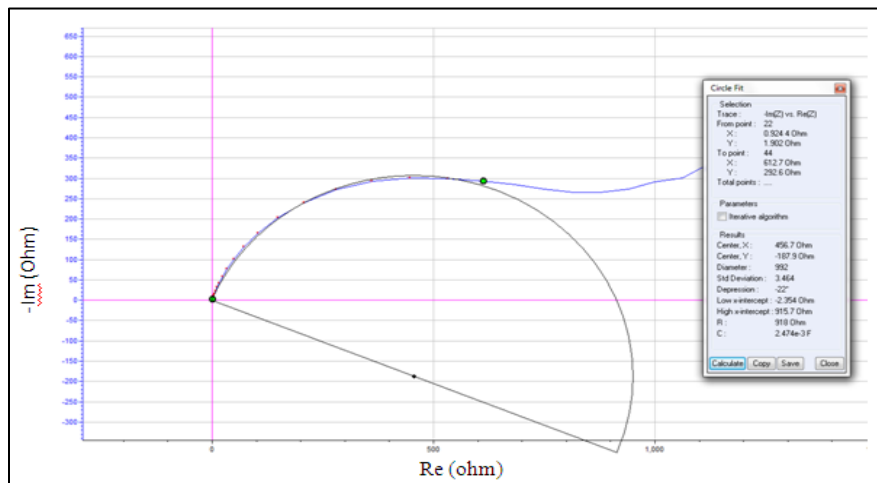
35

Figure 4.12. - Impedance spectroscopy Circle fit of rGO capacitor.
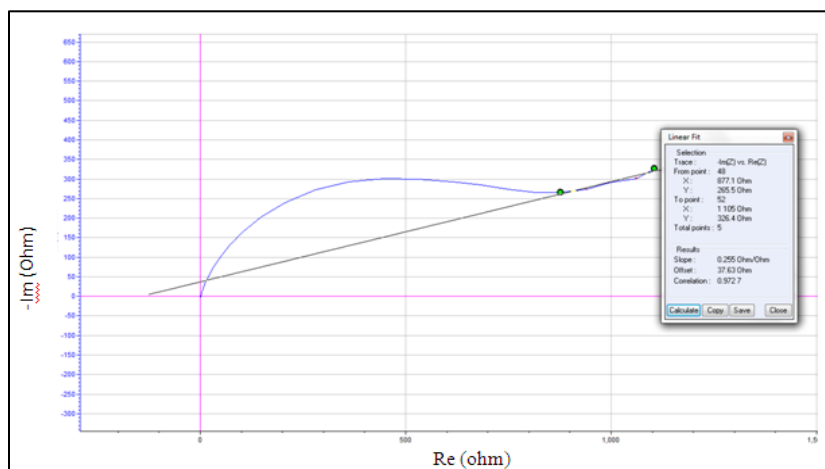
Figure 4.13. - Impedance spectroscopy of linear regression of rGO capacitor.

The Nyquist plot gives very useful information for determining the stability of a system. Figure 4.11 and fig. 4.12. shows the Circle fit and linear regression of Nyquist plot was obtained for rGO supercapacitor. The plot shows a linear line at short frequency region and well-established arc in the elevated frequency region in fig. 4.11. This arc is related to the electronic resistance inside the electrode materials and kinetic control of the system. At low frequency, the incline of the rGO impedance curve is closer to 45∘, representative that the supercapacitor is closer to the

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electrical double-layer capacitor characteristic [11] and mass-transfer control of the system. Therefore, this constructed capacitor shows EDLC behavior. Due to the large circle fit of the Nyquist plot, it was representing high resistance. Therefore, this capacitor has elevated specific capacitance value.

5. CONCLUSIONS AND RECOMMENDATION.

This research study focused on value addition to Sri Lankan graphite and synthesis of graphene based supercapacitor. The morphology of rGO sample was analysed through SEM to get the information related with porosity, shape and thickness. XRD results show that broad nanocrystalline peak due to rGO. The obtained capacitance value for rGO was 0.45 Fg^{-1}. This value can be considered as a reasonable value for capacitance as the investigation was done using two electrode systems. The Nyquist diagrams were described about the stability and EDLC behaviours of the system and this is very essential information to validate the capacitive performance.

In this research, we were able to develop high performance modified carbon material from locally available graphite for supercapacitor without surface activation, better capacitances values, to value addition to local sources.

Based on discharge profiles, the capacitor show better shapes at an applied charging current 1mA and discharge with different rates and it was observed that the maximum retention of charges calculated for 300 s therefore 0.6 mA was indicate the improved discharge time. It was recommended to use this capacitor in domestic purposes. The charge discharge profile confirms the durability during day to day uses. Hence in this preliminary investigation can be concluded that locally available graphite based capacitor has supercapacitor features.

Surface activation of rGO is highly recommended to make metal oxide-rGO composite material to obtaining high supercapacitor properties. The improvement of capacitor properties depends on maybe high pure graphite.

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