Supercapacitor Electrode based on Graphene with Nano Composites for Flexible Nano-Electronics

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***Abstract*-To meet the growing demands for regenerative energy storage applications. In this regard, supercapacitors are very attractive power storage devices in comparison with batteries since they are essentially maintenance-free; possess a longer cycle-life, etc. The aim of this work is to design and synthesize a Supercapacitor electrode material. Graphene is a carbon material with potential in energy storage application such as supercapacitor electrode. In this context, it is planned to utilize graphene oxide and grapheme(Reduced Graphene Oxide) nano particles may fulfil the requirements in the field of supercapacitor. Graphene with graphene oxide combination possess a good super capacitor property .Graphene oxide and graphene materials are prepared from chemical method. All the prepared materials will be characterized using FTIR, XRD, FESEM, etc.**

Keywords:- Supercapacitor, graphene, graphene oxide,characterization.

I. INTRODUCTION

Over the past few years, considerable effort has been devoted to the development of alternative energy storage/conversion devices with high power and energy densities because of the ever-increasing environmental problems and the up-coming depletion of fossil fuels[1-3]. Generally, there are two types of supercapacitors based on the electrode materials:(1) high surface area, inert and conductive materials that store and release energy by nano - scopic charge separation at the electrochemical interface between an electrode and an electrolyte and (2) some redox active materials that use fast, reversible redox reactions at the surface of active materials, which is known as the pseudocapacitance[4-7]. Supercapacitors based on electrochemical double layer capacitance (EDLC) are electrical energy storage devices that store and release energy by charge separation at the electrochemical interface between an electrode and an electrolyte [8].

Prasanna karthika et al, simple process to synthesis the Exfoliated Graphene Oxide (EGO) at two different oxidation levels leading to different level of oxygen groups, (A and B) and Reduced Exfoliated Graphene Oxide (REGO) using gas based reduction, and fabricated supercapacitor devices using these as electrode materials and investigated their performance[9].

In this experiment, Graphene oxide act as electrode, to increase conductive property provide by oxygen reduction agent.

Sheng Chen et al, simple approach of using GO_MnO_2 nanocomposites as electrode material for supercapacitors The electrochemical properties of as obtained Nano composites with different mass ratios were investigated, together with their individual components (nano-MnO_2 and GO) and bulk MnO_2 for comparison. The typical route, for example, when the feeding ratio of MnO_2/GO is 3:1 this method provides a facile and straight forward approach to deposit MnO_2 nanoparticle on to the graphene oxide sheet[10].

Mihnea et al, report the direct preparation of graphene-based films using magnetron sputtering of graphite target. The nanomaterial was deposited at a low temperature of 620 °C on silicon wafers and on metallic foils including aluminium. The films were used in fabrication of supercapacitors with a planar geometry . An efficient, rapid, low-cost, and scalable approach for the synthesis of multilayer graphene sheets by using magnetron sputtering of graphite target[11].

In this experiment super capacitor electrode form by a PEN substrate electrode and graphene film are developed by physical vapour deposition.

Yuxi xu et al, reported a novel flexible solid-state supercapacitor with 120 μm thick graphene hydrogel films to achieve a high gravimetric specific capacitance (186 F/g at 1 A/g), an unprecedented area specific capacitance (372 mF/cm^2), excellent rate capability (70% retention at 20 A/g), cycling stability (8.4%capacitance decay over 10 000 charge/discharge cycles), and outstanding mechanical flexibility[12].

In this experiment, performance are not achieve due to thermal evaporation Of gel substrate.

In the previous research aim to improve a conductive performance of supercapacitor electrode.so metal particles injected to graphene. Herein, we form an scalable approach for the Synthesis of grapheme(Reduced Graphene oxide) using hydrazine method. The graphene based film were used as a electrode material for fabrication of super capacitor. This gives high specific surface area performed by grapheme film. These can be utilized an capacitive performance and stability over a large number of charge – discharge cycles.

II. METHODOLOGY

Among various nanocomposite materials developed so far, hybrid graphene/GO/graphene nanostructures based supercapacitor electrodes prepared with low cost materials and scalable processes hold particular promise for potentially large-scale energy storage systems. To realize many practical applications that require large capacitance and high energy storage, the high mass loading of active Graphene oxide (GO) materials usually leads to the increased electrode resistance and the decreased specific capacitance, because GO becomes densely packed with limited electrochemically active surface area, resulting in only a very thin top layer (up to a few hundreds of nanometers) of oxide nanomaterials participating in the charge storage process.

2.1 Schematic for the preparation of chemically reduced graphene

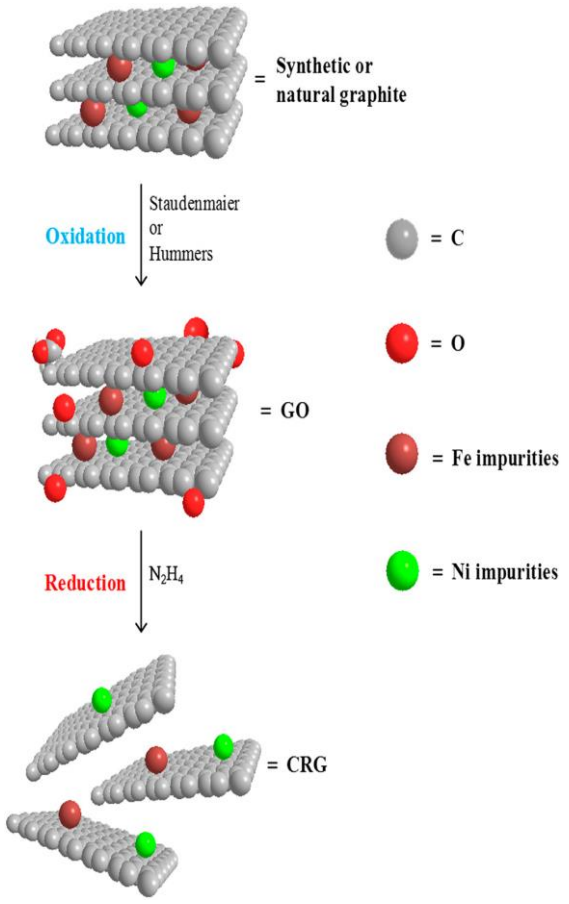


Fig1: Synthesis or natural graphite are preliminarily oxidized to GO using the Hummers methods. CRG is obtained by the chemical reduction of GO using N_2H_4.

2.1 *Synthesis of Nanoparticles*

Chemicals required

Graphite flakes, sodium nitrate, Potassium permanganate, Hydrogen peroxide, sulphuric acid, Hydrochloric acid .

2.1 .1 synthesis of graphene oxide

Graphite flakes (0.5 g) and $NaNO_3$(0.5 g) were mixed in 90 mL of H_2SO_4 (98%) in a 1000 ml volumetric flask kept under at ice bath (0-5°C) with continuous stirring. The mixture was stirred for 4 hrs at this temperature and potassium permanganate (3g) was added to the suspension very slowly. The rate of addition was carefully controlled to keep the reaction temperature lower than 15° C. The mixture is diluted with very slow addition of 184 ml water and kept under stirring for 2 hrs. The ice bath was then removed, and the mixture was stirred at 35°C for 2 hrs. The above mixture is kept in a reflux system at 98°C for 10-15 min. After 10 min, change the temperature to 30°C which gives brown colored solution. Again after 10 min, change it to 25°C, and maintain the temperature for 2 hrs. The solution is finally treated with 14 ml H_2O_2 by which color changes to bright yellow.100 ml of water is taken in two separate beakers and equal amount of solution prepared is added and stirred for 1 hr. It is then kept without stirring for 3-4 hrs, where the particles settles at the bottom and remaining water is poured to filter. The resulting mixture is washed repeatedly by centrifugation with 10% HCl and then with deionized (DI) water several times until it forms liquid like substance (pH-neutral).

Fig 2: prepared Graphene oxide

2.1.1 synthesis of graphene

The Graphene oxide was heat refluxed for 2hours with hydrazine hydrate with a ratio 1:2 in the presence of water. The hydrazine hydrate acts as reducing agent and reduces Graphene oxide to Graphene.

Fig 3: prepared liquid suspension of graphene

Chemically reduced graphene was obtained from the synthesis GO (S-CRG) using hydrazine as reducing agent. Dry graphite oxide powder (5 mg) was dispersed in ultrapure water to give a 0.5 mg mL^{-1} colloidal solution and ultrasonicated (140 W) for 3 h. Hydrazine hydrate was

added dropwise at 50 °C and the reaction mixture was heated up to 100 °C for 24 h. After cooling to room temperature, the mixture was washed periodically with methanol and ultrapure water using centrifugation (8,000 rpm, 10 min). The sample was dried at glass substrate.

The graphene (RGO) suspension was then spin coated at 1000 rpm for 30 seconds with a spin coating machine.

Fig 4:Deposition of graphene on glass

2.1.3 deposition of graphene oxide over on graphene

Reduced Graphene oxide(graphene) liquid suspension with a concentration of 0.05grams of GO was suspended in 10ml Water of and 10ml of Ethylene Glycol in two different beakers. Then after the solutions sonicated by probe type sonicator for 2 hrs for uniform liquid solution.2g of PVP(Polyvinyl Pyrrolidine) was added to the liquid solution and stirred at 800°C for 5hrs. The GO suspension was then spin coated at 1000 rpm for 30 seconds with a spin coating machine.

Fig 5: *Graphene oxide over on graphene(RGO.)*

2.2 mechanism of electrochemical measurement

The electrochemical properties were examined by Using AUTOLAB PGSTAT302N electrochemical workstation In 1 M KOH solution as an electrolyte. the electro chemical analyses were carried out in three electrode configuration with graphene coated substrate(1cm×1cm) as working electrode, platinum as a counter electrode and Ag as a reference electrode respectively. The cells were tested by the cyclic voltammetry (CV) at scan rates 5mV/s, 20mV/s, and 500mV/s, galvano static charge/discharge (GD), and electrochemical impedance spectroscopy (EIS) in frequency range from 100 kHz to 100mHz.

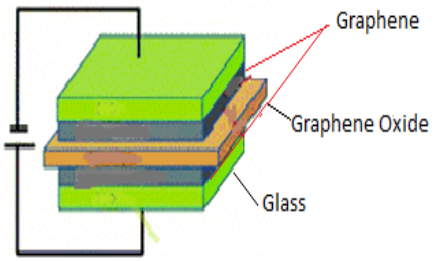


Fig 6:layout of super capacitor

III RESULT &DISCUSSION

3.1 x-ray diffraction

The X-ray diffraction (XRD) is the most widely used technique for general crystalline material characterization. It shows the diffraction peak at $2\theta=10^0$, which is mainly due to the oxidation of graphite. The disappearance of the peak at 26^0 and appearance of the peak at 10^o shows that the product is completely oxidized after the chemical oxidation and exfoliation, indicating an increase in d-spacing from 0.34 nm to 0.82 nm[13].

The XRD pattern for synthesized GO by Hummer's method is shown in Figure

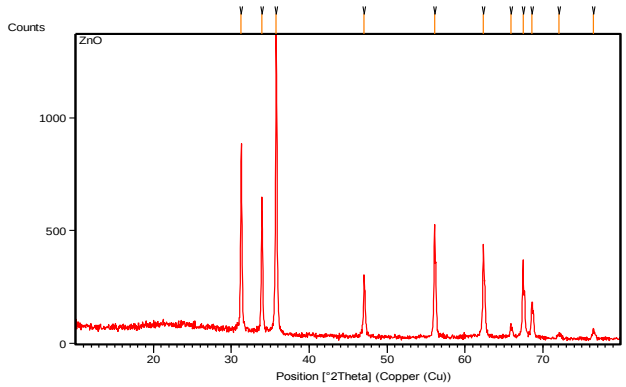
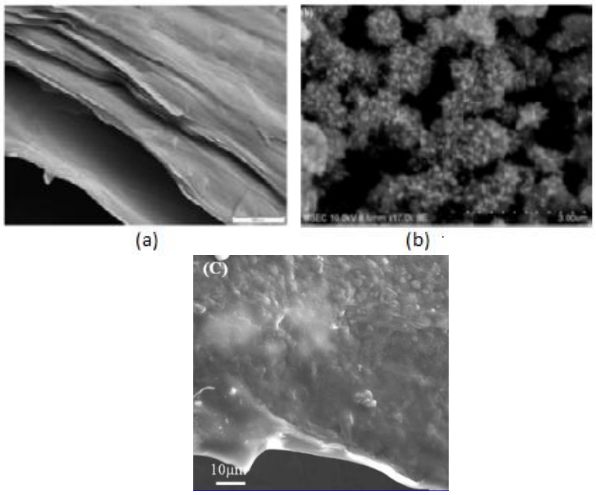


Fig 7:XRD patterns of Graphene oxide

The diffracted peaks at 31.351, 33.703, 35.835, 47.127, 56.281, 62.445, 65.975, 67.538, 68.677, 72.13, and 76.55 were assigned to (1 0 0), (2 0 0), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1), (0 0 4) and (2 0 2) lattice planes respectively.

3.2 scanning electron microscopic analysis

Scanning Electron microscopy provides morphology and structure of nanomaterials. Figure 5a shows the SEM image of typical graphite From SEM image it is clear that how the sheets are stalked together in Fig 8a. Fig 8b shows the SEM image of chemical exfoliated GO. It clearly shows that how the graphene sheets are exfoliated. Fig 8c shows that image of Graphene.



(c)

Fig 8:SEM image of(a) graphite,(b) graphene oxide and (c) graphene(RGO).

3.3 field emission scanning electron microscopic analysis

The grain size and surface morphology were observed by the field emission scanning electron microscope (FESEM). FESEM images of the Graphene Oxide (GO) have well defined and interlinked three-dimensional Graphene sheets, forming a porous network that resembles a loose sponge like structure as shown in Figure [13].

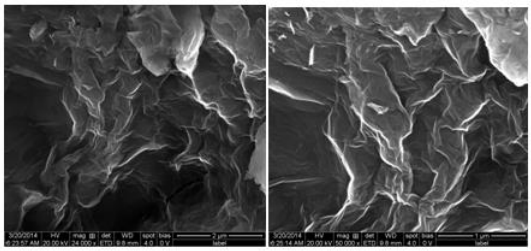


Fig 9;FESEM images of GO at magnification (a) 20000 and (b) 50000.

3.4 fourier transform infra red spectroscopic

It is a technique adopted to obtain an infrared spectrum of absorption, emission, and photoconductivity of a solid, liquid or gas. Also it can be utilized to quantitative analysis of an unknown mixture. FTIR measurement was employed to investigate the bonding interactions in graphene before and after the oxidation process. It assumes the intensities of the peaks are directly related to the amount of sample present.

Figure 4 shows that synthesized GO has a peak at 1098 cm^{-1} which is attributed to the C-O bond, confirming the presence of oxide functional groups after the oxidation process. The peaks in the range of 1660 cm^{-1} to 1680 cm^{-1} show that the C=C bond still remained before and after the oxidation process. The absorbed water in GO is shown by a broad peak at 2885 cm^{-1} to 3740 cm^{-1}, contributed by the O-H stretch of H_2O molecules. This supports the fact that GO is a highly absorptive material, as verified by its ability to become a gel-like solution[13].

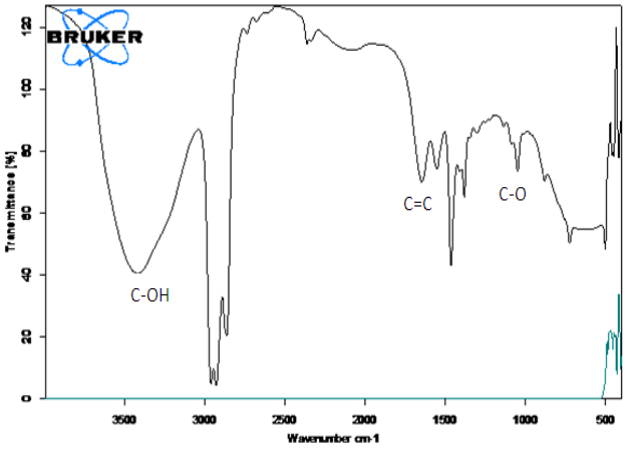


Fig 10: FTIR of Graphene oxide particles.

3.5 UV SPECTROSCOPY ANALYSIS

The size of the nanoparticles plays an important role in changing the properties of materials. Thus, size evolution of conducting nanoparticles becomes very important to explore the properties of the materials. UV-visible absorption spectroscopy is widely being used technique to examine the optical properties of nanoparticles. The absorption spectrum of Graphene oxide powder is shown in Figure 2 .The reflectance spectrum of GO is recorded in the range from 220 nm to 810 nm in solid mode. From the figure, about 98% of the visible light wavelengths from 800 nm to 510 nm were reflected. The low reflectance in the UV region denotes the absorption of photons with higher energy. The lesser reflectance in the UV-region is attributed to the absorption of UV-photons to excite e^- from the valence band to the conduction band[14].

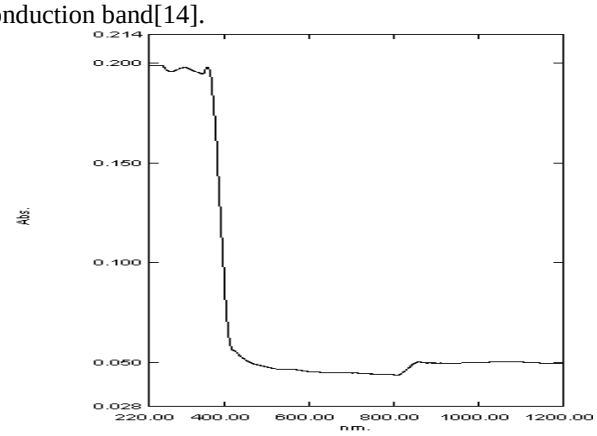


Fig 11: Graphene Oxide solid State UV

3.6 electrochemical impedance spectroscopy:

3.6.1 cyclic voltammetry studies:

The well-developed supercapacitor has to satisfy two conditions, namely, operate in a possibly high current and have a box-like rectangular shape. Based on a Figure 12, it can be noticed that the most rectangular shape was recorded for the reduced graphene oxide . It should be pointed out that better shape was obtained in−40to +40V.

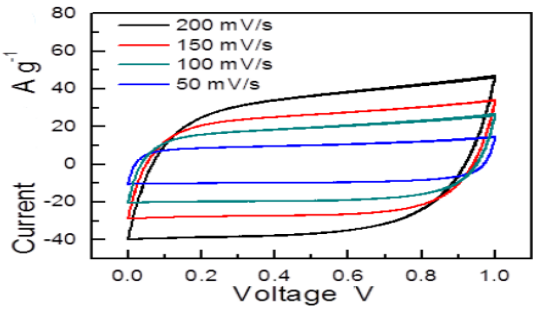


Fig 12 : The CV curves at a scan rate 50, 100, 150 and 200 mV s^{-1} with graphene manufacture at 5 mg.

3.6.2 charge and discharge cycles:

Galvano static charge–discharge curves were obtained at constant current densities of 0.5,1, and 2 A/g (Fig. 13). The charge–discharge curves are close to a triangular shape with the discharge curves nearly symmetric with their corresponding charge counterparts, confirming good charge propagation across the graphene film electrodes and good electrochemical reversibility. super capacitor.

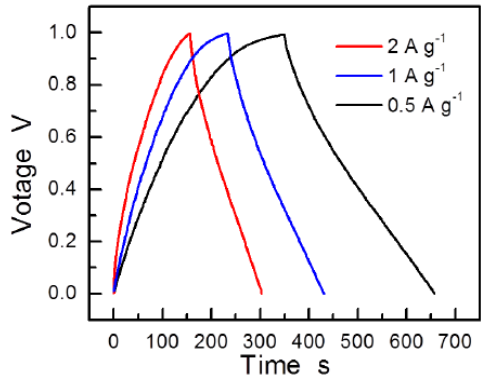


Fig 13:Galvano static charge/discharge curve of various Current(Ag^{-1}).

3.6.3 scan rate vs. capacitance:

The maximum specific capacitance obtained from the CV Curve about 84 Fg^{-1} at scan rate of 50 mV/s. The specific capacitance of graphene is also calculated from the galvano static charge-discharge cycle graphene electrodes using the relation[20].

$$C_{sp} = \frac{I\Delta t}{m\Delta V}(F/g)$$

where I is the discharge current (mA), Δt is the discharge time (s),m is the mass of the electro-active material (mg), ΔV is the potential window.

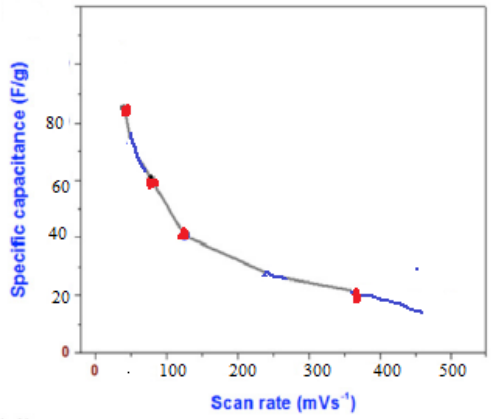


Fig 14: plot of scan rate vs. specific capacitance

IV CONCLUSION

In this phase the synthesis of all the nanoparticles which can be required for the making of super capacitor can be done .The graphene can be prepared from graphene oxide using modified hummer's method. Graphene/Graphene oxide composite is prepared for using it as electrode/dielectric layer in capacitor. The characterization methods such as UV Spectroscopy, x ray Diffraction (XRD),Scanning Electron Microscopy(SEM),Fourier Transform Infra-Red (FTIR)analysis can be performed. This analysis shows that the prepared materials are graphene – graphene oxide solid state capacitor. XRD peaks indicates that the prepared material consist of particles in nanoscales range. The size of the nanoparticles can be determined by using UV spectroscopy. The structure of the prepared composite was supported by FTIR spectroscopy.

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